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Effect of Lattice Misfit on Microstructural Evolution and Mechanical
Properties in Gamma-Prime Strengthened Cobalt-Based Superalloys

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Abstract

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Superalloys strengthened by γ' (L1₂)-precipitates in γ (f.c.c.)-matrix exhibit superior high temperature mechanical properties and environmental resistance over long periods of operation, making them ideal candidates for aerospace and energy conversion applications. The emerging class of superalloys based on Co-Al-W ternary system was identified with a melting temperature 50-100 °C higher than conventional Ni-based superalloys, which after decades of incremental development, are operating at their temperature limit. However, before Co-based superalloys may be considered for practical applications, numerous materials related challenges, such as the inferior mechanical properties, need to be addressed.

Studies are performed to investigate the effect of lattice misfit on microstructural and mechanical properties of Co-based superalloys, where Cr alloying is used to adjust the lattice misfit. The evolution of microstructure is studied using scanning electron microscopy (SEM) to characterize the stability of γ - γ' microstructure and morphology of

γ' -precipitates. Atom-probe tomography (APT) provides accurate measure of elemental distribution between the γ' -precipitate and γ -matrix phase. The elevated temperature mechanical properties are assessed by creep experiments. The effect of alloying addition and lattice misfit are then correlated to the observed microstructure and mechanical properties.

Additions of Cr have shown to gradually alter the lattice parameter of γ - and γ' -phases leading to a decreased lattice misfit and a transition from cuboidal to spherical γ' -morphology. The Cr-containing alloy has demonstrated a superior environmental resistance due to an improved ability to form a passivating chromium and aluminum oxide upon exposing to an oxygen atmosphere. Chromium was found to deteriorate the compressive creep resistance in quaternary (Co-9Al-9W-xCr) and quinary (Co-30Ni-10Al-7W-xCr) alloys but poses minimal impact in multicomponent systems with more than 7 alloying components. The discrepancy in creep behavior is attributed to the combined weakening effect of a reduced lattice misfit and a strengthening effect from additions of Ni, Ti and Ta.

Through both phase-field simulation and experimental observation, lattice misfit was shown to alter the stress induced directional coarsening (rafting) behavior, where tensile stress results in p-type rafts while compressive stress leads to a n-type rafted microstructure. After creep, the alloy with a higher lattice misfit exhibit an extensively rafted microstructure while alloys with a low lattice misfit maintain its initial microstructure. APT analysis suggests that compositional re-distribution occur along the γ - γ' interface and within the γ -matrix to facilitate the rafting driven diffusion during creep. The impact of γ' -raft orientation on the creep resistance was also assessed via tensile creep, and

show that a n-type rafted microstructure demonstrates a creep resistance that is twice of p-type rafted microstructure. However, the instability of n-type morphology under prolonged tensile load prompts additional work to maintain the microstructure during creep.

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CHAPTER 1

Introduction

1.1. Ni-Based Superalloys

The superior mechanical properties at high homologous temperature coupled with the minimal degradation in highly corrosive environment over extended operation, Ni-based superalloys have long been the materials of choice for turbine blades and discs in jet engines and thermal electrical power conversion applications. The superior mechanical properties of Ni-based superalloys can be attributed to the coherent ordered intermetallic γ' -precipitate (Ni_3Al) with L1_2 crystal structure embedded in the disordered face center cubic (f.c.c.) γ -matrix (see Figure 1.1). Over the last 70 years, significant effort has been devoted to improve the performance of Ni-based superalloys through composition tailoring, process optimization and microstructure design. However, after decades of development, Ni-based superalloys are reaching their performance limits. The materials properties and underlying strengthening mechanisms in Ni-based superalloys are summarized below.

In a typical precipitation strengthened metallic system, mechanisms such as stacking fault energy, interfacial energy and Orowan strengthening all contribute to the increased critical resolved shear stress (CRSS) of the materials. However, in Ni-based superalloys, the effect of order strengthening outweighs other contributions. In the γ -phase, slip deformation occurs by dislocation glide on the $a/2 \langle 1\bar{1}0 \rangle \{111\}$ system. In order for the

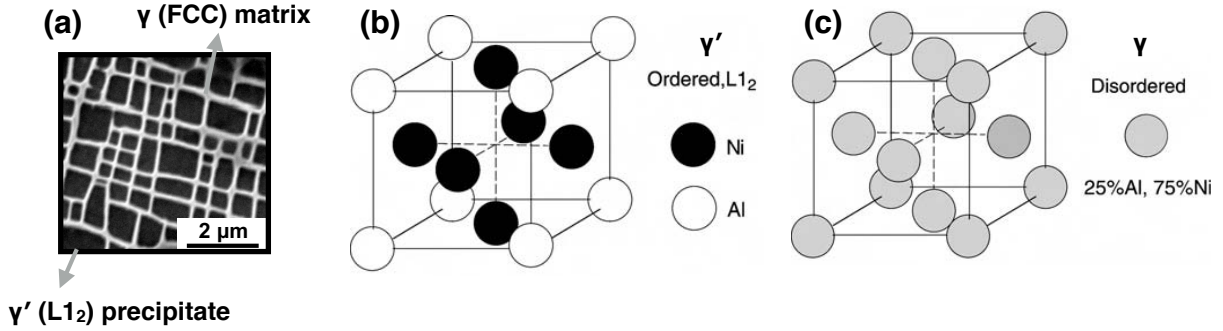


Figure 1.1. (a) γ - γ' microstructure in γ' -strengthened Ni-based superalloy. Crystal structure of (b) L1₂ ordered intermetallic γ' -phase and (c) disordered f.c.c. γ -matrix.

dislocation to shear through an ordered γ' -precipitate, a pair of superpartial dislocation must form to prevent the energetically unfavorable bond in Ni₃Al. The superpartial dislocation pair is referred to as the superdislocation. Superdislocation creates a faulted strip, anti-phase boundary (APB), raising the system energy. The energy cost for superdislocation formation upon shearing defines the CRSS in the system [18].

At a low homologous temperature, when γ' -particles are small, with a low volume fraction and a low APB energy, the superdislocation is considered as weakly coupled since they do not necessarily reside in a single γ' -particle (region 1 in Figure 1.2). In this case, the CRSS scales with $(fr)^{1/2}$ where f is the γ' volume fraction and r is the γ' particle radius. In the case where APB spacing is comparable to the particle size (large γ' particle size), the elastic repulsion force between two superpartial dislocations becomes critical since they now reside in one γ' -particle and are considered to be strongly coupled (region 2 in Figure 1.2). The energy penalty for superdislocation to shear through γ' particle scales with $r^{-1/2}$ when $r \rightarrow \infty$. Thus, the peak CRSS occurs at the transition from weakly to strongly coupled superdislocation as shown by region 3 in Figure 1.2.

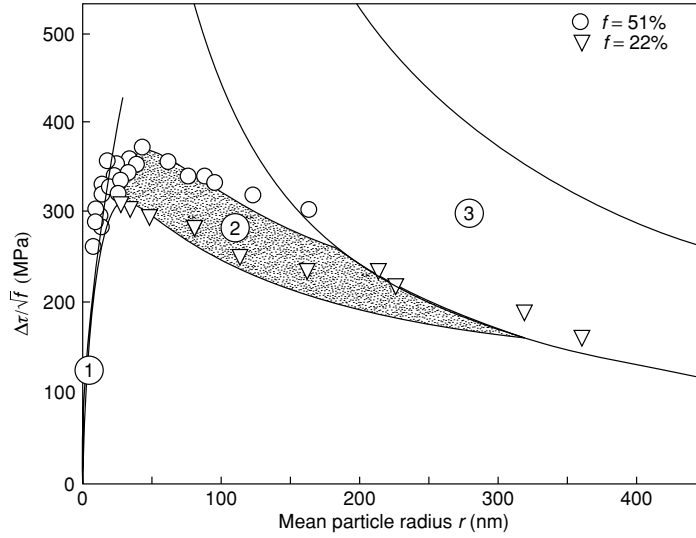


Figure 1.2. Variation of CRSS as a function of mean particle radius. Region 1 corresponds to strengthening by weakly coupled superdislocation, region 2 to the strongly coupled superdislocation, and region 3 to the Orowan mechanism [3].

In contrast to most materials which have a yield strength that decreases with temperature, Ni-based superalloys exhibit anomalous yielding where yield stress increases with temperature. Figure 1.3 shows the anomalous yielding behavior in various single crystal Ni-based superalloys. The peak stress is reached around 800 °C followed by a rapid decline. The specific mechanism of anomalous yielding behavior is still subjected to debate, but it is widely accepted that upon deformation at elevated temperature, superpartial dislocation cross-slip from the octahedral $\{111\}$ planes to the cubic $\{100\}$ planes. Upon cross-slip, the leading superpartial dislocation is immobilized on the cubic $\{100\}$ plane without its trailing superpartial. Additional stress is needed to promote a cross-slip back to the octahedral $\{111\}$ planes. With increasing temperature, more superdislocations are thermally activated onto the $\{100\}$ planes, resulting in an increase in γ' yield strength.

Beyond the peak stress, the materials become cubic $\{100\}$ slip dominant and the yield strength of γ' -phase decreases with temperature.

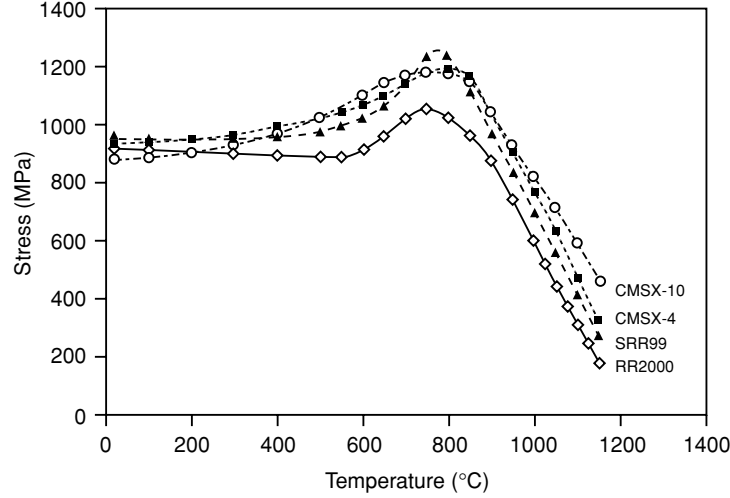


Figure 1.3. Anomalous yield stress for various single crystal Ni-based superalloys.

When Ni-based superalloys are subjected to mechanical stress at elevated temperature, the primary deformation mechanism is creep. During creep, plastic deformation accumulates over time, ultimately leads to failure. Typical creep processes are classified into three regimes, primary, secondary and tertiary creep as shown in Figure 1.4. The rapid initial transient primary creep is characterized by rapid dislocation accumulation within the γ -matrix, which is more compliant compared to the γ' -phase. In secondary creep, dislocation annihilation and multiplication is balanced, resulting in a constant dislocation density. During the secondary creep, as the γ -matrix becomes saturated with dislocations, fractions of matrix dislocations begin to shear through γ' -precipitates via various mechanisms such as stacking fault and superdislocation reaction at the interface [10]. The final tertiary creep regime is characterized by a rapid increase in strain rate and internal cavity

formation. Since superalloys spend majority of operation in secondary creep, quantification of steady state creep rate is critical in predicting the creep resistance. Assuming no significant microstructural evolution occur during creep, the steady state creep strain rate $\dot{\epsilon}_{ss}$ of the alloy is characterized by:

$$(1.1) \quad \dot{\epsilon}_{ss} = A\sigma^n \exp \left\{ -\frac{Q}{RT} \right\}$$

where A is a constant, σ is the applied stress, n is the stress exponent, Q is the creep activation energy, R is the gas constant and T is the temperature. In Ni-based superalloys, creep resistance may be improved through various methods, such as solid-solution strengthening, optimization of γ' volume fraction, increased stacking fault and APB energy, etc.

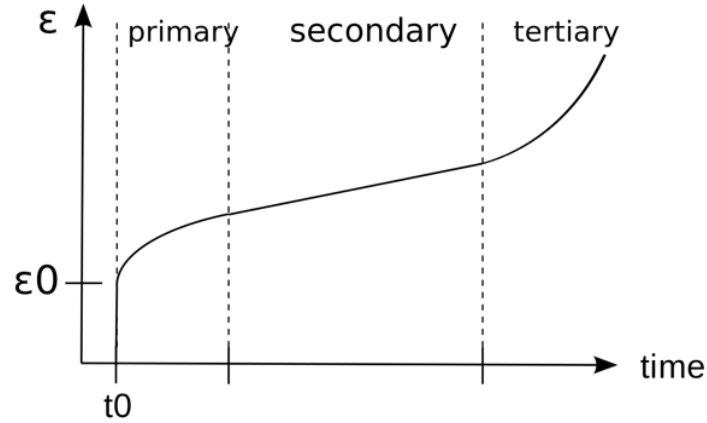


Figure 1.4. Typical creep behavior of a Ni-based superalloy, plotting creep strain as a function of time under constant stress.

At elevated temperature, Ni-based superalloys are required to exhibit superior oxidation and corrosion resistance to avoid surface or grain boundary embrittlement. To ensure an adequate intrinsic environmental resistance, Ni-based superalloys usually contain high

concentration of Al and/or Cr, which facilitate formation of self-passivating oxide when exposed to an oxygen atmosphere. Following that, a metallic bond coat is applied along with ceramic thermal barrier coatings (TBCs) to further enhance Ni-based superalloy's environmental and thermal resistance [19]. In the interest of bulk metallic properties, only the intrinsic oxidation properties of the alloy will be addressed here.

Under an oxidizing environment, layer of oxide scale will form on metal surface spontaneously. Figure 1.5 shows an oxidized surface microstructure of a superalloy. The formation of oxide consumes certain γ' forming elements resulting in a γ' depletion zone. In general, an oxide layer is thin, dense and thermodynamically stable within the operation temperature and adheres to the metal surface. Chromium forms a protective chromia scale, Cr_2O_3 , when exposed to oxygen at an intermediate temperature. Chromia exhibits a low oxygen ion conductivity, effectively passivates further oxidation. However, at temperature above 1000 °C, chromia is further oxidized to form a volatile CrO_3 . In contrast to Cr, Al promotes high temperature stability above 1000 °C by forming α -alumina, Al_2O_3 . The oxygen ion conductivity of alumina is lower than that of chromia, and is stable within the operating temperature of Ni-based superalloys. Nonetheless, at low temperature, other metastable allotrope of alumina, namely γ -, δ - and θ -alumina are formed. Metastable alumina allotrope are porous and contain larger concentration of vacancies, thus less effective in passivating further oxidation[20].

As shown in Figure 1.6, in an oxidizing metallic system, the kinetics of oxide growth may be categorized into: parabolic, logarithmic, and linear growth. Under the conditions where the oxide layer is dense and ion diffusion is rate limiting, the oxide growth follows the parabolic law. This is the most common method to characterized the passivating

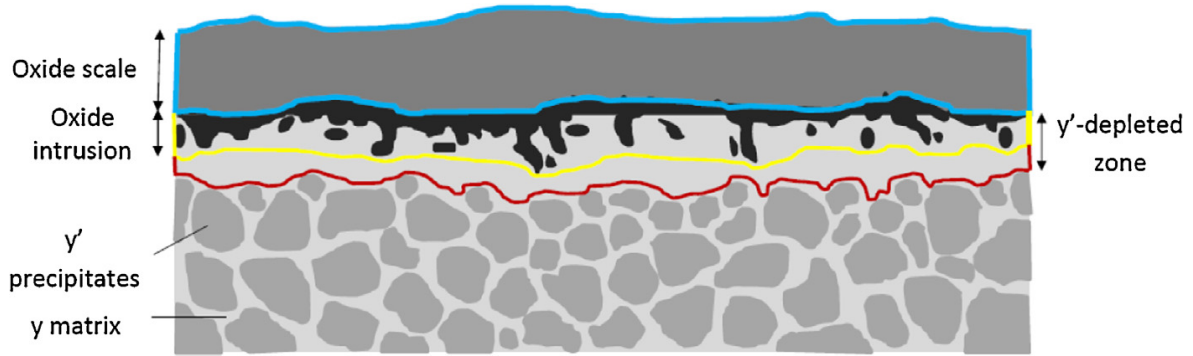


Figure 1.5. Cross sectional schematic of a typical oxidized surface structure in γ' -strengthened superalloys.[4]

ability of a superalloy. At moderate or low temperature, oxidation profile may follow the logarithmic kinetics at the initial growth stage that is determined by interfacial kinetics. In the condition where the oxidation is not limited by ion diffusion or interfacial reaction rate, a linear trend may occur. This is commonly observed in cracked or porous oxide films [5]. The breakdown of the protective oxide layer may result in breakaway oxidation and facilitate mechanical failure.

1.2. Co-Based Superalloys

In 2006, Sato *et al.*[16] re-discovered the ternary Co-Al-W system with a γ - γ' microstructure parallel to that of Ni-based superalloys*. With the performance of Ni-based superalloys approaching its thermodynamic limit, γ' -strengthened Co-based superalloys with a melting temperature 50-100 °C higher than that of Ni-based superalloys offer a potential to supplant traditional Ni-based superalloys in turbine applications. However, for

*Co-Al-W γ' -strengthened Co-based superalloys was originally discovered by C.S. Lee in 1971, but the finding was never published [21].

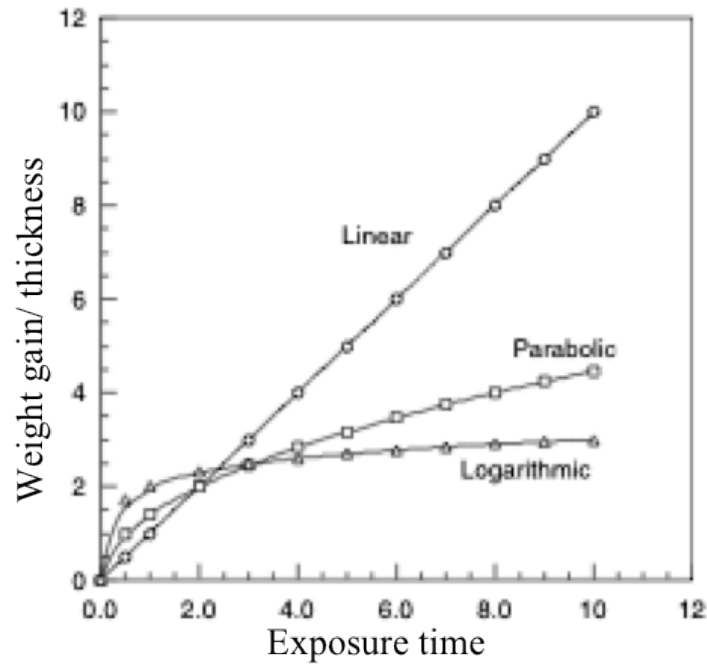


Figure 1.6. Plot of weight gain as a function of oxidation time for different oxide growth kinetic mechanisms[5].

Co-based superalloys to be considered for practical usage, numerous materials challenges need to be overcome:

- The Co-Al-W system exhibits a lower γ' -solvus temperature, such that the strengthening γ' -precipitates dissolve back into the γ -matrix at a lower temperature than commercial Ni-based superalloys.
- Due to the heavy reliance on W, Co-based superalloys have a higher mass density, imposing additional mechanical stress when used in a rotating turbine blade.
- Co-based superalloys exhibit a lower intrinsic oxidation resistance since Co is more likely to be oxidized compared to Ni.

- Co-based superalloys, in general, have a worse high temperature mechanical properties, *e.g.*, creep resistance, compared to commercial Ni-based superalloys.

To overcome these materials challenges, approaches such as multicomponent composition design, microstructural engineering and process control were used to improve individual or collective materials properties. Gaining insight on the fundamental difference between Ni- and Co-based system in terms of atomistic, meso-scale properties and microstructure evolution may also allow us to devise an improved alloy.

Early experiments and first principle calculations shown that γ' in the ternary Co-Al-W system is metastable. After prolong aging at 900 °C, the volume fraction of γ' decreases and decomposes into D0₁₉ and B₂ phase[**22**, **23**]. To stabilize γ' -phase and enhance the performance of Co-based superalloys, numerous alloying elements have been added to study their effect [**24**, **25**].

Nickel additions expand the γ' phase field, allowing the addition of other elements without forming topological close-packed (TCP) phases. Figure 1.7 compares the γ' phase field in 10 and 30 at.% Ni system. Since Ni₃Al γ' is the strengthening phase in Ni-based superalloys, a continuous γ' phase field exist from the Co side to the Ni side in Co-Ni-Al-W system. Nickel also increases the γ' solvus temperature [**6**, **26**]. Recently designed Co-based superalloys include up to 30 at.% of Ni to ensure accommodation of elements such as Cr, Ti and Ta does not result in TCP formation.

Tantalum serves as a γ' -former in Co-based superalloy as it partitions strongly to the γ' -phase in replacement of Al and W in the Co₃(Al,W) superlattice [**27**, **28**]. Tantalum stabilizes the γ' -phase, resulting in an increased γ' volume fraction and solvus

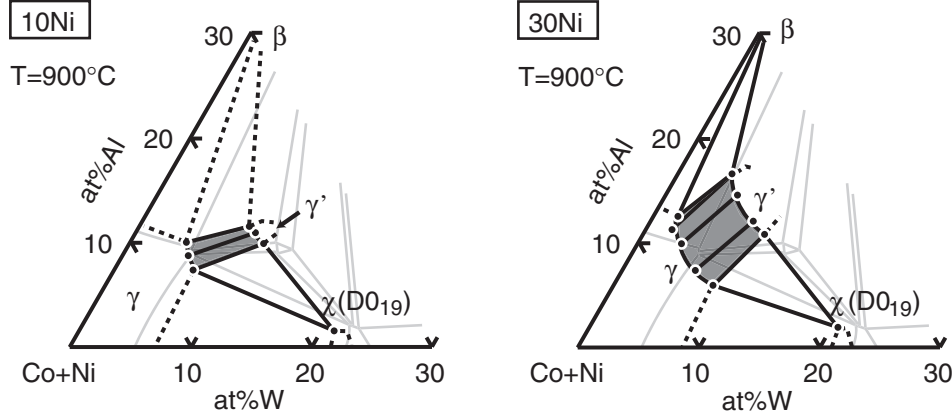


Figure 1.7. Comparison between 10 and 30 at.% on the effect of γ' phase field in Co-Ni-Al-W system [6].

temperature[29, 30, 31]. It also increases the anomalous yield strength due to the increased stacking fault energy [32, 33, 34]. Nano-indentation experiments show that Ta increases the hardness of γ' -phase while the hardness of γ -channel remain constant [28]. However, due to the high atomic weight of Ta, mass density increases significantly with Ta addition.

Similar to Ta, Ti addition stabilizes γ' , raises γ' solvus temperature and improves mechanical properties by increasing the stacking fault energy [28, 29, 35, 36, 37, 38]. Figure 1.8 illustrates the significant creep resistance enhancement of Ti in a quinary Co-Al-W-2Ta-2Ti alloy when compare to a quaternary Co-Al-W-2Ta alloy. In addition, Ti also increases the lattice misfit between γ - and γ' -phase which improve the ability for γ - γ' interface to impede dislocation motion. However, during prolong aging, phases such as D0₁₉ and B2 may form and degrade the mechanical properties [39, 40]. Combination of Ni, Ti and Ta alloying results in a solvus temperature compared to that of commercial Ni-based superalloys [41].

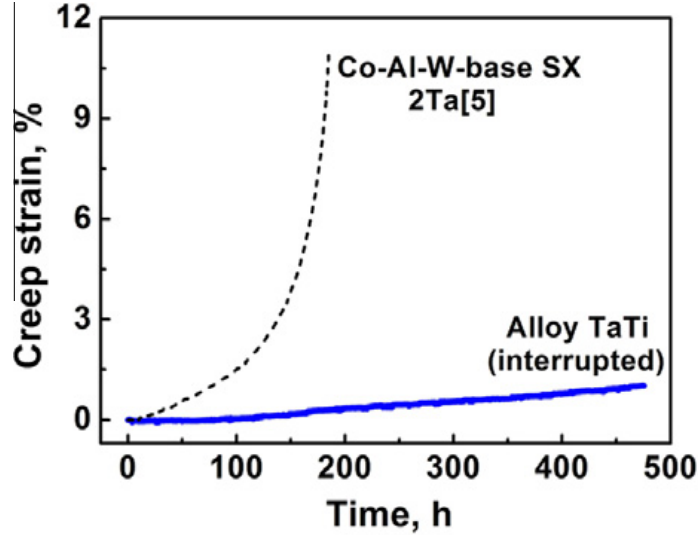


Figure 1.8. Creep behavior of Co-Al-W-2Ta and Co-Al-Ta-2Ta-2Ti at 1000 °C / 137 MPa, demonstrating the creep strengthening effect of Ti addition [7, 8].

In the effort to further lower the alloy density, numerous W-free variants have been developed based on ternary and quaternary system such as Co-Ta-V [42], Co-Nb-V [42], Co-Ti-Cr [43], Co-Ti-Mo [44] Co-Al-Mo-Nb [45, 46, 47]. However, W-free Co-based superalloys generally exhibit a lower γ' solvus temperature compared to the W-containing alloys. Addition of Mo, Nb and V in partial substitution for W were also extensively studied due to the opportunity to reduce mass density. Atom-probe tomography shows that Mo partitions equally between γ - and γ' -phase, with occasional segregation at the γ - γ' interfaces to lower the interfacial excess free energy [1]. Nb and V both weakly partition toward the γ' -phase. To date, there are no systematic study on how Mo, Nb and V impact the mechanical properties. However, these elements generally weaken the creep resistance of Co-based superalloys as less strengthening effect is provided compared to the W substitute [48].

In polycrystalline Co-based superalloys, grain boundary sliding is a primary failure mechanism during creep and fatigue testings. Addition of elements such as B and Zr which segregate to grain boundaries prevents grain boundary sliding and improves ductility [49, 50]. The enhancement is based from the cohesion provided by the ductile boride or zirconide formed at the grain boundary.

Similar to Ni-based superalloys, oxidation resistance in Co-based superalloys relies on formation of thin, dense and thermodynamically stable oxide films upon exposure to oxygen atmosphere. While the exact oxide layer formation mechanisms in Co-based superalloys are not fully understood, the effect of different elements in forming passivating oxide film have been studied. Yan *et al.* [51] show that the mass gain profile under oxidizing conditions follow the parabolic behavior with the following oxidation resistant trend: $10\text{Cr} > 20\text{Fe} > 1\text{Si} > 20\text{Ni} > 2\text{Ta} > \text{Co-Al-W} > 2\text{Mo} > 2\text{Ti} > 6\text{Ni-4V} > 2\text{V}$. Results suggest ≤ 10 at% of Cr is sufficient in forming a continuous oxide film. Furthermore, Yan and coworkers [4] showed that a high Co concentration causes a worsen oxidation resistance, indicating the weaker oxidation resistance of a Co-based system. Moreover, B addition which tends to segregate to grain boundary and surface results in an improved oxidation resistance due to an improved adhesion of surface oxide scale [52, 53].

1.3. Rafting in γ' -Strengthened Superalloys

One of the primary distinction between Ni- and Co-based superalloys that impacts both the microstructural evolution and mechanical properties is the difference in lattice misfit. Lattice misfit, δ , is characterized by the difference in lattice parameter between

the γ' -precipitates and γ -matrix:

$$(1.2) \quad \delta = \frac{2(a_{\gamma'} - a_{\gamma})}{a_{\gamma'} + a_{\gamma}}$$

where $a_{\gamma'}$ and a_{γ} are the lattice parameter of the γ' - and γ -phase, respectively. The magnitude of lattice misfit influences the microstructural properties such as γ' particle size and morphology. For an alloy that exhibits a large magnitude of lattice misfit, *i.e.*, $|\delta| > 0.2\%$, γ' -precipitates typically display a cuboidal morphology. With increasing magnitude of lattice misfit showing a more cuboidal γ' -morphology with a larger $\{100\}$ facet and sharper $\{110\}$ edges and $\{111\}$ corners. As the magnitude of lattice misfit decreases, *i.e.*, $|\delta| < 0.2\%$, the precipitates transition toward a spherical morphology.

Co-based superalloys primarily exhibit a positive misfit ($a_{\gamma'} > a_{\gamma}$) [2, 26, 37, 38, 54], while Ni-based superalloys often show a negative misfit ($a_{\gamma'} < a_{\gamma}$) [18]. The difference in lattice misfit amounts to different elevated temperature stress induced directional coarsening (rafting) behavior during creep as shown in Figure 1.9. In a positive misfit superalloy, γ' rafts perpendicular to the applied compressive stress axis and parallel to the applied tensile axis, forming n-type and p-type rafted microstructures, respectively. On the other hand, the rafting direction is reversed in a negative misfit superalloy, where p-type rafts form under compression and n-type rafts form under tension. The difference in rafting direction leads to a different microstructural evolution pathway, hence a different mechanical properties between Ni- and Co-based superalloys.

During rafting, the creep resistance of a superalloy is impacted by the ability for γ' -rafts to impede dislocation motion. In general, the creep behavior can be categorized into two separate mechanisms: low temperature high stress (LTHS) and high temperature low

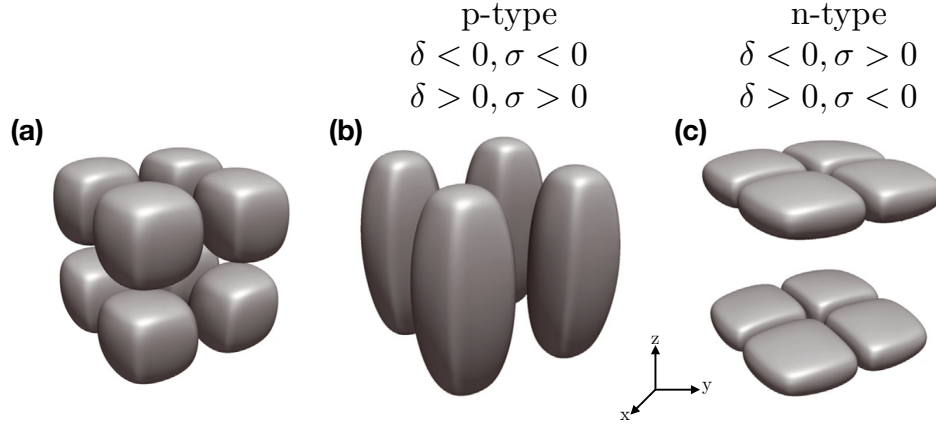


Figure 1.9. (a) Simulated morphology of γ' -precipitate under stress-free condition. Simulated morphology of (b) p-type and (c) n-type rafted γ' -precipitates that occur when tensile or compressive stress is applied along z-axis [9].

stress (HTLS) [10, 18, 55]. Under LTHS, the dominant creep deformation mechanism is via dislocation shearing of γ' -phase; whereas in HTLS, dislocation motion is primarily restricted within γ -matrix since the applied stress is insufficient for dislocations to cut through the stiffer γ' -phase. At LTHS, a rafted microstructure provides a lower creep resistance since dislocation can directly cut through the elongated γ' -rafts. In HTLS, the rafted γ' leads to a lengthen γ - γ' interfaces. This increases the dislocation glide/climb distance needed to circumvent the precipitates, thus enhances the creep resistance. However, as microstructure continues to evolve during creep, the mechanical properties will deteriorate from an extensively rafted microstructure under a prolong creep condition. The non-uniform γ' -morphology and spatial distribution will negatively impact the creep resistance. Therefore, rafting is generally considered as an unavoidable microstructural evolution that negatively impact the mechanical properties of a superalloy.

1.4. Present Research

The effect of Cr on microstructural stability, coarsening-, oxidation- and creep-resistance was first investigated in multicomponent Co-based superalloys that are designed via CALPHAD approach (Chapter 2 and Ch 3). Addition of Cr is facilitated by the the need for an improved oxidation resistance. Through Cr alloying, it was found that Cr progressively alters lattice misfit and, unlike existing studies in the literature, poses minimal impact on the creep resistance. An in-depth study on the influence of lattice misfit on both the creep resistance and rafting behavior was conducted, where the lattice misfit is adjusted by adding 0, 2, 4 and 6 at.% of Cr to a Co-Ni-Al-W-B alloy (Chapter 4). APT characterizations of both rafted and unrafted microstructure shed light to a potential diffusion mechanism that enables γ' -rafting. The influence of γ' -raft orientation on the macroscopic tensile creep resistance is assessed by pre-rafting a monocrystalline Co-based superalloy in both tension and compression to achieve p- and n-type rafts (Chapter 5). The contrasting creep behavior between the p- and n-type rafted microstructure provides opportunity for microstructural engineering to enhance the creep resistance in Co-based superalloys. Finally, to gain a more mechanistic understanding on the parameters and properties that influence γ' -morphology, phase field method was used to study γ' -morphology evolution under different conditions (Chapter 6). Simulation results show a qualitative agreement with the experimentally obtained rafted microstructure.

The effects of lattice misfit are extensive within Co-based superalloys, from mesoscale interaction along the γ - γ' interfaces to determining γ' -precipitate morphology to the stress-coarsening behavior, which all impact the bulk mechanical properties. This thesis

aims to correlate the influence of lattice misfit on multiple length-scale for both understanding the fundamental mechanisms that govern microstructural evolution and facilitate design of commercially viable Co-based superalloys with improved mechanical properties.

CHAPTER 2

Effects of Cr on the Properties of Multicomponent Cobalt-Based Superalloys with Ultra High γ' Volume Fraction

Chromium is known to confer oxidation resistance on Co-based superalloys. Herein we studied the influence of Cr concentration on the properties of a Co-based superalloy, Co-30Ni-11Al-2Ti-5.5W-2.5Ta-0.1B (at.%), with high γ' -volume fractions (up to 98%). Additions of 4, 8, or 12 at.% Cr decreased the γ' -solvus temperature and the γ' -volume fraction, while also reducing the mean radius of γ' -particles. Synchrotron X-ray diffraction and atom-probe tomography confirmed that Cr reduces the lattice parameter misfit by altering the partitioning behavior of W between the γ - and γ' -phases. Concomitantly, an increase in Cr content significantly improved the oxidation resistance of the alloy. The results indicate that 4 at.% Cr is sufficient to decrease the oxidation rate by two orders of magnitude. A creep study at 850 °C revealed that Cr does not affect adversely the creep performance in high γ' -volume fraction Co-based superalloys, but the tendency toward γ' rafting changes with Cr concentration. Compared to Ni₃Al intermetallic compounds, the materials with high γ' -volume fraction studied exhibited a significantly higher creep resistance. This may be attributed to the increase in antiphase boundary energy caused by the addition of Cr, Ti, or Ta, and significant solid-solution hardening in the Co-based intermetallic γ' -phase.

2.1. Introduction

Over the past decade, the need for more efficient aviation and power generation materials, has fueled a heightened interest in the development of Co-based superalloys consisting of a FCC matrix (γ) strengthened by $L1_2$ precipitates (γ'). These alloys, which are based on the Co-Al-W system, exhibit high solidus and liquidus temperatures, so that their maximum operating temperature may be higher than for Ni-based γ - γ' superalloys [16]. Nevertheless, several challenges need to be overcome before these γ' -strengthened Co-based superalloys can be employed commercially. The currently available Co-based superalloys exhibit a lower γ' -solvus temperature than Ni-based superalloys, which limits their mechanical and microstructural stability at high temperatures [6]. Members of the Co-Al-W system, are also susceptible to oxidation and corrosion when prepared without the presence of Cr, a strong oxidation-retarding element [51, 56, 57]. Moreover, Co-based superalloys currently exhibit a lower mechanical creep strength than Ni-based superalloys [26].

The necessity of adding chromium to all Co-based superalloys to improve their oxidation resistance, is generally accepted. However, Cr additions may affect different properties ranging from precipitate size to creep performance. Yan and Dye [24] reported that Cr alloying destabilizes the γ - γ' structure by forming topologically close-packed (TCP) phases, and the addition of Ni widens the γ - γ' phase field, thereby restoring the γ - γ' microstructure [25]. Chromium has been shown to partition strongly to the γ -matrix, although its effect on the γ' -solvus temperature and volume fraction is not fully understood. There is some evidence that Cr decreases the γ' -solvus temperature and also decreases the volume fraction [34, 35, 58], while others have shown that Cr increases the

γ' -volume fraction [36, 59]. Studies of the oxidation resistance of Cr containing Co-based superalloys have verified that increasing the concentration Cr results in reduced oxidation kinetics [25, 52]. Recently, Povstugar *et al.* [2] systematically studied the effect of increasing Cr concentration in Co-Al-W, and found that Cr decreases the lattice parameter misfit between the γ - and γ' -phases and increases the minimum strain rate during creep. Using a computational thermodynamic approach [41], the base alloy without Cr was designed to maximize the γ' -solvus temperature for a fixed Ti-content of 2 at.%. The high γ' -solvus temperature of the base alloy results in a very high γ' -volume fraction for the base and Cr-containing alloys at the aging and creep temperature. The smaller Ti concentration compared to other Co-based superalloys was intended to limit the detrimental effects of Ti on oxidation resistance and solidification, while providing an adequate degree of γ' -stability [25, 39].

Herein, we present a systematic study of the influence of Cr on a multinary Co-based superalloy in order to investigate the progressive effect of Cr on different superalloy properties. The Cr concentration was increased in 4% increments to 12 at.%, to assess the effect on microstructure, elemental partitioning, oxidation, and creep performance.

2.2. Experimental Methods

The initial alloy had a Cr-free composition of Co-30Ni-11Al-2Ti-5.5W-2.5Ta-0.1B (at.%), representing a Co-Al-W basis, with the addition of Ni to broaden the γ - γ' phase field, Ti and Ta to increase the γ' -solvus temperature, and B (in trace amounts) to strengthen the grain boundaries [49, 50, 60]. The computational thermodynamic approach reported previously [1, 41] was used to maximize the γ' -solvus temperature of the

Table 2.1. Nominal composition (at.%), with values in parentheses given in (wt.%) and phase transformation temperatures measured by DSC of the L24 series of Cr-containing high γ' -volume fraction Co-based superalloys. The composition of the alloys are measured using SEM-EDS in at.% to compare with the nominal composition.

Alloy	Co	Ni	Al	Ti	W	Ta	B	Cr	γ' -solvus ($^{\circ}$ C)	γ -solidus ($^{\circ}$ C)	γ -liquidus ($^{\circ}$ C)
0Cr	48.9 (44.3)	30 (27.1)	11 (4.6)	2 (1.5)	5.5 (15.6)	2.5 (6.7)	0.1 (0.02)	0 (0)	1225	1337	1399
EDS	48.3	29.0	12.1	2.24	5.8	2.66	-	0			
4Cr	45.7 (41.8)	30 (27.3)	10.9 (4.4)	1.92 (1.4)	5.3 (15.1)	2.4 (6.7)	0.1 (0.02)	4 (3.2)	1188	1318	1390
EDS	45.6	29.2	11.1	2.04	5.68	2.28	-	4.1			
8Cr	42.5 (39.2)	30 (27.5)	10.1 (4.3)	1.85 (1.4)	5.1 (14.6)	2.3 (6.5)	0.1 (0.02)	8 (6.5)	1152	1308	1380
EDS	42.3	29.5	10.5	1.85	5.14	2.69	-	8.02			
12Cr	39.3 (36.5)	30 (27.7)	9.7 (4.1)	1.77 (1.3)	4.9 (14.1)	2.2 (6.3)	0.1 (0.02)	12 (9.8)	1118	1299	1368
EDS	39.3	28.9	10.1	1.86	5.09	2.3	-	12.5			

base alloy, termed L24-0Cr. This base alloy was modified by the addition of 4, 8, or 12 at.% Cr to obtain L24-4Cr, -8Cr, and -12Cr, alloys, respectively. For a given amount of Cr, the concentration of Co was reduced by 4/5 and the concentrations of Al, Ti, W and Ta by 1/5, to maintain a constant γ' -volume fraction. The characteristics of each alloy are described in Table 2.1. The composition distribution ratio was based on the Cr partitioning coefficient, $\kappa_{\text{Cr}} \approx 0.25$, where approximately 80% of the Cr partitions to the γ -matrix and 20% to the γ' -phase [24, 61]. The Ni concentration was maintained at 30 at.% to maintain a wide γ' -phase-field and to minimize the formation of the topologically close-packed (TCP) phases expected after addition of Cr [6]. Table 1 also presents the γ' -solvus, γ -solidus, and γ -liquidus temperatures of the four alloys. All three parameters decreased with increasing Cr content, to yield slopes of 8.4, 3.4, and 1.8 $^{\circ}\text{C}/\text{at.}\%$ Cr, respectively (Fig. 2.10).

The alloys were prepared from pure metals (99.9+% purity) by arc-melting under an argon atmosphere and each ingot (≈ 50 g) was remelted eight times to ensure homogeneity. The material was then homogenized at 1250 °C for 48 h in sealed argon-backfilled quartz tubes, followed by furnace cooling. Aging was performed at 900, 1000, and 1100 °C in evacuated and sealed quartz tubes for 24, 168, and 1000 h, which was terminated by water quenching to room temperature. The liquidus, solidus and γ' -solvus temperatures were measured using as-homogenized samples under a flowing Ar atmosphere (20 mL/min) employing differential scanning calorimetry (DSC) (Netzsch 404c), with a 10 K/min heating and cooling rate. DSC results were analyzed following the guideline provided by National Institute of Standard and Technology [62] where the liquidus, solidus and γ' -solvus temperatures are determined from the first visible onset of phase transformation in the heating curve.

An Hitachi SU8030 scanning electron microscope (SEM) equipped with a cold-field-emission source was used for microstructural characterization and energy dispersive spectroscopy (EDS). An operating voltage of 25 kV and a 15 mm working distance were utilized. X-ray Diffraction (XRD) for phase identification was performed employing a Cu source X-ray diffractometer (XDS 2000, Scintag Inc). Each sample was scanned from $2\theta = 30^\circ$ to 100° with a step size of 0.05° and a dwell time of 2 s per step. Room-temperature lattice parameter misfit measurements were performed using the 5ID beam line of the Advanced Photon Source (Argonne National Laboratory, IL, USA). Due to the coarse grains produced by arc-melting, only the most intense γ - γ' peaks were used for peak deconvolution and misfit calculations. Phase identification and lattice misfit were both measured on samples heat treated at 900 °C for 168 h.

Isothermal oxidation tests were performed using thermal gravimetric analysis (TGA/SDTA851, Mettler Toledo) with a ground cylindrical specimen, 4 mm in diameter and 3 mm in height, aged at 900 °C for 168 h. Specimens were placed in an alumina crucible to prevent spallation. Dry air was supplied at 50 mL/min for 20 h at 900 °C and the resulting mass change was calibrated using a reference alumina crucible.

Atom-probe tomography (APT) specimens were prepared using an FEI Helios Nanolab microscope equipped with focused ion-beam (FIB) capability (FEI Helios Nanolab 600 dual-beam FIB/SEM) [63]. APT of L24-0Cr, -4Cr and -8Cr aged at 900 °C for 168 h were performed using a local-electrode atom-probe tomograph (CAMECA 4000X-Si) with a pulse laser energy of 30 pJ, pulse frequency of 200 kHz, temperature of 25 K, and a maximum evaporation rate of 5% [1] using a picosecond laser (355 nm wavelength). APT data were analyzed using the IVAS software package, version number 3.6, from CAMECA Instruments Inc [64, 65, 66, 67, 68, 69].

Cylindrical samples with a 5 mm diameter and a 10 mm height were prepared by electro-discharge machining from samples aged at 900 °C for 168 h. Each sample was placed between boron-nitride-lubricated silicon carbide platens and heated without an applied load to the creep temperature of 850 ± 2 °C. For each stress, the applied load was held constant until a minimum strain rate was observed to be two orders of magnitude larger than the sampling error. Sample displacements were measured using a linear variable displacement transducer with a resolution of 10 μm . A test was terminated at the onset of tertiary creep, typically below 8% strain.

2.3. Results and Discussion

2.3.1. Microstructure

Fig. 2.1 displays the microstructure of the four alloys with Cr concentrations ranging from 0 to 12 at.%, aged at 900 °C for 168 h. The Cr-free alloy displayed a γ - γ' microstructure with a high volume fraction of cuboidal γ' -precipitates. As the Cr concentration increases, the γ' -precipitate morphology transitions from cuboidal with sharp corners to rounded corners. Concomitantly, the increase in Cr, results in a decrease in the γ' -volume fraction, which in turn is correlated with a decrease in the γ' -solvus temperature (Figs. 2.10 and 2.11). In addition, an increase in Cr caused a decrease in the size of γ' , with the γ' edge length decreasing by approximately an order of magnitude; from 2 μm in L24-0Cr to 200 nm in L24-12Cr. This decrease in size also affects their appearance. While, both the γ - and γ' -phases appear highly aggregated and percolating in L24-0Cr and -4Cr, the degree of γ' -percolation decreases with a decrease in the γ' -volume fraction. This is also observed in alloys, such as Co-9Al-8W (at.%) with a 64% volume fraction of the γ' -phase [70] and in L24-8Cr and -12Cr, where fewer γ' -precipitates coalesce into aggregates.

Chromium additions are known to destabilize the γ - γ' microstructure in both Ni- and Co-based superalloys by facilitating the formation of TCP phases [18, 25]. The effect becomes more pronounced in high γ' -volume fraction alloys because they have a smaller γ -volume to accommodate Cr in solid-solution. Figs. 2.1c) and 2.1d) demonstrate that the addition of Cr at 8 and 12 at.% results in the formation of the μ -phase (Co_7W_6). In L24-8Cr, the μ -phase was only observed along grain boundaries as discrete precipitates with an irregular morphology, Fig. 2.1c). In contrast, in L24-12Cr, the μ -phase is observed

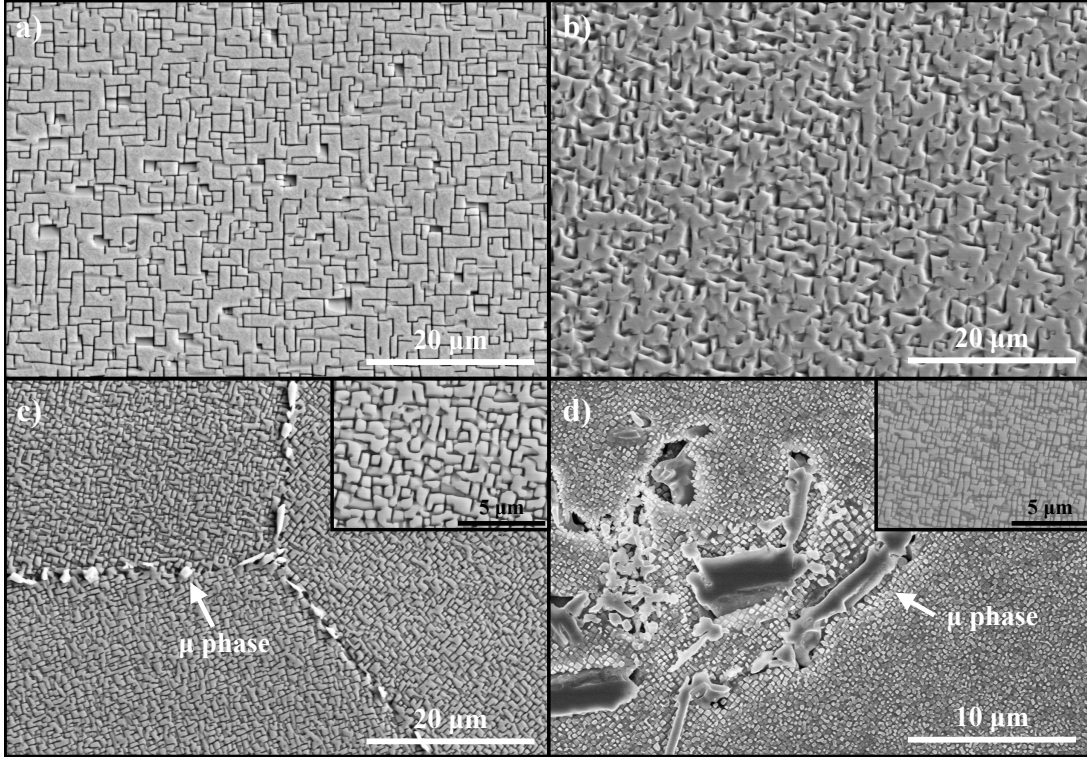


Figure 2.1. Microstructure of a) L24-0Cr, b) -4Cr, c) -8Cr and d) -12Cr aged at 900 °C for 168 h. In, L24-8Cr, the μ -phase precipitates can be seen around the grain boundaries, while in L24-12Cr, the μ -phase appears throughout the microstructure. Insets of c) and d) illustrate the morphologies of the γ' -precipitates.

throughout the microstructure as rods, 20 to 50 μm in length, at approximately 3% volume fraction. The μ -phase, with a binary composition of Co_7W_6 , was first identified by measuring the elemental ratio in the precipitates, where the $(\text{Co} + \text{Ni}):(\text{W} + \text{Cr})$ ratio correlates closely to the $\text{Co}:\text{W}$ atomic ratio in binary Co_7W_6 . The phase, identified as $(\text{Co},\text{Ni})_7(\text{W},\text{Cr})_6$, was further verified using XRD, Fig. 2.2. In L24-0Cr and -4Cr, the diffraction peaks correspond to the γ - and γ' -phases, whereas multiple μ -phase diffraction peaks were identified in L24-8Cr and L24-12Cr. Due to the coarse grains resulting from

arc-melting, peak intensities vary among samples and the unidentified peak in L24-4Cr may represent a surface oxide.

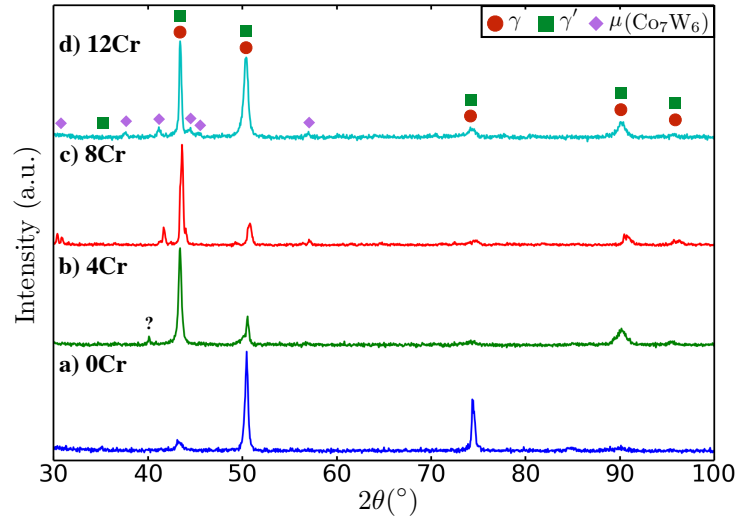


Figure 2.2. X-ray diffraction pattern displaying γ - and γ' -peaks for: a) L24-0Cr, b) -4Cr, c) -8Cr, and d) -12 Cr aged at 900 °C for 168 h. Peaks for the μ -phase are observed in both L24-8Cr and -12Cr.

Klob *et al.* [60] reported that the solubility of B in a Co-Al-W ternary system is less than 0.04 at.%, so that the addition of boron beyond the solubility limit segregates at grain boundaries forming tungsten boride [50, 60]. The alloys described herein all include 0.1 at.% of B for grain-boundary cohesion. Interestingly, no boride was observed in the grain boundary microstructure. Their absence may be due to increased B solubility in both the γ - and γ' -phases, produced as a result of alloying with additional elements, such as Ti, Ta, and Cr.

2.3.2. Lattice Misfit

Lattice misfit, δ , which affect the γ' -particle size and strength in superalloys [11, 71], is defined as:

$$(2.1) \quad \delta = \frac{2(a_{\gamma'} - a_{\gamma})}{a_{\gamma'} + a_{\gamma}}$$

where $a_{\gamma'}$ and a_{γ} are the lattice parameter of the γ' - and γ -phase, respectively. In high γ' -volume fraction superalloys, the mechanical properties may be significantly influenced by the internal misfit strain in the narrow γ -channels [72]. Furthermore, the narrow γ -channels may result in a higher dislocation density and a more localized stress upon loading.

Fig. 2.3 displays the room temperature lattice misfit in L24-0Cr, -4Cr, -8Cr, and -12Cr. The lattice parameter misfit decreases from 0.64% in L24-0Cr to 0.20% in L24-12Cr. The measured misfit in L24-0Cr is smaller than the room-temperature misfit (0.78%) for the ternary Co-9Al-9W ternary system [73]. Chromium, which partitions preferentially to the γ -matrix, is also present in the γ' -phase where it displaces W to the γ -matrix. Povstugar *et al.* [2] reported that Cr decreases $a_{\gamma'}$, while increasing a_{γ} due to W being displaced from the γ' -to the γ -phase. A trend consistent with these observation is observed with a decrease in $a_{\gamma'}$, and an increase in a_{γ} (and thus an overall decrease in lattice parameter misfit) from L24-0Cr to L24-4Cr. However, due to the formation of a W-rich μ -phase in the γ -matrix, a further increase in the Cr concentration depletes W from both the γ - and γ' -phases, resulting in decrease in both $a_{\gamma'}$ and a_{γ} [74]. The reduction in a_{γ} and $a_{\gamma'}$ is more pronounced between L24-8Cr and L24-12Cr than between L24-4Cr and L24-8Cr due

to the larger volume fraction of the μ -phase, which is formed in alloys with a higher Cr concentration. The increase in the μ -phase in L24-12Cr means that more W is removed from the γ - and γ' -phases, leading to a larger decrease in both $a_{\gamma'}$ and a_{γ} .

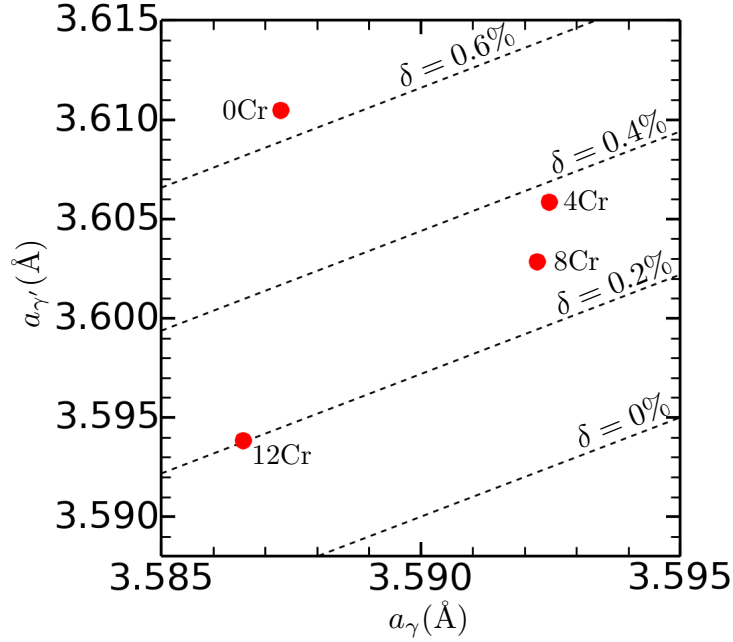


Figure 2.3. Lattice parameters and lattice parameter misfits between the γ - and γ' -phases measured employing high-energy synchrotron X-ray diffraction.

2.3.3. Elemental Partitioning

The L24-0Cr, -4Cr and -8Cr alloys were analyzed by atom-probe tomography (APT). Fig. 2.4 shows the reconstruction and proximity histogram across γ - γ' interfaces. The γ - γ' interfaces are highlighted by isoconcentration surfaces of Co at 56, 50 and 47 at.% for L24-0Cr, -4Cr and -8Cr, respectively. The γ -channels in both L24-0Cr and -4Cr are less than 5 nm thick as a result of the high γ' -volume fraction. The decrease in the γ' volume fraction results in a wider γ -channel (≥ 10 nm) in L24-8Cr.

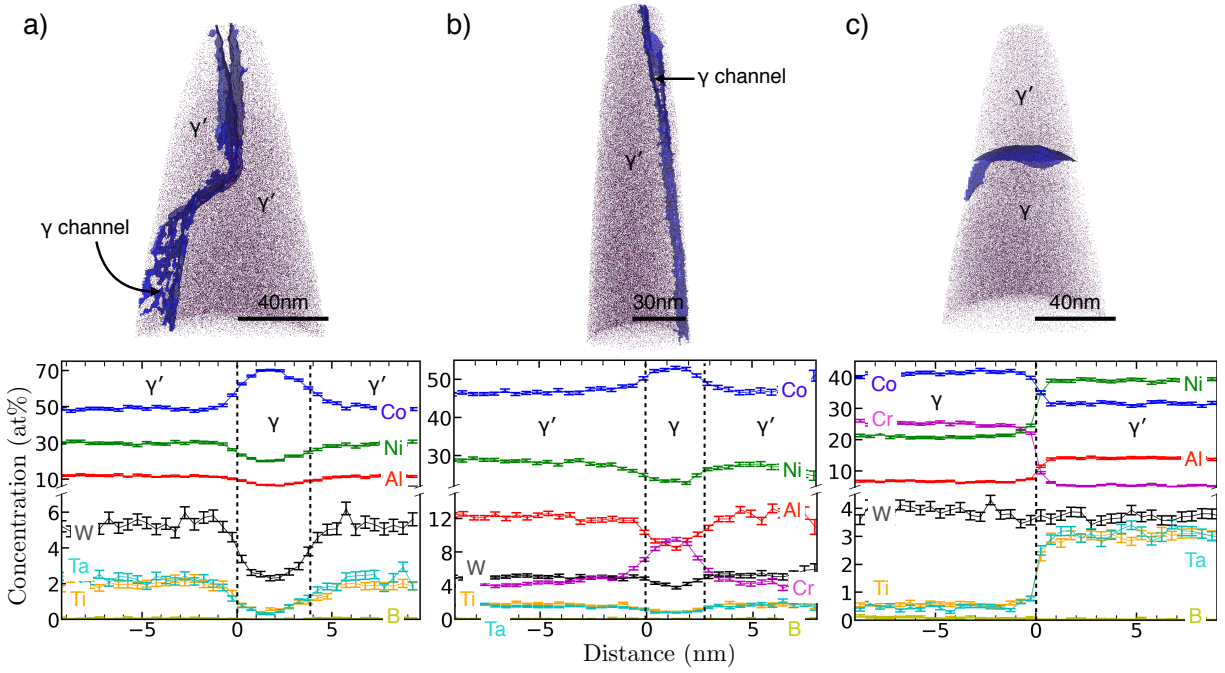


Figure 2.4. APT reconstruction and elemental proximity histogram of: a) L24-0Cr, b) -4Cr, and c) -8Cr heat treated for 24 h at 900 °C.

The partitioning behavior of each element can be clearly seen from the proximity histograms [75, 76]: (i) Co and Cr partition toward the γ -matrix and (ii) Ni, Al, W and Ta partition to the γ' phase [28, 31, 39, 77]. The elemental partitioning is described by the partitioning coefficients:

$$(2.2) \quad \kappa_i = \frac{C_i^{\gamma'}}{C_i^{\gamma}}$$

where $C_i^{\gamma'}$ is the concentration of element i in γ' and C_i^{γ} is the concentration in the γ -phase. Table 2.2 displays the nanotip composition, elemental concentration in both phases, partitioning coefficients κ for each element, and the γ' -volume fraction derived from the lever rule based on the nanotip composition and stereological analyses [78].

The larger reduction of the γ' -volume fraction in L24-8Cr indicated by the APT analysis is probably due to local inhomogeneities, since stereological analysis demonstrated that L24-8Cr exhibits 83% of γ' (see Fig. 2.11).

As shown in Table 2.2, the APT measured tip composition does not wholly agree with the EDS-measured composition. This discrepancy may arise from spatial inhomogeneity between the bulk sample and the miniscule tip volume. The composition of B was shown to be approximately 0.04 at.% with majority partitions toward the γ' phase in L24-0Cr and -4Cr while the partitioning was reversed in L24-8Cr. The remaining B probably segregates to the grain boundaries [49, 50, 52, 60]. The switch in partitioning behavior of B may be induced by the addition of Cr or may be caused by the spatial inhomogeneity in the sample or lack of a sufficient number of B atoms in the miniscule tip. While B-solubility changes with Cr content, no grain boundary boride formation was observed in the sampled alloys suggesting that the increase in γ' -volume-fraction compared to ternary Co-Al-W system [60] may result in a lower degree of B segregation at grain boundaries.

In L24-8Cr, Ni has supplanted Co to become the major component within the $L1_2$ structure in the γ' -phase. As the Cr concentration increases, an analysis of the composition distribution of the alloys reveals a dramatic decrease in the Co content. In this context, the majority element switches from Co=30.9% to Ni=40.4% in the γ' -phase of L24-8Cr. The formation of $(\text{Ni,Co})_3(\text{Al,W,Ti,Ta})$ may be explained by an increase in the γ -volume fraction in L24-8Cr, allowing more Co to be accommodated in the γ -phase.

Fig. 2.5 displays the evolution of κ as a function of Cr concentration. As the Cr content increases, the partitioning trend for most γ' -forming elements remain relatively constant. In the case, however, of Al, Ti, and Ni, an increase in the concentration of

Table 2.2. Composition of γ - and γ' -phases, γ'/γ partitioning coefficient κ , lever-rule and stereologically derived γ' -volume fraction of L24-0Cr, -4Cr and -8Cr.

		Composition (at.%)								$\phi_{\gamma'}\text{-lever (\%)}$	$\phi_{\gamma'}\text{-stereological (\%)}$
		Co	Ni	Al	W	Cr	Ti	Ta	B		
0Cr	nanotip	54.5	27.5	11.6	2.90	-	1.77	1.40	0.04	98 $\pm$ 1.3	90 $\pm$ 0.7
	γ	70.0	20.5	6.80	1.49	-	0.52	0.35	0.02		
	γ'	50.5	28.4	13.4	3.60	-	2.39	1.64	0.04		
	κ	0.72	1.39	1.97	2.42	-	4.58	4.69	2.88		
4Cr	nanotip	55.2	31.5	14.7	3.60	6.50	2.00	1.20	0.04	98 $\pm$ 1.8	86 $\pm$ 3.1
	γ	58.4	18.3	6.2	1.70	15.0	0.39	0.82	0.02		
	γ'	46.5	29.0	13.6	3.39	4.46	1.92	1.49	0.04		
	κ	0.80	1.59	2.19	1.99	0.30	4.89	1.88	1.56		
8Cr	nanotip	41.2	33.9	11.6	2.88	18.6	1.88	1.45	0.06	59 $\pm$ 12	83 $\pm$ 0.4
	γ	42.2	21.4	6.31	2.56	26.5	0.58	0.36	0.08		
	γ'	30.9	40.4	15.0	2.62	5.72	2.93	2.36	0.03		
	κ	0.73	1.89	2.37	1.02	0.22	5.09	6.63	0.38		

Cr concentration results in a strong degree of partitioning toward the γ' -phase, probably because Cr partitions primarily toward the γ -phase. The elements Ta and B do not follow the same trends as other γ' -forming elements. Tantalum partitions strongly towards the γ' -phase in L24-0Cr and -8Cr, although the partitioning was reduced in L24-4Cr. The peculiar partitioning behavior of Ta may be attributed to the very narrow γ -channels in L24-0Cr and L24-4Cr in which low concentration components such as Ta and B may be influenced by the interdiffusion between the two phases in the narrow γ -channels. The proximity histogram shows that the widths of the γ -channels are 4 and 3 nm for L24-0Cr and L24-4Cr, respectively. The γ - γ' interface is diffusive with an interfacial width of 3-5 nm [28, 79]. The narrow γ -channels may also be not representative of the bulk partitioning behavior, where diffusion fields between neighboring γ' -precipitates do not overlap. The opposite partitioning trends for Ta may also be a result of precipitation of the μ -phase, which affects the γ - γ' phase equilibrium.

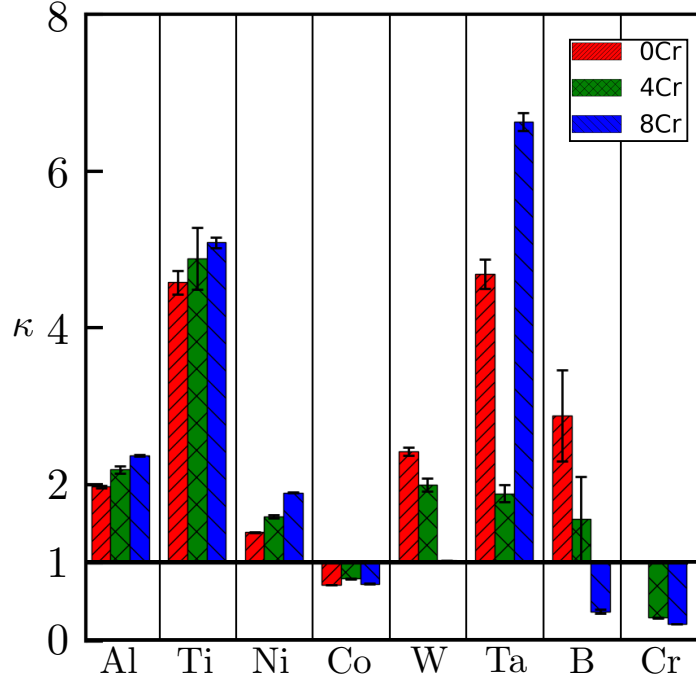


Figure 2.5. Plot of elemental partitioning coefficient, κ , of L24-0Cr, -4Cr and -8Cr.

Tungsten, unlike other elements, becomes increasingly equipartitioned between the γ - and γ' -phases upon addition of Cr. In the absence of Cr, W partitions strongly to the γ' -phase with $\kappa_W = 2.42$. In contrast, in L24-8Cr, W shifts toward equipartitioning with $\kappa_W = 1.02$. This change in partitioning behavior is probably due to the preferential displacement of W by Cr in the $L1_2$ structure. Povstugar *et al.* [2] showed that κ_W decreases from $\kappa_W = 2.3$ in the Co-Al-W ternary system to $\kappa_W = 1.5$ in a quaternary composition (Co-Al-W-8Cr). In the present study, the partitioning tendency of W was even further reduced. The equipartitioning of W in L24-8Cr is probably due to the competition of additional γ' -forming elements, such as Ta and Ti for W lattice sites in the $\text{Co}_3(\text{Al}, \text{W}) L1_2$ lattice structure. Precipitation of the W-rich μ -phase in L24-8Cr may result in additional

W accommodating capacity in the γ -matrix, further shifting W partitioning from the γ' to the γ -phase. A similar partitioning reversal behavior has been observed in Ni-based superalloys where Ta preferentially displaces W from the γ' -phase into the γ -phase [80]. In addition, it is also possible that the increased Ni to γ' forming elements ratio, *i.e.*, Al, W, Ti and Ta, promotes formation of $(\text{Ni,Co})_3(\text{Al,W,Ti,Ta})$, leading to a lower partitioning coefficient of W between γ -and γ' -phases.

2.3.4. Oxidation

Fig. 2.6 shows the surface oxide structure and the corresponding elemental distribution. Oxidation damaged surface layers are typically composed of an outermost oxide scale, followed by an oxide intrusion zone, and a deeper γ' -depletion zone [4]. The oxidation resistance of an alloy is characterized by the cohesion and oxygen-ion impedance of the oxide scale [81]. The surface oxide structure of L24-0Cr after 20 h of 900 °C isothermal oxidation is displayed in Fig. 2.6a), where the outermost oxide scale is composed primarily of CoO and NiO. Based on their porous nature and high-oxygen ion-diffusivities, these oxides can not prevent further oxidation [82]. The oxide intrusion zone for L24-0Cr is composed mainly of Al_2O_3 with Ti and W impurities. It is known that the oxidation resistance of the Al_2O_3 layer diminishes when doped with Ti due to the vacancies introduced by Ti ions [83]. Additionally, the sluggish formation kinetics of Al_2O_3 may result in the formation of less oxidation resistant Al_2O_3 allotropes, *e.g.*, $\gamma\text{-Al}_2\text{O}_3$ instead of the thermodynamically stable $\alpha\text{-Al}_2\text{O}_3$ [82]. Following the oxide intrusion zone, there is a thin layer of a Ni-rich γ' -depletion zone. Nickel enrichment is likely a consequence of the

rejection of Ni from the oxide intrusion layer. Constituents such as W and Ta contribute less to the formation of surface oxides due to their smaller mobilities.

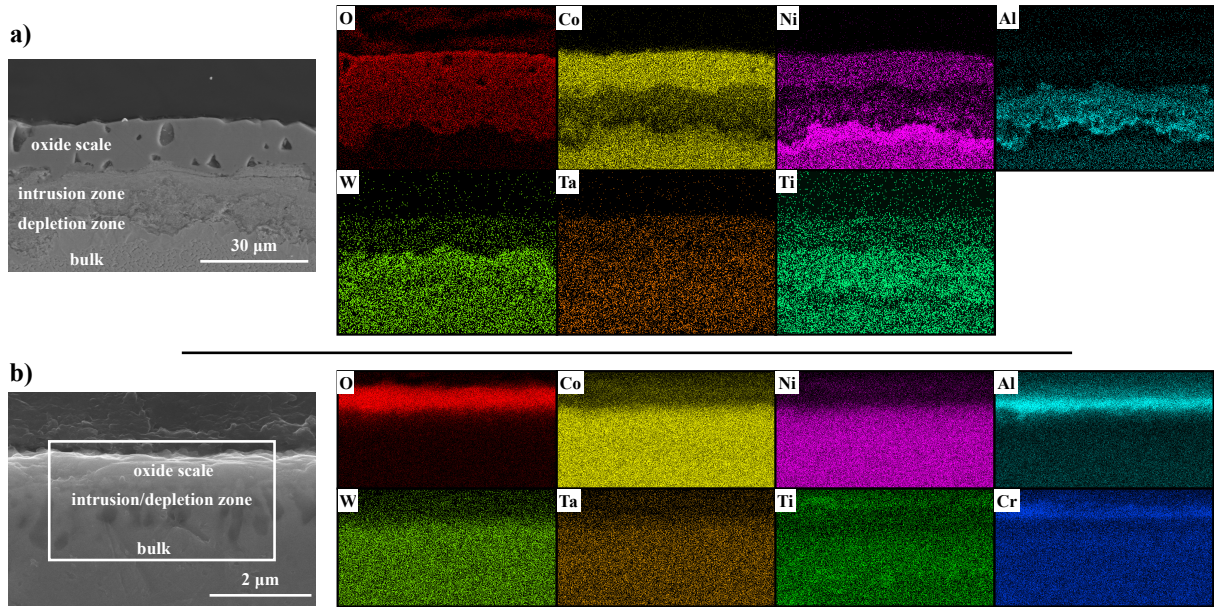


Figure 2.6. Oxide structure and elemental distribution of a) L24-0Cr and b) -12Cr measured by SEM-EDS after 20 h at 900 °C to permit isothermal oxidation.

Fig. 2.6b) and 2.13 shows the surface oxide structure of L24-12Cr. In contrast to L24-0Cr, L24-12Cr exhibits a thinner oxide scale and an oxide intrusion zone. In fact, the thickness of the oxide layer is an order of magnitude smaller than that observed in L24-0Cr. The oxide scale of L24-12Cr contains a layer of Cr_2O_3 followed by Al_2O_3 . Both these oxides are highly passivating, hence the thinner oxide scale. Due to the protective oxide scale formed on the surface, the adjacent oxide intrusion zone and depletion zone are also thin with no significant CoO or NiO. Like 0Cr, neither W or Ta contribute to the formation of a surface oxide. Fig. 2.14 presents the surface oxide structure and elemental

distribution of L24-4Cr and L24-8Cr. With an increase in Cr content, the surface oxide becomes progressively thinner and more Cr_2O_3 is formed.

For most alloys, steady state oxidation follows a parabolic growth behavior [84]:

$$(2.3) \quad (\Delta m)^2 = kt$$

where Δm is the oxidation mass gain, k is the parabolic rate constant and t is the time. Transient oxidation was observed for the first 5 h of isothermal oxidation, followed by steady state parabolic growth (see Fig. 2.15). Fig. 2.7 displays the the oxide scale thickness and the parabolic rate constant k as a function of Cr concentration. The results indicate that 4 at.% of Cr lowers k by two orders of magnitude as compared to L24-0Cr. Increasing the Cr concentration to 12 at.% resulted in a further order of magnitude reduction in k . The oxide scale thicknesses measured from cross-sectional SEM correlates closely with k indicating that with increasing Cr concentration, a thinner oxide scale is sufficient to form an oxidation resistant surface. A higher Cr concentration facilitates the formation of Cr_2O_3 and Al_2O_3 , which exhibit a low oxygen ion diffusivity, effectively passivating the alloy surface and preventing further oxygen ion diffusion into the bulk [26, 51, 52].

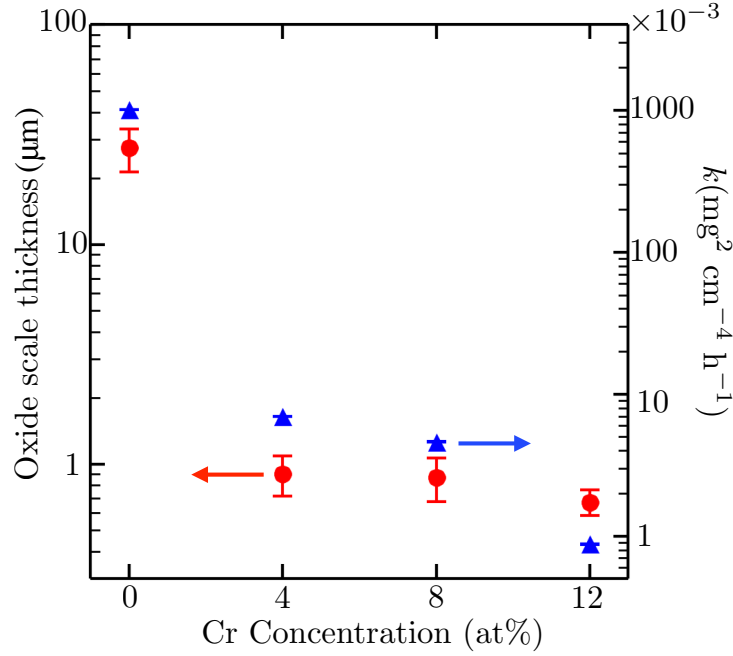


Figure 2.7. Oxide scale thickness and parabolic rate constant, k , as a function of Cr concentration. The oxidation tests were performed at 900 °C for 20 h.

2.3.5. Creep

Fig. 2.8 displays a double-logarithmic plot of the minimum creep strain-rate vs. applied compressive stress for L24-0Cr, -4Cr, and -8Cr. The data were fitted using the Mukherjee-Bird-Dorn power-law equation

$$(2.4) \quad \dot{\epsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right)$$

where $\dot{\epsilon}$ is the steady state strain rate, A is a constant, σ is the applied stress, n is the stress exponent, Q is the activation energy, R is the gas constant and T is the absolute temperature. Fig. 2.8 demonstrates the effect of Cr on creep resistance. Increasing the Cr

concentration increases the stress exponent from $n = 3.2$ to 9.5 and to 11.6 in L24-0Cr, -4Cr and -8Cr, respectively, suggesting that the addition of Cr is associated with a change in the deformation mechanism. The relative strength also increased moderately with increasing Cr concentration, where L24-8Cr was more creep resistant than L24-0Cr in the tested stress range. Given the very high γ' -volume fraction, the samples show cracking along the grain boundaries and tertiary creep was initiated after 8% accumulated strain (see Fig. 2.16 for strain *vs.* time plots of each sample).

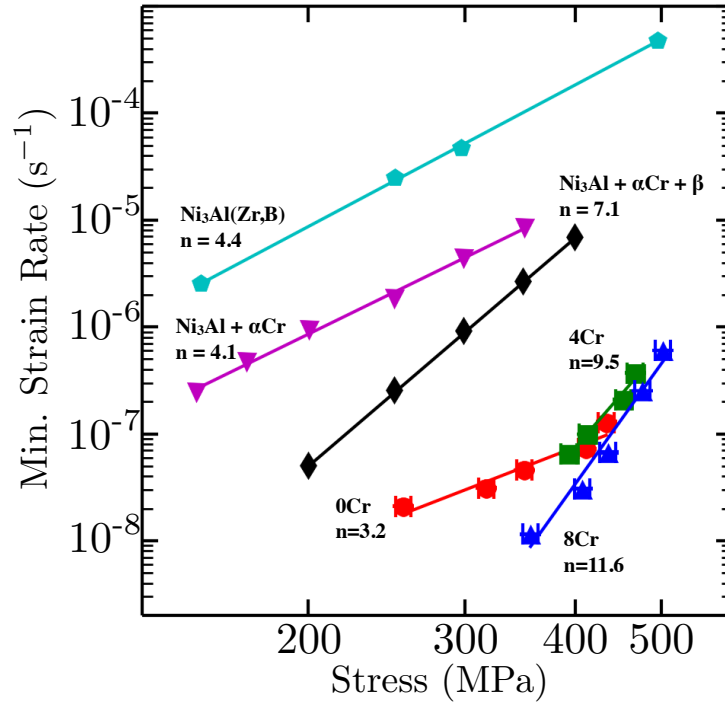


Figure 2.8. Norton plot of L24-0Cr, -4Cr and -8Cr subjected to compression creep at 850 °C. The stress exponents, n , are derived from the Mukherjee-Bird-Dorn power law creep model.

Povstugar *et al.* [2] showed that Cr is detrimental to creep performance in Co-9Al-9W-xCr alloys, and reported a two order of magnitude increase in the steady-state strain-rate

when the Cr concentration was increased from 0 to 8 at.%. The diminishing effect of Cr can be attributed to a reduction in the lattice parameter misfit. While a similar reduction in misfit can be observed from L24-0Cr to L24-8Cr, which did not result in a significant change in the strain rate in the alloys studied herein. The discrepancy between these results is probably due to the γ' -volume fraction difference in the two studies. The alloys studied by Povstugar *et al.* exhibited γ' -volume fractions ranging from 38 to 64%, while the materials L24-0Cr to -8Cr described herein, contain up to 98% of the γ' -phase. Our current results suggest that the effect of lattice parameter misfit reduction on creep properties may be diminished as the γ' -volume fraction increases and percolates through the microstructure. Moreover, as the microstructural evolution during the creep was not presented by Povstugar *et al.*, it is plausible that the increase in strain rate caused by their Cr addition was a consequence of changes in the microstructure after creep, *e.g.*, rafting or decomposition of γ' due to a lack of Ni to serve as a γ' -stabilizing element.

Fig. 2.8 further compares the L24-Cr alloy series, which is very close to pure γ' (albeit with a highly alloyed composition) with the intermetallic polycrystalline γ' -Ni₃Al containing trace amounts of Zr and B added to enhance the grain-boundary ductility (Ni-21.7Al-0.3Zr-0.1B at.%) [85]. An additional comparison was made with α -Cr precipitation-strengthened (Ni-20.2Al-8.2Cr-2.44Fe at.%) [86] and multiphase-strengthened (Ni-21.9Al-8.1Cr-4.2Ta-0.9Mo-0.3Zr at.%) [87] Ni₃Al based alloys. To the best of our knowledge, no creep studies on a pure γ' Co-rich intermetallic have been reported in the literature. The results of the comparison revealed that Ni₃Al intermetallic compounds are significantly weaker than their Co counterparts, with the steady-state strain-rate up to three orders of magnitude higher. While Co₃(Al,W) was demonstrably weaker than Ni₃Al [88, 89],

the increase in creep strength in the Co-based superalloys studied herein may be attributed to an increase in anti-phase boundary energy resulting from the addition of Cr, Ti, and Ta, and the large extent of solid-solution strengthening [90]. A comparison among Ni_3Al compounds revealed that precipitate hardening may improve the creep properties of Ni_3Al , since the addition of elements such as Fe achieve the same creep resistance as seen in the heavily alloyed high γ' -volume fraction Co-based superalloys.

Directional coarsening of γ' -precipitates during mechanical creep, commonly referred to as rafting [91, 92, 93], is observed in the post-creep microstructure of L24-0Cr, as displayed in Fig. 2.9. Unlike their Ni counterparts, cobalt-based superalloys exhibit a positive lattice parameter misfit. Under compression, the γ' -phase undergoes n-type rafting where the precipitates coarsen perpendicular to the applied stress axis. Figs. 2.9a) and 2.9b) show the post-creep microstructure of L24-0Cr. No rafting was detected in the plane perpendicular to the applied load. In contrast, rafting could be seen in the plane parallel to the applied load, where the γ' -precipitates coarsen and coalesce along the $\langle 100 \rangle$ crystal direction. Due to the polycrystallinity of the samples, rafting behavior varies among grains (Fig. 2.17). The variation in grain-to-grain crystallography orientation and inter-grain load transfer results in multiple rafting directions. Under certain conditions, misalignment with the load axis may prevent certain grains from undergoing rafting [9, 18].

Figs. 2.9c) and 2.9d) show the post-creep microstructure of L24-4Cr, which is single-phase γ' . From the original γ' -volume fraction of 98% created during aging at 900 °C, the remaining γ -matrix transforms into γ' -phase upon creep at 850 °C. The trace

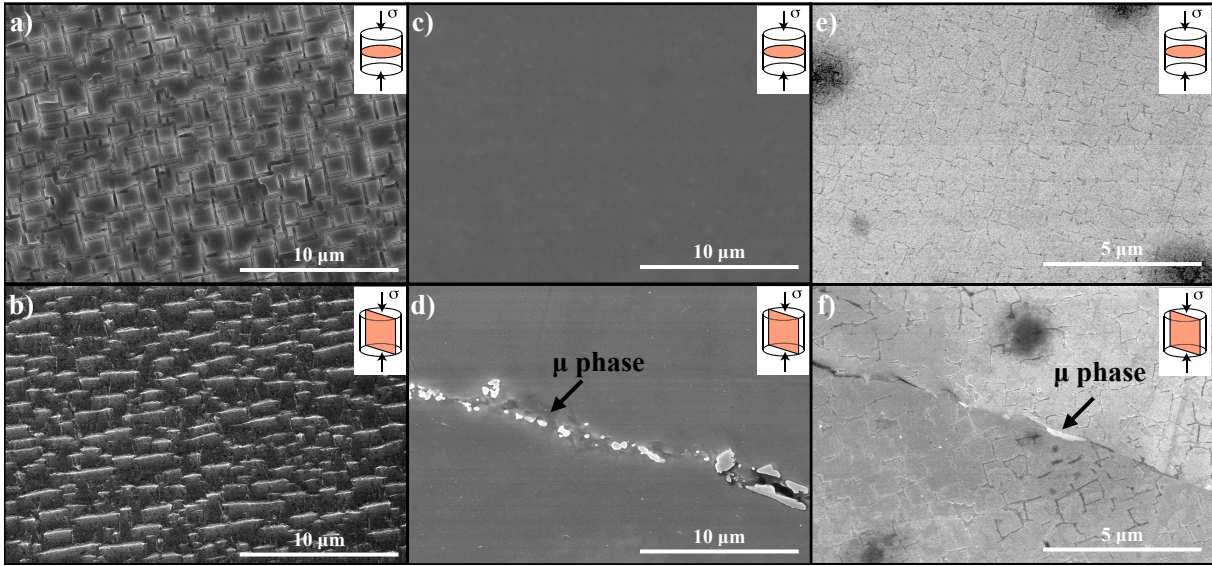


Figure 2.9. Post-creep microstructure of a), b) L24-0Cr, c), d) -4Cr and e), f) -8Cr. Planes perpendicular and parallel to the loading direction are shown to illustrate γ' rafting direction.

amounts of the μ -phase along the grain boundaries, are probably the consequence of a creep temperature lower than the aging temperature.

The post-creep microstructure of L24-8Cr is shown in Figs. 2.9e) and 2.9f). Like L24-4Cr, the γ' -volume fraction increased significantly, from 83% before creep to 92% after creep. The increase in γ' -volume fraction is responsible for the percolated γ' -network observed in L24-0Cr and -4Cr. L24-8Cr does not raft at the testing temperature and stress range. This is probably because of the reduction in the lattice-parameter misfit at elevated temperatures resulting from the higher coefficient of thermal expansion of the γ -phase [8, 48, 73, 94, 95]. At 850 °C, the lattice-parameter misfit between the γ and γ' approaches zero as evident by the rounded morphology of the γ' -precipitates, which significantly reduces the rafting driving force [79, 96]. A similar effect is observed in other Co superalloys with zero lattice-parameter misfit at their creep temperature [97]. In the

absence of a lattice-parameter misfit, γ' -precipitates are not subjected to an anisotropic local stress-field, and hence there is no rafting [98, 99].

2.4. Summary and Conclusion

A Cr-free Co-based superalloy, L24-0Cr, with the composition Co-30Ni-11Al-2Ti-5.5W-2.5Ta-0.1B (at.%), was cast. The composition of this material was selected according to a computational thermodynamic method to maximize the γ' -solvus temperature and volume fraction [1, 41]. This alloy was then modified by increasing the concentration of Cr (4, 8, or 12 at.%) with the primary goal of increasing the oxidation resistance. The following conclusions are drawn from the results of the study:

- Microstructural characterization indicated that increasing the concentration of Cr caused the morphology of the γ' -precipitates to become increasingly spherical. Upon aging at 900 °C, the volume fraction of the γ' -phase remained high at 98% for L24-0 and L24-4Cr and decreased to 83% and 69% for L24-8Cr and -12Cr, respectively, coinciding with the formation of a $(\text{Co,Ni})_7(\text{W,Cr})_6$ μ -phase at the grain boundaries and within grains.
- The lattice parameter misfit decreased with increasing Cr concentration, decreasing from 0.64% in L24-0Cr to 0.2% in L24-12Cr. This reduction may be attributed to the shift in W partitioning, when Cr is added to the alloy. Chromium preferentially displaces W from the L1_2 lattice to the γ -matrix decreasing the lattice parameter of the γ' -phase and increasing the lattice parameter of the γ -phase.
- Atom-probe tomographic analyses of the L24-Cr alloys revealed that Ni, Al, W, Ti, Ta, and B partition to the γ' -phase, while Co and Cr partition to the γ -phase.

With the exception of W, the partitioning coefficient of all γ' -forming-elements decreased for L24-4Cr, but increased for L24-8Cr.

- Oxidation resistance improved monotonically with increasing Cr concentration. Based on the oxide parabolic growth rate, adding 4 at.% of Cr proved sufficient to reduce the oxidation rate by two orders of magnitude. Without a Cr addition, Al alone cannot form a protective oxide scale on the surface at 900 °C. However, chromium could facilitate the formation of stable Cr_2O_3 and Al_2O_3 .
- Chromium did not significantly affect the steady-state strain-rate, but did increase the stress exponent, indicating a change in the deformation mechanism during creep. The rafting behavior of the alloy depends on the lattice parameter misfit at the loading temperature, so that reducing the lattice parameter misfit by adding Cr, results in a lower degree of γ' -precipitate rafting.
- A comparison between L24-Cr and Ni_3Al intermetallic compounds revealed that L24-Cr is significantly more creep resistant than single-phase Ni_3Al and precipitation strengthened Ni_3Al . The enhancement in creep properties is probably a consequence of the extensive solid-solution strengthening of the γ' -phase in L24-Cr.

Supplemental Information

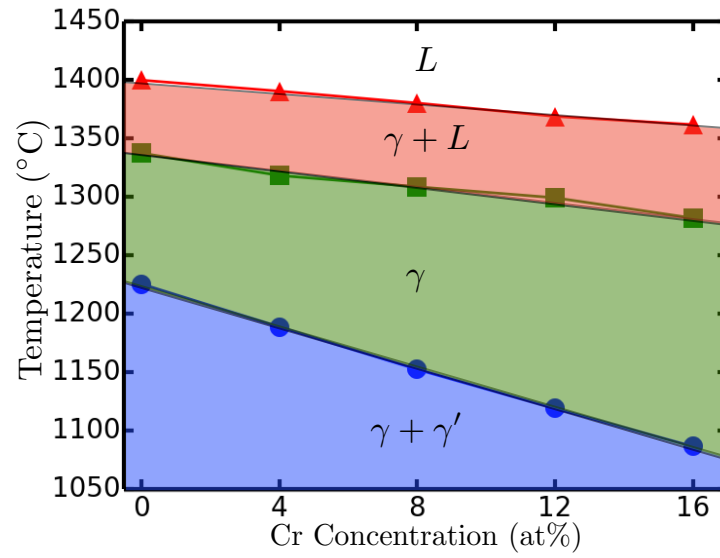


Figure 2.10. γ' -solvus, γ -solidus and γ -liquidus temperature as a function of Cr concentration.

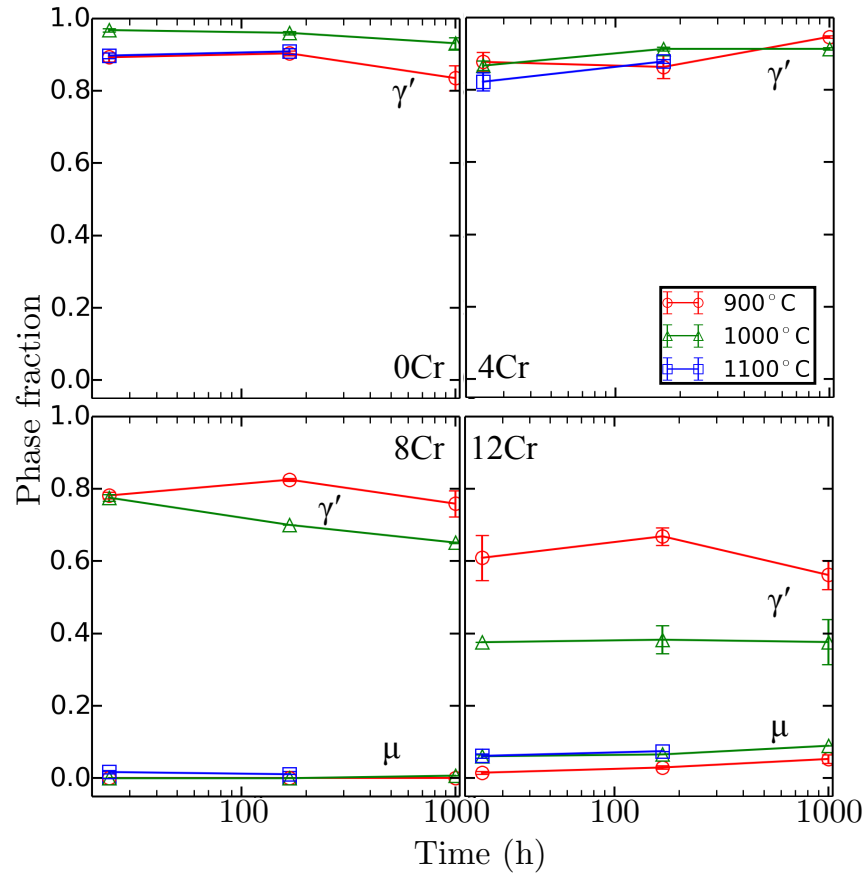


Figure 2.11. Volume fraction of γ' and μ phase for -0Cr, -4Cr, -8Cr and -12Cr heat treated at different temperature and duration. The volume fraction was estimated using stereological method.

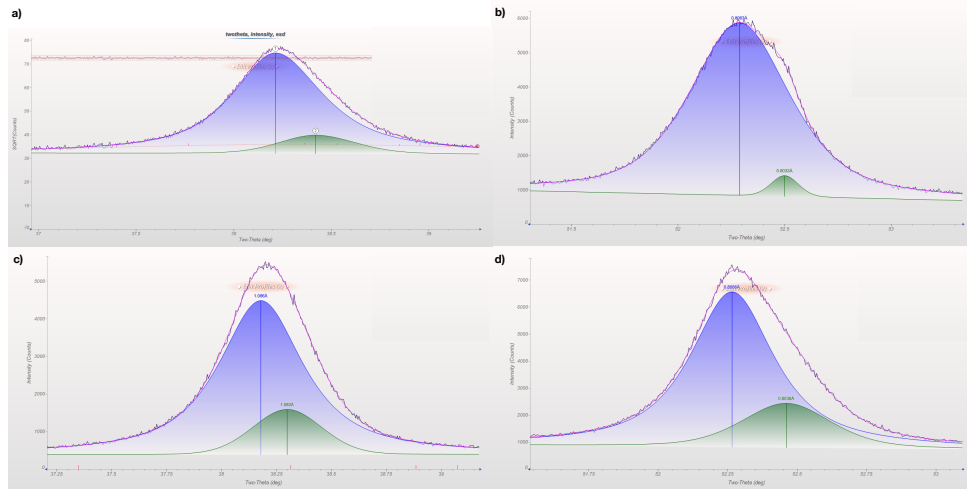


Figure 2.12. Pseudo-Voigt fitting of the superimposed γ and γ' synchrotron x-ray diffraction peaks for L24 a)-0Cr, b)-4Cr, c)-8Cr and d)-12Cr. Using the stereologically derived volume fraction as the constraint, the fitting was performed via JADE, x-ray diffraction analysis software. The blue peaks correspond to the γ' diffraction and the green peaks to the γ .

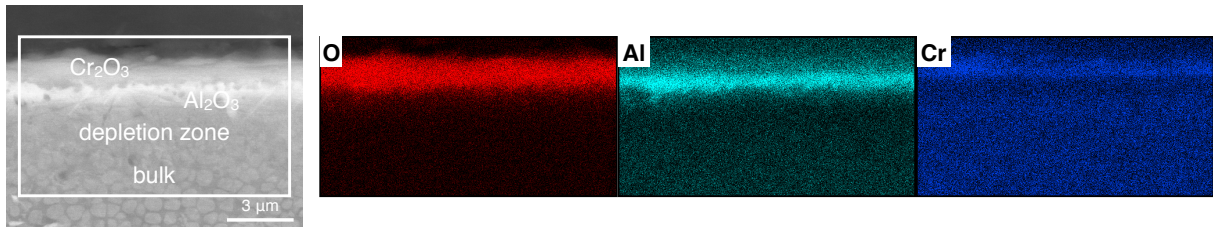


Figure 2.13. (Color online) Oxide scale elemental distribution of L24-12Cr after 900°C 20 h of isothermal oxidation which illustrate the distinct layer between the top Cr_2O_3 scale and the bottom Al_2O_3 scale.

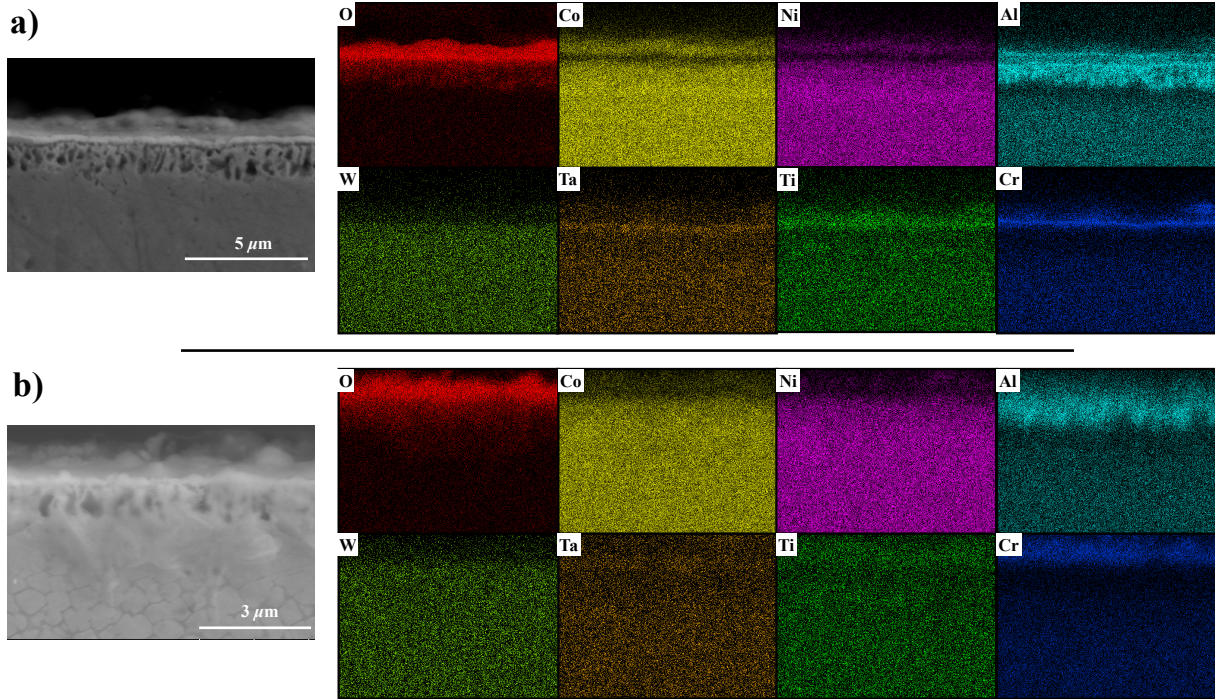


Figure 2.14. (Color online) Oxide scale elemental distribution of a) -4Cr and b) -8Cr after 900°C 20 h of isothermal oxidation.

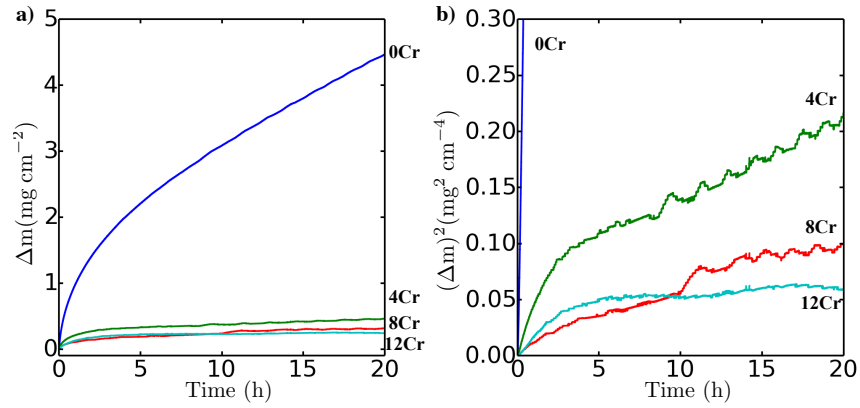


Figure 2.15. a) Δm and b) $(\Delta m)^2$ for -0Cr, -4Cr, -8Cr and -12Cr during isothermal oxidation at 900°C for 20 hours.

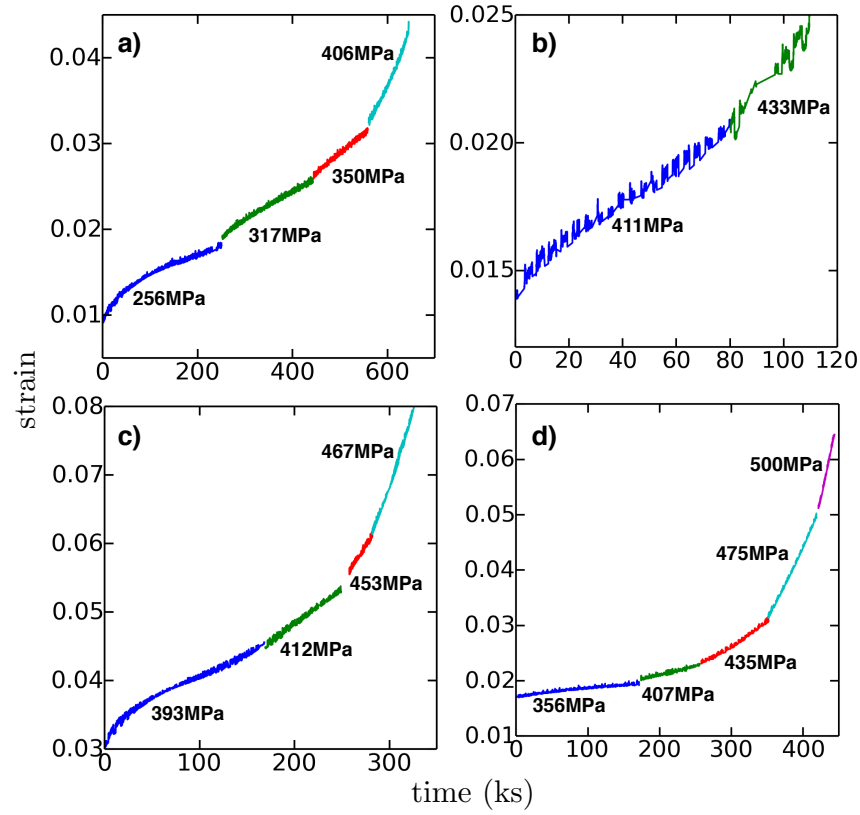


Figure 2.16. Strain as a function of time for the mechanical creep tests. a), b) two distinct -0Cr samples, c) -4Cr and d) -8Cr. -0Cr sample is highly brittle and enter tertiary creep earlier than -4Cr and -8Cr, thus two samples were crept to ensure data validity.

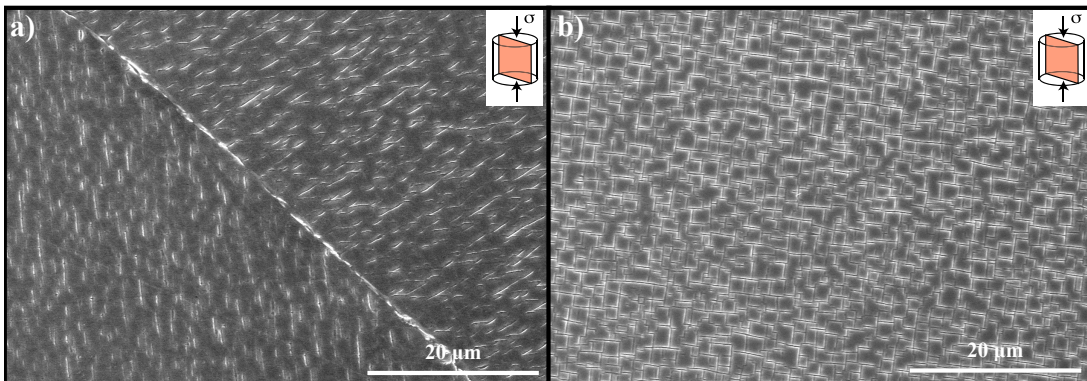


Figure 2.17. Post-creep microstructure of -0Cr, a) different rafting direction between grains and b) grain that does not raft.

CHAPTER 3

Effect of Cr Additions on a γ - γ' Microstructure and Creep Behavior of a Cobalt-Based Superalloy with Low W Content

Nickel- and cobalt-based superalloys derive their excellent oxidation and corrosion resistance from the surface oxidation of Al and Cr, which form protective oxide layers. Starting from an existing Cr-free cobalt-based superalloy (Co-30Ni-7Al-4Ti-3Mo-2W-1Nb-1Ta-0.1B at.%) with a γ - γ' microstructure, we create three alloys with 4, 8 and 12 at.% Cr additions. Chromium lowers the γ' solvus temperature (from 1129 °C for 0% Cr to 1075 °C for 12 at.% Cr) and alters the γ' precipitate morphology (from cuboidal-to-spherical), but does not affect the coarsening kinetics (which follow the Lifshitz-Slyozov-Wagner model). The alloys with 8 and 12 at.% Cr exhibit minor amounts of a Mo-rich intermetallic phase at grain boundaries after homogenization, and the 12 at.% Cr alloy displays an additional 3 vol.% intragranular refractory-rich secondary precipitates upon aging at 850 °C for 168 h. Atom-probe tomography reveals that Cr partitions strongly to the γ -matrix, with a partitioning coefficient of $\kappa^{\gamma'/\gamma} = 0.33$ and 0.26 for Cr additions of 4 and 8%, respectively. These additions halve the creep rate of the original alloy at stresses between 275 and 400 MPa, reflecting significant changes in γ' precipitate composition, volume fraction, morphology, and rafting tendency.

3.1. Introduction

Research into Ni-based superalloys has largely been driven by the need for creep-, fracture-, oxidation-, corrosion-, and coarsening-resistant alloys capable of withstanding the extreme operating conditions of aircraft engines and industrial gas turbines for generating electricity [18]. Building upon decades of research and development, many commercial precipitation-strengthened Ni-based superalloys have been developed, with a microstructure consisting of a γ -(f.c.c.) matrix containing a high-volume fraction of submicron γ' -(L1₂) precipitates. The 2006 discovery by Sato *et al.* [16] showed that Co₃(Al,W) γ' -precipitates could be formed in the ternary Co-Al-W system, which opened new possibilities for Co-based superalloys with γ - γ' microstructures as potential alternatives to Ni-based superalloys in high temperature applications [29, 51, 100, 101, 102].

The incorporation of additional alloying elements to the ternary Co-Al-W system has demonstrated that Ti and Ta are beneficial for γ' -stability [28, 29], while an alloy's mass density is decreased by replacing W with Mo and Nb [45, 103]. Furthermore, replacing some Co with Ni results in a larger γ plus γ' phase-field and minimizes the formation of secondary intermetallic phases [6]. Additions of elements such as Ti, Ta, Mo and W increase ambient- and elevated-temperature strength via solid-solution and precipitation strengthening [104, 105, 106], while refractory elements such as Ta, Mo, Nb, Re, and Ru decelerate γ' coarsening kinetics [96, 103, 107]. The rapid development of compositionally complex Co-based alloys to match or exceed the mechanical performance of conventional Ni-based alloys has not focused substantially on chromium [35, 61, 106, 108], despite it being of utmost importance for oxidation and corrosion resistance [51, 52, 102], provided by the protective oxide scale formed by Cr and Al, as in Ni-based

superalloys [109]. The few studies on Cr-containing Co-based superalloys report that Cr additions lowers the γ' solvus temperature, alters precipitate morphology, and destabilizes the γ plus γ' microstructure by forming additional intermetallic phases [25, 34, 58], changes that may have detrimental impacts on mechanical performance. In particular, Povstugar *et al.* [2] reported that the minimum creep rate at 850 °C of the Co-9Al-9W ternary alloy was increased dramatically, by two orders of magnitude, when 8% Cr was added to the alloy. While additions of 8 at.% Cr or more indeed promote secondary phase formation in Ni-free Co-based alloys, Knop *et al.* [61] and Neumeier *et al.* [110] have demonstrated that as much as 12-15 at.% Cr can be added to Co-based alloys containing 30-35 at.% Ni without degrading the two-phase microstructure.

Lass *et al.* [1, 41] recently reported a multicomponent Co-based alloy, Co-30Ni-7Al-4Ti-3Mo-2W-1Nb-1Ta-0.1B at.%, labeled L19. This alloy exhibits an excellent combination of a high γ' solvus temperature (1126 °C), high γ' volume fraction (65 %), low mass density (8.89 g/cm³) due to its low W plus Ta content, and excellent γ' coarsening resistance (at 900 °C) [1]. To obtain acceptable oxidation resistance at elevated temperatures, Cr additions as high as 15 at.% are required without significantly affecting microstructural stability and creep resistance. In the present study, three levels of Cr-additions to the base alloy of Lass *et al.* [1] (4, 8 and 12 at.% Cr) are investigated. Characterization of microstructure, phase stability, composition, coarsening resistance, and creep performance are carried out to study how these Cr additions affect microstructural evolution and mechanical performance.

3.2. Experimental Methods

Table 3.1 displays the nominal compositions of the studied alloys, which were based on the Cr-free L19 alloy composition reported by Lass *et al.* [1] (labeled herein as 0Cr). Also listed are the compositions as measured via inductively coupled plasma optical emission spectroscopy (ICP- OES) and energy dispersive spectroscopy (EDS) (for the 12Cr alloy), which were performed to verify that the alloys had the expected compositions. For the three alloys containing Cr at concentrations of 4, 8, and 12 at.% Cr (labeled herein as 4Cr, 8Cr and 12Cr), the Ni concentration was fixed at 30 at.% to ensure a consistently wide γ plus γ' phase-field [6]. Likewise, the B concentration was also maintained at a constant value of 0.1 at.% to improve grain-boundary cohesion, either by forming borides or via solid solution partitioning along grain boundaries [49, 60]. Previously measured partition coefficients of Cr in Co-based superalloys are $\kappa^{\gamma'/\gamma} \approx 0.25$ [49, 61], indicating that 80 % of the Cr partitions to the γ matrix. With the goal of maintaining a constant γ' phase-fraction, Co was thus replaced by 80% of the total Cr-addition, while the remaining 20% was subtracted from the γ' -forming alloying elements (Al, Ti, Mo, W, Nb, and Ta), maintaining the same ratio between these elements as found in the base alloy.

Alloys with a ≈ 50 g mass were created via arc-melting under an argon atmosphere (Arc Melting System AM0.5, Edmund Buhler GmbH) of pure elements (99.9+% purity). Approximately five additional percent (by mass) of Al was added to the melt to compensate for evaporation losses (*e.g.*, for the 0Cr alloy with a Al target composition of 7.00 at.%, 7.35 at.% was added). The charge was remelted at least eight times to ensure composition homogeneity, resulting in 10 x 15 x 50 mm ingots. These ingots were then encapsulated in argon-backfilled quartz capsules, homogenized at 1250 °C for 48 h and

Table 3.1. Nominal (Nom.) and ICP-OES and EDS-measured compositions (at.%) of Co-based superalloys with their solvus, solidus, and liquidus temperatures ($^{\circ}\text{C}$). The 0Cr alloy has the same nominal composition as alloy L19 in Ref. [1]. An asterisk (*) indicates that the value is below the EDS detection limit.

Alloy	Cr	Ni	Al	Ti	Mo	W	Nb	Ta	B	γ' -solvus ($^{\circ}\text{C}$)	γ -solidus ($^{\circ}\text{C}$)	γ -liquidus ($^{\circ}\text{C}$)
0Cr												
Nom.	0	30.0	7.00	4.00	3.00	2.00	1.00	1.00	0.10	1129	1305	1378
EDS		29.3	7.72	4.17	3.33	2.02	1.10	1.16	*			
ICP-OES	0	30.7	7.48	4.15	3.19	2.14	1.04	1.11	0.068			
4Cr												
Nom.	4	30.0	6.69	3.82	2.87	1.91	0.96	0.96	0.10	1114	1295	1373
EDS	3.94	30.2	7.03	4.22	3.28	2.09	1.07	1.07	*			
ICP-OES	4.18	31.3	5.56	3.92	3.15	2.10	0.95	1.02	0.119			
8Cr												
Nom.	8	30.0	6.38	3.64	2.73	1.82	0.91	0.91	0.10	1095	1285	1366
EDS	8.11	28.8	7.05	3.86	3.19	1.91	1.14	1.04	*			
ICP-OES	8.11	31.0	6.29	3.73	2.95	1.97	0.89	0.96	0.084			
12Cr												
Nom.	12	30.0	6.07	3.47	2.60	1.73	0.87	0.87	0.10	1075	1280	1359
EDS	12.2	28.7	7.12	3.49	2.94	1.76	0.94	1.05	*			

air-cooled. After homogenization, aging studies were performed at 900°C in sealed, evacuated quartz capsules for times ranging from 24 to 2000 h, terminated by water quenching to room temperature.

For each alloy, the γ' solvus, solidus, and liquidus temperatures were measured using a Netzsch differential scanning calorimetry (DSC) 404C thermal analyzer with a $10^{\circ}\text{C}\cdot\text{min}^{-1}$ heating rate under a $20\text{ mL}\cdot\text{min}^{-1}$ argon flow rate. The γ' solvus temperatures were obtained by averaging values from four heating cycles and the solidus and liquidus temperatures were measured once.

Due to the corrosion resistance provided by Cr, different etchants were necessary for the low- and high-Cr alloys. The 0Cr and 4Cr alloys were etched with Carapella's reagent (5 g FeCl_3 , 2 mL HCl , 100 mL methanol) for 5 and 30 s, respectively, while the 8Cr and 12Cr alloys were etched with waterless Kalling's reagent (5 g CuCl_2 , 100 mL HCl , 100 mL

ethanol), both for 90 s. A Hitachi SU8030 scanning electron microscope (SEM) equipped with a cold-field-emission source was used for microstructural characterization and energy dispersive spectroscopy (EDS) under an operating voltage of 25 kV and a working distance of 15 mm. SEM micrographs were analyzed with the NIH ImageJ software, using Otsu's method for binary thresholding to determine the γ' -precipitate outlines [111]. Average precipitate area A was determined as the product of precipitate edge-lengths, which were measured for at least 30 randomly-selected precipitates per sample. The area equivalent precipitate radii were calculated from $R = \sqrt{A/\pi}$, from which a mean value was calculated. Precipitate areal number density N_A was determined by a manual counting method for areas totalling at least $100 \mu\text{m}^2$, from which the volumetric number density N_V was calculated from the stereological relationship $N_V = N_A/(2\langle R \rangle)$ [112].

Atom probe tomography (APT) specimens were prepared using an FEI Helios Nanolab microscope equipped with focused ion beam (FIB) capability (FEI Helios Nanolab 600 dual-beam FIB/SEM microscope). Specimens for 0Cr, 4Cr and 8Cr alloys were characterized using a local electrode atom probe (LEAP) tomograph (CAMECA LEAP4000X-Si) with a picosecond pulse ultraviolet (wavelength = 355 nm) laser energy of 30 pJ, pulse frequency of 200 kHz, temperature of 25 K, and evaporation rate of 5 %. APT data were analyzed with the proprietary IVAS 3.6 software package from CAMECA Instruments Inc.

Cylindrical compression samples (5 mm in diameter and 10 mm in height) were produced through electro-discharge machining for the 0Cr, 4Cr, and 8Cr alloys aged at 900 °C for 168 h. For testing, each sample was placed between silicon carbide platens lubricated by boron nitride and then deformed in air at 850 °C under a series of monotonically

increasing nominal stresses in the range 275-400 MPa. For each stress, a minimum creep strain rate was determined from the sample displacement rate after exhaustion of primary creep, measured using an extensometer connected to a linear variable displacement transducer with a resolution of 10 μm . Tests were terminated at the onset of tertiary creep, when the strain rate was observed to increase at a constant stress. The total strain accumulated in each sample was no more than 16 %, while the total time accumulated ranged from 52 to 146 h.

3.3. Results and Discussion

3.3.1. Microstructure and phase stability

Table 3.1 presents the solvus, solidus, and liquidus temperatures of all the alloys, with the base alloys (0Cr) exhibiting values of 1129, 1305, and 1378 °C, respectively. All three temperatures decrease with increasing Cr concentrations at rates of 4.6, 2.2 and 1.5 °C/at.% Cr, respectively (Supplemental Figure 3.8). An 8 at.% Cr addition, which is expected to provide significant oxidation resistance in Co-based superalloys [51, 52] as well as a small decrease in mass density (1.2 %), exacts a relatively modest penalty of 20 °C for the solidus and 12 °C for the liquidus temperatures, but a sizeable 34 °C decrease of the solvus temperature (from 1129 to 1095 °C). For comparison, addition of 8% Cr to the Co-9Al-9W ternary system decreases the solvus temperature by 39 °C (from 986 to 947 °C) [58].

The homogenized alloys exhibited a single-phase γ free of other phases, except for γ' formed on cooling. Figure 3.1 displays the microstructure of the four studied alloys aged at 900 °C for 168 h. Figure 3.1(a) illustrates the cuboidal morphology of γ' -precipitates

in grains with different crystallographic orientations in the 0Cr alloy. As the Cr concentration increases, Figures 3.1(b-d), the γ' -precipitates gradually lose their sharp cuboidal morphology and become increasingly spherical, which is likely due to a decrease in the γ - γ' lattice parameter misfit with Cr-additions to Co-based alloys as reported in Ref [2]. Despite the use of more extreme etching conditions, the etchant only selectively etches the γ - γ' interfaces in 8Cr and 12Cr samples, which is consistent with a higher corrosion resistance with increased Cr concentration.

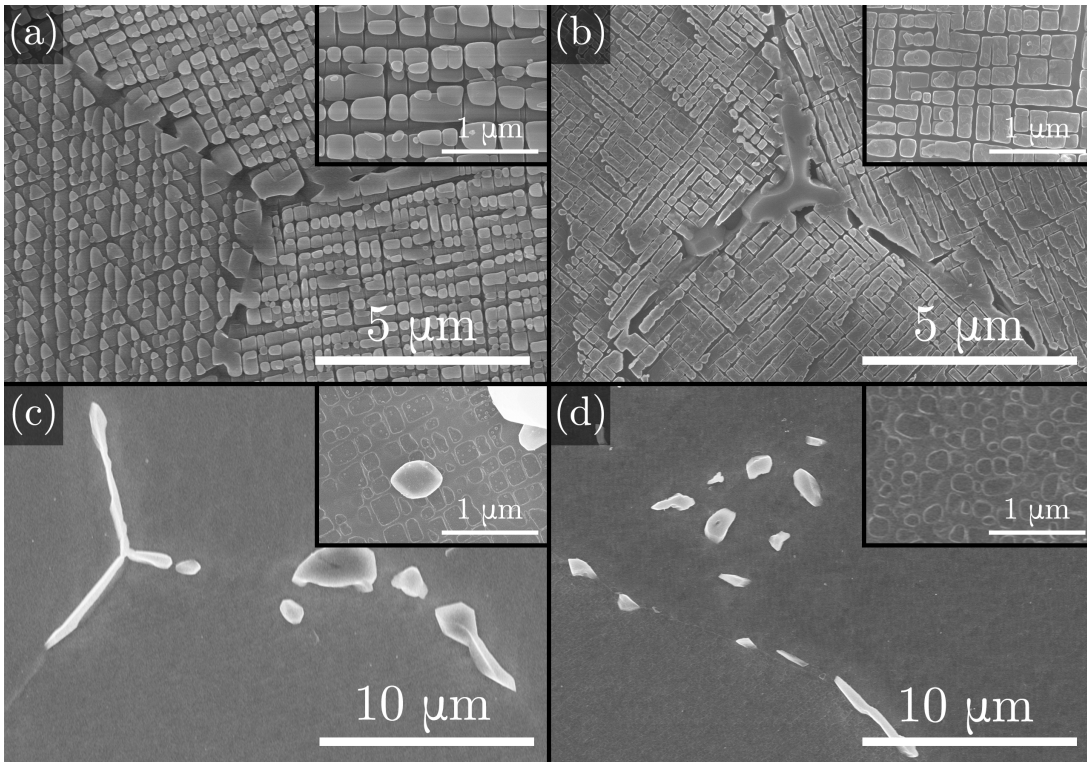


Figure 3.1. Secondary electron micrographs of: (a) 0Cr; (b) 4Cr; (c) 8Cr; and (d) 12Cr alloys aged at 900 °C for 168 h, showing γ - γ' microstructures in grains (seen at higher magnification in insets), as well as grain-boundary precipitates consisting of coarsened γ' (0Cr and 4Cr) and μ phase (8Cr and 12Cr).

Figures 3.1(c-d) show that the aged alloys with 8 and 12 at.% Cr additions exhibit secondary phases at, or near, grain boundaries. The addition of Cr in the range 8-20 at.% is known to destabilize the $\gamma+\gamma'$ microstructure in Co-based superalloys by facilitating the formation of $D0_{19}-\chi$ and topologically-closed-packed (TCP) secondary-phases such as $D8_5-\mu$ [25]. The morphology of the grain-boundary precipitates is similar to the μ -phase found in other Co-Al-W alloys with Cr and Ni additions [25] and Co-Al-W alloys with refractory elements such as V, Ti, Mo, Nb, and Ta [113]. EDS measurements for 8Cr and 12Cr samples also show that the mole fraction of Co plus Ni in the secondary-phase is approximately 54%, and the precipitates are significantly enriched in Mo (25-30 at.%), which is consistent with a $\mu-(Co,Ni)_7(Mo,X)_6$ type intermetallic phase where X consists of the remaining refractory elements [18]. Other studies have found the μ -phase in Co superalloys to be W-rich based on the binary composition of Co_7W_6 , but this has only been observed in systems with higher nominal W concentrations (> 5 at.%) [25, 113], whereas the alloys studied here contain ≤ 2 at.% W.

These grain-boundary precipitates could also be σ -phase or a boride phase. The σ -phase has not been previously reported in γ' -strengthened Co-based alloys and is therefore unlikely to form in the present alloys. However, since B was added to promote grain boundary strengthening via boride formation, it is possible that these precipitates are a Mo-rich boride. Indeed, their size and morphology are similar to W-rich borides reported in other Co-based superalloys [35, 36, 58]. Further, Figure 3.2, which presents the microstructure of the 12Cr alloy after aging at 900 °C for 1000 h, shows that the size of the grain boundary precipitates does not change significantly with increasing aging time.

This is consistent with the observations W-rich borides observed by Bauer *et al.* in Co-Al-W-B alloys [35]. Indeed, the B concentration of 0.1 at.% is well beyond the solubility limit (< 0.04 at.%) in the Co-9Al-9W ternary system, which should result in precipitation of borides at grain boundaries [60]. Since the concentration of Mo is higher than that of W, it is possible that Mo substitutes for W in the grain boundary boride phase. Positive identification of the grain boundary phases via transmission electron microscopy and APT will be a subject of future work.

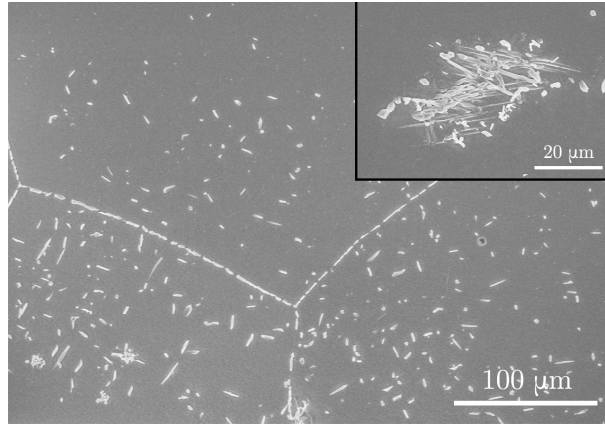


Figure 3.2. Secondary electron micrograph of a 12Cr alloy aged at 900 °C for 1000 h, showing needle-like secondary precipitates at grain boundaries and within the grains. Inset shows a cluster of intragranular secondary precipitates.

Figure 3.2 also demonstrates that further aging of the 12Cr alloy for 1000 h at 900 °C results in precipitation of a small volume fraction ($\approx 3\%$) of an intragranular secondary phase with plate-like morphology. This phase, which was observed in only the 12Cr alloy, is expected to be the hexagonal $D0_{19}$ - χ phase (Co_3W and Co_3Mo) based on its characteristic elongated morphology, as observed in several other similar Co-based alloys [113, 114]. These precipitates were determined by EDS analysis to be significantly enriched in Mo,

Nb, Ta, and Ti, which are known to substitute for W in D0₁₉ Co₃W-type precipitates in Co-based alloys with little or no W content [1, 103, 113]. The appearance of intragranular D0₁₉ after extended aging times suggests that the two-phase γ - γ' microstructure is not stable in the 12Cr alloy. Further, the formation of TCP and other deleterious phases in superalloys is undesirable due to possible deleterious effects on the mechanical properties, as extensive secondary-phase precipitates within the grains are likely to act as sites for crack nucleation and growth. The compositions of the secondary phases in this study also suggest that they deplete refractory alloying elements from the matrix, which may deteriorate mechanical properties by decreasing the effectiveness of solid-solution and precipitation strengthening, and by accelerating coarsening via diffusion in the γ -channels [115]. As a two-phase γ plus γ' grain microstructure without additional phases is a design goal in Co-based superalloys, the 12Cr sample was not considered for further investigation in this study due to its significant fraction of intragranular secondary phase.

3.3.2. Coarsening Kinetics

Figures 3.3(a-c) show the temporal-evolution at 900 °C of microstructural parameters for the γ' -precipitates (volume fraction, radius, and number density) in alloys with 0, 4 and 8 at.% Cr. For the shortest time of 24 h, Figure 3.3(a), the volume fraction of γ' -precipitates hasn't yet reached its steady-state value, indicating that the alloy microstructures are still in the growth stage. The γ' volume fractions plateau in the range of 70-80% after 168 h and beyond, indicating a quasi-steady-state coarsening regime [116]. Figure 3.3(a) shows that the γ' volume fraction plateau increases slightly from $\approx 78\%$ to 81% with addition of 4 at.% Cr, then decreases to 72% with 8 at.% Cr. An increase in γ' volume fraction has

also been observed in a ternary Co-9Al-9W alloy with up to 4 at.% Cr addition, but the γ' -precipitates lose their cuboidal morphology upon adding 8 at.% Cr [58].

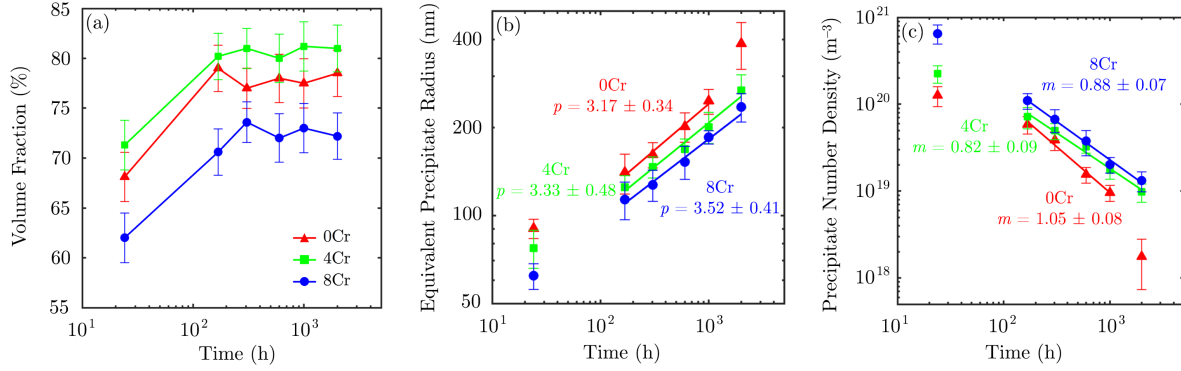


Figure 3.3. Microstructural evolution of alloys aged at 900 °C in terms of: (a) γ' volume fraction, (b) equivalent precipitate radius, and (c) number density. Error bars represent a 95% confidence interval.

Figure 3.3(b) shows the precipitate radius evolution with aging time, which can be compared to the Lifshitz-Slyozov-Wagner (LSW) [117, 118] model:

$$(3.1) \quad \langle R(t) \rangle^p = Kt$$

where $\langle R(t) \rangle$ is the precipitate radius at aging time t , p is the temporal exponent, and K is the associated coarsening rate constant. The LSW model predicts a temporal exponent of $p = 2$ for interface-limited coarsening, and $p = 3$ for diffusion-limited coarsening. A nonlinear multivariable regression was performed using Equation 3.1 on data given in Figure 3.3(b), resulting in values of p with uncertainties given by the standard error calculated from regression analysis. In Figures 3.3(b) and (c), the data for the 24 h aging time were not included in the regression analysis since the steady-state coarsening regime had not been reached. The data for the 0Cr samples aged for 2000 h were also

not included because the micrographs showed significant coalescence of the γ' precipitates (see Supplemental Figure 3.9). In contrast, individual particles were still distinguishable for the 4Cr and 8Cr samples aged for 2000 h. The best-fit temporal exponents are $p = 3.17 \pm 0.34$, 3.33 ± 0.48 , and 3.52 ± 0.41 for the 0Cr, 4Cr, and 8Cr alloys, respectively; this is close to $p = 3$, indicating that diffusion is the dominant rate-limiting mechanism in these alloys. Lass *et al.* [1] previously determined $p = 2.96 \pm 0.34$ for the Cr-free L19 alloy aged at the same temperature of 900 °C, which is in agreement with the present results for 0Cr condition.

Under steady-state conditions, with a constant γ' volume fraction, precipitate number density decreases as t^{-q} with $q = 1$ according to the LSW theory [119]. Figure 3.3(c) gives $q = 1.05 \pm 0.08$, 0.82 ± 0.09 , and 0.88 ± 0.07 for the 0Cr, 4Cr, and 8Cr alloys, respectively. While experimental p and q exponents are reasonably close to theoretical predictions, minor discrepancies with the LSW model may indicate that a true steady-state has not quite been achieved. Also, the LSW theory may be inaccurate in the present, multicomponent system with a high precipitate volume fraction [120]. However, the addition of Cr to a Co-based superalloy is expected to alter the γ - γ' interfacial energies and lower matrix diffusivity for most alloying elements [115], thereby hindering coalescence, as well as slowing coarsening, consistent with the higher temporal exponents p and lower values for q observed in the 4Cr and 8Cr alloys, as compared to 0Cr.

3.3.3. Elemental Partitioning

Figure 3.4 shows APT reconstructions and proximity histograms for samples aged at 900 °C for 168 h, at the onset of steady-state coarsening. The reconstructions display 1 or 2

partial γ' -precipitates (which are larger than the nanotip), separated by thin γ -channels, with the γ - γ' interface highlighted by isoconcentration surfaces of 56, 51, and 46 at.% Co for the 0Cr, 4Cr, and 8Cr alloys, respectively. The concentration profiles for each phase are obtained from the proximity histograms, in which vertical dotted lines at the origin of the ordinate represent the center of the diffuse heterophase interfaces (≈ 3 -5 nm in width). Following Lass *et al.* [1], the error attributed to the concentration measurements is given by:

$$(3.2) \quad \sigma = \sqrt{C_i(1 - C_i)/N_T}$$

where σ is the statistical counting uncertainty, C_i is the measured concentration of species i , and N_T is the total number of type i -atoms collected in the sampled region. The concentration data is quantitatively summarized in Table 3.2, which gives far-field (ff) concentration values in each phase averaged over the range between 3 and 9 nm away from the interface, along with corresponding partitioning coefficients $\kappa^{\gamma'/\gamma}$ calculated as the ratio between $C^{\gamma'}$ and C^γ , the ff concentrations of an element in γ' and γ , respectively. These $\kappa^{\gamma'/\gamma}$ values are displayed graphically in Figure 3.5.

In 0Cr, only Co partitions to the γ matrix with $\kappa^{\gamma'/\gamma} = 0.70$, while all other elements partition to the γ' -precipitates. The Co partitioning behavior remains relatively constant with 4 and 8 at.% Cr addition. As expected from previous studies, Ta, Ti and Nb, which are known to stabilize γ' , show strong partitioning to the γ' -phase [28, 29]. Chromium additions slightly increase the partitioning of Ta, but have little effect on partitioning of Ti and Nb; however, the changes in partition coefficient are within the experimental uncertainty and therefore statistically insignificant. Both Ni and Al show partitioning

Table 3.2. Elemental compositions (at.%) of the bulk material and far-field (ff) concentrations in γ - and γ' -phases measured by atom-probe tomography, and the calculated partitioning coefficients $\kappa^{\gamma'/\gamma}$. The far-field concentrations have a global average error of ± 0.12 at.%. A range of values is given for the B concentration in γ' due to the lack of a plateau.

Alloy		Cr	Co	Ni	Al	Ti	Mo	W	Nb	Ta	B
0Cr	Bulk	-	57.39	27.51	6.51	3.25	2.55	1.42	0.66	0.67	0.045
	C^γ	-	64.53	24.32	4.95	1.86	2.49	1.13	0.41	0.29	0.01
	$C^{\gamma'}$	-	45.31	33.09	9.03	5.55	2.59	1.91	1.06	1.35	0.10
	$\kappa^{\gamma'/\gamma}$	-	0.70	1.36	1.82	2.98	1.04	1.69	2.57	4.58	9.65
4Cr	Bulk	3.98	49.47	29.69	6.98	3.67	2.69	1.70	0.73	0.91	0.18
	C^γ	6.55	58.86	23.82	4.24	1.49	2.98	1.32	0.34	0.31	0.09
	$C^{\gamma'}$	2.16	41.78	33.97	9.12	5.35	2.54	1.98	1.03	1.39	0.30-1.20
	$\kappa^{\gamma'/\gamma}$	0.33	0.71	1.43	2.15	3.60	0.85	1.50	2.99	4.41	3-13
8Cr	Bulk	6.62	42.61	32.19	7.91	4.81	2.35	1.56	0.79	1.08	0.072
	C^γ	13.88	52.72	22.44	4.28	1.91	2.92	1.25	0.34	0.24	0.03
	$C^{\gamma'}$	3.62	38.28	36.4	9.37	6.01	2.12	1.70	0.98	1.44	0.09
	$\kappa^{\gamma'/\gamma}$	0.26	0.73	1.62	2.19	3.15	0.72	1.36	2.87	5.89	3.51

coefficients increasing slightly with Cr content, possibly indicating the energetically favorable formation of a Ni_3Al -like γ' -phase instead of $\text{Co}_3(\text{Al},\text{W})$ [1]. In contrast, Cr slightly decreases the W partitioning ratio, which is consistent with the literature values suggesting that Cr partially replaces W in the L_{12} sublattice and hence decreases the concentration of W in γ' precipitates [2]. Boron has the highest partitioning coefficients ($\kappa^{\gamma'/\gamma} = 9.65$ in 0Cr), which decreases with Cr addition. However, as a trace element, the limited number of detected B ions during APT experiments resulted in very large associated measurement uncertainty especially for the 8Cr alloy. Also, for the 4Cr alloy, no concentration plateau was observed for B in the γ' -phase in the proximity histogram (Figure 3.4(b)), hence a range of values are given in Table 3.2. Finally, unlike the other elements, Mo has nearly equipartitioning behavior in the 0Cr alloy ($\kappa^{\gamma'/\gamma} = 1.04$) and it

segregates at the γ - γ' interface, as seen from the proximity histogram in Figure 3.5(a). However, Mo begins to favor the γ -matrix upon Cr addition, possibly because the two elements compete for sites in the W sublattice of the $\text{Co}_3(\text{Al,W})$ γ' -structure [121]. Furthermore, the formation of Mo-rich secondary phases in the 8Cr alloy may allow a greater capacity in the matrix to accommodate Mo, thereby shifting the partitioning of Mo to the γ .

Chromium itself partitions strongly to the γ matrix with $\kappa^{\gamma'/\gamma} = 0.33$ for the 4Cr and 0.26 for the 8Cr alloy. The sum of the Co and Ni concentrations in the γ' -phase is 78.4 at.% for the 0Cr alloy, suggesting that Co and Ni mostly occupy the X sublattice of the X_3Z L_{12} -compound (as expected from the Ni_3Al and $\text{Co}_3(\text{Al,W})$ parent compounds [16]) and that all other elements occupy the Z sublattice based on known substitutions for Al and W on the Z sublattice [121, 122, 123]. The deviation of 3.4 at.% from the 75 at.% stoichiometric value for the X sublattice is comparable to deviations reported in nano-precipitates from $\text{Ni}_3(\text{Al,Z})$ and $\text{Co}_3(\text{Al,W,Z})$ in Ni- and Co-based superalloys, with deviations from the 3:1 ratio of several at.% [28, 104, 123]. If Cr is fully assigned to the X sublattice, the sums of the Co, Ni, and Cr concentrations in the γ' -phase are 77.9 and 78.3 at.%, for the 4Cr and 8 Cr alloys, respectively, which are comparable to the 0Cr alloy value. However, Cr has been shown to displace some γ' -forming elements, such as Mo and W, on the Z sublattice sites [2, 124], which could explain the decreased partitioning coefficient of Mo and W with Cr additions. In the present case, the increase in partitioning of Al and Ta (and possibly Ti and Nb) seem to offset these decreases at least partially, which is consistent with previous observations demonstrating Ta displacement of Cr on the Z sublattice sites [124]. The slight increase in γ' volume fraction in the 4Cr

alloy compared to 0Cr, from $\approx 78\%$ to 82% suggests that Cr indeed displaces some of the γ' -forming elements. By contrast, the decrease in γ' volume fraction observed from 4Cr to 8Cr consistent with the consumption of γ' -forming elements Mo, W, Nb, and Ta in the secondary phases (μ or borides) observed in Figures 3.1 and 3.2.

3.3.4. Compressive Creep Behavior

3.3.4.1. Mechanical Properties. Figure 3.6 shows double logarithmic plots of minimum steady-state strain rate vs. applied stress σ for the three alloys, 0Cr, 4Cr and 8Cr, with the data fitted to the Arrhenius-Norton power-law equation

$$(3.3) \quad \dot{\epsilon} = A\sigma^n \exp\left(\frac{-Q}{RT}\right)$$

where A is a constant, n is the stress exponent, Q is the activation energy, R is the gas constant, and T is the absolute temperature in Kelvin. Comparable stress exponents ($n = 6.4 \pm 1.4$, 6.1 ± 2.4 , and 7.6 ± 2.2 for our 0Cr, 4Cr, and 8Cr alloys, respectively) suggest that our three alloys have the same deformation mechanism, namely dislocation creep. Furthermore, all samples displayed cracking along grain boundaries after compressive creep deformation of $\approx 10\%$ (Supplemental Figure 3.10), indicating limited high-temperature ductility. The data of Povstugar *et al.* for three Co-9Al-9W-0.04B alloys with 0, 4, and 8 at.% Cr additions (abbreviated as CoAlW, CoAlW-4Cr, and CoAlW-8Cr) [2] are also shown in Figure 3.6. Despite its smaller γ' volume fraction and lack of additional alloying elements, the CoAlW alloy from Povstugar *et al.* has comparable creep strength to our alloys, most likely due to a combination of effects including higher W content to slow diffusion, and a high enough B content high to avoid grain-boundary decohesion.

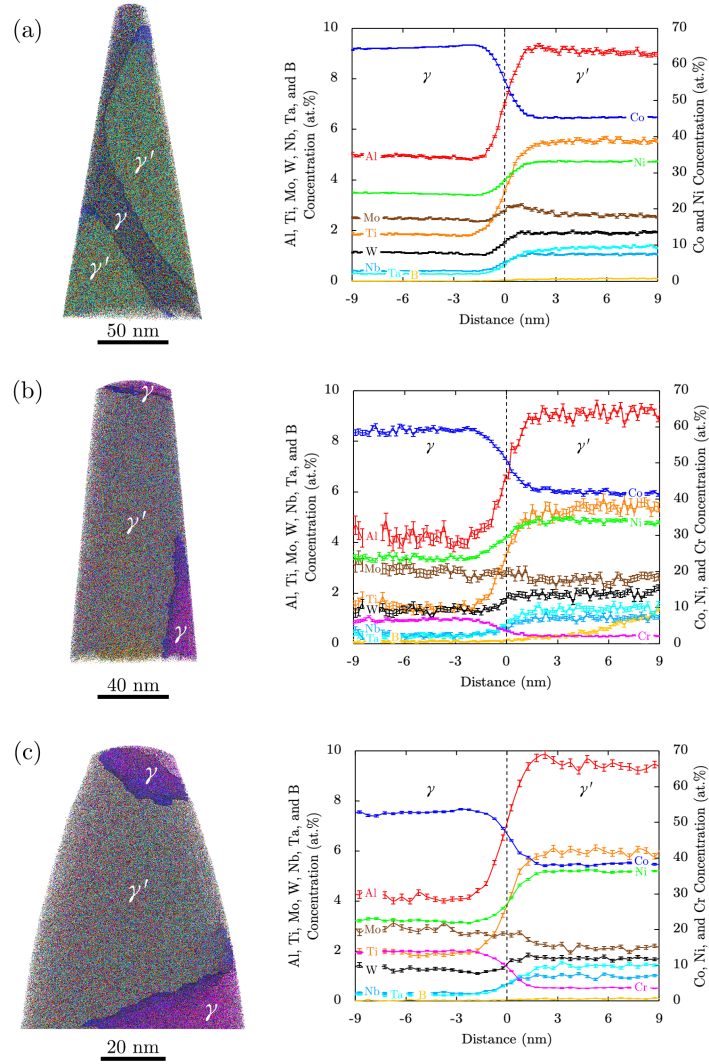


Figure 3.4. APT reconstructions and proximity histograms for (a) 0Cr, (b) 4Cr, and (c) 8Cr samples heat-treated at 900 °C for 168 h. Concentration profiles in the proximity histograms are labeled with their corresponding elements and can be read on one of the two concentration axes.

Nevertheless, our Cr-free multicomponent alloy achieves a similar degree of creep performance with a lower mass density of 8.89 g/cm³ [1], compared to 9.36 g/cm³ for the

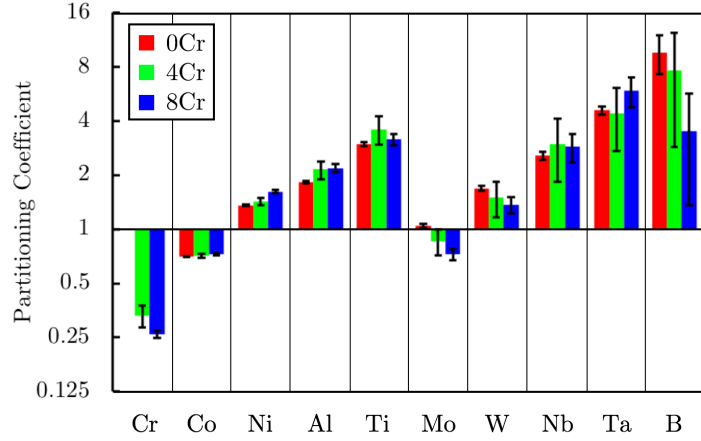


Figure 3.5. Partitioning coefficient κ' / γ in 0Cr, 4Cr, and 8Cr samples heat treated at 900 °C for 168 h, with values greater than 1 indicating partitioning to the γ' -phase.

Co-9Al-9W-0.04B alloy [36]. Density is further reduced to 8.84 and 8.78 g/cm³ for the 4Cr and 8Cr alloys, respectively.

In comparing the Cr-additions to the present alloy with those of Povstugar *et al.*, our multicomponent alloys with 4 and 8 % Cr additions exhibit slightly improve creep resistance (decreasing minimum strain rates by a factor of ≈ 2); whereas the ternary alloy exhibits a dramatic deterioration in the creep resistance upon the addition of Cr, with minimum strain rates increasing by factors of ≈ 8 for CoAlW-4Cr and ≈ 35 for CoAlW-8Cr compared to Cr-free CoAlW. However, direct comparison is difficult for two reasons. First, because Povstugar *et al.* added Cr only by replacing Co (*i.e.*, without altering the Al and W content to account for changes in partitioning behavior), their alloys had varying γ' volume fractions (38, 57, and 64% for CoAlW, CoAlW-4Cr, and CoAlW-8Cr, respectively). Given that optimal creep resistance is typically achieved for γ' volume fractions of 65-70% [125], this suggests that the negative influence of Cr addition on the

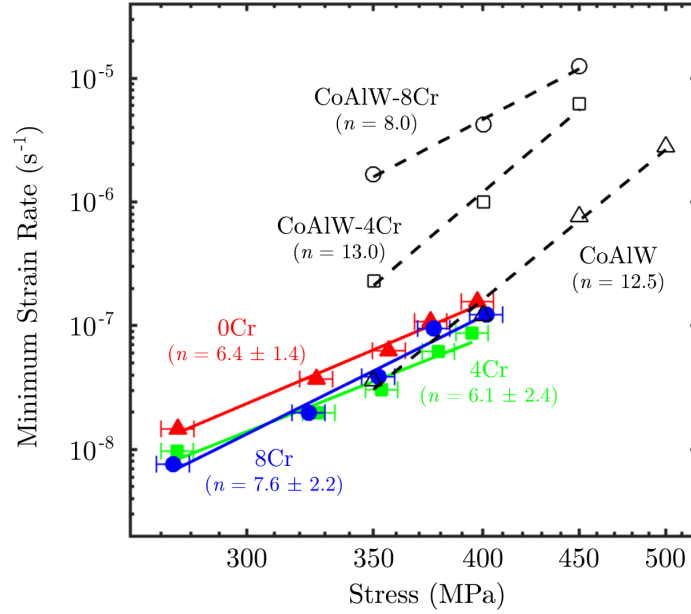


Figure 3.6. Double logarithmic plot of minimum, steady-state strain rate at 850 °C vs. compressive stress for our 0Cr, 4Cr, and 8Cr alloys, compared to literature data for Co-9Al-9W-0.04B alloys containing Cr (dashed lines labeled CoAlW-xCr) from Povstugar *et al.* [2]. Stress exponents n are given in parentheses.

creep strength of CoAlW is not caused by changes to γ' volume fraction, as the CoAlW-8Cr alloy has the worst creep performance despite being the closest to this optimal γ' -fraction range. In contrast, the multicomponent alloys in the present study have relatively high γ' -volume fractions of 78, 81, and 72% for 0Cr, 4Cr, and 8Cr, respectively (see Figure 3.3(a)). The volume fraction decreasing towards the optimal range in the 8Cr alloy may play a role in its slightly improved creep resistance, although this does not account for the lower strain rate of the 4Cr alloy as compared to 0Cr. Second, the quaternary CoAlW-8Cr alloy from Povstugar *et al.* exhibited W-rich secondary precipitates within the grains with a $\approx 2\%$ volume fraction (as estimated from their published micrographs [58]), which

may deteriorate mechanical properties (*e.g.*, by decreasing ductility and removing solid-solution strengthening elements from the matrix), but their absence in the CoAlW-4Cr alloy also cannot explain the reduced creep strength when compared to ternary CoAlW.

Povstugar *et al.* [2] suggested that the addition of Cr to Co-9Al-9W-0.04B, beside creating undesirable intermetallic secondary phases, may alter the energy of stacking faults and thereby deteriorate creep properties. However, the observed improvement in creep resistance as Cr is added to our multicomponent alloy suggests that more compositionally complex alloys may in fact be strengthened at elevated temperature by Cr additions. An important factor explaining this discrepancy may be the presence of 30 at.% Ni in our alloy: additions of 18 at.% Ni to the CoAlW-8Cr alloy were shown to progressively improve creep resistance (decreasing strain rates by a factor of ≈ 4) [2]. Furthermore, a study of a series of Co-[0-83]Ni-9Al-8W superalloys showed that the addition of 8 at.% Cr resulted in similar minimum creep rates for Cr-free and Cr-modified alloys with ≈ 20 at.% Ni, and Ni-rich alloys experienced almost two orders of magnitude decrease in creep rate upon Cr addition [126]. This was justified by the improvement in solid-solution strengthening provided by Cr to the γ -phase, due to its pronounced partitioning behavior in Ni-rich alloys. The stacking fault energy and antiphase boundary energy of the γ' may also change with high Ni-content. Further investigation is needed to help clarify the possible beneficial effects of Cr in Ni-containing Co-based superalloys. Thus, the inclusion of at least 20 at.% Ni may be sufficient to offset or mask any detrimental effects of Cr in Co-based superalloys, if they exist. The additional alloying elements (*e.g.*, Ti, Ta, Mo, Nb) may also aid in preventing Cr-induced degradation of creep performance by providing additional solid-solution strengthening and by improving microstructural stability.

3.3.4.2. Post-Creep Microstructure. Figure 3.7 displays SEM micrographs of the 0Cr, 4Cr and 8Cr samples after the creep experiments at 850 °C, with total strains of 14, 9 and 13%, respectively. For a typical 5 mm diameter cross-section, about 40 grains were counted, with grain diameters ranging from 0.3-2.0 mm. Rafting of the γ' -precipitates is clearly visible in the 0Cr and 4Cr samples, with elongated γ' -rafts oriented along $\langle 100 \rangle$ perpendicular to the applied compressive load (n-type rafting), as also reported in other Co-based superalloys and consistent with a positive γ - γ' misfit (*i.e.*, γ' lattice parameter larger than γ) [18, 58, 94]. Directional coarsening and coalescence are especially apparent in the plane parallel to the applied load, Figures 3.7(a) and (c). This rafting behavior is present in the majority of the grains observed in 0Cr and 4Cr samples, and the degree of rafting is more significant in grains with crystallographic orientations such that precipitates can raft perpendicular to the applied stress. Other, less well oriented grains do not exhibit rafting.

By contrast, no rafting is observed in the 8Cr sample after creep testing, as illustrated in Figure 3.7(e). This is consistent with the reported observation that Cr additions decrease the γ - γ' lattice misfit by substitution of the large W atoms in the γ' structure [2]: a smaller lattice misfit results in a reduced driving force for rafting due to the lack of anisotropic stress field around precipitates during unidirectional loading [99], and it has been shown that an alloy with zero misfit when undergoing creep exhibits isotropic γ' coarsening without rafting [97]. The lack of rafting for the 8Cr alloy may indicate a near zero γ - γ' lattice misfit at 850 °C. Furthermore, as observed earlier, the coarsening rate of the γ' -precipitates appears to decrease upon the addition of Cr, and this effect may also contribute to the decreased degree of rafting.

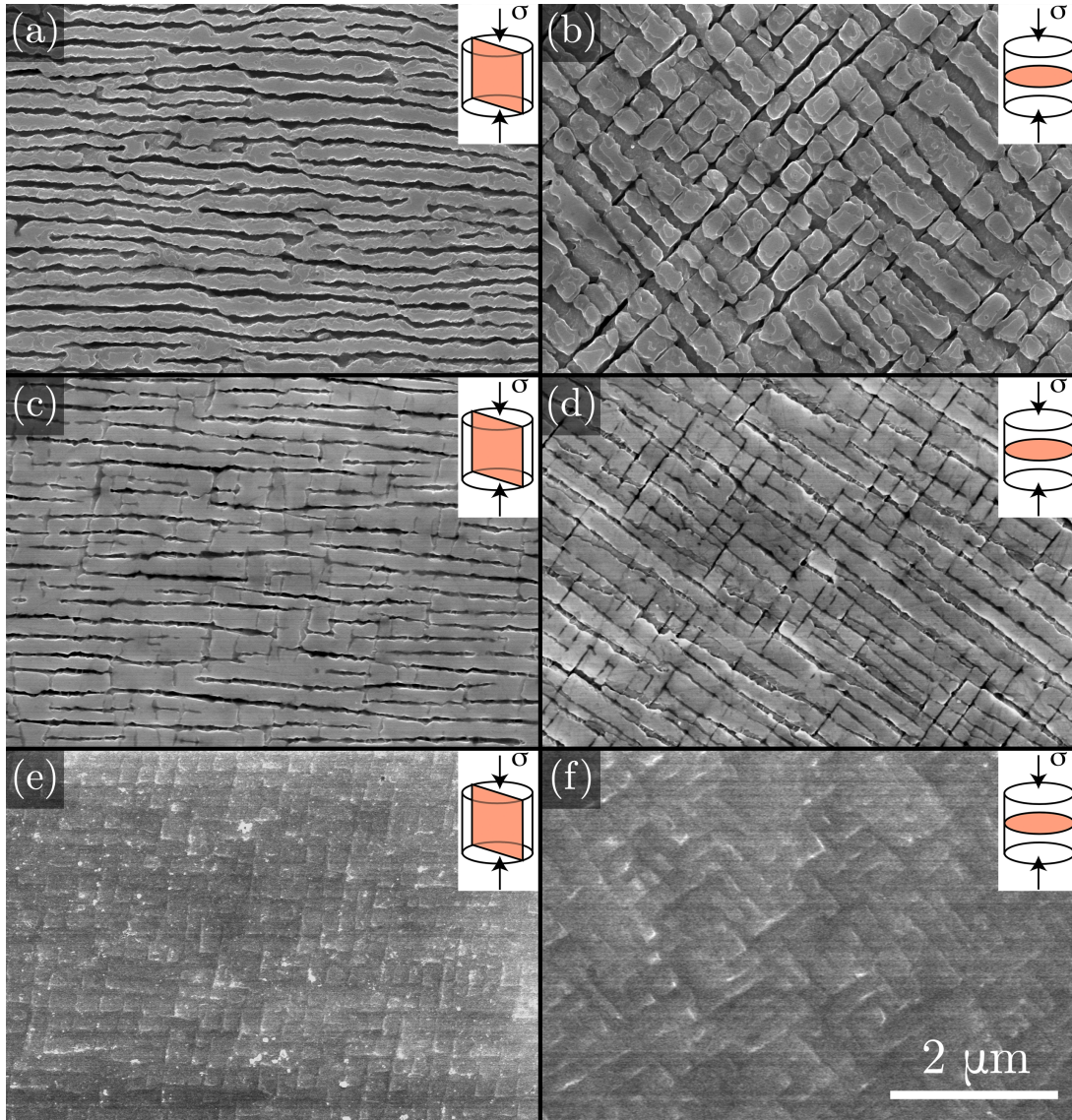


Figure 3.7. Post-creep SEM micrographs of (a, b) 0Cr, (c, d) 4Cr, and (e, f) 8Cr samples, showing rafted γ' structure for 0Cr and 4Cr in two orientations with respect to applied stress σ .

Another Co-based superalloy with significant Ni content was shown to exhibit antiphase boundaries created from dislocation shearing of the γ' -precipitates at stresses over 275 MPa at 900 °C [127]. It has been suggested that rafting has a negative impact

on creep performance in Ni-based superalloys, when the main deformation mechanism involves dislocations shearing through precipitates at low temperature and high stress creep regime [97]. In our 8Cr alloy, the absence of rafting due to Cr addition may thus offset any potential weakening effects such as changes to stacking fault energies or precipitation of additional phases that scavenge solid-solution strengthening elements. However, other studies of Co-based superalloys have suggested that rafting may improve creep resistance even when γ' shearing occurs [93, 94]. Differences between our 0Cr, 4Cr, and 8Cr alloys in grain structures, including dimensions, morphology, and orientation with respect the applied load may also impact the creep behavior, so a more systematic study is needed to explain the creep strengthening effect observed here upon Cr addition to the 0Cr base alloy.

3.4. Conclusion

We investigate herein the effect of adding 4, 8, and 12 at.% Cr to the multicomponent Co-30Ni-7Al-4Ti-3Mo-2W-1Nb-1Ta-0.1B (at.%) alloy with γ - γ' structure in terms of microstructure and creep properties.

- Chromium additions monotonically reduce the γ' solvus temperature, as well as the alloy solidus and liquidus temperatures, thereby reducing the maximum operating temperature of the alloy.
- Cr-modified alloys display γ' -precipitates that are less cuboidal in shape and coarsen more slowly. While the alloy with 4% Cr displays a two-phase γ - γ' structure, the alloy with 8 at.% Cr exhibits some Mo-rich intermetallic phases at grain boundaries, and the alloy with 12 at.% Cr additionally shows extensive

secondary phase within the grains upon aging. For this particular alloy series, the optimum Cr content (to balance oxidation resistance and microstructural stability) is therefore in the vicinity of 8 at.%.

- Atom-probe tomography measurements of aged alloys show that Co and Cr partition to the γ -matrix, while Ni, Al, W, Ti, Ta, Nb, and B partition to the γ' -phase. Chromium additions generally increases the partitioning of elements to the γ' -precipitates, except for B and W, which Cr displaces from the Z sublattice into the X_3Z ($L1_2$)-structure, and Mo, which initially has equipartitioning behavior but mildly partitions to the γ -matrix upon Cr addition.
- The two alloys with 4 and 8% Cr show a two-fold decrease in creep rate (at constant stress at 850 °C) as compared to the base, Cr-free alloy, as well as a decreased degree of rafting during creep, which is attributed to a reduction of γ - γ' lattice misfit. This small, but significant improvement in creep resistance upon Cr addition is in contrast to the previously reported behavior of Co-9Al-9W-0.04B, but agrees with results for Ni- containing Co-Al-W alloys, suggesting that the inclusion of Ni in the multicomponent Co-based alloy is crucial to prevent any detrimental effects of Cr on creep resistance.

Supplemental Information

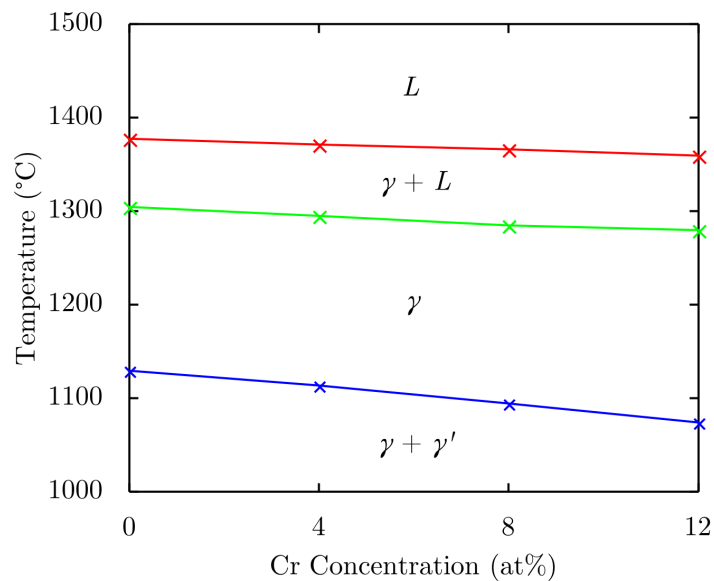


Figure 3.8. Phase diagram of γ' solvus and γ solidus and liquidus temperatures determined by differential scanning calorimetry.

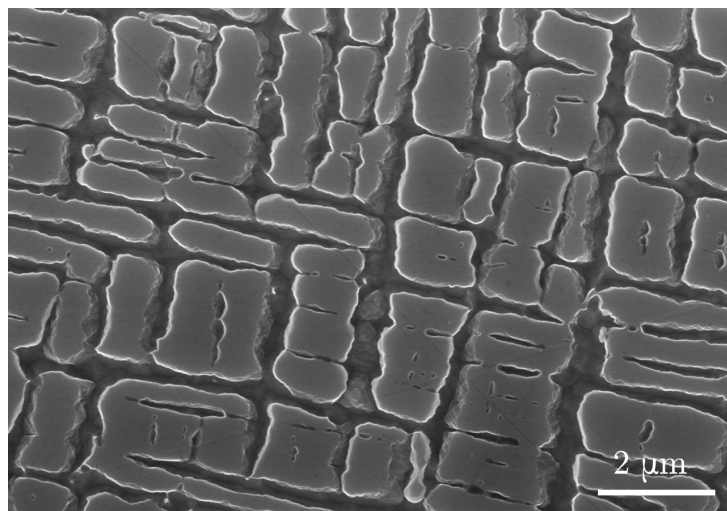


Figure 3.9. Secondary electron SEM micrograph of 0Cr aged at 900 °C for 2000 h showing coalescence of γ' -precipitates.

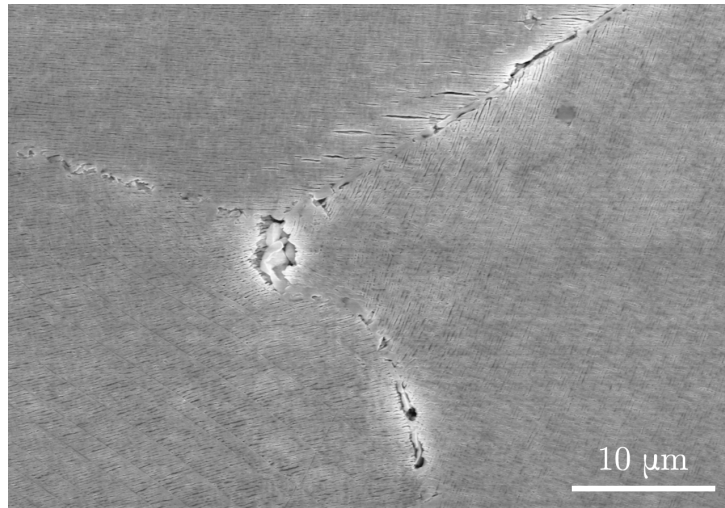


Figure 3.10. Post-creep SEM micrograph of 4Cr sample displaying grain-boundary cracking.

CHAPTER 4

Creep Behavior and Rafting Mechanisms in Cr-Containing γ' -Strengthened Cobalt-Based Superalloys with Different Lattice Misfit

The creep resistance and γ' -rafting mechanism are studied in a series of Cr-containing Co-based superalloy, Co-30Ni-10Al-7W-0.1B-xCr (x=0-6 at.%). As Cr concentration increases, the γ' -morphology changes from cuboidal to spherical, and the γ' -rafting tendency decreases, consistent with a reduction of γ/γ' -lattice misfit. The creep resistance of the alloys is unaffected by additions of up to 4% Cr, but decreases significantly for 6% Cr, consistent with a reduced tendency in the latter alloy to create a rafted γ' -microstructure which impedes dislocation motion during creep. Atom-probe tomography (APT) measurements reveal that the rafted microstructure exhibits a local enrichment of γ -stabilizers (Co and Cr) in the γ -matrix, specifically adjacent to a γ - γ' interface or within a narrow γ -channel in between two coalescing γ' -precipitates. For comparison, APT shows that an unrafted microstructure does not display a local enrichment in γ -stabilizers. These results suggest that γ' -rafting leads to a inhomogeneous elemental distribution within the γ -matrix channels, and help elucidate the underlying diffusion mechanism that occur during γ' -rafting.

4.1. Introduction

Co-based superalloys [16] have attracted significant research efforts since the rediscovery of γ - γ' microstructure in the Co-Al-W ternary system, following an early report by Lee [21]. The higher solidus and liquidus temperatures, as compared to Ni-based superalloys, provide opportunity for more efficient jet engines and gas turbines. However, for the Co-based superalloys to be adopted for such critical applications, their deformation-, coarsening- and corrosion-resistance need to be further improved at elevated temperature [59, 101, 128]. In particular, it is crucial to understand the microstructural evolution of Co-based superalloys under creep conditions (combined high temperatures and stresses), as the difference in lattice misfit between the γ' -precipitates and the γ -matrix, affect the latter directional coarsening (rafting). Whereas Co-based superalloys commonly exhibit a positive misfit, Ni-based superalloys typically have a negative misfit [91], thus affecting the direction of γ' -rafting and the resulting mechanical properties. Therefore, understanding the effect of lattice misfit on creep resistance and the underlying mechanism that governs γ' -rafting is key to the development of Co-based superalloys.

In Co-based superalloys, the magnitude of the positive γ - γ' lattice misfit is affected by the partitioning of alloying elements in these two phases. Alloying elements that partition toward the precipitate (γ' -formers) typically increase the lattice misfit by increasing the lattice parameter of the γ' -phase [38]. Conversely, elements which partition toward the γ -matrix (γ -stabilizers) typically decrease the lattice misfit through expanding the lattice spacing in the γ -phase [58]. In particular, addition of Cr to Co-based superalloys has been shown to consistently reduce the lattice misfit, evident from the change in γ' -morphology, γ' -rafting, and lattice parameter measurement from X-ray and neutron diffraction [129].

However, the effect of reduced lattice misfit on creep resistance of Co-based superalloys has yet to be clearly elucidated. Povstugar *et al.* [2] showed that creep resistance of a quaternary Co-Al-W-xCr is negatively impacted by Cr addition, and attributed the deterioration in mechanical properties to the lower lattice misfit in Cr-containing alloys. However, recent studies by Ng *et al.* [130] and Chung *et al.* [131] in multicomponent Co-based superalloys (with 10 and 8 elements, respectively) show that, while Cr reduces the γ - γ' lattice misfit, the creep resistance of the alloy is only weakly reduced, even for additions as high as 8 at.% Cr.

To understand the microstructural evolution and the corresponding vacancy-assisted transport phenomena during creep, previous works have utilized both transmission electron microscopy (TEM) and atom-probe tomography (APT) to study the post-creep micro-segregation behavior in Co-based superalloys. Freund *et al.* [132] employed TEM to study the elemental segregation that occurs during micro-twinning of a polycrystalline Co-based superalloy. It was shown that Co and Cr preferentially segregate toward the twin boundary, lowering local fault energy to facilitate slip of partial dislocations. Makineni *et al.* [133] used APT to show that both partial dislocations and anti-phase boundaries within γ' -precipitates are enriched in Co and Cr. Similar creep-induced defect-assisted segregation behavior has been observed in Ni-based superalloys [134, 135]. While numerous efforts have been focused on characterization of nanoscale creep-induced segregation in γ' -phase of Co-based superalloys, few studies have addressed the effect of rafting on segregation in the γ -phase matrix. Understanding of rafting-induced compositional redistribution on the nanoscale may help design Co-based superalloys with better coarsening- and creep-resistance.

In this paper, Cr alloying is used to adjust the lattice misfit in a moderately complex Co-Ni-Al-W-B alloy. The effect of the reduced γ - γ' misfit on the high temperature creep resistance is investigated via compressive creep. The effect of γ' -rafting on the local γ -phase composition is then studied by APT to explain the underlying elemental redistribution mechanism that occur during γ' -rafting in Co-based superalloys.

4.2. Experimental Methods

Table 4.1. Nominal composition of the D-xCr series alloy given in at.% and (wt.%) along with the phase transformation temperatures measured by DSC.

Alloy	Co	Ni	Al	W	B	Cr	γ' -solvus ($^{\circ}$ C)	γ -solidus ($^{\circ}$ C)	γ -liquidus ($^{\circ}$ C)
0Cr	53.0 (48.5)	30 (27.3)	10 (4.2)	7 (20.0)	0.1 (0.02)	0 (0)	1038	1451	1468
2Cr	51.8 (47.7)	30 (27.5)	9.5 (4.0)	6.7 (19.2)	0.1 (0.02)	2 (1.6)	1016	1448	1464
4Cr	50.6 (46.9)	30 (27.7)	9.1 (3.8)	6.3 (18.3)	0.1 (0.02)	4 (3.3)	1043	1462	1469
6Cr	49.4 (46.1)	30 (27.9)	8.6 (3.7)	6.0 (17.5)	0.1 (0.02)	6 (4.9)	987	1442	1460

The base alloy (0Cr), with a Cr-free composition of Co-30Ni-10Al-7W-0.1B (at.%), was designed from a Co-Al-W basis with Ni addition to broaden the γ - γ' phase field to accommodate subsequent Cr alloying without formation of topologically closed-packed phases [6]. Boron was added to strengthen the grain boundary based on previously observed grain boundary cracking [49, 50, 60]. The base alloy (labelled as 0Cr) was then modified by addition of 2, 4 or 6 at.% Cr (labelled as 2Cr, 4Cr and 6Cr) to examine the effect of Cr on creep resistance and rafting behavior. For a given amount of Cr, the concentration of Co was reduced by 4/5 and the concentration of γ' -formers (Al and W)

by 1/5 to maintain a constant γ' volume fraction based on a Cr partitioning coefficient of $\kappa_{\gamma'/\gamma} \approx 0.25$ [61]. The nominal composition of each alloy is shown in Table 4.1 along with the measured γ' -solvus, γ -solidus and γ -liquidus temperatures.

The alloys were prepared by arc-melting pure metals (99.9+% purity) under argon atmosphere. Each ingots (with a mass of 100g) was remelted at least eight times to ensure compositional homogeneity. After arc-melting, the alloys were subjected to a three-step heat treatment : (i) homogenization at 1200 °C for 24 h ; (ii) boride precipitation at 1050 °C for 12 h. and (iii) γ' -precipitation at 900 °C for 168 h. The boride precipitation step promotes formation of grain-boundary boride without a reduced γ' depletion zone, thus enhancing the high temperature mechanical properties [60].

The γ' -solvus, γ -solidus and γ -liquidus temperatures were measured via differential scanning calorimetry (DSC) (Netzsch 404c) using as-homogenized samples under flowing argon (20 mL/min) and heating and cooling rates of 10K/min. DSC results were analyzed following the National Institute of Standard and Technology guideline [62] where the phase transformation temperatures were determined from the first visible onset of deviation from the heating curve. Microstructural studies were conducted on a Hitachi SU8030 scanning electron microscope (SEM) equipped with a cold-field-emission source and energy dispersive spectroscopy (EDS). An operating voltage of 25 kV and a 15 mm working distance were utilized.

All compressive creep experiments were conducted at 900 ± 2 °C. Creep specimens were machined into compressive cylinders with a 5 mm diameter and a 10mm height via electro-discharge machining from as-aged ingots. Creep specimens were placed between

boron-nitride lubricated silicon carbide platens and heated without load to the test temperature. For the multi-stress creep tests, each applied stress was held constant until the minimum strain rate was measured to be two orders of magnitude larger than the sampling error. The multi-stress creep specimens were furnace-cooled with load after the tests. For the single-stress creep experiment, a compressive load of 150 MPa was applied for 50 h before unloading and immediately quenching the specimen in water to avoid further microstructural evolution during cooling for atom-probe tomographic (APT) study. Sample displacements were measured using a linear variable displacement transducer with a resolution of 10 μm .

APT [64, 65] was used to study the rafting induced compositional inhomogeneity before and after creep. For rafted samples, to target the specific rafted microstructure, a FEI Helios Nanolab microscope equipped with focused ion-beam (FIB) capability (FEI Helios Nanolab 600 dual-beam FIB/SEM) was used to prepare the region specific APT specimen (see Supplemental Figure 4.11) [63]. For as-aged and unrafted samples, where region specific sample preparation is not needed, APT specimens were prepared via a two-step electropolishing [136]. A coarse-polishing step in 20% chromic acid, 30% hydrochloric acid (12.1M) and 50% deionized water was performed at 5.5 V dc under room temperature. The final sharpening was performed at 20V dc in a 2% perchloric acid, 1% hydrochloric acid, 1% chromic acid in 2-butoxyethanol solution [78]. All APT experiments were conducted on a local-electrode atom-probe tomograph (LEAP 5000XS, Cameca) with a pulse laser energy of 30 pJ, pulse frequency of 500 kHz, temperature of

25 K and a maximum evaporation rate of 5% using a picosecond laser (355 nm wavelength) [137]. APT data were analyzed using the IVAS software package, version number 3.6, from CAMECA Instruments Inc.

4.3. Results and Discussion

4.3.1. Microstructure Under As-aged Condition

Figure 4.1 shows the microstructure of the four D-xCr alloys, with Cr concentration of 0, 2, 4 and 6 at.%, after 168 h of γ' -aging at 900 °C. The microstructures prior to γ' -aging (after boride precipitation at 1050 °C) are presented in Supplemental Figure 4.12 and show a single γ -phase with borides along grain boundaries. Figure 4.1 shows that, with increasing Cr concentration, the alloys exhibit a similar γ' volume fraction of $\approx 50\%$ ($V_f^{0Cr} = 55 \pm 4\%$, $V_f^{2Cr} = 49 \pm 1\%$, $V_f^{4Cr} = 46 \pm 1\%$ and $V_f^{6Cr} = 46 \pm 2\%$), suggesting that the composition balance based on $\kappa_{\gamma'/\gamma} \approx 0.25$ is effective in maintaining a constant γ' volume fraction when adding Cr. The γ' -morphology transitions from cuboidal to spherical with increased Cr content, where the spherical morphology is most apparent in the 6Cr alloy shown in Figure 4.1(d). This morphological transition suggests a reduced lattice parameter misfit, based on similar morphological changes observed in both Ni- and Co-based superalloys [138, 139, 140]. Specifically, in Cr-containing Co-based superalloys, Povstugar *et al.* [2] and Chung *et al.* [131] have shown that Cr preferentially displaces W from the L1₂ lattice site towards the γ -phase. The change in W partitioning results in an increased and decreased lattice parameter of the γ - and γ' -phase, respectively, producing a lower γ - γ' misfit.

Insets of Figure 4.1 show the grain-boundary microstructure of the D-xCr alloys decorated with boride precipitates whose fraction progressively decreases as the Cr concentration increases, evident by the increasingly thinner and more dispersed boride along the grain boundaries. A previous study by Klob *et al.* [60] showed that ternary Co-Al-W exhibits a very low B solubility, $< 0.04\text{at.}\%$. Thus, any addition of B beyond the solubility limit is expected to segregate toward the grain boundary [50], consistent with the large fraction of grain boundary boride observed in the 0Cr alloy. However, in our case, the boride fraction decreases with increasing Cr concentration. In particular, the 6Cr alloy exhibit significantly less grain boundary boride compared to other alloys. Investigation of multicomponent Co-based superalloys, with up to 9 elemental constituents, has shown that these heavily alloyed systems show relatively little grain-boundary borides, even though B segregates to grain boundaries. Ng *et al.* [130] proposed that B solubility in γ' -phase increases in multicomponent alloy, reducing B segregation at grain boundaries. Long *et al.* [141] further confirmed the increased B solubility in a single-phase $L1_2$ -ordered Co-based alloy (pure γ'), from 0.04 at.% in Co-Al-W to 0.08 at.% in the multinary γ' -intermetallic alloy. These results suggest that, as the Cr content increases in D-xCr alloys, the B solubility in the γ' -phase increases concomitantly, reducing the B segregation (and thus boride formation) at γ -grain-boundary. Detailed AP measurements of grain-boundary segregation will have to be done to confirm this hypothesis.

4.3.2. Creep Results and Microstructure

Figure 4.2 plots the minimum strain rate against the applied compressive stress for each of D-xCr alloys during creep at 900 °C. The creep behavior is assumed to follow the

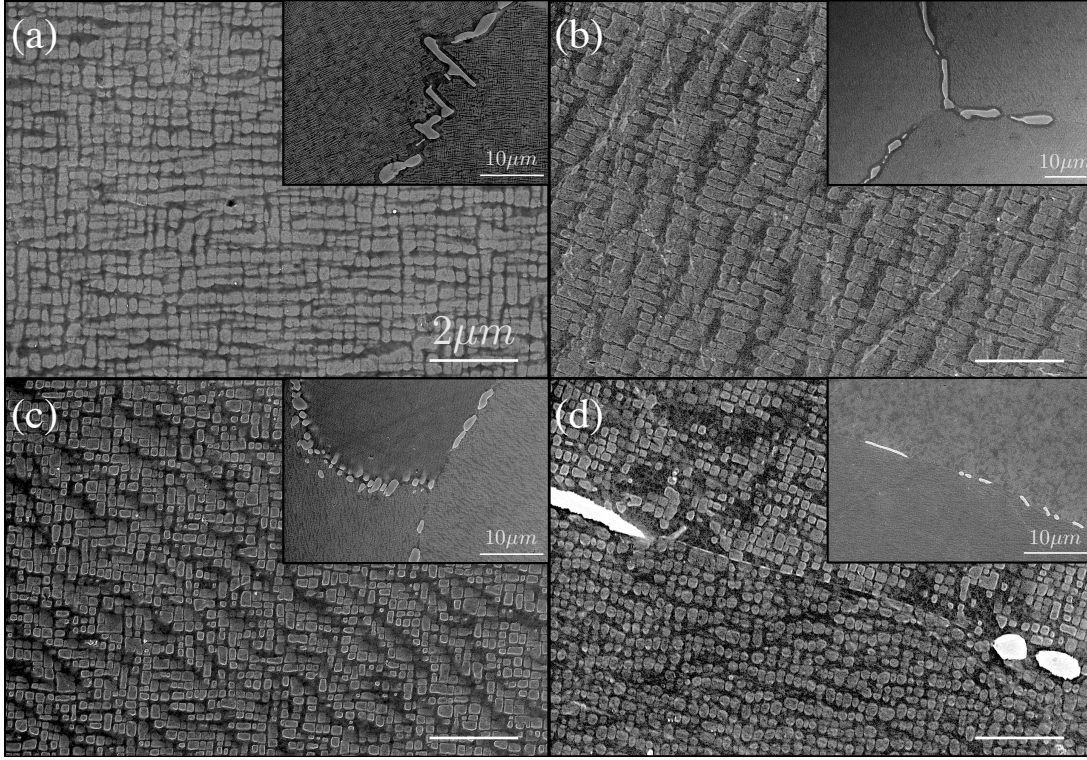


Figure 4.1. Microstructure of D-xCr alloys, (a) 0Cr, (b) 2Cr, (c) 4Cr and (d) 6Cr aged at 900 °C for 168 h. Insets show the grain boundary of each alloy decorated with boride precipitates.

Mukherjee-Bird-Dorn power-law equation:

$$(4.1) \quad \dot{\epsilon} = A\sigma^n \exp(-Q/RT)$$

where $\dot{\epsilon}$ is the strain rate, A is a constant, σ is the applied stress, n is the stress exponent, Q is the creep activation energy, R is the gas constant, and T is the temperature. The creep data show that 0Cr, 2Cr and 4Cr alloys demonstrate a comparable power-law creep behavior with similar minimum strain rates. The 6Cr alloy shows a minimum strain rate approximately an order of magnitude higher, at a given stress, than those with a lower Cr content, indicative of a lower creep resistance.

Povstugar *et al.* [2] show that Cr additions significantly weaken the high temperature creep strength of ternary Co-9Al-9W, with an addition of 4 at.% of Cr (Co-9Al-9W-4Cr) increasing the minimum strain rate by an order of magnitude and 8 at.% (Co-9Al-9W-8Cr) by two orders of magnitude. The authors attribute the weakening effect to the reduced lattice misfit. However, previous study on multinary Co-based superalloys conducted by others show that Cr does not impact the creep resistance. Specifically, Ng *et al.* [130] show that Co-30Ni-7Al-2W-4Ti-3Mo-1Nb-1Ta-0.1B-xCr (x=0-12 at.%) alloys exhibit a similar creep resistance between the Cr-free and the 8 at.% Cr variant. Similar results were obtained in a study of multinary Co-30Ni-11Al-5.5W-2Ti-2.5Ta-0.1B-xCr (x=0-12 at.%) alloy performed by Chung *et al.* [131]; while Cr alloying progressively reduces the lattice misfit from 0.6 to 0.2%, as measured via synchrotron XRD, creep resistance was not impacted as significantly as in the quaternary Co-9Al-9W-xCr alloys. The confounding effects of Cr on creep resistance suggest that in addition to the reduced lattice misfit, other factors are also influencing the creep strength of Co-based superalloys. Potential discrepancy may arise from multicomponent alloying, TCP phase precipitation in the Co-9Al-9W-xCr system, change in γ' volume fraction with Cr.

Zenk *et al.* [26] and Titus *et al.* [127] theorize that a high Ni content of 30 at.%, when used in multi-component Co-based superalloys, may increase the stacking fault and anti-phase boundary energy, thus compensating the weakened creep resistance from the reduced lattice misfit. However, present results show that creep resistance is degraded for 6% Cr additions, even with a constant Ni concentration at 30 at.%. Therefore, it is likely that other alloying elements commonly employed in multinary Co-based superalloys, such as Ti, Mo, Nb and Ta, are effective in maintaining the creep resistance with Cr addition.

Among these elements, Ti is shown to be most effective in enhancing the mechanical properties of Co-based superalloys. Xue *et al.* [29] and Zenk *et al.* [28, 38] show that a small fraction of Ti addition leads to a significantly improved creep resistance via multiple mechanisms, *i.e.*, an increased lattice misfit and formation of dislocation network in γ -phase which both inhibit dislocation motion within the γ -matrix, and an increased stacking fault and APB energy to prevent shearing in γ' -phase. Hence, it is possible that strengthening by Ti overshadows any weakening by Cr explaining the stable creep resistance observed up to 4% Cr addition in our multicomponent Co-based superalloy.

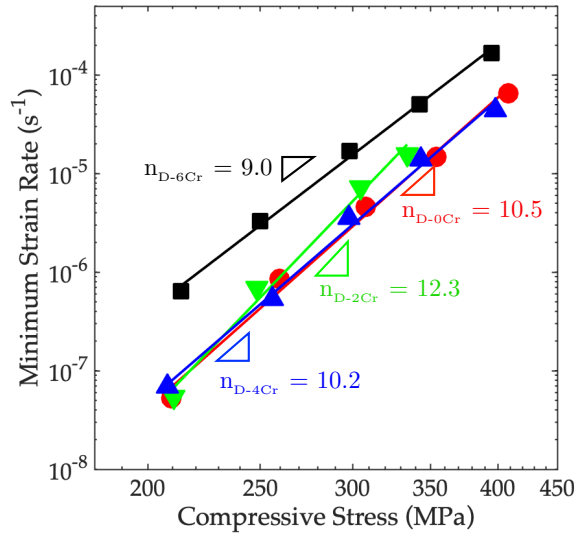


Figure 4.2. Double-logarithmic plot of minimum creep strain-rate vs. applied compressive stress at 900 °C for D-xCr alloys. The slope of each alloy corresponds to the stress exponent, n , derived from the power law creep model Eq. 4.1. Total accumulated creep strain and elapsed time of each creep specimens is as follow, 0Cr: $\epsilon_f = 10\%$, $t_f = 75h$; 2Cr: $\epsilon_f = 14\%$, $t_f = 47h$; 4Cr: $\epsilon_f = 11\%$, $t_f = 43h$; 6Cr: $\epsilon_f = 9\%$, $t_f = 15h$.

The microstructures of D-xCr after multi-stress compressive creep are shown in Figure 4.3. Under compressive stresses, positive-misfit Co-based superalloys are expected to

exhibit n-type rafting where γ' -precipitates coarsen preferentially in a direction perpendicular to the applied compressive stress axis [58, 94, 98, 108]. Due to the polycrystallinity of arc-melted samples, grains with various crystallographic orientation with respect to the uniaxial stress are expected to exhibit varying rafting behavior. Figure 4.3 highlights the most rafted grain within the studied cross-section.

As visible in cross-sections parallel to the applied stress axis (Figure 4.3), the degree of rafting decreases with increasing Cr concentration. The reduced rafting in alloys with a higher Cr concentration is indicative of the reduced lattice misfit [2, 129, 130, 131]. The perpendicular cross-sections of the post-creep 0Cr alloy (Figure 4.3) illustrates the horizontal γ' -platelets formed via n-type rafting. In a heavily rafted microstructure such as in the 0Cr alloy, all γ' -precipitates exhibit either a coalesced irregular or cubic, plate-like cross-section. The morphology of the γ' -platelet is determined by the coherency of the γ - γ' interface after creep; if an interface has relaxed via interfacial dislocation pile-up, the γ' -platelet likely exhibit an irregular morphology [99, 142]. The coalescence along the perpendicular cross-section is not evident in the 2Cr, 4Cr and 6Cr alloys shown in Figure 4.3(b)-(d) consistent with a reduced degree of rafting from a smaller lattice misfit. The grain-to-grain mechanical interaction may also alter the rafting direction, as shown in the perpendicular cross-section of the 2Cr alloy (Figure 4.3(b)) where γ' can be found directionally rafted perpendicular to the applied stress.

Figure 4.3 further illustrates the post-creep grain boundary microstructure of D-xCr alloys. Grain-boundary boride fracture is often observed after 8% of accumulated compressive creep strain, corroborating the lack of grain-boundary ductility in Co-based superalloys [49, 50, 60]. The borides in the 0Cr alloy fractured in a piece-wise manner

suggesting significant stresses are present at the grain-boundaries during creep. In the 2Cr alloy, the boride precipitates are fractured with cracks propagating in multiple directions. Grain-boundary microstructure of the 2Cr alloy shows a larger precipitate-depleted zone compared to the 0Cr alloys. Krol *et al.* [143, 144, 145] demonstrate that the yield strength of Ni-based superalloys decreases drastically when the width of the precipitate-depleted zone exceeds a certain limit. This mechanism may explain the higher prevalence of grain boundary boride failure in the 2Cr alloy. The 6Cr alloy exhibits an even higher grain boundary brittleness compared to the other alloys. The cracks propagate from the fractured grain boundary into the adjacent grains. The extensive grain boundary cracking may contribute to the increased creep strain rate observed in the 6Cr alloys shown in Figure 4.2, at which point the Cr effect on creep resistance may be related to the γ' -morphology change less than expected. Finally, unlike the other D-xCr alloys, the 4Cr alloy does not exhibit any grain boundary boride failure. The amount of grain boundary decorated with boride in the crept 4Cr alloy is also less than for the other alloys studied herein. In addition to the brittleness of the grain boundary, the different fracture behavior may be due to the different grain-to-grain mechanical interaction in the coarse-grain arc-melted samples.

The multi-stress creep experiments used here do not allow for a straightforward comparison of post-creep microstructures, due to variation in accumulated creep strain and time between specimens, thus preventing an accurate rafting comparison between D-xCr alloys. In addition, in multi-stress experiments, creep results are often convoluted with different microstructural evolution at different creep stresses which may influence the measured creep response.

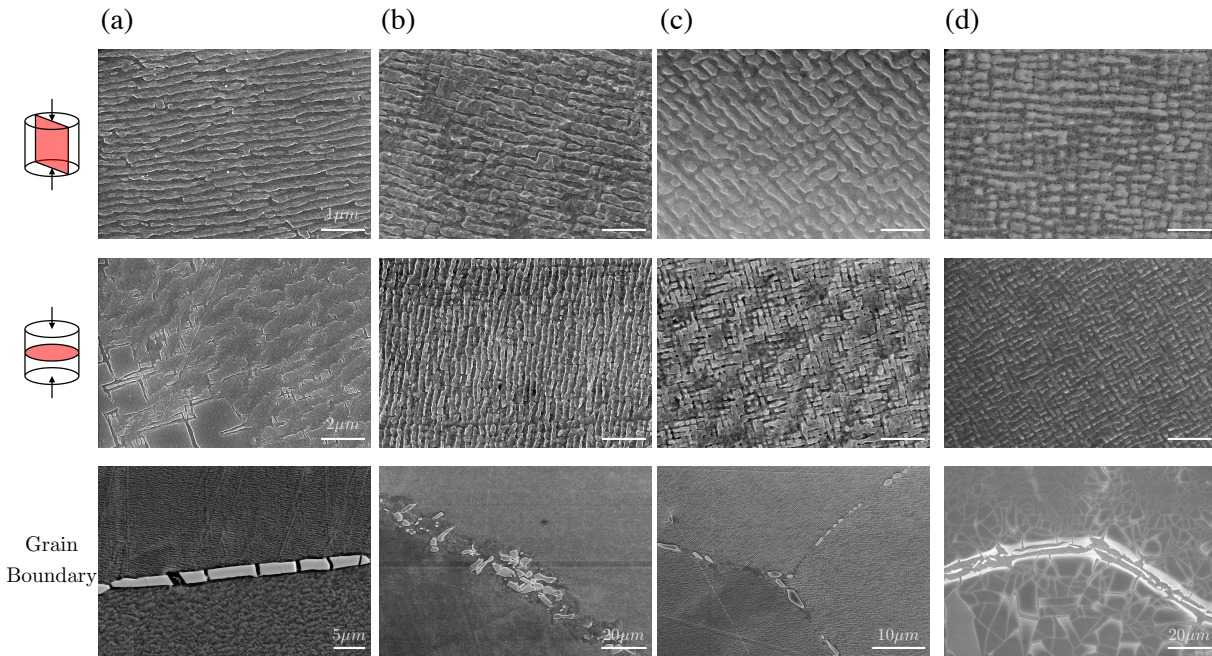


Figure 4.3. Post-creep microstructure of D-xCr alloys (a) 0Cr, (b) 2Cr, (c) 4Cr and (d) 6Cr after multi-stress creep at 900 °C. Micrographs shows the planes parallel, perpendicular to the loading axis and the post-creep grain boundary microstructure.

Figure 4.4 shows the single-stress compressive creep behavior of D-xCr alloys performed at 150 MPa / 50 h / 900 °C. The measured strain rate at the end of the creep experiment shows that increasing Cr concentration (*i.e.*, reduced lattice misfit) resulted in a small, but measurable increase in strain rate, where the strain rate is approximately doubled between the 0Cr alloy and the 4 and 6Cr alloys. The difference in the single-stress creep behavior can be attributed to the change in lattice misfit and the corresponding rafting behavior. Alternatively, it is possible that the creep variation arise from the grain-to-grain interaction from polycrystal specimens. The shorter primary creep regime observed in the 0Cr alloy may also be due to the larger lattice misfit. When subjected to a compressive stress, the γ -channels, in alloys with a larger lattice misfit, experience a higher stress

due to the larger coherency stress between the precipitates and the matrix [55, 99, 146]. This might result in a faster dislocation accumulation in, and hardening of, the γ -phase, and thus a shorter primary creep regime in the 0Cr alloy. The lower strain rate measured in the alloy with a lower Cr concentration is likely due to the creep strengthening from γ' -rafting. Figure 4.5 shows the microstructure of D-xCr alloys after single-stress creep, where the extent of rafting is reduced as the Cr content is increased. Previous studies on Co-based superalloys [7, 108, 147] have shown that rafting under both compressive and tensile stress is associated with a reduced creep strain rate, where the primary strengthening mechanism is via a lengthened glide/climb path for matrix dislocation, needed to circumvent rafted γ' -precipitates. Similar observations have also been made in Ni-based superalloys [10, 148]. Therefore, it is plausible that the 2Cr, 4Cr and 6Cr alloys exhibit a somewhat higher strain rate from the lack of rafting-induced strengthening. For the low strain rate studied here (Figure 4.4), the difference is relatively modest, about a factor 2.

The rafted microstructure after the single-stress creep shown in Figure 4.5 more accurately illustrates the rafting tendency from Cr addition than multi-stress creep. Here, the alloy with the largest lattice misfit, 0Cr, clearly exhibits the highest degree of rafting, with γ' -precipitates coalescing to form high-aspect ratio rafts. The γ - γ' interfaces in the post-creep 0Cr specimen are also more jagged, consistent with a partial or full loss of coherency after creep [99, 142]. Alloys with a lower lattice misfit, *i.e.*, 2Cr and 4Cr, show a lower degree of rafting as some γ' -precipitates have directionally coarsened but have yet to coalesce, as seen in Figure 4.5(b) inset. Jokisaari *et al.* [9], using a phase field approach that consider elastic interaction between γ' -precipitates, have demonstrated that coalescence during rafting depends on the magnitudes of both the applied stress and lattice

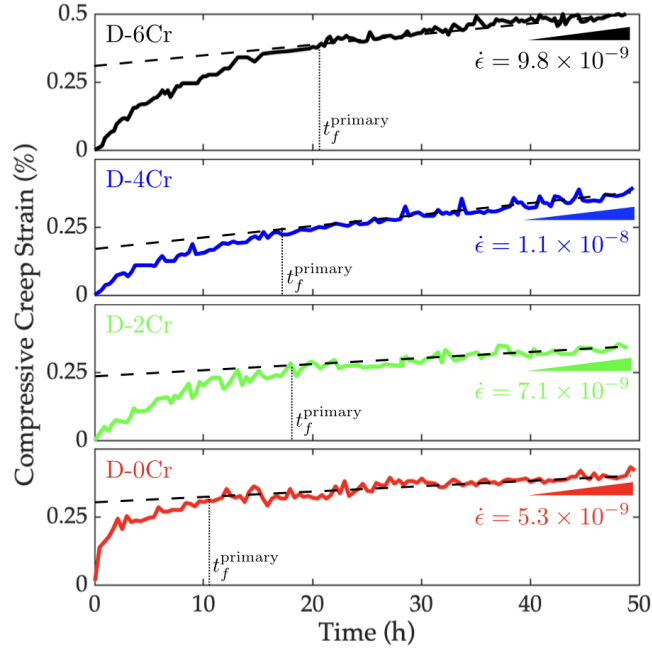


Figure 4.4. Plot of creep strain as a function of time for each of the D-xCr alloy during 150 MPa / 900 °C compressive creep experiments lasting for 50 h. The strain rates measured from the last 10 h of the experiment are shown for each alloy. Primary creep strain and elapsed time are estimated by extrapolating steady-state creep strain rate to $t = 0$.

misfit. A sufficiently large applied stress or a lattice misfit is needed to overcome the elastic interaction between two neighboring γ' -precipitates, leading to their coalescence. In the crept 2Cr alloy, coalescence is stalled for numerous γ' -precipitates, leaving narrow γ -channels between the precipitates; this is likely because the reduced lattice misfit does not provide sufficient driving force to overcome the elastic interaction between two γ - γ' interfaces. In the 6Cr alloy, no rafting is observed after the single-stress creep, as expected since the alloy has the lowest lattice misfit from its highest Cr content (see Figure 4.5(d)). However, it can be inferred that the 6Cr alloy still exhibits a positive lattice misfit at 900 °C, since γ' -rafting occurs after multi-stress creep where the specimen was stressed

to 400 MPa (Figure 4.2). The gradual change in rafting behavior from 0Cr to 6Cr alloy, illustrated via single-stress creep experiments, provides a more representative illustration of the effect of Cr on affecting the lattice misfit and rafting tendency.

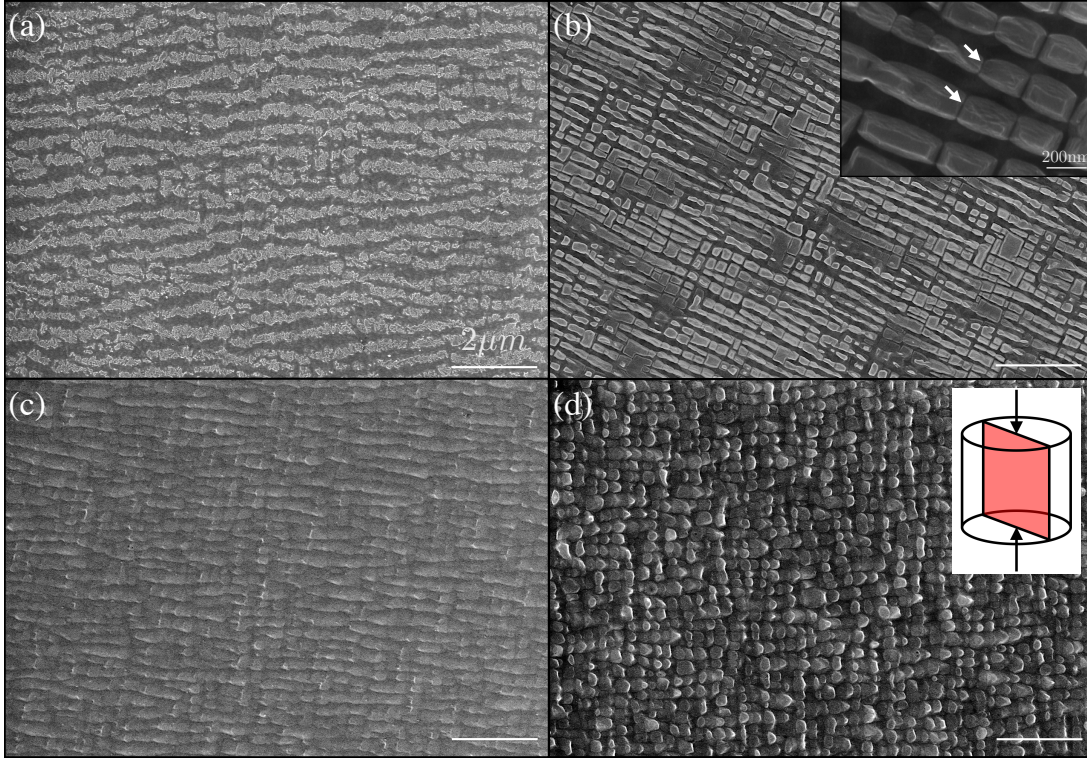


Figure 4.5. Post-creep microstructure of D-xCr alloy series (a) 0Cr, (b) 2Cr, (c) 4Cr and (d) 6Cr after the 150 MPa / 50 h / 900 °C of compressive creep. All microstructures correspond to cross section parallel to the applied stress.

4.3.3. Atom-Probe Tomography Analysis of As-aged and Crept Specimens

Figure 4.6 shows the APT reconstruction of the as-aged and single-stress crept 2Cr alloy, which was selected due to its rafting state, where the γ' -precipitates had directionally coarsened but not yet coalesced. The examined nanotip of the as-aged 2Cr alloy exhibits a highly cuboidal γ' -morphology with $\{100\}$ facets and sharp $\{110\}$ edges and $\{111\}$

corners. In addition of featuring the γ' -morphology, Figure 4.6 further highlights the effect of creep and rafting on local composition in the γ -matrix. Specifically, the nanotip is obtained from a rafted region shown in the inset of Figure 4.6(b). After the single-stress creep experiment, where compressive stress is applied along the x-y direction, the two γ' -precipitates at the center of the nanotip were directionally coarsened and left a narrow γ -channel between them as shown in Figure 4.6(b). Analysis of γ -matrix composition, via iso-concentration thresholding (Co=64% and Cr=4%) of both as-aged and crept 2Cr alloy, shows that significant enrichment of γ -stabilizers developed in the crept 2Cr alloys. A higher concentration of Co and Cr is observed in the matrix, both adjacent to the γ - γ' interfaces and within the narrow γ -channel, while the as-aged nanotip does not show such local enrichment of γ -stabilizers (via iso-concentration thresholding).

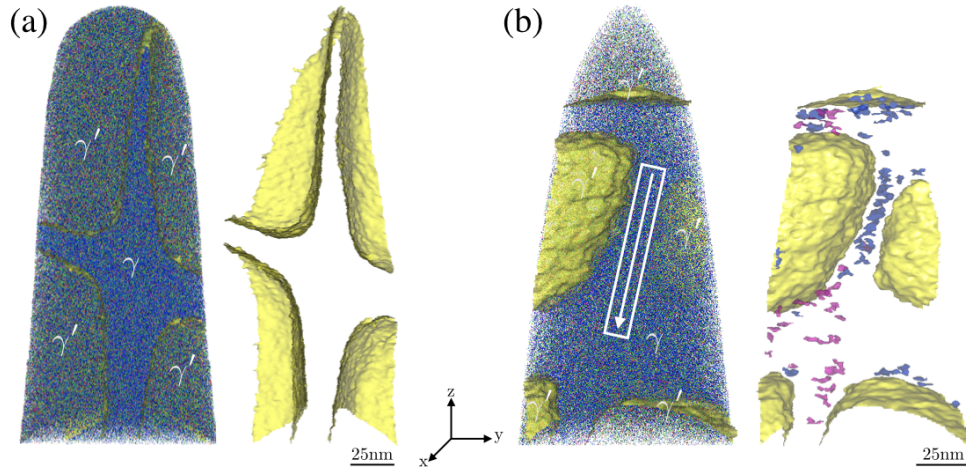


Figure 4.6. APT reconstruction of the 2Cr alloy (a) in as-aged condition and b) after compressive creep for 50 h (150 MPa / 900 °C). Iso-concentration surface inset of both (a) and (b) highlights the γ - γ' interface in yellow (Co=52 at.%). Co (Co=64 at.%) and Cr (Cr = 4 at.%) enrichment within the γ -matrix are highlight by blue and magenta surfaces, respectively. The compressive stress was applied along the x-y direction and γ' -precipitate is rafting along the y-direction.

The concentration profile of the crept 2Cr alloy analyzed across both the narrowing transverse γ -channel and the opened horizontal γ -channel is shown in Figure 4.7. The sampling volume for the profile is shown in Figure 4.6(b). The transverse γ -channel corresponds to the region of γ -matrix between two coalescing γ' -precipitates while the horizontal γ -channel refers to a volume of γ -matrix parallel to the rafting direction. The crept 2Cr alloy exhibits a discernible Co enrichment in the narrow transverse γ -channel while the horizontal γ -channel has a composition comparable to the as-aged γ -phase at Co = 60.2 at.% (see Table 4.2 for phase composition in both as-aged and post-creep 2Cr alloy). In contrast, the concentrations of Ni and Al are less in the transverse channel and again return to their as-aged values in the horizontal channel. The observed local concentration enrichment in the crept 2Cr alloy may be attributed to a stress/rafting-induced compositional redistribution. For rafting to occur during creep, γ' -formers and γ -stabilizers must diffuse towards the transverse and horizontal γ - γ' interfaces, respectively [10, 11, 12]. The Co- and Cr-enrichment within the γ -matrix and adjacent to the γ - γ' interfaces are thus a result of the corresponding cross fluxes between alloy constituents. Kontis *et al.* [13] utilized APT to confirm that γ -matrix interfacial dislocation network in Ni-based superalloys is enriched in Co and Cr after creep, suggesting that γ -stabilizers migrate from interface to interface via dislocation-assisted pipe diffusion. The concentration of Cr and W do not vary significantly across the two analyzed γ -channels, likely because both Cr and W exhibit a diffusivity one to two orders of magnitude or more lower compared to Co, Ni and Al [149, 150, 151].

Alternatively, the enrichment in γ -stabilizers in the γ -channel adjacent to the γ - γ' interfaces may be attributed to supersaturation of the γ -phase during cooling from creep.

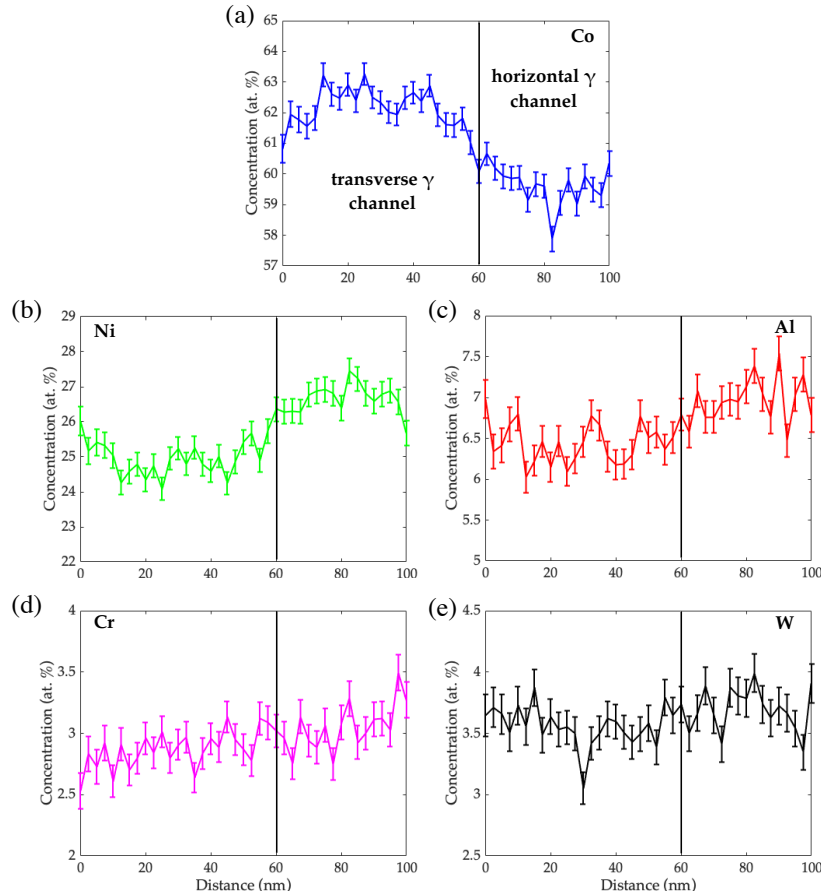


Figure 4.7. Compositional profile of Co, Ni, Al, Cr and W in the crept 2Cr alloy, across both the transverse and horizontal γ -channel, in a n-type rafted microstructure. Compositional gradients exist for Co, Ni and Al across the γ -channels while Cr and W concentrations remain unchanged.

Studies on Ni-based superalloys have demonstrated that composition variations within the γ -matrix occur during γ' growth from a slower cooling rate [152, 153]. While both the as-aged and crept specimens are water-quenched, the cooling rate for the crept specimen is slower due to the additional time needed to be removed from the creep fixture. Table 4.2 shows that after creep, with the exception of W, the average concentration of γ -stabilizers in γ -phase exhibits a modest increase compared to the as-aged alloy. Conversely, the

concentration of γ' -formers decreases within the γ -phase. The supersaturation of Co and Cr in the γ -matrix occur during γ' -precipitate growth while cooling from the creep temperature. As the precipitates grow, γ' -formers are consumed, leaving a matrix enriched in γ -stabilizers and depleted in γ' -formers. The change in composition is also reflected in the as-aged and post-creep partition coefficients listed in Table 4.2. In contrast to other γ' -formers, W exhibit a decreased partition coefficient. This is likely due to W being a slower diffusing element, but W inhomogeneity within the bulk alloy cannot be excluded. The APT reconstruction, proximity histogram, phase composition of all D-xCr alloys under as-aged condition are shown in Supplemental Figure 4.13, 4.14, and Supplemental Table 4.4.

Table 4.2. APT measured composition (at.%) of γ -, γ' -phase and $\kappa_{\gamma'/\gamma}$ partitioning coefficient in the as-aged and post-creep 2Cr alloy.

	Co	Ni	Al	W	B	Cr
As-aged						
γ	60.2	26.4	7.1	3.6	0.004	2.7
γ'	45.3	33.8	13.4	6.2	0.01	1.2
$\kappa_{\gamma'/\gamma}$	0.75	1.28	1.89	1.73	4.11	0.45
post-creep						
γ	60.7	25.9	6.8	3.8	0.007	2.9
γ'	44.3	34.4	14.2	5.8	0.02	1.3
$\kappa_{\gamma'/\gamma}$	0.73	1.33	2.1	1.55	2.52	0.45

Figure 4.8 shows the APT reconstruction of the as-aged and crept 6Cr alloy for which no rafting was observed, unlike the post-creep 2Cr alloy. While the smaller nanotip volume of the as-aged 6Cr alloy shown in Figure 4.8(a) does not capture the spherical morphology of its γ' -precipitates, the post-creep 6Cr alloy (Figure 4.8(b)) displays a spherical γ' -morphology with no distinct crystallographic facet. This further confirms the lack of

rafting from the lower misfit 6Cr alloy. A iso-concentration threshold ($\text{Co}=61\%$ and $\text{Cr}=11\%$) shows that, unlike the rafted 2Cr alloy, the unrafted 6Cr alloy does not exhibit a measurable enrichment in γ -stabilizers within the γ -matrix, indicating that lack of γ' -rafting yield a more compositionally homogeneous γ -phase.

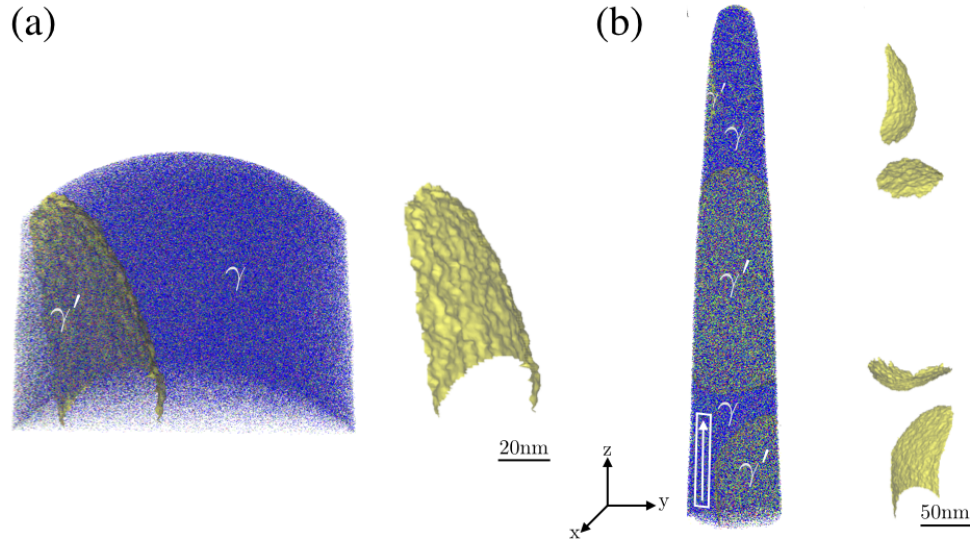


Figure 4.8. Atom-probe tomographic reconstruction of the 6Cr alloy in (a) as-aged condition and b) after compressive creep for 50 h (150 MPa / 900 °C). Iso-concentration surface inset of both (a) and (b) highlights the γ - γ' interface in yellow ($\text{Co}=49$ at.%). Iso-concentration threshold of γ -stabilizers at $\text{Co}=61$ at.% and $\text{Cr} = 11$ at.% reveal no local solute enrichment in these nanotips. The compressive stress was applied along the z direction in the crept specimen.

The homogeneity of the γ -matrix in the crept 6Cr alloy is further illustrated in Figure 4.9, where the concentration of a volume containing both a transverse and a horizontal γ -channel is analyzed. The assessed volume is shown in Figure 4.8(b). In contrast to the rafted 2Cr alloy, the unrafted 6Cr alloy exhibits no apparent compositional variation across different γ -channels. Co, Ni and Al, which previously showed inhomogeneous distributions in the rafted 2Cr alloy (Figure 4.7), all exhibit a uniform concentration in

Figure 4.9. These results provide further evidence that the local enrichment in γ -stabilizers in the rafted 2Cr specimen arise from rafting-induced compositional re-distribution.

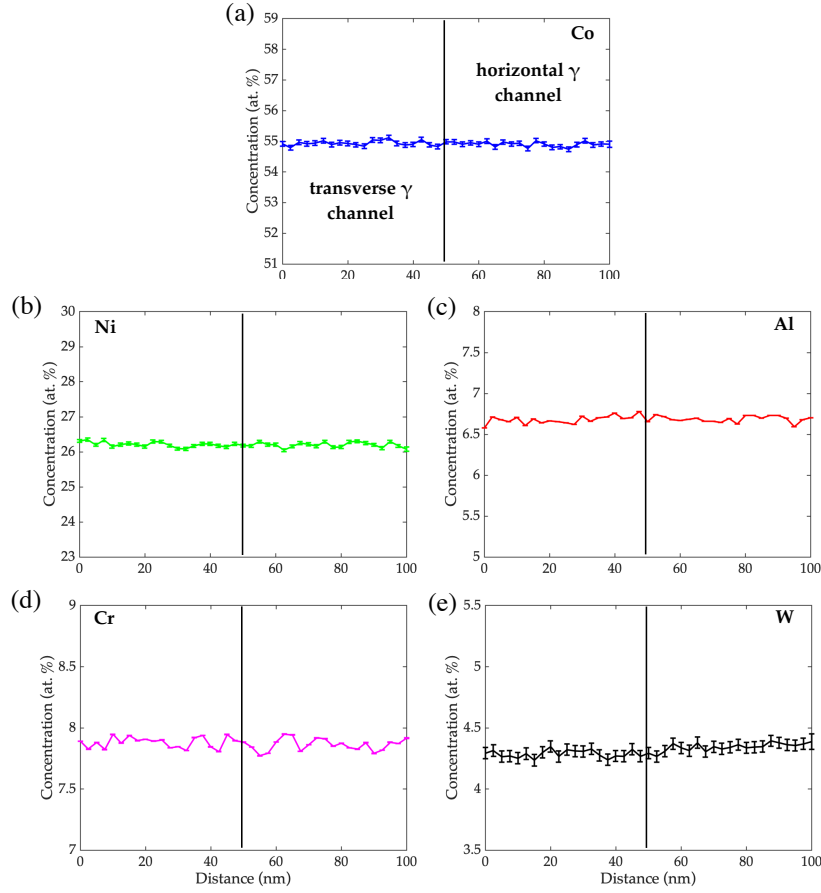


Figure 4.9. Compositional profile of constituent elements of crept 6Cr alloy across both the transverse and horizontal γ -channel shown in Figure 4.8. No significant inhomogeneity is observed across the γ -channels.

Table 4.3 shows the APT measured γ - and γ' -phase composition in the 6Cr alloy before and after creep. Although there are no discernible segregations of γ -stabilizers observed via both iso-concentration thresholding (Figure 4.8) and concentration profile (Figure 4.9), the overall composition of the γ -phase, like the crept 2Cr alloy, still shows a slight increase in γ -stabilizers and a decrease in γ' -formers after creep.

Here, we attribute the change in the overall composition of the γ -phase in crept 6Cr alloy to supersaturation. While cooling from the creep temperature, both the 2Cr and 6Cr alloy exhibit γ' growth and possibly nucleation of secondary γ' -precipitates. The growth of the γ' phase leads to saturation of γ -stabilizers within the γ -matrix as shown previously in the 2Cr (Table 4.2) and here for the 6Cr alloy (Table 4.3). While both crept 2Cr and 6Cr alloys exhibit a higher overall concentration of γ -stabilizers in the γ -phase, only the rafted 2Cr alloy displays distinct local enrichment in Co and Cr, measurable through iso-concentration thresholding and concentration profiles across γ -channels (Figure 4.6 and 4.7). This is strong indication in favor of the hypothesis that the compositional redistribution via γ' -rafting is responsible for the local enrichment observed in the rafted 2Cr alloy, but the overall change in γ -matrix composition after creep is the result of supersaturation from a slower cooling rate. While no secondary γ' -precipitates are observed in the nanotips, the supersaturation suggests that secondary γ' -precipitates are likely present, but not detected through the iso-concentration surface. A more complex cluster analysis [154, 155, 156] may be necessary to resolve secondary γ' -nuclei.

Table 4.3. APT measured composition (at.%) of γ and γ' phases and $\kappa_{\gamma'/\gamma}$ partitioning coefficient for the as-aged and post-creep 6Cr alloy.

	Co	Ni	Al	W	B	Cr
As-aged						
γ	55.3	26.0	6.6	4.1	0.005	7.9
γ'	42.2	35.2	13.2	6.2	0.01	3.2
$\kappa_{\gamma'/\gamma}$	0.76	1.35	1.99	1.50	2.61	0.40
post-creep						
γ	55.7	25.7	6.4	4.1	0.004	8.1
γ'	42.0	35.0	13.5	6.3	0.02	3.2
$\kappa_{\gamma'/\gamma}$	0.75	1.36	2.12	1.54	3.97	0.40

4.3.4. Rafting Mechanisms

The mass transport mechanisms which results in γ' -rafting are often subject to debate, as numerous hypotheses and studies suggest different diffusional processes [10, 11, 12, 13]. Previous studies have established that a cross-flux of γ -stabilizers and γ' -formers must occur in order for rafting to proceed. In addition, the rate of diffusional cross flux is higher than those during classical Ostwald ripening since rafting-related coarsening occur at a higher rate [142, 157, 158]. Here, APT measured compositional variation in the γ -matrix provide understanding to the diffusion mechanism during rafting. The proposed mechanism is illustrated in Figure 4.10.

Under compressive stress, Co-based superalloys with positive γ' - γ misfit raft perpendicular to the applied stress axis, forming n-type rafts. For rafting to occur, γ' -formers must diffuse to the transverse interfaces for directional coarsening of the γ' -precipitates. Since no segregation of γ' -formers is observed in either the horizontal or the transverse γ -channels, the current study suggests that diffusion of γ' -formers likely occur along the γ - γ' interfaces as shown in Figure 4.10(a). Neutron diffraction measurements have shown that lattice misfit is relaxed via dislocation pile-up and loss of coherency along the γ - γ' interfaces during creep of Co-based superalloys [159]. Therefore, γ - γ' interfaces may serve as short-circuit diffusion pathways for the accelerated diffusion of γ' -formers from one interface to another. As the γ' -precipitates coarsen directionally into the transverse channels, γ -stabilizers are rejected into the γ -channels, resulting in local enrichment of γ -stabilizers near the interface. Enrichment of γ -stabilizers in the vicinity of γ - γ' interfaces corroborates with the Co and Cr enrichment near γ - γ' interfaces observed in the rafted 2Cr alloy (see Figure 4.6(b)).

Following the onset of γ' directional coarsening toward the transverse γ -channels, the horizontal γ - γ' interfaces are expected to recede to ensure a constant phase fraction of γ' . The reduction in thickness of γ' -precipitates during rafting has been shown in superalloys that have been extensively rafted [142]. The recession of the horizontal γ - γ' interfaces facilitates the diffusion of γ -stabilizers from the transverse channel toward the horizontal channels through the γ -matrix as shown in Figure 4.10(b), completing the diffusion cross-flux circuit. The enrichment of γ -stabilizers in the narrowing transverse γ -channels is substantiated by the concentration comparison between the transverse and the horizontal γ -channels shown in Figure 4.7, where a significantly higher enrichment of Co is observed in the transverse γ -channel.

It is unclear from the current study if the diffusion of γ -stabilizers occurs via a dislocation network, since dislocations are not resolved within the γ -matrix in our APT analysis. In addition, a total accumulated creep strain of $< 1\%$ after 50 h of compressive creep at 150 MPa may not provide a sufficient dislocation density for formation of a matrix dislocation network [160, 161]. Theoretical studies suggest that rafting may occur both with and without dislocation-assisted diffusion [9, 162]. The rafting phenomenon and cross-flux of γ -stabilizers and γ' -formers persists even after γ' -coalescence as the rafts continue to lengthen (see Figure 4.10(c)).

4.4. Summary and Conclusions

Chromium, from 0 to 6 at.%, was systematically added into a base alloy with composition of Co-30Ni-10Al-7W-0.1B, to study the effect of reduced lattice misfit on creep resistance and γ' -rafting. Microstructure investigation shows that, with an increased Cr

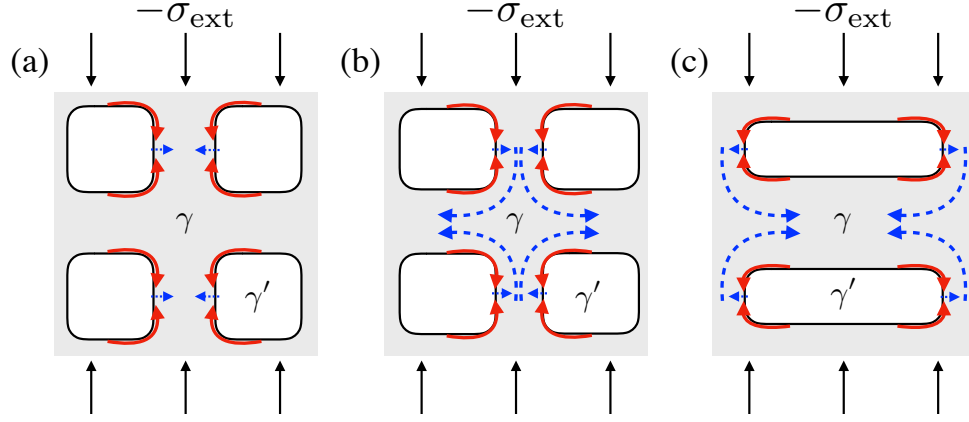


Figure 4.10. Schematic illustration of rafting mechanism [10, 11, 12, 13] in a compressively crept positive-misfit superalloy. (a) Under applied load, γ' forming elements (*i.e.*, Ni, Al and W) diffuses from horizontal to transverse interfaces. Directionally coarsened γ' exudes γ -stabilizers into transverse γ -channel. (b) Local enrichment of γ -stabilizers coupled with a receding horizontal γ - γ' interfaces lead to cross-flux of γ -stabilizers toward the horizontal channels. (c) γ' -precipitates coalesce forming a rafted microstructure.

concentration, γ' -morphology transitions from cuboidal to spherical upon aging, indicating a decreased lattice parameter misfit. Moreover, the degree of rafting under compressive stress also decreases with increasing Cr content: the 0 at.% Cr alloy is heavily rafted, while the 6 at.% Cr alloy exhibit no sign of rafting after compressive creep for 50 h at 150 MPa / 900 °C. The compressive creep strain rate of the alloys is observed to progressively increase with Cr additions, possibly due to a reduced lattice misfit and absence of strengthening from γ' -rafting. APT was used to compare the compositional distribution in an as-aged and post-creep alloy. Analysis show that, in a rafted alloy, local enrichment of γ -stabilizers (Co and Cr) is observed both in the vicinity of γ - γ' interfaces and the narrow γ -channel in between two coalescing γ' -precipitates. In contrast, no measurable γ -stabilizers are observed in alloy that is unrafted after creep.

These observations, combining microstructural characterization and APT analyses, can be explained via a diffusional cross-flux mechanism occurring during γ' -rafting. At the on-set of n-type rafting that occur during compressive creep of Co-based superalloy, γ' -formers (Ni, Al, W) diffuse via the γ - γ' interface toward the transverse γ - γ' interfaces parallel to the applied stress. This leads to directional coarsening of γ' -precipitates toward the transverse γ -channels at the expense of receding horizontal interfaces. The directional coarsening of γ' -precipitates leads to local enrichment of γ -stabilizers in the transverse γ -channels, which facilitates diffusion of γ -stabilizers toward the horizontal γ -channels, completing the cross-flux of γ' -formers and γ -stabilizers. The γ' -precipitates continue to coalesce under stress, forming the long γ' -rafts observed after creep in this (and other) Co-based superalloys.

Supplemental Information

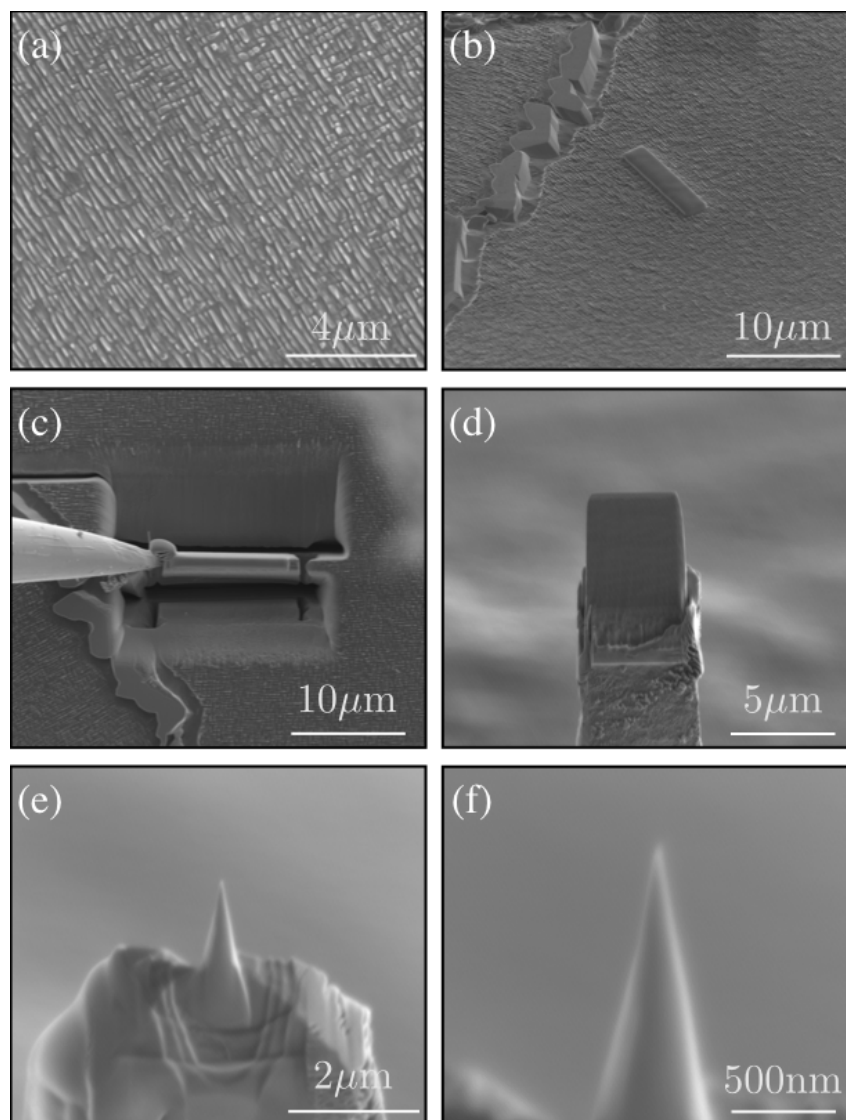


Figure 4.11. Illustration of focus-ion beam lift out of a rafted region in post-creep D-2Cr. (a) Microstructure of a rafted region. (b) Pt deposition was applied onto the region to prevent ion-beam damage during life-out. (c) Lift-out of the region of interest. (d) Specimen is mounted onto Si pillar, (e) sharpen via ion milling for atom-probe experiment. (f) Final tip shape with a tip radius of ≈ 20 nm.

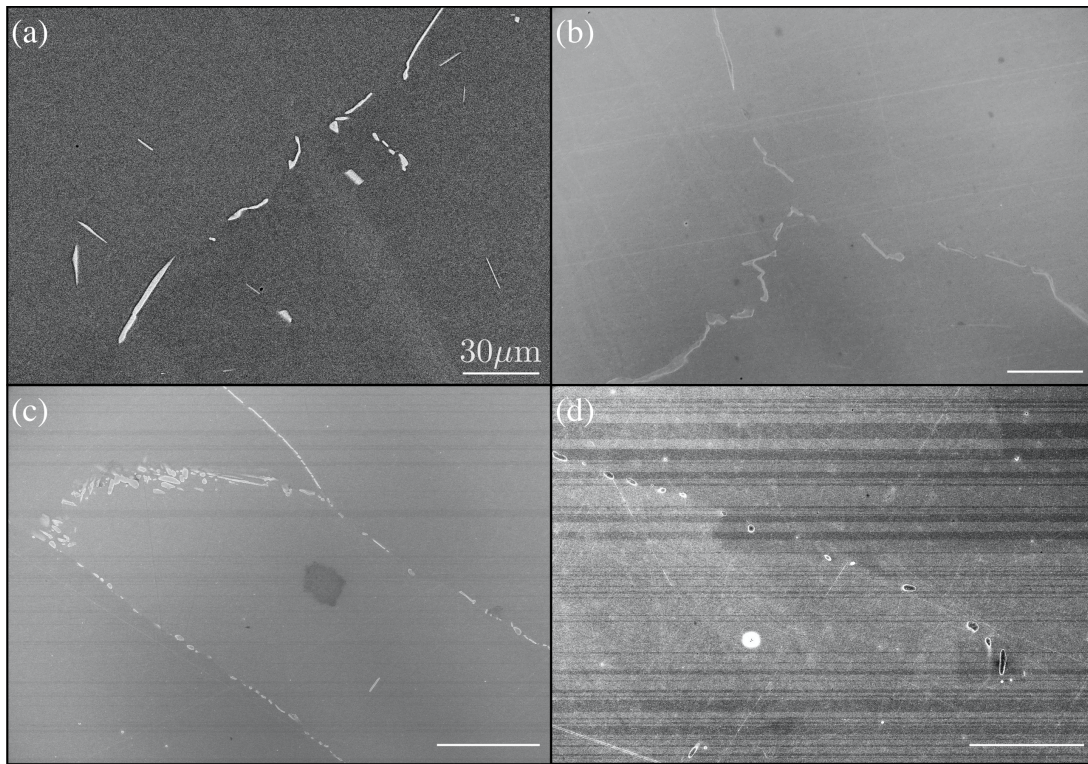


Figure 4.12. Microstructure of boride decorated grain boundaries of (a) 0Cr, (b) 2Cr, (c) 4Cr and (d) 6Cr after boride precipitation heat treatment at 1050 °C for 12 h.

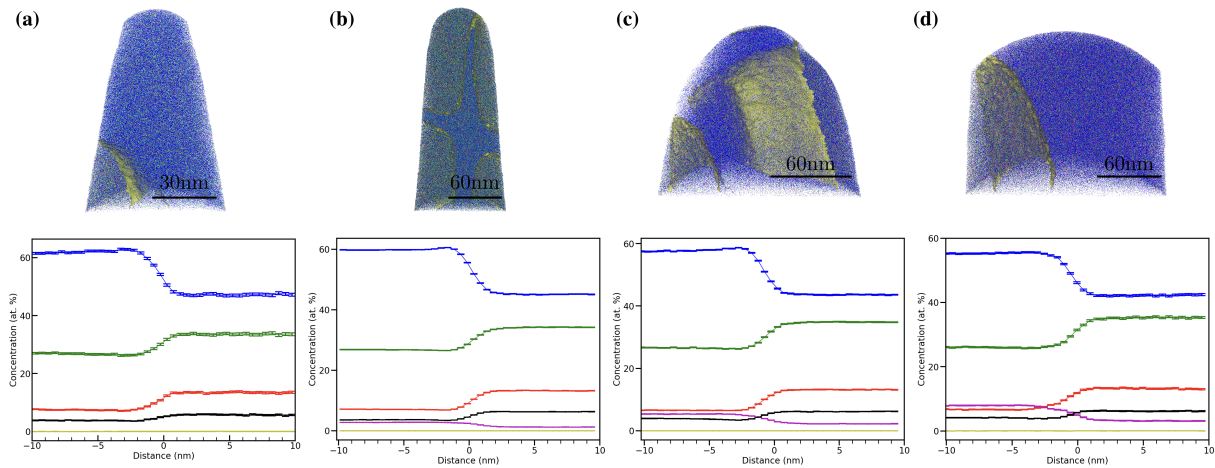


Figure 4.13. Atom-probe tomographic reconstruction and proximity histogram of D-xCr after heat treatment at 900 °C for 168 h; (a) 0Cr, (b) 2Cr, (c) 4Cr and (d) 6Cr.

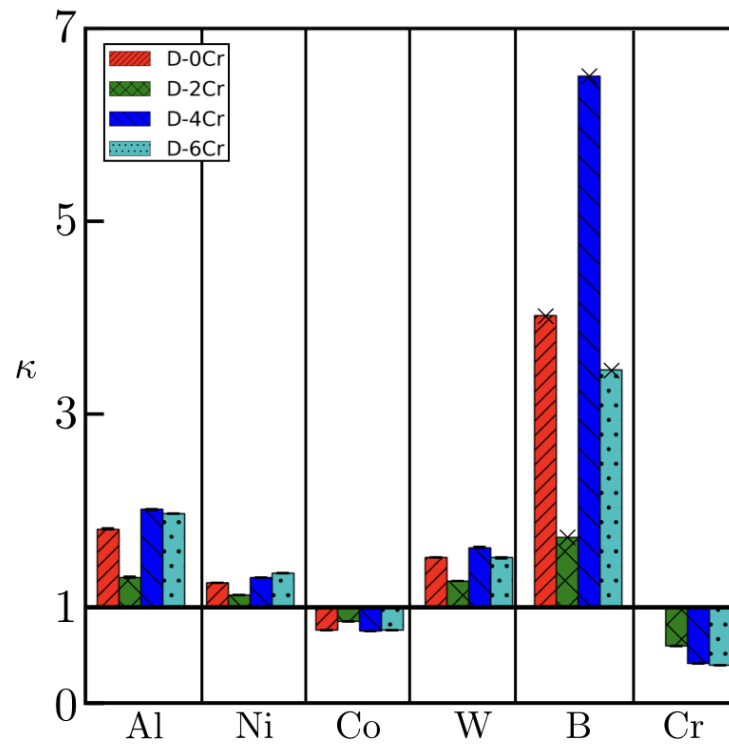


Figure 4.14. Plot of elemental partitioning coefficient, $\kappa_{\gamma'/\gamma}$, of D-xCr. The uncertainty of B partitioning coefficient is not plotted due to its miniscule concentration.

Table 4.4. APT measured tip composition (at.%) of γ -and γ' -phases, $\kappa_{\gamma'/\gamma}$ partitioning coefficient of each of the D-xCr alloy under 900 °C / 168 h as-aged condition.

Alloy	Co	Ni	Al	W	B	Cr
D-0Cr						
γ	62.0	26.8	7.4	3.8	0.002	-
γ'	47.2	33.6	13.4	5.8	0.01	-
$\kappa_{\gamma'/\gamma}$	0.76	1.25	1.80	1.52	5.71	-
D-2Cr						
γ	60.2	26.4	7.1	3.6	0.004	2.7
γ'	45.3	33.8	13.4	6.2	0.01	1.2
$\kappa_{\gamma'/\gamma}$	0.75	1.28	1.89	1.73	4.11	0.45
D-4Cr						
γ	57.9	26.6	6.6	3.6	0.003	3.6
γ'	43.8	35.0	13.2	5.8	0.01	2.2
$\kappa_{\gamma'/\gamma}$	0.76	1.32	2.01	1.61	3.36	0.62
D-6Cr						
γ	55.3	26.0	6.6	4.1	0.005	7.9
γ'	42.2	35.2	13.2	6.2	0.01	3.2
$\kappa_{\gamma'/\gamma}$	0.76	1.35	1.99	1.50	2.61	0.40

CHAPTER 5

Influence γ' -Raft Orientation on Creep Resistance of Monocrystalline Cobalt-Based Superalloys

The creep behavior of a monocrystalline Co-based γ - γ' superalloy (Co-28.8Ni-6.2Al-1.8Ti-2.0W-2.7Mo-1.8Nb-0.9Ta, at.%) is investigated for two types of rafted γ' -phase: (i) rods parallel (p-type) to [001] and (ii) plates perpendicular (n-type) to [001], created by subjecting specimens to tensile or compressive stresses, respectively, at 900-940 °C along [001]. The tensile creep behavior of these two rafted microstructures (and a control unrafted microstructure) is measured at 900 °C for various creep stresses, again along [001], up to a creep strain of 3%. At the highest stress of 305 MPa (2-4 h creep to 3% strain), microstructures with n-type γ' -rafts provide better creep resistance than p-type γ' -rafts and unrafted γ' -cuboids, consistent with n-type γ' -plates oriented perpendicular to stress being more effective at hindering dislocation motion in the γ -matrix compared to γ' -cuboids (unrafted) and γ' -rod (p-type rafted) morphologies. At an intermediate stress of 250 MPa (10-20 h to 3% creep strain), n-type rafts still provide the highest overall creep resistance, but this effect is less pronounced due to the rafts disintegrating under tensile load under prolonged creep duration. Specimens with initially unrafted γ' -cuboids show a creep resistance comparable to the p-type rafts after the cuboids directionally coarsen into p-type rafts. At the lowest stress of 205 MPa (100-220 h to 3% creep strain),

n-type rafts provide the least creep resistance, as they first disintegrate and then transform into p-type rafts. Specimens starting with p-type γ' -rods and unrafted γ' -cuboids microstructures show better creep resistance, but start to exhibit onset of tertiary creep from their extensively rafted microstructure. The evolution of creep strain rate (and thus the time to reach 3% strain) for the three stresses and three microstructures studied is affected by the rafting evolution, as well as γ - γ' topological inversion and development of inhomogeneous γ' spatial distribution.

5.1. Introduction

Cobalt-based superalloys strengthened by ordered L1₂-ordered γ' -precipitates (with typical composition Co₃(Al,W)) have been extensively studied in the past decade, as they exhibit an outstanding combination of deformation-, coarsening-, oxidation-, and corrosion-resistance that may exceed those of Ni-based superalloys [1, 16, 29, 59, 101, 129, 163]. In particular, the creep resistance of the Ni- and Co-based superalloys is crucial for efficient jet engines and gas turbines due to the high temperatures and stresses experienced by the turbine materials under operation [128]. One important distinction between Ni- and Co-based superalloys is their lattice parameter misfit, $\delta = 2(a_{\gamma'} - a_{\gamma}) / (a_{\gamma'} + a_{\gamma})$, where $a_{\gamma'}$ and a_{γ} are the lattice parameters of the γ' -precipitates and the γ matrix, respectively. Co-based superalloys mostly exhibit a positive misfit ($a_{\gamma'} > a_{\gamma}$) [2, 26, 37, 38, 54], while their Ni-based counterparts typically have a negative misfit ($a_{\gamma'} < a_{\gamma}$) [18]. The sign of the lattice parameter misfit strongly affects γ' -precipitate rafting behavior, a stress-induced directional coarsening phenomenon that occurs during creep of precipitation-strengthened materials with a coherent or semi-coherent misfit [164]. Specifically, in

positive-misfit systems such as Co-based superalloys, γ' coarsens and coalesces into rafts that are elongated along the stress axis during tensile creep (p-type raft) and perpendicular to the stress axis during compressive creep (n-type raft). In negative-misfit alloys such as Ni-based superalloys, the rafting direction is reversed, with γ' rafts having their long axis perpendicular to the stress axis after tensile creep (n-type raft) and parallel to the stress axis after compressive creep (p-type raft). The difference in rafting directionality amounts to differing microstructural evolution between the Co- and Ni-based superalloys, which impacts the creep performance before, during, and after the rafted microstructure has developed.

Previous works have studied the effect of rafting on creep resistance in Ni-based superalloys, and have engineered rafted microstructures to improve creep properties. Specimens with n-type rafts are more creep resistant (*i.e.*, they show a lower minimum tensile creep strain rate), especially under high-temperature, low-stress conditions. Reed *et al.* [148] attribute this effect to a reduction in the number of vertical γ -channels, which hinders the glide and climb of dislocations. However, the creep strain rate was found to increase rapidly after extensive rafting rendered the overall microstructure inhomogeneous. Tetzlaff and Mughrabi [14, 165] sought to enhance the tensile creep strength in a monocrystalline Ni-based superalloy by first inducing p-type rafts in compression. They observed that these p-type “pre-rafts”, with their axis aligned with the subsequent creep tensile stress, offered significant short-term strengthening in tensile creep; however, a deterioration of creep resistance occurred at longer times, as the p-type rafts evolved into an irregular γ' -microstructure.

For Co-based superalloys, the effect of rafting on creep properties of Co-based superalloys has not been studied as extensively as in their Ni counterparts. Xue *et al.* [93] showed that a monocrystalline Co-based superalloy strain-hardens as n-type γ' -rafts are created under compressive creep. Lu *et al.* [147] and Titus *et al.* [108] found interfacial dislocation interactions and p-type rafting to be responsible for strengthening observed during tensile creep of a Co-based superalloy. Coakley *et al.* [91, 159] used *in-situ* neutron diffraction to study the lattice parameter evolution of γ - and γ' -phases during tensile creep rafting, the concomitant loss of coherency, and its potential to degrade creep resistance. Existing studies focus on γ' -rafts that form *in-situ* during testing, with the raft orientation given by the applied stress direction, *i.e.*, p-type for tensile or n-type for compressive deformation. However, there are currently no studies in Co-based superalloys on how pre-rafting - achieved through deformation in one direction (*e.g.*, in compression) - influences subsequent creep resistance with stress applied in the opposite direction (*e.g.*, tension).

In this paper, the effects of pre-existing γ' -rafts upon the subsequent tensile creep resistance is studied in a monocrystalline Co-based superalloy. Three initial γ' -microstructures are created: p-type rafted, n-type rafted, and unrafted. Tensile creep tests are then performed at three stresses, on specimens with each of these microstructures to study the evolution of their γ' -morphology and the corresponding creep resistance.

5.2. Experimental Methods

We use here Co-based superalloy monocrystalline bars with a composition of Co-27.3Ni-2.7Al-1.4Ti-5.8W-4.2Mo-2.8Nb-2.8Ta wt.% (Co-28.8Ni-6.2Al-1.8Ti-2.0W-2.7Mo-1.8Nb-0.9Ta at.%) (labelled as L19C), which were directionally casted by the Alcoa-Howmet Research Center, and previously studied by us [91, 159]. Electron backscatter diffraction of selected bars shows that the mis-orientations between the [00l] direction and the length of the bar are within 2° . A previous study via neutron diffraction measured the lattice parameter misfit of L19C to be between 0.52 and 0.45% [91]. The bars (length: 200 mm; diameter: 15 mm) were homogenized at 1250 °C for 24 h, furnace-cooled to 900 °C to age at that temperature for another 24 h in a flowing Ar atmosphere, and then furnace-cooled to room temperature.

Each specimen was subjected to a two-step creep test. First, a pre-raftered microstructure was created by subjecting dog-bone-shaped specimens to tensile stress or cylindrical specimens to compressive stress. The p-type rafted microstructure was developed during +150MPa tensile creep at 900 °C while the n-type microstructure was developed during -150MPa compressive creep at 940 °C, both lasting for 50 h. The different pre-raftering temperatures were used to account for tension/compression asymmetry in the rafting behavior, where tensile creep was shown to promote a greater degree of rafting [15]. The control specimens with the cuboidal microstructure were heat treated for the same duration of 50 h at 900 °C in air to ensure a comparable thermal history with the pre-raftered specimens. Following the pre-raftering step, each specimen was tensile-crept at 900 °C to 3% creep strain at 205, 250, or 305 MPa to study the effect of pre-raftered γ' -morphology on creep resistance. During all creep tests, specimen displacement was measured using

a linear variable displacement transducer with a resolution of 10 μm and temperature was measured using a K-type thermocouple with an accuracy of ± 2 $^{\circ}\text{C}$. After reaching a 3% creep strain limit, all specimens were air-cooled under load to prevent further microstructural evolution.

For p-type pre-raftered and cuboidal specimens, the aged bars were machined into tensile dogbone specimens with a cylindrical gauge length of 30 mm and gauge diameter of 5 mm. For n-prerafter specimens, the aged bars were first machined into cylindrical rods with 10 mm diameter and 30 mm height. After the compressive pre-raftering, these compressed cylindrical rods were further machined into tensile dogbone specimens with a gauge diameter of 3 mm and gauge length of 12 mm. All specimens were machined such that the applied uniaxial stress was parallel to the $[001]$ crystallographic direction.

A Hitachi SU8030 scanning electron microscope (SEM) equipped with a cold-field-emission source was used for microstructural characterization, under operating conditions of 25 kV, 10 μA and a 15 mm working distance. Samples were etched using Carapella's reagent (5 g FeCl_3 , 2 mL HCl , 100 mL methanol) for 5 s to reveal the γ - γ' microstructure.

5.3. Results

5.3.1. Pre-raftering in tensile/compressive creep

Figure 5.1 shows the creep behavior of the monocrystalline Co-based superalloy, L19C, during tensile and compressive deformation at 150 MPa to form p-type and n-type rafts. As shown in Figure 5.1(a), the total accumulated creep strain during the 50 h creep experiments is much higher during compressive creep as compared to tensile creep (1.7 vs. 0.4%, respectively), consistent with the higher compressive creep temperature (940

vs. 900 °C). The creep strain rate evolution in Figure 5.1(b) shows that both tensile and compressive creep curves exhibit a transient maximum in creep strain rate at ≈ 18 h, a phenomenon referred to as double-minimum creep observed in both Ni- and Co-based superalloy single crystals, which has been shown to occur concurrently with the onset of rafting [93, 166]. Supplemental Figure 5.13 shows the 150 MPa tensile rupture test of an originally unrafted specimen, with a total accumulated creep strain of 9% and a rupture life of ≈ 800 h. The strain evolution of the other pre-rafting experiments to produce p-type rafted microstructure are plotted in Supplemental Figure 5.14, showing a degree of primary creep variability during tensile creep.

The corresponding pre-rafted microstructures, at the end of the 50 h deformation, are shown in Figure 5.2. The microstructure of the control specimen not subjected to externally applied stress is shown in Figure 5.2(a). This sample, labelled as “cuboid”, exhibits γ' -precipitates which maintain their initial, post-aging cuboidal morphology. Figure 5.2(b) shows that the p-type specimen (labelled as “p-preraft”) that was deformed under tension underwent directional coarsening where the as-aged γ' -cuboids coalesced into γ' -rods aligned parallel to the applied stress axis. The cubic cross-sections of these rods is seen in the (001) plane SEM cross section. Figure 5.2(c) shows the n-type alloy (labelled as “n-preraft”) where the original γ' -cuboids coalesced in planes perpendicular to the applied stress axis, in both [100] and [010] directions, into γ' -rafts with plate-like morphology. The wavy γ - γ' interface in both p- and n-preraft samples is consistent with onset of coherency loss between the γ -matrix and γ' -precipitates. The cuboid edge lengths are measured at 0.21 ± 0.06 μm with a volume fraction of $53 \pm 3\%$. The p-preraft γ' -rods have an average width of 0.17 ± 0.04 μm and an average length of 2.75 ± 1.01 μm . The

n-preraft γ' -platelets have an average width of $3.05 \pm 2.04 \text{ }\mu\text{m}$ and an average height of $0.14 \pm 0.04 \text{ }\mu\text{m}$. Although the variances in measurement are large, the trend shows that the cuboid sample has the largest edge length of $0.21 \text{ }\mu\text{m}$ compared to rafted γ' -precipitates. This suggests that the γ' -phase becomes progressively thinner with rafting.

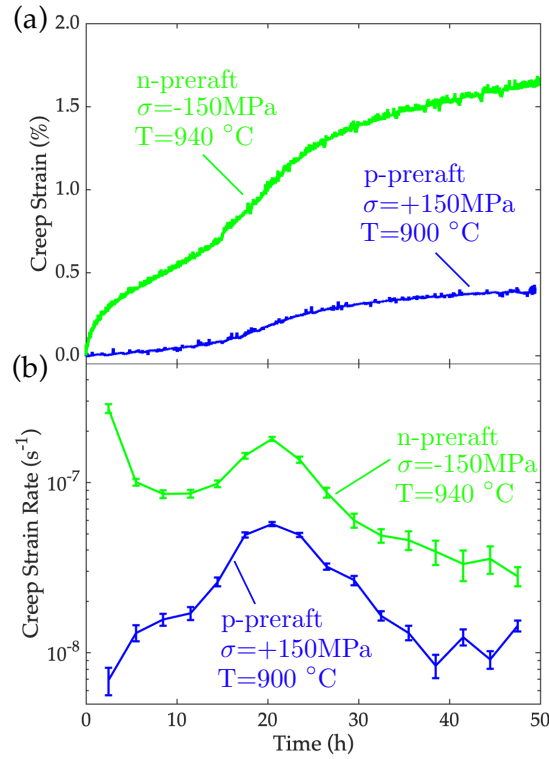


Figure 5.1. Pre-raftering experiments lasting 50 h, showing time dependence of (a) creep strain (absolute value) and (b) creep strain rate (absolute value) as a function of time for monocrystalline Co-based superalloys (L19C) under +150 MPa tensile stress at 900 °C (blue) and -150 MPa compressive stress at 940 °C (green).

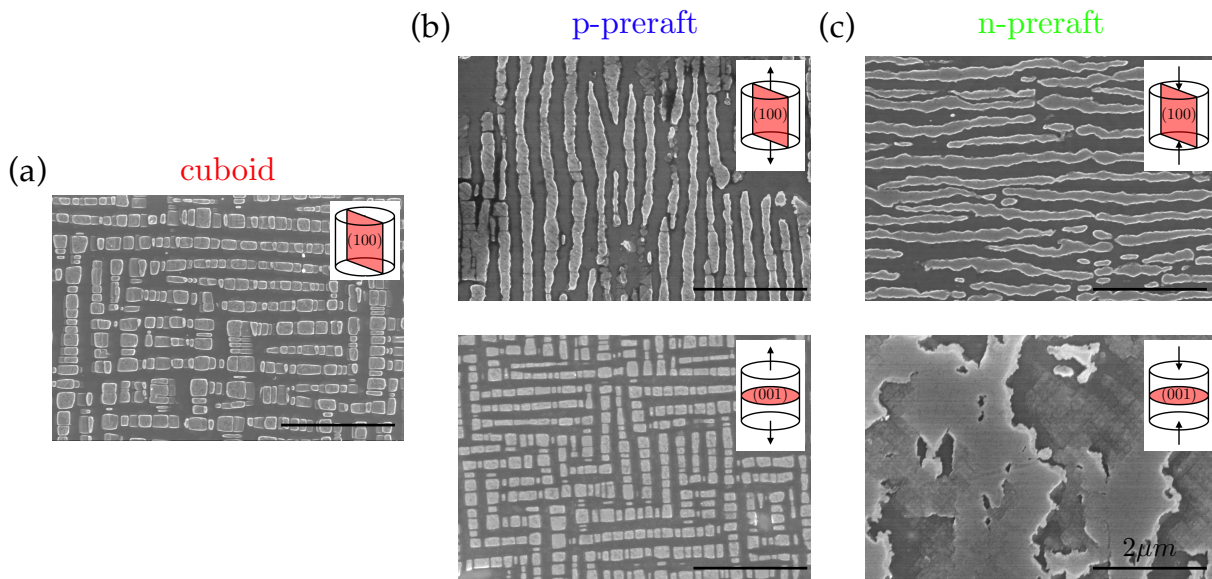


Figure 5.2. Secondary electron micrographs of L19C after 50 h of pre-raftering creep (as shown in Figure 5.1). (a) Control specimen (not subjected to an applied stress during 50 h) showing (100) planes with cuboidal γ' -precipitates, (b) rafted specimen showing p-type γ' -precipitates on (100) and (001) planes after +150 MPa tensile stress at 900 °C / 50 h, and (c) rafted specimen showing n-type γ' -precipitates on (100) and (001) planes after -150 MPa compressive stress at 940 °C / 50 h.

5.3.2. Tensile creep at high stress (305 MPa)

The creep behavior of the cuboid, p-, and n-preraft alloys are shown in Figure 5.3 for the highest tensile stress of 305 MPa. At this high stress, creep experiments lasted from 1.5 to 4 h until the cutoff 3% creep strain was reached. Experiments for both types of pre-raftering were performed in duplicate to assess reproducibility of the creep results. The creep curves in Figure 5.3(a) show that the creep resistances of alloys with γ' -cuboids (cuboid) and γ' -rods (p-preraft) are nearly indistinguishable, with the three curves largely overlapping each other. By contrast, the alloy with γ' -plates (n-preraft) exhibits a significant increase in creep resistance, doubling the time needed to reach 3% creep strain. Figure 5.3(b) shows

that the n-preraft alloy's minimum strain rate is approximately an order of magnitude lower compared to the cuboid and p-preraft specimens. After the n-preraft alloy reaches its minimum strain rate at 0.5% strain, its strain rate increases gradually; by contrast, the cuboid and p-preraft specimens approach their minimum creep rates at the end of the experiment, for a strain of 3%. At this point, the n-preraft alloy displays a creep strain rate similar to those of the cuboid and p-preraft specimens ($\approx 4 \times 10^{-6} \text{ s}^{-1}$).

The post-creep microstructures are shown in Figure 5.4. For the cuboidal specimen (Figure 5.4(a)), after tensile creep for ≈ 2 h, the originally cuboidal γ' -precipitates maintain their mostly cuboidal morphology with occasional instances of p-type rafts, indicative of the onset of p-type rafting. The p-preraft specimens (Figure 5.4(b)) display a post-creep γ' -microstructure that is similar to the pre-rafterd microstructure. Finally, the n-preraft specimens (Figure 5.4(c)) maintain their horizontally aligned n-type raft, but the γ - γ' interface has become significantly rougher, indicating a further loss of coherency. In summary, for all three initial microstructures, the extent of γ' -morphology evolution is relatively modest after the short times (1.5-4 h) needed to achieve 3% strain under the highest tensile stress of 305 MPa.

5.3.3. Tensile creep at intermediate stress (250 MPa)

Figure 5.5 shows the tensile creep behavior at 250 MPa for the cuboid, p-preraft, and n-preraft specimens. Under this intermediate stress, the creep experiments lasted between 10 and 20 h until the 3% cutoff strain was reached. The cuboid alloy exhibits the highest average strain rate and reaches 3% creep strain within 10 h. The cuboid also exhibits double-minimum creep (with a peak of creep strain rate after ≈ 4 h, Figure 5.5(a)), as

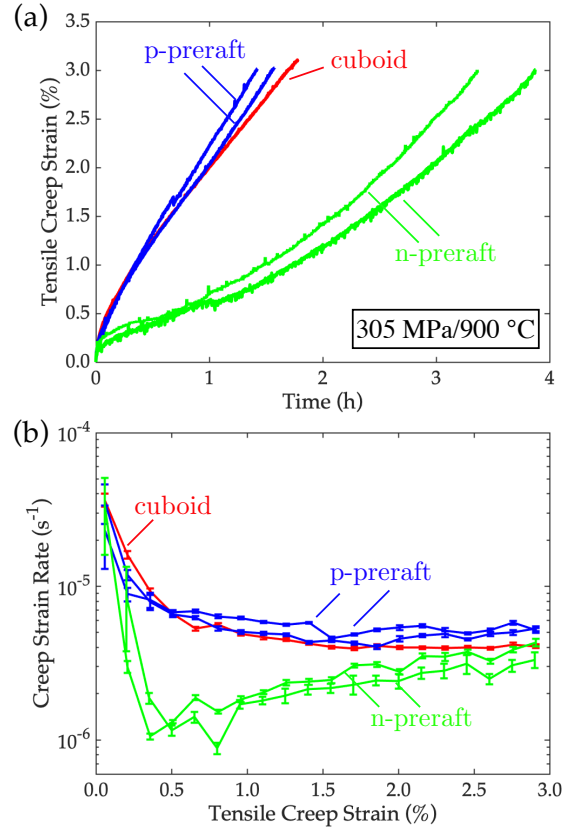


Figure 5.3. 305 MPa tensile creep at 900 °C of (a) creep strain and (b) creep strain rate for cuboid (red), p-prerafted (blue), and n-preraft (green) specimens. Two specimens of p-preraft and n-preraft were crept to ensure reproducibility.

also observed during the p- and n-preraft experiments (peak at ≈ 20 h, Figure 5.1). The differences in times (20 vs. 4 h) are expected from the different magnitude of applied stresses, 150 MPa during pre-raftering and 250 MPa during subsequent creep. In contrast to tensile creep at the higher stress of 305 MPa, the p-preraft sample deformed at 250 MPa shows a better creep resistance as compared to the cuboid sample. The n-preraft alloy, while exhibiting the lowest average creep strain rate at 250 MPa among the three types of microstructure, does not offer a creep enhancement as significant as under 305

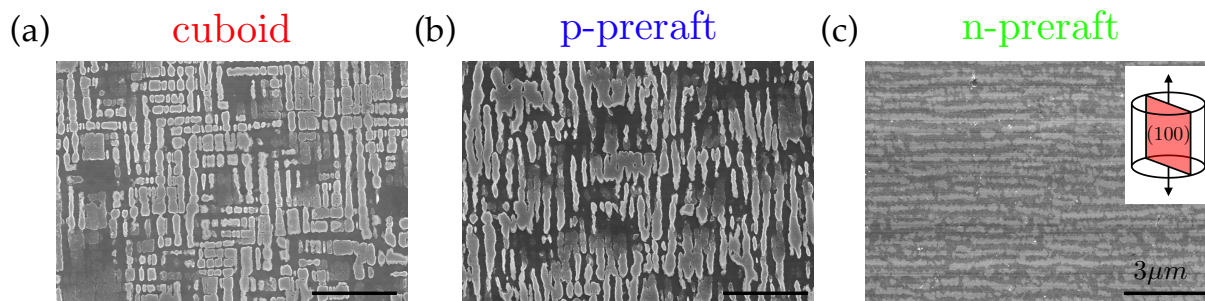


Figure 5.4. Secondary electron micrographs of the (a) cuboid, (b) p-preraft, and (c) n-preraft microstructure after tensile creep at 305 MPa at 900 °C. All micrographs show the (100) plane that is parallel to the applied stress axis.

MPa tensile stress. Specifically, the n-preraft alloy exhibits two distinct creep regimes, highlighted by the averaged strain rate marked (i) and (ii) on the n-preraft creep curve in Figure 5. In regime (i), the creep resistance of the n-preraft alloy is significantly higher than for the cuboid and p-preraft specimens. However, in regime (ii), the creep strain rate of the n-preraft alloy increases gradually, and much like the case of the n-preraft alloy under 305 MPa after reaching a minimum strain rate, becomes comparable to those of the cuboid and p-preraft specimens toward the end of the experiment (*cf.* averaged strain rate (i) for both cuboid and p-preraft specimens in Figure 5.5).

Figure 5.6 shows the post-creep microstructure after 250 MPa creep. As expected, with the additional time given for the microstructure to evolve as compared to the 305 MPa condition, the initially cuboidal γ' -precipitates have rafted vertically along the applied tensile stress axis (Figure 5.6(a)). The p-preraft alloy continues to raft parallel to the applied tensile stress axis, as shown in Figure 5.6(b). The extent of p-type rafting is more significant as compared to the microstructure after 305 MPa creep. By contrast, the n-preraft alloy undergoes a notable microstructural evolution during the 250 MPa creep, as

shown in Figure 5.6(c). The initially horizontally aligned γ' -platelets have disintegrated into a near-isotropic γ' -morphology. These γ' -precipitates (Figure 5.6(c)) do not appear as cuboidal as those in the as-aged microstructure (Figure 5.2(a)), but rather exhibit an irregular morphology with rounded $\langle 110 \rangle$ and $\langle 111 \rangle$ corners.

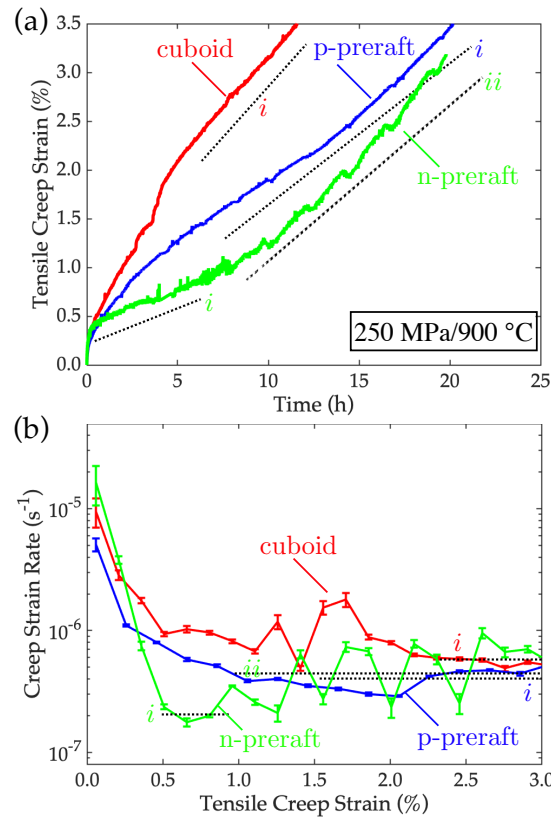


Figure 5.5. 250 MPa tensile creep at 900 °C of (a) creep strain and (b) creep strain rate as a function of strain for cuboid (red), p-preraft (blue), and n-preraft (green) specimens. Dotted lines correspond to the average creep strain rate at different times during the creep experiment, highlighting the different creep behavior regimes after primary creep.

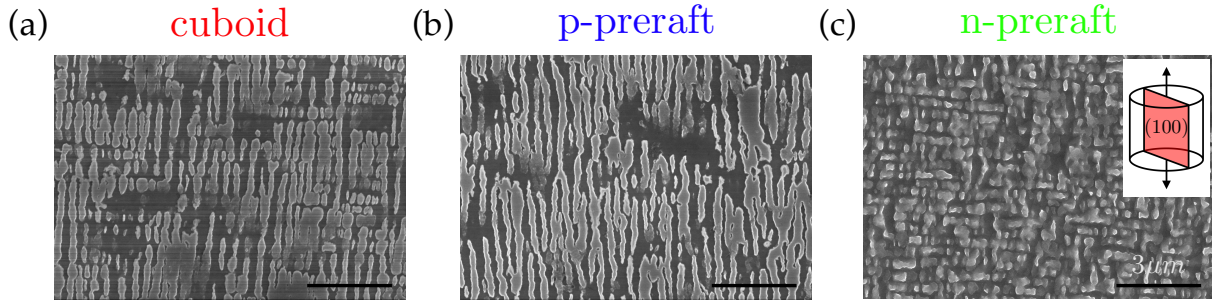


Figure 5.6. Secondary electron micrographs of the (a) cuboid, (b) p-preraft, and (c) n-preraft microstructures after tensile creep at 250 MPa. All micrographs show the (100) plane that is parallel to the applied stress axis.

5.3.4. Tensile creep at low stress (205 MPa)

Figure 5.7 highlights the creep response and the corresponding strain rate evolution for each of the three microstructures under 205 MPa creep. The lowest applied stress resulted in the longest time for each specimen to reach the 3% cutoff strain, between 100 and 220 h. No long-term steady-state creep is observed at this stress; rather, the strain rate increases shortly after reaching a minimum. In Figure 5.7, the average creep strain rate during the strain rate minimum is labeled with (i) for each of the cuboid, p-, and n-preraft microstructure, while the strain rates towards the end of the creep experiments are labelled with (ii), highlighting two distinct creep regimes for each alloy. The n-preraft alloy exhibits an overall creep resistance worse (*i.e.*, reaching 3% strain in half the time) than the cuboid and p-preraft specimens, unlike its superior creep performance at 305 and 250 MPa. While the n-preraft alloy shows a marginally lower primary creep strain rate as compared to the cuboid and p-preraft specimens, the minimum strain rate (i) is higher than the other two microstructures. The creep resistance of the n-preraft alloy also deteriorates rapidly thereafter (see (ii)). As a result, the n-preraft alloy took about 100 h

to reach 3% creep strain, half the time needed for the cuboid and the p-preraft specimens. The latter two specimens show a comparable overall creep resistance, both taking ≈ 200 h to reach 3% creep strain. Unlike the double minimum creep seen in both 250 MPa and the pre-rafter specimens, the cuboid specimen does not exhibit double minimum creep at 205 MPa. This is likely due to the local maximum strain rate peak being hidden in the large primary creep. Once the cuboid and p-preraft specimens reach a similar minimum strain rate in regime (i), their strain rate increases gradually in a similar fashion. The strain rate in regime (ii) of the cuboid specimen is slightly lower than that of the p-preraft specimen, likely due to the lack of pre-rafter deformation in the cuboid sample delaying the onset of secondary creep.

Figure 5.8 shows the post-creep microstructure of the three different γ' -morphologies. For creep at 205 MPa, each specimen is allowed more time for its microstructure to evolve than in the two experiments at higher stresses. The initially cuboidal microstructure in the cuboid alloy has evolved to form extensive p-type rafts, as illustrated in Figure 5.8(a). In the p-preraft alloy, the rafted γ' -rods become thinner and a topological inversion, where γ is surrounded by γ' , is apparent in some regions (arrows) in Figure 5.8(b). The post-creep microstructure of the n-preraft alloy is shown in Figure 5.8(c). The initially horizontal γ' -platelets have reversed their rafting direction to form vertical rods parallel to the applied tensile load, *i.e.*, a p-type microstructure. However, these p-raftered γ' -rods resulting from tensile creep of n-type pre-raftered γ' -plates are less uniform than the p-type γ' -rods derived from a cuboidal γ' -morphology, as seen in Figure 5.8(a).

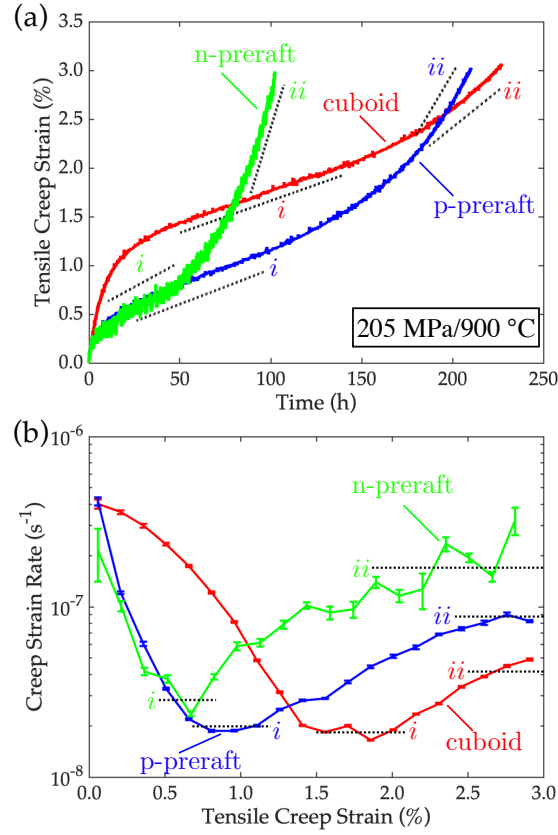


Figure 5.7. 205 MPa tensile creep at 900 °C of (a) creep strain and (b) creep strain rate for the cuboid (red), p-preraft (blue), and n-preraft (green) specimens. Dotted lines correspond to the average creep strain rate at different time during the creep experiment, highlighting the different creep behavior regimes after primary creep.

5.4. Discussion

5.4.1. Creation of γ' -rafts during pre-rafting creep

Figure 5.9 depicts the local stress state in a positive-misfit Co-based superalloy under different loading conditions. For a sample aged under stress-free conditions, the positive γ - γ' misfit results in coherency stresses between the γ' -particles and γ -channels. Specifically,

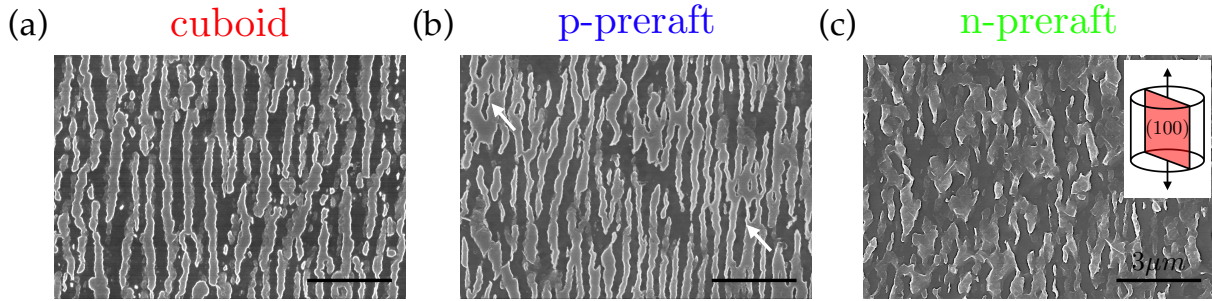


Figure 5.8. Secondary electron micrographs of the (a) cuboid, (b) p-preraft, and (c) n-preraft microstructures after tensile creep at 205 MPa. All micrographs show the (100) plane that is parallel to the applied stress axis.

the γ -channels along $[001]$ are subjected to a tensile stress, whereas the γ' -precipitates are under a triaxial compressive stress [11, 99]. With an equivalent stress magnitude in each $\langle 100 \rangle$ crystallographic direction, the γ' -precipitates remain cuboidal as they coarsen, as shown in Figure 5.2(a) and 5.9(a) [167].

The characterization and formation mechanisms of p-type and n-type rafted microstructure have been studied extensively in negative-misfit Ni-based superalloys [11, 167, 168, 169, 170, 171]. However, due to the more recent development of Co-based superalloys, the rafting behavior of positive-misfit superalloys is less well studied [9, 92, 172]. In both cases, a rafted microstructure is generated from the asymmetric local coherent and plastic stresses produced by the applied external stress [164]. Figure 5.9(b) illustrates the local stress state under a tensile load for a positive-misfit Co-based superalloy. The vertical γ -channels (aligned along $[001]$) experience an increased tensile stress from the superimposed external stress while the horizontal γ -channels along $[100]$ (and along $[010]$ when seen in three dimensions) are subjected to a reduced tensile stress due to the Poisson effect. The γ' -precipitates are subjected to an increased and decreased compressive stress along the $[001]$ and $[100]$ direction, respectively. The difference in

strain energy density between the two crystallographic directions results, upon coarsening, in the p-type rafts observed in Figure 5.2(b), where γ' -cuboids directionally coarsen into rods oriented parallel to the tensile stress axis to reduce interfacial strain energy density. The local stress state is reversed under applied compressive load (Figure 5.9(c)), where γ' -cuboids coalesce in the $[100]$ and $[010]$ directions to form horizontal n-type rafted platelets, as demonstrated in Figure 5.2(c).

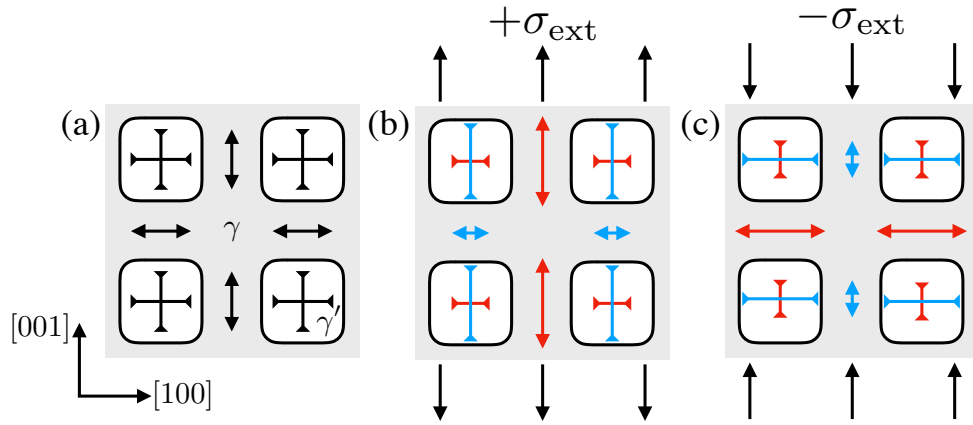


Figure 5.9. Schematic illustration of local stress state on γ -matrix and γ' -precipitates in a positive-misfit superalloy during (a) stress-free, (b) tensile stress, and (c) compressive stress. Red arrows indicate a more tensile and blue arrows a more compressive stress state with respect to the stress-free condition.

5.4.2. γ' -microstructure evolution during tensile creep

The evolution of the γ' -microstructure contributes significantly to the creep resistance of each pre-raftering condition. Figure 5.10 schematically depicts the pre-raftered (inset a) and post-tensile creep microstructure (inset b-d) of the cuboid, p-, and n-prerafter specimens at three different stresses, 305, 250 and 205 MPa.

Shown in Figures 5.4 and 5.10(b), the morphology of the γ' -phase after 305 MPa creep remains very similar to its pre-rafterd microstructure. This is primarily due to the short creep time under the high stress condition, where the creep tests were terminated in less than 4 h for all specimens. Since microstructural evolution is diffusion dependent, the short creep time does not allow for significant microstructural change to occur.

After tensile creep at 250 MPa, which took between 12 and 20 h, additional time is given for the microstructure to evolve (Figures 5.6 and 5.10(c)). The initially cuboidal γ' in the cuboid specimen has begun to form p-type rafts. The p-prerafterd alloy remains largely the same before and after 250 MPa creep, suggesting that the coarsening kinetics, while rapid at the onset of rafting, slow down after γ' -precipitates coalesce [157].

Out of the three microstructures, the n-prerafterd alloy evolves the most substantially after 250 MPa tensile creep. The initial n-type rafted γ' -platelets are observed to disintegrate into smaller γ' -particles as shown in Figure 5.6(c). Based on the irregular morphology of γ' , the γ - γ' interface is likely semi-coherent or incoherent from the accumulation of interfacial dislocations. With a loss of coherency, the γ' -precipitates are also irregularly arranged as opposed to aligning along $\langle 100 \rangle$ when γ' -precipitates are cuboidal. After the disintegration of n-type rafts, the γ' -precipitates continue to evolve toward a p-type raft microstructure. This is evident from the numerous γ' -particles coarsened and coalesced along $[001]$. Similar γ' morphological evolution has been reported in Ni-based superalloys. Yu *et al.* [173] proposed that the change in strain energy density between the vertical and horizontal interfaces induces local concentration inhomogeneity which ultimately decomposes the pre-rafterd γ' before promoting rafting according to the direction of applied stress. The decomposition mechanism of the n-type rafted γ' likely occurs from

the defect-assisted nucleation of γ -phase at the γ - γ' interface. Lenz *et al.* [15] shows that intruding γ -kinks bounded by microtwin and stacking faults form at the γ - γ' interface of a monocrystalline Co-based superalloy compressively crept to 5% creep strain. The defects are observed to be enriched with γ -forming elements such as Co and Cr while depleted with γ' formers, Ni and W. Similar defect-assisted phase transformation has been observed in Ni-based superalloys [134, 174, 175].

The micrographs and schematic depicting the γ' -morphologies after 205 MPa tensile creep are shown in Figure 5.8 and 5.10(d). The lowest applied stress results in the longest creep time, between 100 and 200 h. The cuboid alloy shows an extensive p-type rafted microstructure after creep. The γ' -rafts of the p-preraft alloy have become comparably narrower in width compared to the initial p-type raft [176, 177]. In addition, topological inversion between γ and γ' , where significant coarsening of γ' results in engulfing of γ -phase, are seen throughout the microstructure. This inversion between the matrix and the precipitate phases are frequently observed in Ni-based superalloys after extended periods of creep and are frequently associated with creep performance degradation [157, 178]. Moreover, the combination of the narrowing γ' -raft and topological inversion render the γ' spatial distribution less homogeneous.

As expected from the disintegration of the horizontally-rafterd γ' in the n-preraft alloy observed for 250 MPa creep (Figure 5.6), the post-creep microstructure after 205 MPa tensile creep shows further morphological evolution. The micrograph highlighted in Figure 5.8(c) and schematically illustrated in Figure 5.10(d) show that the initially n-type horizontal γ' -platelets, after 100h of tensile creep, have completely reversed their rafting direction by forming p-type raft. Since the coherency stress between the γ - and

γ' -phase is the primary driving force for rafting to occur [99, 146], this reversed rafting suggests that the γ - γ' interface did not completely lose coherency after the n-type rafts were disintegrated. Thus, it is likely that the interface remains as semi-coherent even after interfacial dislocation build up from creep deformation [12, 13, 55, 179]. The irregular γ' -morphology after n-type rafts transition to p-type rafts, however, forms a highly inhomogeneous microstructure with varying γ' -precipitate spacing, width and length.

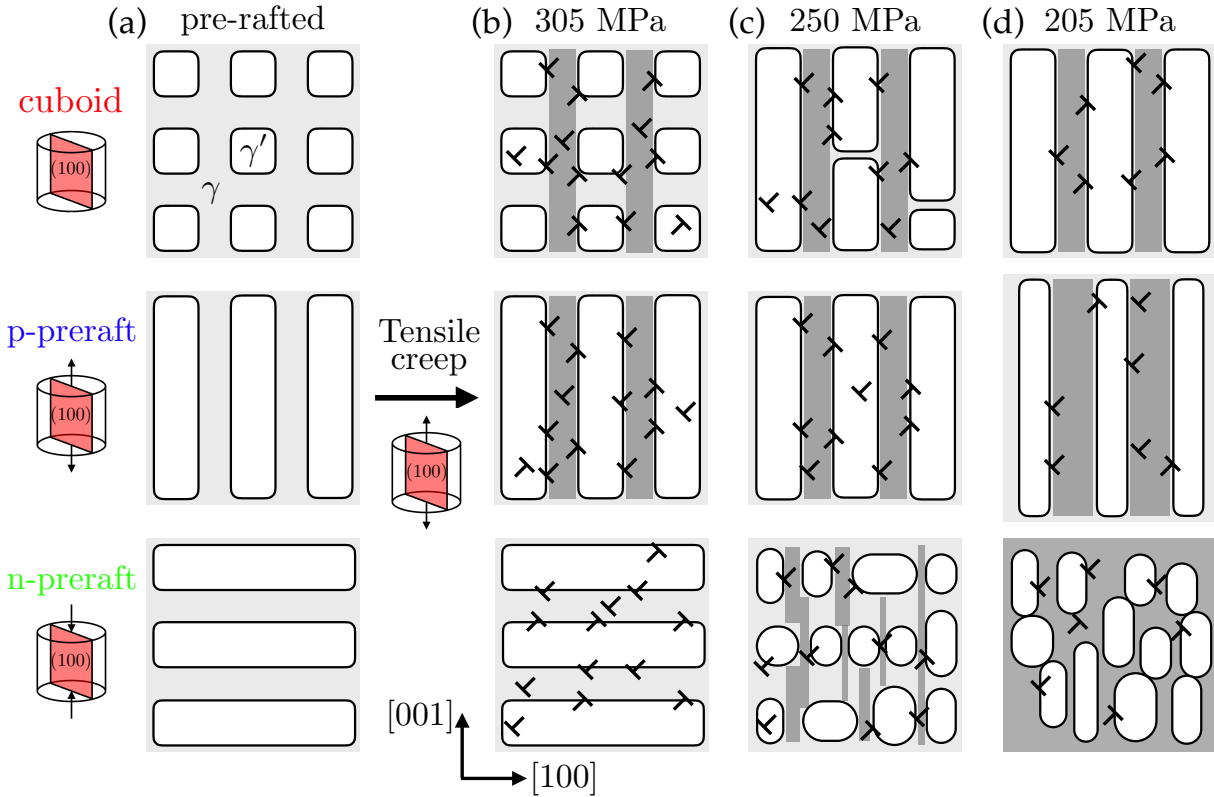


Figure 5.10. Microstructure and creep deformation mechanism for the cuboid, p- and n-praft specimens after (a) pre-rafterd, (b) 305 MPa, (c) 250 MPa and (d) 205 MPa tensile creep. The gray shades correspond to the primary deformation γ -volume during tensile creep.

5.4.3. Influence of γ' -microstructure on creep properties

Figures 5.3, 5.5 and 5.7 demonstrate that creep resistance differs significantly depending on γ' -microstructure. While illustrating the γ' -microstructural evolution from cuboids to rafts, Figure 5.10 also depicts the dislocation-creep deformation mechanisms of each cuboid, p-, and n-preraft specimens at different stresses.

As shown previously in Figure 5.9(b), due to the tensile coherency stress from the positive misfit Co-based superalloys, tensile creep deformation occurs primarily via the vertical $[001]$ γ -channels parallel to the applied stress [94, 180]. In contrast, the horizontal $[100]$ γ -channels perpendicular to the applied stress experience a lower magnitude of tensile stress. The asymmetry in local stress between the parallel and perpendicular γ -channels leads to dislocation glide occurring largely within the vertical channels during early stages of creep, which is likely responsible for most of the 3% creep strain accumulated in this study. The volume of γ -matrix allowing for dislocation glide is shaded in gray in Figure 5.10.

Under the high stress condition, *i.e.*, 305 MPa, as depicted in Figure 5.10(b), since the microstructures of the cuboid and p-preraft specimen were not given sufficient time to evolve, the dislocation glide is concentrated largely in the vertical γ -channels. Therefore, while the cuboid and the p-preraft specimens exhibit a different γ' -morphology, the similar orientation of the primary deforming γ -channel results in a similar creep response (see Figure 5.3). On the other hand, the n-preraft microstructure is devoid of vertical γ -channels, effectively trapping matrix dislocations between the horizontal γ' -platelets. Since the intermetallic γ' has a higher strength compared to the disordered

FCC γ -matrix [181, 182], the creep strain rate of the n-preraft alloy is smaller than the cuboid and p-preraft specimen, as observed experimentally.

The deformation mechanism under the intermediate stress condition, *i.e.*, 250 MPa, is illustrated in Figure 5.10(c). The primary source of creep deformation in the cuboid specimen originates from the large primary creep and the local strain rate maximum occurring in conjunction with rafting [93]. After the local strain rate maximum, the cuboid and p-preraft specimens exhibit a comparable strain rate as shown by their averaged strain rate (*i*) in Figure 5.5. This is likely due to the similar orientation and width of the deforming vertical γ -channels. The n-preraft alloy, however, shows a more distinct macroscopic creep behavior. The initial horizontal γ' -platelets effectively immobilize dislocations within the horizontal γ -channels as shown by the lower initial strain rate (*i*) in Figure 5.5. However, as the n-type rafted γ' -platelets disintegrate under tensile stress, the creep strain rate increases gradually as γ' evolves into p-type rafts. The increased strain rate in the n-preraft alloy (regime (*ii*) in Figure 5.5) thus likely arises from the vertical γ -channels that begin to percolate for dislocation glide once the horizontal γ' -platelets disintegrated. The connected vertical γ -channels provide an easier glide path for dislocation, leading to an increased strain rate.

Figure 5.10(d) shows the creep deformation mechanisms under the low stress condition, *i.e.*, 205 MPa. After the initial cuboidal γ' coalesces to form p-type rafts, the cuboid and p-preraft specimens exhibit very similar microstructures. From Figure 5.7, these specimens follow a similar strain rate evolution, reaching comparable minimum strain rates in regime (*i*) with the strain rate increasing thereafter. The cuboid alloy has a larger primary creep and the minimum strain rate occurs later, since it did not undergo

pre-rafting. The similar strain rate trajectory indicates a similar deformation mechanism between the cuboid and p-preraft specimens. Previous creep mechanistic studies on Ni-based superalloys suggest that rafting in accordance with the applied tensile or compressive stress is effective in slowing dislocation glide within γ -channels by promoting dislocation climb [10, 148]. However, as the rafts continue to evolve, generating a topologically-inverted and inhomogeneously-distributed γ' microstructure, the creep resistance is expected to decrease [178, 183]. The onset of increased strain rate (regime (ii)) seen in the cuboid and p-preraft specimens shown in Figure 5.8(b) likely corresponds to the emergence of the irregular γ' -microstructure from extensive rafting.

For low-stress creep, the creep resistance of the n-preraft alloy is significantly worse than those of the cuboid and p-preraft specimens (Figure 5.8). The lower strain rate during primary creep is likely the consequence of horizontal γ' -platelets being more effective at inhibiting dislocation motion. After the primary creep, a short steady-state creep regime (i) likely corresponds to disintegration of horizontal γ' -platelets. Thereafter, as the n-type rafted microstructure evolves towards a p-type rafted structure, the strain rate increases rapidly in regime (ii), which may be attributed to various microstructure-dependent dislocation motion. First, as the horizontal γ' -platelets disintegrate and raft along the stress axis, the initially separated vertical γ -channels become connected, allowing dislocations to glide over long distances throughout the γ -matrix. Second, the p-type rafts evolved from n-type rafts exhibit a more irregular morphology and a less homogeneous spatial distribution than the p-type rafts coalesced from cuboidal γ' . This inhomogeneity may further promote local stress concentration, dislocation glide and shearing of γ' [55, 178, 183].

Third, since rafting is a diffusion-driven coarsening process, the associated n-type to p-type diffusional flux may contribute to dislocation climb at the γ - γ' interface, further accelerating the creep deformation.

The overall creep behavior of the pre-rafterd monocrystalline L19C study herein has numerous similarities to the pre-rafterd Ni-based superalloys (SRR99) studied by Tetzlaff and Mughrabi [14] (Supplemental Figure 5.15 shows the creep behaviors of SRR99 at different stresses and the corresponding microstructure). In both studies, it was found that the pre-rafterd microstructure formed via compression (n-type in Co-based and p-type in Ni-based superalloy) offers a temporarily improved creep resistance under tensile creep. The enhanced creep resistance is particularly apparent under high stress conditions due to the shorter creep duration for microstructural evolution. This improvement becomes progressively attenuated for samples crept at a lower stress (and hence a longer duration) since the rafts formed via compression are not stable under tension. While the rafting directions are reversed between the positive misfit Co-based superalloys and the negative misfit Ni-based superalloys, the underlying strengthening and weakening mechanisms from pre-rafterd microstructure are analogous.

5.4.4. Minimum strain rate comparison

Figure 5.11 shows, for monocrystalline L19C, the influence of pre-rafterd on the minimum strain rate, as determined from Figures 5.3, 5.5 and 5.7. It is apparent that the cuboid and p-prerafter specimens have near identical minimum strain rates at 205, 250 and 305 MPa. This further illustrates that the p-type γ' rafted microstructure deforms via the same mechanism and has a similar microstructural evolution pathway when compared

to the cuboidal γ' microstructure. On the other hand, the n-preraft alloy exhibits a lower minimum strain rate under high stress and a higher minimum strain rate under low stress. In all the investigated microstructures, especially the n-preraft alloy, the continuous microstructural evolution entails significant influence on the measured strain rate, evident from L19C's deviation from the power law creep. While the Mukherjee-Bird-Dorn power-law equation: $\dot{\epsilon} = A\sigma^n \exp(-Q/RT)$ governs the creep behavior assuming a non-evolving microstructure, microstructure of γ' -strengthened superalloys with a non-zero misfit continuously evolves during creep, rendering a less effective minimum strain rate prediction.

Due to the lack of pre-rafter creep results of Ni-based superalloys at 900 °C, comparison is made with a Ni superalloy SRR99 crept at 1000 °C [14] (with a γ' -volume fraction of 72%, significantly higher than the 53% value of L19C). Supplemental Figure 5.15 shows the creep behavior and microstructure of SRR99 at different stresses. Similar to L19C, the compressive pre-rafter treatment leading to p-type rafts in SRR99 (but n-type rafts in L19C) enhances the tensile creep resistance, as evidenced by the lower minimum strain rates in p-preraftered SRR99 as compared to SRR99 with cuboidal γ' -precipitates (Figure 4.2). However, in SRR99, the improvement in creep resistance is present across all tested stresses from 150 to 300 MPa, while the n-prerafter improvement in L19C is only apparent under intermediate and high stresses (250 and 305 MPa).

5.4.5. Overall creep resistance comparison

Figure 5.12 summarizes for L19C the effect of the three initial γ' -microstructures on the time to reach 3% creep strain. This 3% creep time contains contributions from primary,

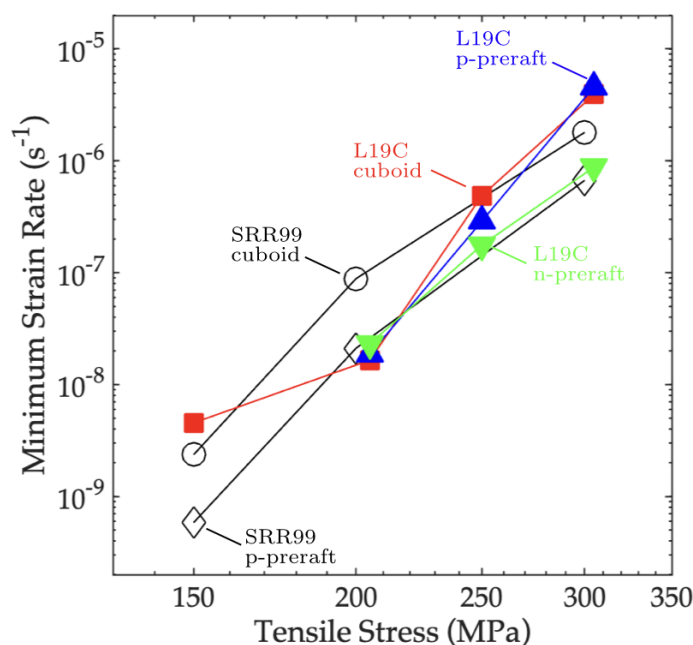


Figure 5.11. Double-logarithmic plot of minimum strain rate vs. tensile stress for creep at 900 °C of monocrystalline L19C with cuboid (red squares), p-preraft (blue upward triangles) and n-preraft (green downward triangles) microstructure. The minimum strain rate of the cuboid specimen at 150 MPa is extracted from the rupture test shown in Supplemental Figure 5.13. A Ni-based superalloy, SRR99, with cuboidal (black opened circle) and p-type pre-rafter (black opened diamond) microstructure crept at 1000 °C highlight the similar creep strengthening behavior from the rafted microstructure [14].

secondary (and in some cases, tertiary) creep for the cuboid, p-, and n-preraft specimens. Additional comparison is again made with the Ni-based superalloy SRR99 for two initial microstructures (unrafted and compressive pre-rafter) [14] which were also tensile-crept at three stresses: high stress (300 MPa), intermediate stress (200 MPa) and low stress (150 MPa). For L19C at the highest stress of 305 MPa, the n-preraft specimen takes the longest time to reach the cutoff 3% strain, as compared to both cuboid and p-preraft specimens, which show approximately the same creep time. This illustrates the significance of the

n-type microstructure in hindering creep deformation. A similar behavior is observed in SRR99 at 300 MPa, where the p-type rafted γ' -microstructure provides a moderate enhancement (by $\approx 20\%$) in tensile creep resistance.

For L19C at the intermediate stress of 250 MPa, the improved creep resistance for the n-preraft alloy is small ($\approx 15\%$ more time to reach 3% strain), as its microstructure evolves away from n-type rafts. The cuboid alloy reaches the cutoff strain the fastest, consistent with a larger primary creep strain and the strain associated with transition from a cuboidal to p-type rafted microstructure [93]. The p-prerafted SRR99, at its intermediate stress of 200 MPa, also exhibits no improvement in creep resistance compared to the cuboid SRR99.

Finally, under the low-stress condition of 205 MPa, the n-preraft L19C superalloy reaches the cutoff strain well before either the cuboid or p-preraft specimens, due to the significant morphological evolution of γ' -precipitates. A similar effect is visible for the p-preraft SRR99 alloy at its low stress of 150 MPa, with creep times reduced by $\approx 60\%$ as compared to the cuboid, initially unrafted microstructure.

Present results on our Co-based superalloy, along with comparison with previous work in Ni-based superalloys, show that the overall creep resistance of a superalloys - not solely its minimum creep rate - is affected by the pre-existing rafting of its γ' -microstructure (if present) as well as the evolution of the rafted microstructure during creep. In the case of p-preraft SRR99 and n-preraft L19C, creep resistance is significantly reduced as the γ' -microstructure transforms during creep from one orientation of rafted microstructure to another. The results suggest that maintaining a n-type rafted microstructure in Co-based

superalloys under tensile load may provide improved mechanical properties, in both creep and fatigue [184].

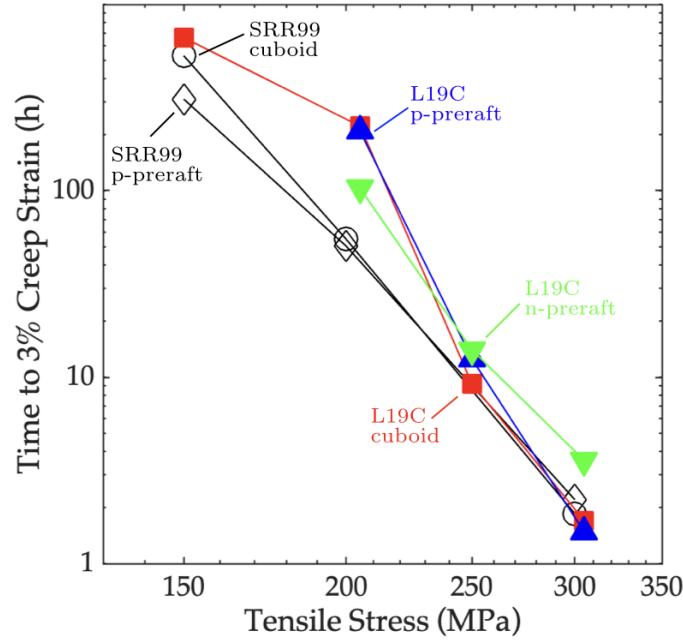


Figure 5.12. Double-logarithmic plot of time to reach 3% creep strain vs. tensile stress for creep at 900 °C of monocrystalline L19C with cuboid (red squares), p-preraft (blue upward triangles), and n-preraft (green downward triangles) microstructure. The time to 3% creep strain of the cuboid specimen at 150 MPa is extracted from the rupture test shown in Supplemental Figure 5.13. Data for the Ni-based superalloy SRR99, with cuboidal (black opened circle) and p-type pre-rafter (black opened diamond) microstructure crept at 1000 °C [14], are plotted for comparison.

5.5. Summary and Conclusions

The influence of pre-existing γ' -rafts on the tensile creep behavior of the monocrystalline Co-based superalloy L19C is studied for two types of raft orientations: p-type and n-type created via pre-raftering at 900-940 °C under tensile and compressive stresses, respectively. Subsequent tensile creep deformation experiments are performed at 900 °C on

both pre-rafterd (and a third unrafterd) specimens at three stresses (305, 250 and 205 MPa). The microstructural evolution during creep and the corresponding creep performance are found to be correlated, with key findings summarized as follow:

- For the as-aged superalloy with cuboidal γ' -morphology, p-type γ' -rafts aligned parallel to the applied stress and n-type γ' -rafts aligned perpendicular to the applied stress, are created after deformation for 50 h (under tensile stress at 900 °C and compressive stress at 940 °C, respectively), as expected from the positive γ - γ' -lattice parameter misfit.
- Upon subsequent tensile creep deformation to 3% strain at 900 °C, the duration of creep determines the degree of γ' microstructural evolution: specimens crept at low stress coarsen more than those crept at a higher stress, due to the longer time of testing for the same amount of creep strain.
- Under high tensile stress (305 MPa) where the creep tests are completed in 2-4 h, the n-type pre-rafterd microstructure delivers a significant enhancement in creep resistance, consistent with the absence of vertical γ -channels. The n-rafterd γ' -platelets oriented perpendicular to the applied tensile stress are effective in preventing dislocation glide and climb. The specimens with p-type γ' -rafts and unrafterd γ' -cuboids perform similarly due to vertically-aligned γ -channels being less effective in impeding dislocation motion.
- At intermediate stress (250 MPa) where the creep tests last 10-20 h, the overall creep resistance of the n-type pre-rafterd microstructure diminishes, as the n-type γ' -rafts disintegrate into a more isotropic morphology. The p-type pre-rafterd

and cuboidal γ' -microstructures performs similarly, as their microstructures both converge into p-type rafts.

- At low stress (205 MPa) when creep tests last 100-220 h, the n-type pre-rafterd microstructure provides creep resistance that is significantly worse than both p-type pre-rafterd and cuboidal γ' -morphologies. The creep duration is long enough for the n-type rafts to transform into p-type rafts, resulting in an irregular microstructure and degraded creep resistance. The p-type pre-rafterd and cuboidal microstructure, while exhibiting a better creep resistance, have both begun tertiary creep from the extensively rafterd (p-type) microstructure. Microstructural evolution such as topological inversion, widening of γ -channels, and spatial inhomogeneity may all affect the onset of increasing strain rate.
- The combined effect of raft orientation and time-dependent γ' -morphology contribute to the creep hardening of n-type pre-rafterd microstructure at high stress and creep softening at low stress, analogous to behavior observed in p-type pre-rafterd Ni-based superalloys.

Supplemental Information

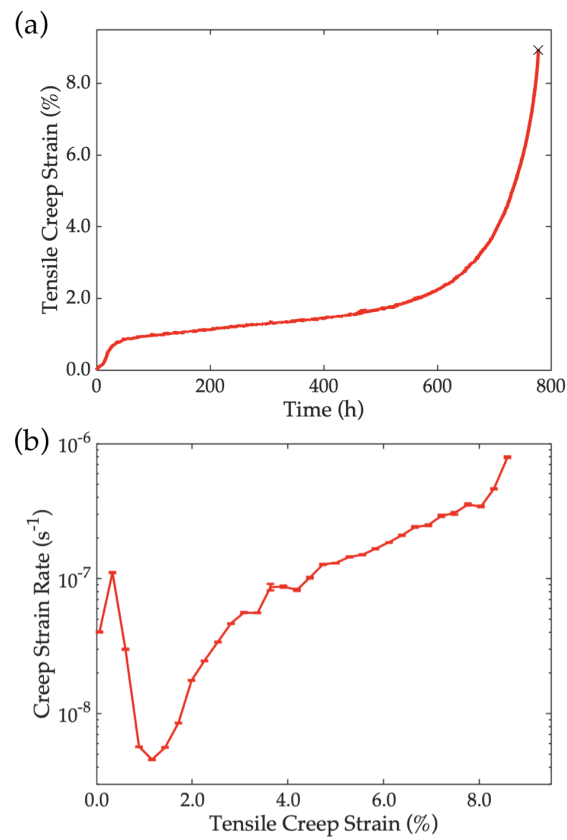


Figure 5.13. Tensile creep rupture test, performed at 150 MPa and 900 °C, for L19C with unrafted cuboidal γ' starting microstructure, showing (a) strain evolution with time and (b) strain-rate evolution with strain.

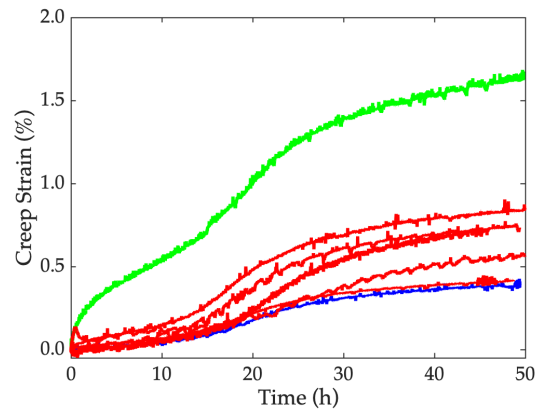


Figure 5.14. Creep strain (absolute value) during pre-raftering for monocrystalline L19C. Blue (tensile 150 MPa at 900 °C) and green (compressive 150 MPa at 940 °C) curves are shown in Figure 5.1(a). Red curves are the tensile pre-raftering creep behavior generated when producing p-prerafter specimens.

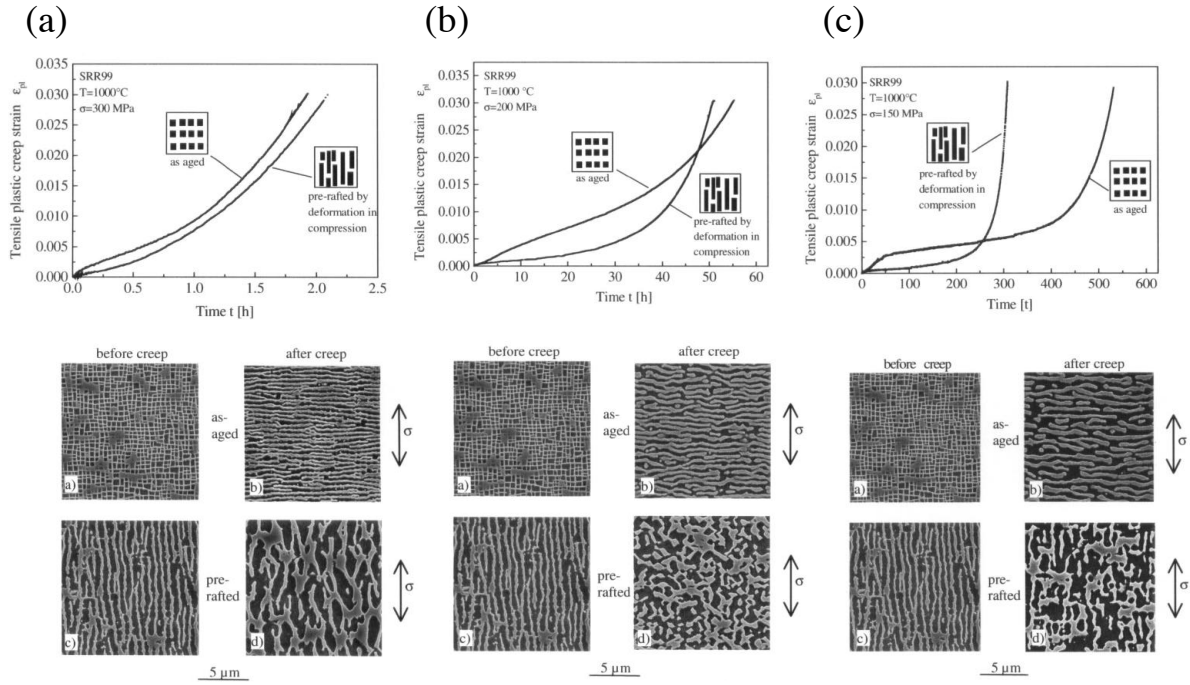


Figure 5.15. Tensile creep behavior, pre- and post-creep microstructure of p-type pre-rafterd and unrafterd Ni-based superalloy SRR99 under (a) 300, (b) 200 and (c) 150 MPa at 1000 °C. Reproduced from Ref. [14].

CHAPTER 6

Predicting Morphology of γ' -Precipitate via Phase Field Simulations

6.1. Introduction

From previous chapters, the effects of lattice misfit on microstructural evolution in Co-based superalloys are well illustrated. Chromium additions alter the lattice misfit which in turn effects the equilibrium morphology of γ' -precipitates. In addition, as the lattice misfit decreases, the degree of rafting is reduced during creep. The influence of rafting ultimately leads to a drastically different creep resistance between rafted and unrafted Co-based superalloys. While the impact of lattice misfit and rafting on bulk mechanical properties are well-discussed in this thesis, the underlying mechanisms that govern the misfit related microstructural evolution have yet to be fully understood. The goal of this work is to gain fundamental insights into the influence of lattice misfit on γ' rafting morphology in Co-based superalloys. With distinction from experimental work presented earlier where the observed microstructural features are confounded with inter-related properties such as alloy composition, processing condition and statistical variation, computational methods enable us to de-convolute individual mechanisms.

In this chapter, using the phase field method, mechanisms that govern the equilibrium morphology of γ' -precipitate are elucidated. We assessed quantitatively how lattice misfit interplays with microstructural evolution under stress. The unraveled mechanisms are

used to explain the experimentally observed microstructures that appeared throughout this thesis.

6.2. Theoretical Framework and Simulation Method

The phase field model formulation is based from the earlier work performed by Jokisaari *et al.* [9], where the phase identity of the system is described using a phase field variable η . Specifically, $\eta = 0$ in γ -phase and $\eta = 1$ in γ' -phase. Thus, there is no concentration dependence in the current framework. The phase field free energy formulation is described by three contributions that determine the microstructural evolution in a coherent γ' -strengthened superalloy system: bulk chemical energy density f_{chem} , interfacial energy density between γ - and γ' -phase f_{int} and elastic energy density f_{el} .

The bulk chemical energy density f_{chem} is described as;

$$(6.1) \quad f_{chem} = w \sum_{j=0}^{10} a_j \eta^j$$

where w determines the energy barrier height between the γ and γ' -phase, a_j is parameterized such that f_{chem} is a double-well function with $f_{chem}(\eta = 0) = f_{chem}(\eta = 1) = f'_{chem}(\eta = 0) = f'_{chem}(\eta = 1) = 0$. Note that the bulk chemical energy density described via this high order parameterized polynomial shown in Eq. 6.1 does not accurately reflect the experimental bulk chemical energy. However, due to lack of the thermodynamic data in the newly discovered Co-based superalloys, Eq. 6.1 is used as a surrogate to study γ' morphology evolution.

Following the theory of phase boundary motion for a diffuse interface by Allen and Cahn [185], interfacial energy density f_{int} is described as:

$$(6.2) \quad f_{int} = \frac{\kappa}{2} |\nabla \eta|^2$$

where κ is the interfacial coefficient and is related to the interfacial energy via $\sigma_{int} = \frac{4\sqrt{2}}{3} \sqrt{\kappa w}$ [186]. Here, it is assumed that Co-based superalloys exhibit an isotropic interfacial energy.

The elastic energy density f_{el} is described as:

$$(6.3) \quad f_{el} = \frac{1}{2} \sigma_{ij} \epsilon_{ij}^{el}$$

where $\sigma_{ij} = C_{ijkl} \epsilon_{ij}^{el}$ is the elastic stress tensor, ϵ_{ij}^{el} is the elastic strain tensor and C_{ijkl} is the stiffness tensor. However, since γ' -strengthen superalloys exhibit a misfit strain between γ - and γ' -phase, the stress-free strain is calculated as $\epsilon_{ij}^0 = \epsilon_{ij}^{misfit} h(\eta)$, where ϵ_{ij}^{misfit} is the misfit strain tensor and $h(\eta) = \eta^3(6\eta^2 - 15\eta + 10)$ is the scaling parameter to ensure the interfacial strain varies smoothly from one phase to another. The lattice misfit will be referred to as δ in the remainder of this chapter. The ϵ_{ij}^{el} is calculated as $\epsilon_{ij}^{el} = \epsilon_{ij}^{total} - \epsilon_{ij}^0$ where ϵ_{ij}^{total} is the total strain calculated from system displacement. Similar to the stress-free strain ϵ_{ij}^0 , the stiffness tensor is scaled between γ - and γ' -phase as $C_{ijkl}(\eta) = C_{ijkl}^\gamma [1 - h(\eta)] + C_{ijkl}^{\gamma'} h(\eta)$ where C_{ijkl}^γ and $C_{ijkl}^{\gamma'}$ is the stiffness tensor of γ - and γ' -phase, respectively.

To simulate the equilibrium morphology of γ' -precipitate, the system is allowed to evolve following the Cahn-Hilliard equation [187, 188, 189]:

$$(6.4) \quad \frac{\partial \eta}{\partial t} = \nabla \cdot [M \nabla \{ \frac{\partial F}{\partial \eta} \}]$$

where t is the time, M is the mobility, which we may control since only the final equilibrium morphology is of interest here and F is the free energy of the system described by the volume integral of the different energy contribution described above:

$$(6.5) \quad F = \int_V (f_{chem}(\eta) + f_{int}(\eta) + f_{el}(\eta)) dV.$$

Table 6.1. Model parameters and materials properties input for the phase field model used to simulate equilibrium γ' -morphology.

Parameters	Value	Material Properties	Value (unit)
a0=a1	0	σ_{int}	98 mJ/m ² [9]
a2	8.072789087	C_{1111}^{γ}	221 GPa [182]
a3	-81.24549382	C_{1122}^{γ}	162 GPa [182]
a4	408.0297321	C_{1212}^{γ}	95.4 GPa [182]
a5	-1244.129167	$C_{1111}^{\gamma'}$	238 GPa [182]
a6	2444.046270	$C_{1122}^{\gamma'}$	141 GPa [182]
a7	-3120.635139	$C_{1212}^{\gamma'}$	127 GPa [182]
a8	2506.663551		
a9	-1151.003178		
a10	230.2006355		

Table 6.1 lists the simulation parameters and the relevant materials properties input for the model. Equations 6.1 to 6.4 were implemented into a customized application of MOOSE, an open-source finite element framework [190]. All simulations were performed in two-dimension with a circular γ' -precipitate embedded in a square γ -domain that is at least ten times the radius of the precipitate, as shown in Figure 6.1. The larger domain size

allows the elastic interaction at the γ - γ' interface to fully relax before reaching the domain boundary. The system is solved via the preconditioned Jacobian-Free Newton-Krylov (PJFNK) method with adaptive meshing and adaptive time-stepping. The simulation is allowed to run until the change in system's total energy over time is less than $1 \times 10^{-5} \frac{aJ}{s}$, which signifies that the system has reached equilibrium and no further γ' morphological evolution will occur.

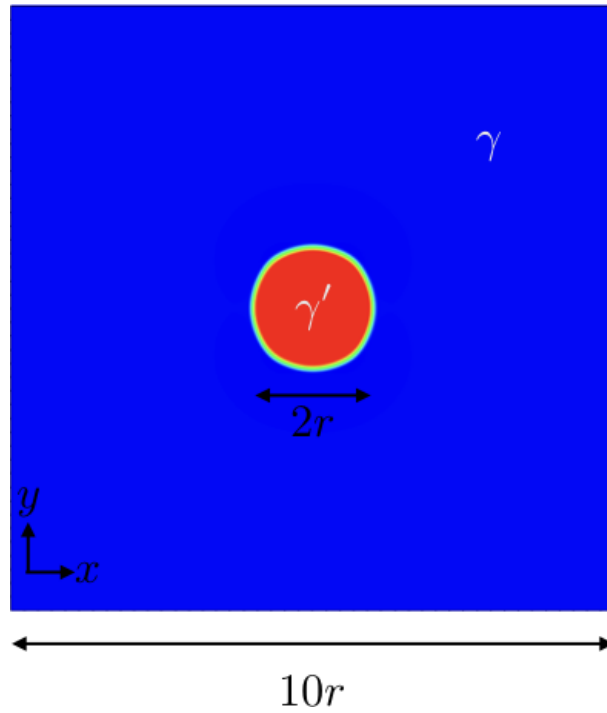


Figure 6.1. Two-dimensional simulation domain with a γ' -precipitate embedded in a γ -volume. All external stress is applied in the y-direction.

6.3. Results and Discussion

Figure 6.2a) shows the equilibrium morphology of γ' with different lattice misfit, ranging from -0.5% to 0.5%. This lattice misfit range covers the conventional Ni-based superalloys which typically has a negative misfit to the Co-based superalloys that usually have a positive misfit. Results show that γ' -morphology is symmetrical for positive and negative misfit superalloys, which agrees with previous phase field simulation and experimental findings. Figure 6.2b) to 6.2d) outline the driving force that determine the equilibrium morphology of γ' -precipitate. Evident from the large shear stress, σ_{xy} , that develops along the $\langle 110 \rangle$ lattice direction at the interface (represented by the corners of the γ' -precipitate in 2D), γ' -precipitate minimizes the area of $\{110\}$ lattice plane. The shear stress developed is equal and opposite in magnitude for both positive and negative misfit, thus resulting in an identical γ' -morphology for Ni- and Co-based system. However, as the lattice misfit reduces toward zero, the shear stress diminished as shown in Figure 6.2c). In the condition where lattice misfit is zero, the precipitate morphology is determined largely by the interfacial energy. It is commonly assumed that the interfacial energy between γ - and γ' -phase to be isotropic since γ' -precipitates exhibit a spherical morphology when the particle size is < 20 nm [9].

The rafting behavior observed during creep is also predicted via phase field simulations. Figure 6.3 shows the effect of lattice misfit on the degree of rafting under applied tensile stress. The degree of rafting is quantified by the aspect ratio of γ' -precipitate, where a more rafted γ' correlates to a higher aspect ratio. In a low misfit superalloy, where misfit approaches 0%, the precipitate does not raft and displays a spherical morphology under stress. As the misfit increases, the precipitate begins to raft more, shown

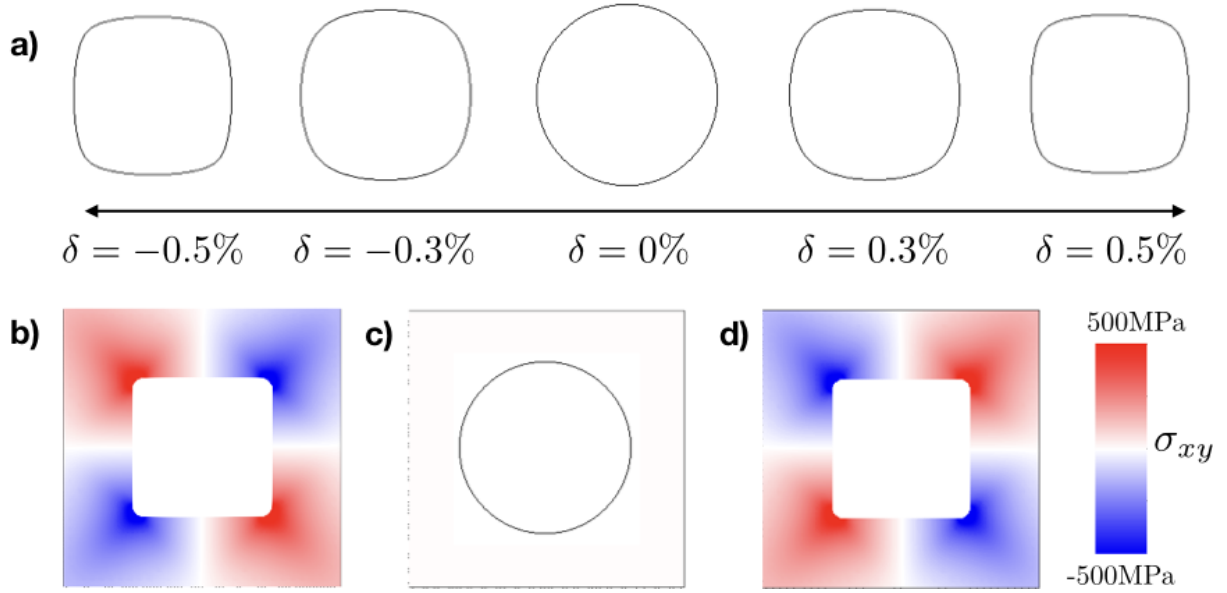


Figure 6.2. (a) Equilibrium morphology of the γ' -precipitate with different lattice misfit, ranging from $\delta = -0.5$ to 0.5% . The shear stress, σ_{xy} component of the γ - γ' system with (b) $\delta = -0.5\%$, (b) $\delta = 0.0\%$ and (c) $\delta = 0.5\%$ highlight the large shear stress at the $\{110\}$ and $\{111\}$ lattice plane that arise from lattice misfit of an superalloy.

by the increasing aspect ratio. This result suggests that lattice misfit can control the microstructural evolution trajectory during creep. In the case where γ' -rafting is shown to influence the mechanical properties, addition of elements that modify the lattice misfit may result in an improve microstructure and possibly a strengthened creep resistance.

Figure 6.4a) compares the aspect ratio of γ' with $\delta = 0.5\%$ when loaded in either tension and compression. Both tensile and compressive stress demonstrate that γ' becomes more rafted with an increased stress magnitude. When loaded in tension, the positive misfit superalloy exhibit p-type rafting behavior where γ' lengthens to a rod-like morphology. On the other hand, when loaded under compression, positive misfit superalloys evolve toward a n-type rafted microstructure where γ' flatten into a horizontal plate.

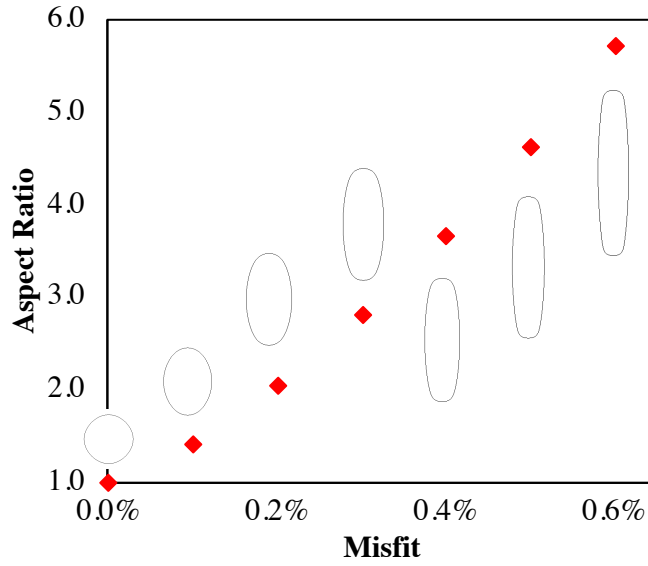


Figure 6.3. Plot of precipitate aspect ratio as a function of lattice misfit when the system is subjected to a 400 MPa of tensile stress.

This result agrees with the work performed in Chapter 5. However, simulation study show that under tensile stress, a γ' -particle forms a longer raft compare to a compression load. This tension-compression asymmetry in rafting behavior is supported by the experimental evidence shown in Figure 6.4b). Lenz *et al.* [15] show that when a single crystalline Co-based superalloy (Co-32Ni-8Al-6Cr-5W-2.5Ti-0.5Ta at.%) is crept to 5% creep strain under either tension or compression, the p-type microstructure is more significantly rafted compared to the n-type microstructure. However, the detailed mechanism behind this rafting asymmetry is not well-understood via experiments.

Figure 6.5 illustrates the driving force for forming a p-type and n-type rafted microstructure in positive misfit superalloy, while also attempt to elucidate the tension/compression asymmetric rafting behavior. Under a stress-free condition, as a result

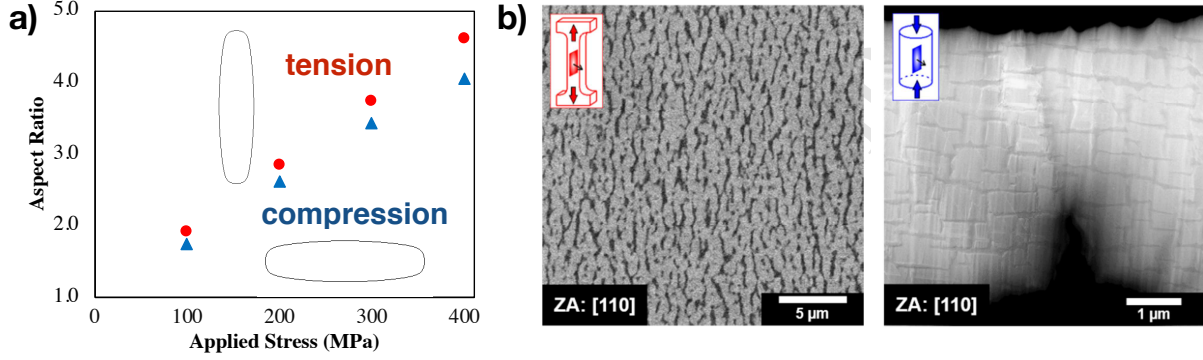


Figure 6.4. (a) Plot of precipitate aspect ratio as a function of applied stress for a superalloy with a lattice misfit of $\delta = 0.5\%$. (b) Experimental observation demonstrating that γ' -precipitates in Co-based superalloy coarsen at a different rate when creep under tension and compression. The γ' -microstructure is significantly more rafted when loaded in tension than in compression. Both micrographs show the 110 cross-section after the creep specimens reached 5% creep strain. The creep experiments was performed along the [100] direction at 850 °C at 400 MPa and lasted 755 h under compression, 380 h under tension [15].

of the larger lattice parameter in the γ' -phase along with a stiffer elastic modulus, γ' -precipitate exerts a tensile stress on the γ - γ' interface and the neighboring γ -matrix along the $\{100\}$ lattice plane (Figure 6.5a)). This internal stress is commonly referred to as the coherency stress.

When a tensile load is applied (Figure 6.5b)), since the γ -phase is more compliant than the γ' -precipitate, the tensile stress is intensified on the interface parallel to the applied stress. Concomitantly, due to the Poisson effect, the interface perpendicular to the applied stress is relaxed from the coherency stress. This difference in stress state leads to a difference in chemical potential between two interfaces. Here, the chemical potential, $\mu = \frac{\partial F}{\partial \eta}$, embodies the contribution from the mechanical energy as described by Eq. 6.5. With vertical interfaces exhibit a higher chemical potential, diffusion is driven from vertical to

horizontal interfaces, and forming a p-type rafted microstructure. Employing the same rationale, when a compressive stress is applied, the tensile stress on vertical interfaces is reduced while the tensile load on horizontal interfaces is intensified (Figure 6.5c)). This difference in stress state results in an opposite chemical potential distribution compared to tensile loaded system (Figure 6.5e)), thus γ' -precipitate directionally coarsening into a n-type rafted microstructure.

The rafting asymmetry may be explained from the tensile coherency stress that occur intrinsically in a positive misfit superalloy. Since the interface is pre-stressed in tension, an external tensile load further intensifies the coherency stress while an external compressive load counteract the coherency stress. As shown in Figure 6.5b) and c), the maximum local stress under the applied tensile stress is ≈ 700 MPa. On the other hand, when a compressive stress is applied, the maximum local stress at the interface is ≈ 250 MPa. This asymmetry in internal stress state results in a different chemical potential between the tensile and compressive stressed system, and likely is responsible for the rafting asymmetry observed both computationally and experimentally. Under this mechanism, a negatively misfit superalloy (*e.g.*, Ni-based superalloy) will exhibit an opposite rafting asymmetry behavior where γ' -precipitates raft more extensively under compression. However, there are no experimental report on rafting asymmetry found in Ni-based superalloys.

The current phase field approach presents few shortcomings and may be addressed via continuous development of the current method. The aforementioned framework did not consider a realistic bulk chemical energy, as the double well function is parameterized through high order polynomial. This prevents the model to consider a concentration dependence microstructural evolution. Effort in utilizing both CALPHAD database Gibbs

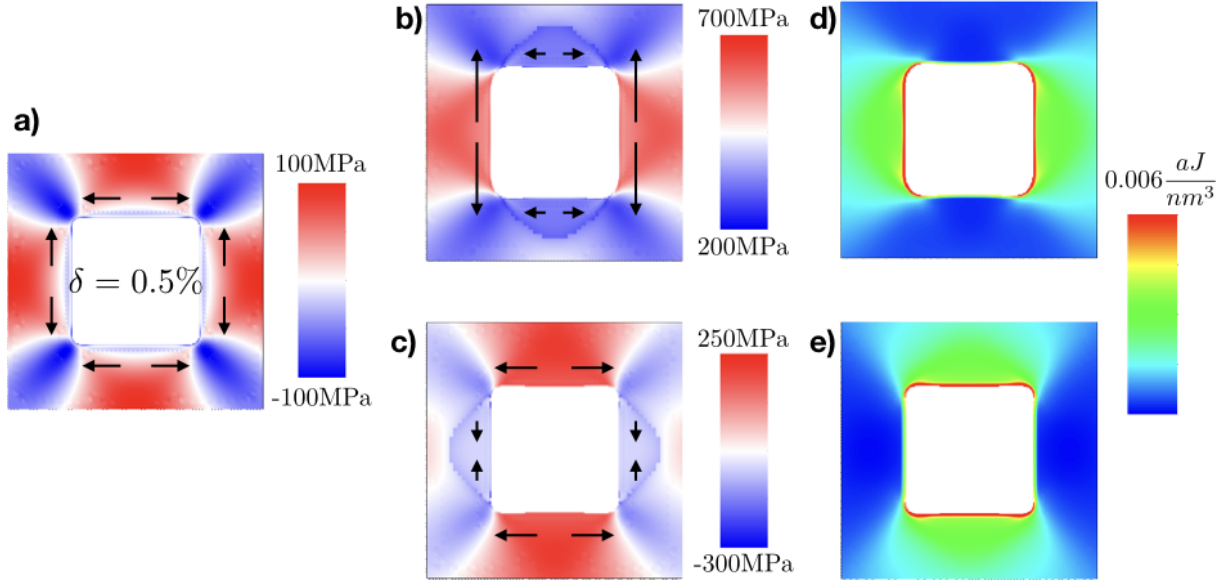


Figure 6.5. Map of stress state at the interface and the γ' -matrix surrounding a γ' -precipitate under (a) zero applied stress, (b) 400 MPa of tensile stress and (c) -400 MPa of compressive stress. The corresponding chemical potential, $\mu = \frac{\partial F}{\partial \eta}$, under (d) 400 MPa of tensile stress and (e) -400 MPa of compressive stress.

free energy and diffusivity data is current being pursued within CHiMaD, and will allow a concentration dependent simulation that can lead to a fully predictive phase field model. Studies where a phase phase framework implemented the CALPHAD thermodynamic database and diffusivity database have been reported in Ni-based superalloy. It allows detailed mechanistic study on the effect of individual alloying component [191].

Present model uses an interfacial energy that is calculated from density functional theory [9], which neglect the thermal effect. This error contribution may be significant since superalloys are usually operating at high homologous temperature. An accurate assessment of interfacial energy either via molecular dynamic simulation (MD), a combined MD-APT simulation or other experimental methods will help improve the accuracy of

the simulation. Moreover, while it is commonly assumed that γ' -strengthened superalloys exhibit an isotropic interfacial energy, the cubic crystal structure of γ' -phase likely has an anisotropic interfacial energy. Additional work had been performed to incorporate an anisotropic interface energy into the model framework, see Appendix B for details of the derivation and validation.

The elastic energy contribution, which is the dominant energy that determined the equilibrium morphology of the γ' -phase, is described most accurately in the current framework. This is due to the accurate misfit and stiffness data reported in the literature. However, it is important to note that the misfit data are commonly collected at room temperature. With the difference in thermal expansion coefficient between γ - and γ' -phase, misfit strain was shown to evolve with temperature. Measurement of lattice misfit or ability to obtain molar volume of individual phase at elevated temperature will further improve the accuracy of the lattice misfit used in the model. Furthermore, experimental studies have shown that rafting behavior is highly dependent on the plasticity that occur within γ -matrix. Extension to incorporate dislocation based crystal plasticity into phase field description may lead to a more accurate prediction of rafting behavior [140, 162, 192].

6.4. Summary and Conclusion

Phase field method that incorporate chemical, interfacial and elastic energy is used to predict the equilibrium morphology of γ' -precipitate. Simulations demonstrate that equilibrium morphology of γ' is largely determined by the mechanical interaction that arise from the misfit strain, whereas the contribution from interfacial energy is minimal. Under as-aged condition, the morphology of γ' -precipitate is symmetrical about $\delta = 0$

for both positive and negative misfit superalloy. With a higher $|\delta|$, γ' -precipitates are expected to show a higher degree of rafting, while a superalloy with $\delta = 0$ will not undergo rafting during creep. Detailed study of the local stress state between γ - and γ' -phase show that the coherency stress that arise from misfit strain provides the driving force rafting in different direction under tension and compression, and it is likely the cause of tension/compression asymmetric rafting behavior.

CHAPTER 7

Summary and Recommendation

7.1. Summary of Results

Unlike Ni-based superalloys which usually exhibit a negative lattice misfit, Co-based superalloys commonly show a positive lattice misfit where the lattice parameter of γ' -precipitates is larger than the γ -matrix. The contrasting lattice misfit between the Ni- and Co-system results in a different microstructural evolution pathway and possibly different mechanical properties. Here, the impact of lattice misfit on microstructural evolution, the associated diffusion mechanisms and bulk mechanical properties is succinctly described for Co-based superalloys.

With an increasing Cr concentration, Co-based superalloys show a reduced lattice misfit evident from both the cuboidal to spherical morphological transition and a lessened tendency of rafting during creep. The mechanisms governing the different morphological features are probed using phase field computational method. Calculations demonstrate that the morphology of γ' -precipitates is driven primarily by the mechanical energy at γ - γ' interfaces. Under high lattice misfit, shear stress at the $\{110\}$ and $\{111\}$ interfaces increases the local elastic energy, thus γ' -precipitate prefers to exhibit a cuboidal morphology. As the misfit reduces toward zero, the coherency stress at the interface diminishes, allowing the γ' -precipitate to exhibit a spherical morphology based on an isotropic interfacial energy. The change in rafting behavior is also correlated with the misfit induced

coherency stress at γ - γ' interfaces. In positive misfit superalloys, due to the heterogeneous stiffness between γ - and γ' -phase, the $\{100\}$ interfaces and the neighboring γ -matrix are under tensile stress exerted from the larger lattice parameter of γ' -phase. Upon application of external stress, interfaces parallel and perpendicular to the stress axis therefore experience a different stress due to Poisson effect. This results in a difference in chemical potential between parallel and perpendicular interfaces that drives rafting. Using monocrystalline Co-based superalloy, it was demonstrated that a tensile stress results in p-type rafts where γ' directionally coarsen parallel to the stress axis while a compressive stress triggers formation of n-type rafts where γ' flatten and coalesce to form plates perpendicular to the stress axis.

Significant amount of compositional re-distribution must occur on the mesoscale in order for rafting to occur. Through APT studies of both rafted and unrafted crept specimens, the underlying diffusional pathway that enable rapid directional coarsening of γ' -precipitates is inferred. During rafting, γ' -formers diffuse toward the γ - γ' interfaces that is migrating outward while γ -stabilizers to the γ - γ' interfaces that is receding. Present work suggests that diffusion of γ' -formers occur along the γ - γ' interfaces, from interfaces perpendicular to the applied stress to interfaces parallel to the applied stress during n-type rafting, possibly via dislocation based pipe diffusion to accelerate the diffusion kinetics. The migration of γ -stabilizers occur through the γ -channels, from channel parallel to the applied stress to channel perpendicular to the applied stress. The diffusion of γ -stabilizers via the γ -matrix is evident from the significant enrichment of Co and Cr observed in the rafted specimen. The rafting diffusional mechanism is illustrated in Figure 4.10. For crept

specimen that does not undergo rafting due to the reduced lattice misfit, no local enrichment of either γ' -formers or γ -stabilizers is observed, indicating that no compositional re-distribution occur in unrafted specimens.

The influence of γ' -rafting on the mechanical properties of Co-based superalloy is assessed by studying the impact of raft orientation on creep resistance. Tensile creep experiments performed on specimens pre-rafted in either the n-type or p-type raft orientation show a drastically different creep resistance. N-type rafted microstructure exhibits a tensile creep resistance twice of the p-type rafted microstructure, requiring double the creep time to accumulate same amount of creep strain. The superior creep performance of the n-type rafted microstructure is attributed to the ability for γ' -platelets to impede dislocation motion. However, under prolonged creep experiments, the n-type rafts are shown to be unstable under tension where γ' -platelets disintegrated into smaller particles. The disintegration of n-type rafts is associated with an increasing strain rate that result in rapid mechanical failure. On the other hand, p-type rafted microstructure, while not as effective in impeding dislocation motion, is stable under tension. Findings suggest that alternative method to stabilize n-type pre-rafted microstructure may significantly enhances the elevated temperature mechanical properties of superalloy, and similar microstructural engineering approach may be used to enhance Ni-based superalloys as well.

7.2. Suggestions for Future Work

With elucidating the effect of lattice misfit being the primary focus, this thesis provides understandings of how lattice misfit influences the microstructure, rafting mechanisms and

creep resistance in Co-based superalloys. To further advance the foundation presented here, the proposed work is categorized into two directions:

- Foundational understanding of rafting mechanisms.
- Construing the impact of rafted microstructure on mechanical properties under different conditions.

7.2.1. Foundational understanding of rafting mechanisms

While Chapter 4 attempted to explain the diffusional pathway resulting in a rafted microstructure, the proposed mechanism is not conclusive and comprehensive. Specifically, the confounding contributions between cooling supersaturation and rafting induced enrichment remain to be de-convoluted. APT, while being an *ex-situ* technique, provides an unparalleled resolution and precision in quantifying compositional inhomogeneity. To ensure each stage of rafting is captured by APT characterization, multiple interrupted creep tests should be adopted such that γ - γ' microstructures at the on-set of rafting, in the midst of directional coarsening, before and after γ' -precipitates coalescence are all analyzed to better describe the concentration distribution at each stage. It is also crucial to develop a standard operating procedure for quenching the crept specimen from the furnace. This will avoid an inequivalent cooling rate between as-aged and crept specimens.

To further understand the elemental diffusion pathway, it will be necessary to perform TEM-APT correlative study on crept specimens. Previous work in Ni-based superalloys have shown that interfacial dislocation network is locally enriched with Co and Cr (γ -stabilizers) at the dislocation core. It was proposed that γ -stabilizers diffuse along the

interfacial dislocation network via pipe diffusion. Correlative TEM-APT offers the opportunity to closely examine such claims, where a nanotip will first be imaged using TEM to ensure dislocation network is observed. Following that, APT will provide compositional information both within γ -matrix and at the dislocation to reveal any compositional inhomogeneity. The results may shed light to which components segregate toward matrix dislocation and if rafting mechanism is controlled by the dislocation network.

On the micro-scale, the kinetics of rafting may be studied via coarsening analysis. Coarsening via rafting has been demonstrated to occur at a higher rate than classical Ostwald ripening [11]. A comparison may be made by studying the particle size evolution for both stressed and un-stressed specimens. With the challenge in quantifying the particle size in extensively rafted microstructure, the coarsening kinetics may also be captured through the evolution of interfacial length per unit area. Furthermore, a study on whether a tensile or a compressive crept specimen exhibit a different stress coarsening behavior may suggest if rafting occur via a different mechanism during tensile and compressive creep. Figure 7.1 shows a preliminary comparison between γ' -microstructure coarsened in three conditions (un-stressed, tensile and compressive stress) along with the measured interfacial length per unit area. Results show that tensile and compressively crept specimens exhibit a lower interfacial length after the same 50 h aging time, further supporting previous findings that coarsening via rafting occur at a higher rate.

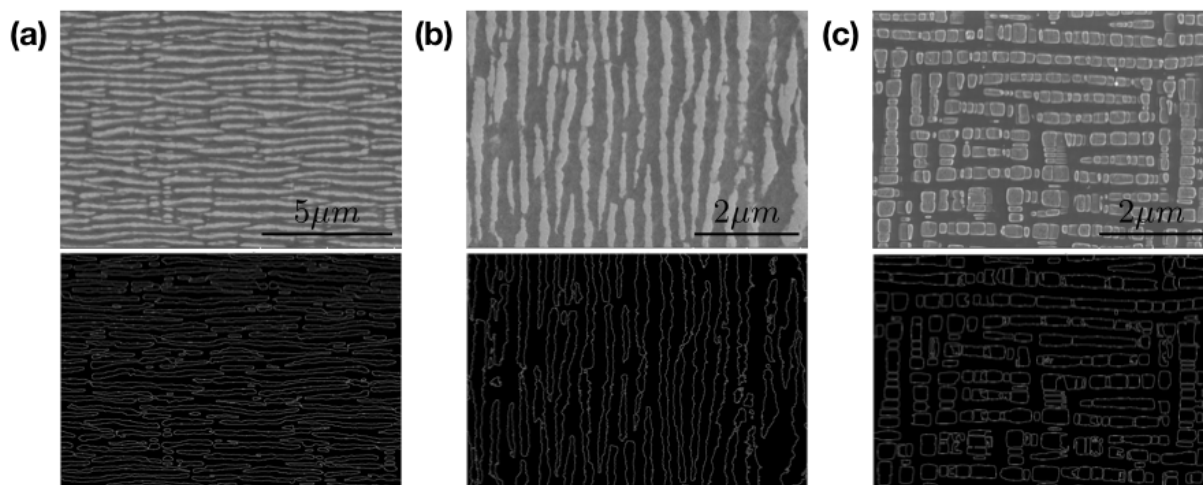


Figure 7.1. Microstructure and interfacial outline of Co-based superalloys after (a) compressive -150 MPa, (b) tensile 150 MPa and (c) un-stressed 0 MPa of creep for 50 h at 900 °C. The compressive, tensile and un-stressed micrograph each exhibit an interfacial length per unit area of 6.57, 7.60 and 8.94 μm^{-1} , respectively.

7.2.2. Construing the impact of rafted microstructure on mechanical properties under different conditions

Chapter 5 demonstrates the effectiveness of n-type rafted microstructure to enhance creep resistance while also showing its instability under tensile load at 900 °C with a stress ranging from 205 to 305 MPa. It will be of great practical interest to investigate the temperature dependence creep strength of n- and p-type rafted microstructure. Previous work in Ni-based superalloys have shown that rafted microstructure in general exhibits an improved creep strength under high temperature low stress condition due to its ability to increase dislocation glide/climb path length [10]. Also, rafted microstructure show a worsen creep resistance under low temperature high stress condition when dislocation begins to shear through γ' under high stress. It is important to note that all these analyses

and conclusion were conceived from pre-rafterd microstructure that raft according to the applied stress while a microstructure pre-rafterd against the applied stress was never investigated. Therefore, for Co-based superalloy, testing the n-type pre-rafterd microstructure under tensile loads at a lower temperature, *e.g.*, 700 °C, and a higher temperature, *e.g.*, 1000 °C, may provide additional insight on creep mechanism and potential strengthening strategy.

While no dislocation study was conducted in this thesis, the ability to visualize dislocation interaction with the γ - γ' interface and superpartial dislocation within γ' -phase will contribute significantly to understanding different creep mechanisms. Specifically, TEM study will provide an even more conclusive evidence on the effect of n-type pre-rafterd microstructure on impeding dislocation motion. It may additionally help explain the mechanism on which n-type rafts disintegrating under tensile load since the process likely occur via defect assisted nucleation of γ -phase at the γ - γ' interface [15]. Moreover, TEM imaging of dislocation at different stage of rafting may assist in explaining how rafting is enhancing or deteriorating the creep strength of Co-based superalloys.

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APPENDIX A

Evaluation of Cobalt-Based Superalloy Thermodynamic Database

A.1. Introduction

This chapter provides the evaluation of Pandat/CompuTherm's thermodynamic database, PanCo_TH, ranging from Co-Al-W ternary system to complex multinary systems with up to eight components. The goal is to assess the strength and shortcomings of the database for γ' strengthened Co-based superalloys and whether the database will add value to CHiMaD's Precipitation Strengthened Alloys Use-Case Group.

A.2. Evaluation

A.2.1. Ternary Co-Al-W and Quaternary Co-Al-W-Ni

Figure A.1 compares the Co-Al-W ternary phase diagrams at 900°C measured experimentally [16] and calculated from PanCo_TH database [17]. The calculated phase diagram closely resembles the experimentally measured phase diagram with γ' , γ , D0₁₉ and B2 phase field predicted relatively accurately. Figure A.2 demonstrates that PanCo_TH database captures the Ni quaternary addition accurately. With increasing Ni content, the γ' phase field expands correspondingly. This results agrees with the observation by Shinagawa *et al.*[6] which show γ' phase exists from the Co side to the Ni side in the Co-Al-W-Ni

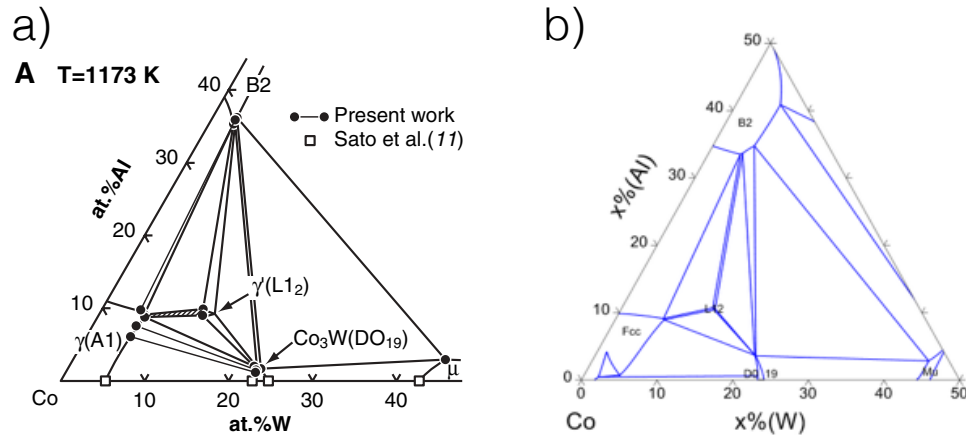


Figure A.1. Co-Al-W ternary phase diagram at 900°C a) measured experimentally [16] and b) reproduced from the PanCo_TH database [17].

quaternary system. In addition, increasing amount of Ni also widen the W solubility in γ' phase.

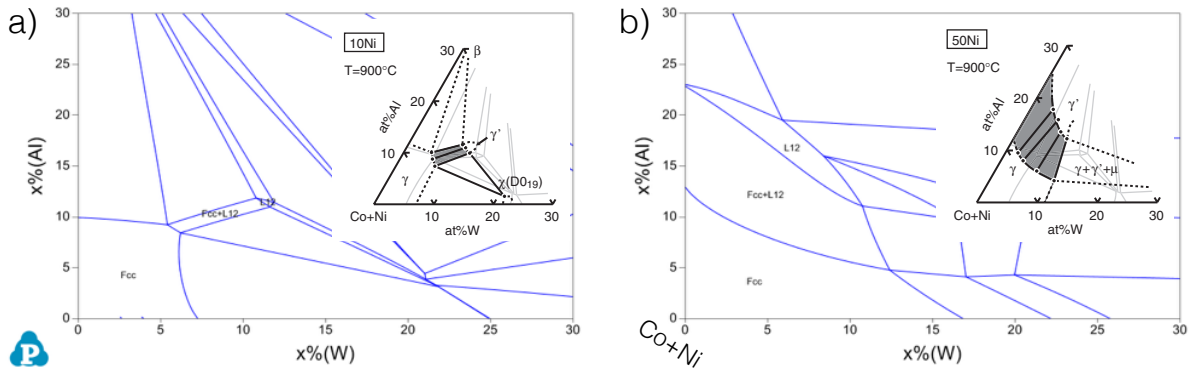


Figure A.2. Comparison of experimentally measured [6] and PanCo_TH calculated quaternary Co-Al-W-Ni 900°C phase diagram with a) 10at% Ni and b) 50at% Ni.

A.2.2. Quinary Co-Al-W-Ni-Cr

A.2.2.1. Comparison with in-house measurement. To assess the accuracy and comprehensiveness of PanCo_TH, testing beyond published quaternary systems were performed. Table A.1 shows the EDS measured composition, SEM derived and thermodynamically calculated volume fraction of an in-house casted quinary Co-Al-W-Ni-Cr alloy series with Cr concentration ranging from 0 to 6at%. Preliminary quantification shows an increase in γ' volume fraction from 0 to 4at% Cr follow by a decrease for the 6at% alloy. However, PanCo_TH predicts a continuous increase of γ' volume fraction from 0 to 6at% Cr.

Table A.1. EDS measured composition, SEM derived and thermodynamically calculated volume fraction of γ' phase in an in-house arc-melted quinary alloy series with varying concentration of Cr.

	Co	Ni	Al	W	Cr	B	SEM volume fraction %	Pandat volume fraction %
0-Cr	53.16	31.26	9.65	5.93	0	–	34.1	24.9
2-Cr	53.03	29.98	9.42	5.5	2.07	–	41.8	28.4
4-Cr	51.33	30.53	9.48	4.72	3.94	–	46.5	30.0
6-Cr	49.87	30.56	9.37	4.22	5.98	–	42.0	31.1

A.2.2.2. Comparison with Literature Reported Measurement by Povstugar *et al.* Table A.2 presents the APT measurements and PanCo_TH calculated composition and volume fraction of five alloys studied by Povstugar *et al.* [2]. Through the lever rule derived volume fraction, the results show that γ' phase fraction increases with higher Cr concentration. However, PanCo_TH predicts that composition of 4Cr and 8Cr samples are out of γ' phase field where only D0₁₉ and B2 phases are present. This indicates PanCo_TH's incapability in predicting the stable phases correctly when there is no Ni present in the alloys. With the addition of 9 and 18at%Ni, PanCo_TH correctly predicts

the stability of γ' phase although with notable deviation in volume fraction. The elemental partitioning behaviors are predicted accurately throughout the 5 alloys evaluated herein.

Table A.2. Comparison of the literature reported phase composition and volume fraction of Cr containing Co based superalloys measured by APT [2] and calculated from PanCo-TH.

Alloy	Method	Phase	Co	Composition at%				γ'	Volume fraction %		
				Ni	Al	W	Cr		D0 ₁₉	B2	μ
Base	APT	γ	85.5	...	8.5	6.0	...	38 $\pm$ 2		0	0
		γ'	76.6	...	9.4	14.0	...				
	Pandat	γ	84.6	...	8.9	6.5	...	26.9	6.7	0	0
		γ'	77.3	...	10.5	12.3	...				
4Cr	APT	γ	80.6	...	7.9	5.9	5.5	57 $\pm$ 2	0	0	0
		γ'	75.9	...	9.5	11.4	3.2				
	Pandat	γ	81.3	...	7.9	6.3	4.5	0	20.0	9.02	0
		γ'	...	...	...	...	...				
8Cr	APT	γ	73.9	...	8.0	6.8	11.2	64 $\pm$ 2	0	0	0
		γ'	73.9	...	9.4	10.4	6.4				
	Pandat	γ	79.2	...	7.4	5.6	7.8	0	0	10.54	10.83
		γ'	...	...	...	...	...				
9Ni8Cr	APT	γ	66.7	8.3	7.8	6.7	10.7	64 $\pm$ 3	0	0	0
		γ'	64.2	9.4	10.1	9.9	6.4				
	Pandat	γ	68.7	8.3	7.2	5.1	10.7	88.02	0	0	0.39
		γ'	64.6	9.1	9.3	9.4	7.6				
18Ni8Cr	APT	γ	59.2	15.6	6.0	7.4	11.8	64 $\pm$ 2	0	0	0
		γ'	54.2	19.7	10.5	9.7	5.6				
	Pandat	γ	60.5	16.3	6.4	5.6	11.1	93.11	0	0	0.05
		γ'	55.7	18.1	9.2	9.2	7.8				

A.2.3. Multinary Systems

A.2.3.1. L24Cr. Table A.3 shows the comparison between APT and PanCo-TH calculated results for an in-house alloy series, L24-Cr. Composition of L24-0Cr was designed by Eric Lass (NIST) using TCNI8 database [193]. Evaluation shows that PanCo-TH predicts elemental partition with high degree of accuracy and captures the trend of phase

Table A.3. Comparison of the phase composition and volume fraction of L24Cr alloy series measured by APT and calculated from PanCo_TH.

L24	Method	Phase	Co	Ni	Composition at%						Volume fraction %		
					Al	W	Cr	Ti	Ta	B	γ'	Ni ₃ Ta	μ
0Cr	APT	γ	...	...	...	...	...	...	...	...	83.5*	0	0
		γ'	48.5	31.0	12.0	3.9	0	2.1	2.3	0.062			
	Pandata	γ	62.5	24.3	6.5	4.1	0	0.47	2.0	...	81.5	0	0
		γ'	45.9	31.3	12.0	5.8	0	2.3	2.6	...			
4Cr	APT	γ	...	...	...	...	...	...	...	...	94.6*	0	0
		γ'	46.4	30.7	11.4	3.5	4.2	1.8	2.0	0.041			
	Pandata	γ	55.9	23.9	5.8	4.0	7.6	0.32	2.3	...	93.0	1.4	0
		γ'	45.0	30.5	11.0	5.5	3.8	2.0	2.1	...			
8Cr	APT	γ	50.4	19.6	6.0	2.4	20.5	0.5	0.4	0.035	86.0	0	trace*
		γ'	41.4	32.0	11.8	3.9	6.3	2.0	2.4	0.041			
	Pandata	γ	48.1	23.2	5.8	4.5	15.2	0.25	2.9	...	82.3	0	0
		γ'	41.4	31.5	11.1	5.2	6.4	2.2	2.2	...			
12Cr	APT	γ	...	...	...	...	...	...	...	...	43.4*	0	trace*
		γ'	...	...	...	...	...	...	...	...			
	Pandata	γ	42.3	23.6	6.3	4.3	19.4	0.26	2.8	...	61.2	0	2.0
		γ'	37.0	34.8	12.1	4.1	7.3	2.7	1.9	...			

*SEM measured volume fraction

fraction with varying Cr content. PanCo_TH correctly predicts trend of γ' volume fraction; with increasing Cr concentration, the volume fraction first increases then decrease accompany by formation of μ phase.

A.2.3.2. L19Cr. L19 is another alloy designed by Eric Lass. This alloy uses Mo and Nb in substitution for W to reduce the density of the material. A series of study with different Cr concentration was added to L19-0Cr base alloy, but only the data for 0-Cr is available at this moment. Similar to L24Cr, Table A.4 shows PanCo_TH captures the elemental partition behavior between γ and γ' with high degree of accuracy except for Ta here. The volume fraction prediction also lies close to the APT lever rule calculated values. Comparison shows that PanCo_TH performs adequately for the 0-Cr samples. However, base on further analysis with higher Cr concentration, PanCo_TH predicts γ

Table A.4. Comparison of the phase composition and volume fraction of L19 alloy measured by APT and calculated from PanCo_TH.

L19	Method	Phase	Co	Ni	Al	Composition at%				Mo	Nb	B	Volume fraction %
						W	Cr	Ti	Ta				γ'
0Cr	APT	γ	63.5	24.1	4.6	1.3	0	1.7	0.3	3.0	1.3	0	54.4
		γ'	41.9	33.6	9.4	2.3	0	5.8	1.5	3.1	2.5	0	
	Pandata	γ	62.8	24.8	4.3	1.9	0	1.4	1.1	3.2	0.5	0	53
		γ'	42.6	34.5	9.3	2.1	0	6.3	0.91	2.8	1.4	0	

and γ' to be the only stable phases up until 12at% Cr, yet SEM microstructure shows secondary precipitate formation higher than 8at% Cr. Thus, the database accuracy with addition of Mo and Nb remains questionable. Future work will assist in determining the reliability of PanCo_TH with Mo and Nb addition.

A.3. Conclusion

PanCo_TH database constructed by CompuTherm LLC is evaluated in this report. Phase diagram and point calculations ranging from ternary to eight elements multinary systems showcase the strength and weakness of the database. The phase diagram constructed for ternary Co-Al-W and quaternary Co-Al-W-Ni systems agree closely with the literature published results. Calculations for alloys beyond quaternary Co-Al-W-Ni systems, especially with addition of Cr, begin to display inconsistency between the experimental measurements and PanCo_TH prediction. For example, Povstugar *et al.* show their Ni-free Cr containing systems contain high volume fraction of γ' , yet PanCo_TH predicts stable D0₁₉ and B2 phases instead. Similarly, preliminary in-house experimental results show TCP phase formation in L19-Cr with Cr higher than 8at%, but PanCo_TH predicts γ' to be stable to 12at% Cr. Overall, the database does not perform well in Ni-free and Mo-, Nb-containing alloys.

APPENDIX B

Derivation of Residuals and Jacobians for Cahn-Hilliard Equation with Anisotropic Interfacial Energy

B.1. Introduction

As discussed in Chapter 6, while elastic energy strongly determines the γ' -precipitate morphology in a superalloy, interfacial energy may contribute toward the equilibrium morphology when lattice misfit or particle size is small. Difference in interfacial energy between the $\{100\}$, $\{110\}$ and $\{111\}$ lattice plane may result in subtle difference in precipitate morphology. However, to this point, no work has been performed to assess the interaction between elastic mechanical energy and anisotropic interfacial energy contribution in a γ' -strengthened superalloy system.

By implementing the anisotropic interfacial contribution to the existing phase field model described in Chapter 6, γ' -morphology, in addition to the elastic contribution, will be further dependent on the interfacial energy anisotropy. Figure B.1 shows the γ' -morphology with different interfacial energy when the lattice misfit is negligible. Figure B.1a) shows the equilibrium morphology where $\{100\}$ plane has the lowest interfacial energy than $\{110\}$ and $\{111\}$. In contrast, in Figure B.1b), by adjusting the interfacial contribution such that $\{100\}$ now has the highest interfacial energy, instead of obtaining a cuboidal morphology, precipitate now exhibit a diamond morphology. In this chapter,

the mathematics necessary for implementation of an anisotropic interfacial energy into the phase field model is derived.

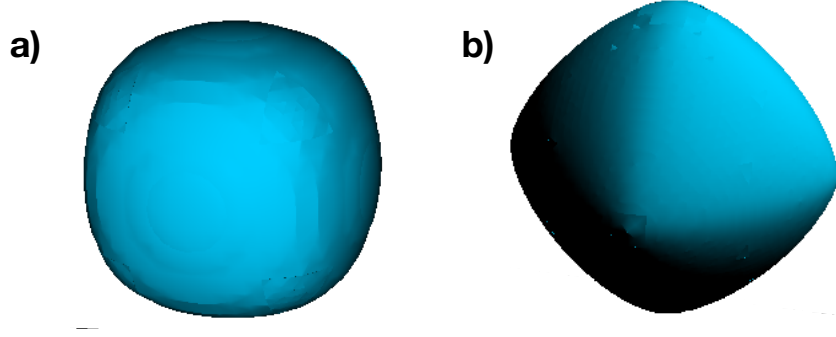


Figure B.1. Precipitate morphology a) with a low $\{100\}$ interfacial energy and b) with a low $\{111\}$ interfacial energy.

B.2. Energy Functional with Anisotropic Gradient Coefficient

Free energy functional for an anisotropic interface system without elastic energy contribution is expressed as:

$$(B.1) \quad F(u_h) = f_o + \frac{1}{2} \epsilon(\mathbf{n})^2 |\nabla u_h|^2$$

The gradient coefficient $\epsilon(\mathbf{n})$ can be model by the cubic harmonic equation as:

$$(B.2) \quad \begin{aligned} \epsilon(\mathbf{n}) &= \epsilon \\ &= W_o(1 - 3\epsilon_4) \left[1 + \frac{4\epsilon_4}{1 - 3\epsilon_4} \frac{(\partial_x u_h)^4 + (\partial_y u_h)^4 + (\partial_z u_h)^4}{|\nabla u_h|^4} \right] \\ &= \epsilon_o \left[1 + \bar{\epsilon} \frac{(\partial_x u_h)^4 + (\partial_y u_h)^4 + (\partial_z u_h)^4}{|\nabla u_h|^4} \right] \end{aligned}$$

where W_o is assumed to be 1 here and ϵ_4 is the anisotropic strength. Note that when $\epsilon_4 > 1/15$, the phase field evolution equation becomes ill-posed. Thus, the present model

may only be used to model system with a weak anisotropy. Here, $\partial_x u_h = \frac{\partial u_h}{\partial x}$, $\partial_y u_h = \frac{\partial u_h}{\partial y}$ and $\partial_z u_h = \frac{\partial u_h}{\partial z}$ are the gradient of the phase field variable in each Cartesian direction, where u_h is equivalent to η phase variable described in Chapter 6.

B.3. Derivation of the Residuals

Using Equation B.1 and B.2, Euler-Lagrange equation yields:

$$\begin{aligned}
\frac{\delta F}{\delta u_h} &= \frac{\partial f_{\text{bulk}}}{\partial u_h} - \\
&\quad \frac{\partial}{\partial x} \frac{\partial}{\partial (\partial_x u_h)} \left[\frac{1}{2} \epsilon^2 |\nabla u_h|^2 \right] - \\
&\quad \frac{\partial}{\partial y} \frac{\partial}{\partial (\partial_y u_h)} \left[\frac{1}{2} \epsilon^2 |\nabla u_h|^2 \right] - \\
&\quad \frac{\partial}{\partial z} \frac{\partial}{\partial (\partial_z u_h)} \left[\frac{1}{2} \epsilon^2 |\nabla u_h|^2 \right] \\
&= \frac{\partial f_{\text{bulk}}}{\partial u_h} - \frac{\partial}{\partial x} (\epsilon^2 (\partial_x u_h)) - \frac{\partial}{\partial y} (\epsilon^2 (\partial_y u_h)) - \frac{\partial}{\partial z} (\epsilon^2 (\partial_z u_h)) - \\
&\quad \frac{\partial}{\partial x} \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_x u_h)} |\nabla u_h|^2 \right) - \frac{\partial}{\partial y} \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_y u_h)} |\nabla u_h|^2 \right) - \frac{\partial}{\partial z} \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_z u_h)} |\nabla u_h|^2 \right)
\end{aligned}$$

Simplifying the above equation yields:

$$\begin{aligned}
\text{(B.3)} \quad \frac{\delta F}{\delta u_h} &= \mu \\
&= \frac{\partial f_{\text{bulk}}}{\partial u_h} - \nabla \cdot (\epsilon^2 \nabla u_h) - \nabla \cdot \left[\epsilon \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} |\nabla u_h|^2 \right]
\end{aligned}$$

where μ is the chemical potential, and $\frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)}$ is a vector corresponding to the derivative of ϵ with respect to $\partial_x u_h$, $\partial_y u_h$ and $\partial_z u_h$. Full derivation of $\frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)}$ is shown in Section B.5.1.

Using the divergence theorem along with product rule, Cahn-Hilliard equation shown in Eq. 6.4 can be expressed into weak form in terms of the inner product of volume $(*,*)$

and surface $\langle *, * \rangle$ integrals. The weak form for the chemical potential μ is:

$$\mathbf{R}_{i,\mu} = \left(\frac{\partial u_h}{\partial t}, \psi_i \right) + (M \nabla \mu, \nabla \psi_i) - \langle M \nabla \mu \cdot \mathbf{n}, \psi_i \rangle$$

where t is the time, M is the mobility. The weak form of the operating phase field variable u_h is

$$\begin{aligned} \mathbf{R}_{i,u_h} = & \left(\left(\frac{\partial f_{\text{bulk}}}{\partial u_h} - \mu \right), \psi \right) + (\epsilon^2 \nabla u_h, \nabla \psi_i) - \langle \epsilon^2 \nabla u_h \cdot \mathbf{n}, \psi_i \rangle \\ & + \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i \right) - \langle \epsilon \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} |\nabla u_h|^2 \cdot \mathbf{n}, \psi_i \rangle \end{aligned}$$

$\mathbf{R}_{i,\mu}$ is implemented in the existing kernel in MOOSE [190], *SplitCHWRes*, and the surface integrals are implemented in the boundary conditions, the remaining Residuals describing an anisotropic interface are

$$\begin{aligned} \mathbf{R}_i &= (\epsilon^2 \nabla u_h, \nabla \psi_i) + \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i \right) \\ &= \mathbf{R1}_i + \mathbf{R2}_i \end{aligned} \tag{B.4}$$

where $\mathbf{R1}_i$ and $\mathbf{R2}_i$ correspond to individual volume integral.

B.4. Derivation of the Jacobian

The Jacobians of the Residuals (Equation B.4) is the derivative of $\mathbf{R}_i$ with respect to u_j :

$$\begin{aligned}
 \mathbf{J}_{i,j} &= \frac{\partial \mathbf{R}_i}{\partial u_j} \\
 &= \frac{\partial}{\partial u_j} (\epsilon^2 \nabla u_h, \nabla \psi_i) + \frac{\partial}{\partial u_j} \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i \right) \\
 (B.5) \quad &= (2\epsilon \frac{\partial \epsilon}{\partial u_j} \nabla u_h, \nabla \psi_i) + (\epsilon^2 \frac{\partial (\nabla u_h)}{\partial u_j}, \nabla \psi_i) \\
 &\quad + \left(\frac{\partial \epsilon}{\partial u_j} \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i \right) + \left(\epsilon \frac{\partial^2 \epsilon}{\partial u_j \partial (\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i \right) + \\
 &\quad \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} \frac{\partial (|\nabla u_h|^2)}{\partial u_j}, \nabla \psi_i \right) \\
 &= \mathbf{J1}_{i,j} + \mathbf{J2}_{i,j} + \mathbf{J3}_{i,j} + \mathbf{J4}_{i,j} + \mathbf{J5}_{i,j}
 \end{aligned}$$

where $\mathbf{J1}_{i,j}$ to $\mathbf{J5}_{i,j}$ correspond to individual volume integral. The following subsection solves for the expression of individual Jacobian.

B.4.1. Calculation of $\mathbf{J1}_{i,j}$

$\mathbf{J1}_{i,j} = (2\epsilon \frac{\partial \epsilon}{\partial u_j} \nabla u_h, \nabla \psi_i)$ where ϵ is shown in Equation B.2. Here we solve for $\frac{\partial \epsilon}{\partial u_j}$:

$$\begin{aligned}
 \frac{\partial \epsilon}{\partial u_j} &= \frac{\partial}{\partial u_j} \left[\epsilon_o + \epsilon_o \bar{\epsilon} \left(\frac{(\partial_x u_h)^4 + (\partial_y u_h)^4 + (\partial_z u_h)^4}{|\nabla u_h|^4} \right) \right] \\
 (B.6) \quad &= \frac{\partial}{\partial u_j} [\epsilon_o + \epsilon_o \bar{\epsilon} (n_x^4 + n_y^4 + n_z^4)] \\
 &= \epsilon_o \bar{\epsilon} \left(\frac{\partial n_x^4}{\partial u_j} + \frac{\partial n_y^4}{\partial u_j} + \frac{\partial n_z^4}{\partial u_j} \right)
 \end{aligned}$$

where $\frac{\partial n_x^4}{\partial u_j}$, $\frac{\partial n_y^4}{\partial u_j}$ and $\frac{\partial n_z^4}{\partial u_j}$ are:

$$\begin{aligned}\frac{\partial n_x^4}{\partial u_j} &= \frac{\partial}{\partial u_j} \left(\frac{(\partial_x u_h)^4}{|\nabla u_h|^4} \right) \\ &= \frac{4(\partial_x u_h)^3(\partial_x \phi_j)|\nabla u_h|^4 - (\partial_x u_h)^4 \frac{\partial |\nabla u_h|^4}{\partial u_j}}{|\nabla u_h|^8}\end{aligned}$$

$$\frac{\partial n_y^4}{\partial u_j} = \frac{4(\partial_y u_h)^3(\partial_y \phi_j)|\nabla u_h|^4 - (\partial_y u_h)^4 \frac{\partial |\nabla u_h|^4}{\partial u_j}}{|\nabla u_h|^8}$$

$$\frac{\partial n_z^4}{\partial u_j} = \frac{4(\partial_z u_h)^3(\partial_z \phi_j)|\nabla u_h|^4 - (\partial_z u_h)^4 \frac{\partial |\nabla u_h|^4}{\partial u_j}}{|\nabla u_h|^8}$$

The full derivation and expansion of $\frac{\partial |\nabla u_h|^4}{\partial u_j}$ is shown in Supplemental Section B.5.2, Equation B.10.

B.4.2. Calculation of $\mathbf{J2}_{i,j}$

$$\begin{aligned}\mathbf{J2}_{i,j} &= (\epsilon^2 \frac{\partial(\nabla u_h)}{\partial u_j}, \nabla \psi_i) \\ &= (\epsilon^2 \nabla \phi_j, \nabla \psi_i)\end{aligned}$$

B.4.3. Calculation of $\mathbf{J3}_{i,j}$

$\mathbf{J3}_{i,j} = (\frac{\partial \epsilon}{\partial u_j} \frac{\partial \epsilon}{\partial(\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i)$ where $\frac{\partial \epsilon}{\partial u_j}$ is derived in Section B.4.1 Equation B.6 and $\frac{\partial \epsilon}{\partial(\partial_{x,y,z} u_h)}$ in Supplemental Section B.5.1, Equation B.8.

B.4.4. Calculation of $\mathbf{J4}_{i,j}$

$\mathbf{J4}_{i,j} = (\epsilon \frac{\partial^2 \epsilon}{\partial u_j \partial(\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i)$. To calculate for $\frac{\partial^2 \epsilon}{\partial u_j \partial(\partial_{x,y,z} u_h)}$:

$$(B.7) \quad \frac{\partial^2 \epsilon}{\partial u_j \partial(\partial_{x,y,z} u_h)} = \left(\frac{\partial^2 \epsilon}{\partial u_j \partial(\partial_x u_h)}, \frac{\partial^2 \epsilon}{\partial u_j \partial(\partial_y u_h)}, \frac{\partial^2 \epsilon}{\partial u_j \partial(\partial_z u_h)} \right)$$

where

$$\begin{aligned}\frac{\partial^2 \epsilon}{\partial u_j \partial (\partial_x u_h)} &= \frac{\partial}{\partial u_j} \left[4\epsilon_o \bar{\epsilon} \frac{\alpha_x}{|\nabla u_h|^6} \right] \\ &= 4\epsilon_o \bar{\epsilon} \frac{\left(\frac{\partial \alpha_x}{\partial u_j} |\nabla u_h|^6 \right) - \left(\alpha_x \frac{\partial |\nabla u_h|^6}{\partial u_j} \right)}{|\nabla u_h|^{12}}\end{aligned}$$

$$\begin{aligned}\frac{\partial^2 \epsilon}{\partial u_j \partial (\partial_y u_h)} &= \frac{\partial}{\partial u_j} \left[4\epsilon_o \bar{\epsilon} \frac{\alpha_y}{|\nabla u_h|^6} \right] \\ &= 4\epsilon_o \bar{\epsilon} \frac{\left(\frac{\partial \alpha_y}{\partial u_j} |\nabla u_h|^6 \right) - \left(\alpha_y \frac{\partial |\nabla u_h|^6}{\partial u_j} \right)}{|\nabla u_h|^{12}}\end{aligned}$$

$$\begin{aligned}\frac{\partial^2 \epsilon}{\partial u_j \partial (\partial_z u_h)} &= \frac{\partial}{\partial u_j} \left[4\epsilon_o \bar{\epsilon} \frac{\alpha_z}{|\nabla u_h|^6} \right] \\ &= 4\epsilon_o \bar{\epsilon} \frac{\left(\frac{\partial \alpha_z}{\partial u_j} |\nabla u_h|^6 \right) - \left(\alpha_z \frac{\partial |\nabla u_h|^6}{\partial u_j} \right)}{|\nabla u_h|^{12}}\end{aligned}$$

where $\frac{\partial \alpha_{x,y,z}}{\partial u_j}$ are derived in Supplemental Section B.5.3 Equation B.12 and $\frac{\partial |\nabla u_h|^6}{\partial u_j}$ in Supplemental Section B.5.2 Equation B.11.

B.4.5. Calculation of $\mathbf{J5}_{i,j}$

$$\mathbf{J5}_{i,j} = \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} \frac{\partial (|\nabla u_h|^2)}{\partial u_j}, \nabla \psi_i \right)$$

where $\frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)}$ in Equation B.8 and $\frac{\partial (|\nabla u_h|^2)}{\partial u_j}$ in Equation B.9.

B.5. Summary

This section provides a summary of the full expression of individual Residuals and Jacobians, that ultimately implemented into the MOOSE finite element framework to enable simulation of anisotropic interfacial energy.

$$\mathbf{R1}_i = (\epsilon^2 \nabla u_h, \nabla \psi_i)$$

Expression	Equation
ϵ	B.2

$$\mathbf{R2}_i = (\epsilon \frac{\partial \epsilon}{\partial(\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i)$$

Expression	Equation
ϵ	B.2
$\frac{\partial \epsilon}{\partial(\partial_{x,y,z} u_h)}$	B.8

$$\mathbf{J1}_{i,j} = (2\epsilon \frac{\partial \epsilon}{\partial u_j} \nabla u_h, \nabla \psi_i)$$

Expression	Equation
ϵ	B.2
$\frac{\partial \epsilon}{\partial u_j}$	B.6

$$\mathbf{J2}_{i,j} = (\epsilon^2 \nabla \phi_j, \nabla \psi_i)$$

Expression	Equation
ϵ	B.2

$$\mathbf{J3}_{i,j} = (\frac{\partial \epsilon}{\partial u_j} \frac{\partial \epsilon}{\partial(\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i)$$

Expression	Equation
$\frac{\partial \epsilon}{\partial u_j}$	B.6
$\frac{\partial \epsilon}{\partial(\partial_{x,y,z} u_h)}$	B.8

$$\mathbf{J4}_{i,j} = (\epsilon \frac{\partial^2 \epsilon}{\partial u_j \partial(\partial_{x,y,z} u_h)} |\nabla u_h|^2, \nabla \psi_i)$$

Expression	Equation
ϵ	B.2
$\frac{\partial^2 \epsilon}{\partial u_j \partial (\partial_{x,y,z} u_h)}$	B.7

$$\mathbf{J5}_{i,j} = \left(\epsilon \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} \frac{\partial (|\nabla u_h|^2)}{\partial u_j}, \nabla \psi_i \right)$$

Expression	Equation
ϵ	B.2
$\frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)}$	B.8
$\frac{\partial (\nabla u_h ^2)}{\partial u_j}$	B.9

Supplemental Information

This section shows the work for more complicated derivation that is needed for Jacobian of anisotropic interfacial energy.

B.5.1. Calculation of $\frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)}$

$$(B.8) \quad \frac{\partial \epsilon}{\partial (\partial_{x,y,z} u_h)} = \left(\frac{\partial \epsilon}{\partial (\partial_x u_h)}, \frac{\partial \epsilon}{\partial (\partial_y u_h)}, \frac{\partial \epsilon}{\partial (\partial_z u_h)} \right)$$

where $\frac{\partial \epsilon}{\partial(\partial_x u_h)}$, $\frac{\partial \epsilon}{\partial(\partial_y u_h)}$ and $\frac{\partial \epsilon}{\partial(\partial_z u_h)}$ are calculated as follow:

$$\begin{aligned}
\frac{\partial \epsilon}{\partial(\partial_x u_h)} &= \epsilon_o \bar{\epsilon} \frac{\partial}{\partial(\partial_x u_h)} \left[\frac{(\partial_x u_h)^4 + (\partial_y u_h)^4 + (\partial_z u_h)^4}{[(\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2]^2} \right] \\
&= 4\epsilon_o \bar{\epsilon} \left[\frac{(\partial_x u_h)^3((\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2) - ((\partial_x u_h)^4 + (\partial_y u_h)^4 + (\partial_z u_h)^4)(\partial_x u_h)}{((\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2)^3} \right] \\
&= 4\epsilon_o \bar{\epsilon} \left[\frac{(\partial_x u_h)^5 + (\partial_x u_h)^3(\partial_y u_h)^2 + (\partial_x u_h)^3(\partial_z u_h)^2 - (\partial_x u_h)^5 - (\partial_x u_h)(\partial_y u_h)^4 - (\partial_x u_h)(\partial_z u_h)^4}{((\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2)^3} \right] \\
&= 4\epsilon_o \bar{\epsilon} \frac{(\partial_x u_h)^3(\partial_y u_h)^2 + (\partial_x u_h)^3(\partial_z u_h)^2 - (\partial_x u_h)(\partial_y u_h)^4 - (\partial_x u_h)(\partial_z u_h)^4}{|\nabla u_h|^6} \\
&= 4\epsilon_o \bar{\epsilon} \frac{\alpha_x}{|\nabla u_h|^6} \\
&= 4\epsilon_o \bar{\epsilon} \frac{\partial_x u_h}{|\nabla u_h|^2} \left[\frac{[\partial_x u_h]^2 [(\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2] - (\partial_x u_h)^4 - (\partial_y u_h)^4 - (\partial_z u_h)^4}{|\nabla u_h|^4} \right] \\
&= 4\epsilon_o \bar{\epsilon} \frac{\partial_x u_h}{|\nabla u_h|^2} \left[\frac{[\partial_x u_h]^2 [(\partial_y u_h)^2 + (\partial_z u_h)^2] - (\partial_y u_h)^4 - (\partial_z u_h)^4}{|\nabla u_h|^4} \right] \\
\frac{\partial \epsilon}{\partial(\partial_y u_h)} &= 4\epsilon_o \bar{\epsilon} \frac{(\partial_y u_h)^3(\partial_x u_h)^2 + (\partial_y u_h)^3(\partial_z u_h)^2 - (\partial_y u_h)(\partial_x u_h)^4 - (\partial_y u_h)(\partial_z u_h)^4}{|\nabla u_h|^6} \\
&= 4\epsilon_o \bar{\epsilon} \frac{\alpha_y}{|\nabla u_h|^6} \\
&= 4\epsilon_o \bar{\epsilon} \frac{\partial_y u_h}{|\nabla u_h|^2} \left[\frac{[\partial_y u_h]^2 [(\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2] - (\partial_x u_h)^4 - (\partial_y u_h)^4 - (\partial_z u_h)^4}{|\nabla u_h|^4} \right] \\
&= 4\epsilon_o \bar{\epsilon} \frac{\partial_y u_h}{|\nabla u_h|^2} \left[\frac{[\partial_y u_h]^2 [(\partial_x u_h)^2 + (\partial_z u_h)^2] - (\partial_x u_h)^4 - (\partial_z u_h)^4}{|\nabla u_h|^4} \right] \\
\frac{\partial \epsilon}{\partial(\partial_z u_h)} &= 4\epsilon_o \bar{\epsilon} \frac{(\partial_z u_h)^3(\partial_x u_h)^2 + (\partial_z u_h)^3(\partial_y u_h)^2 - (\partial_z u_h)(\partial_x u_h)^4 - (\partial_z u_h)(\partial_y u_h)^4}{|\nabla u_h|^6} \\
&= 4\epsilon_o \bar{\epsilon} \frac{\alpha_z}{|\nabla u_h|^6}
\end{aligned}$$

$$\begin{aligned}
&= 4\epsilon_0\bar{\epsilon} \frac{\partial_z u_h}{|\nabla u_h|^2} \left[\frac{[\partial_z u_h]^2 [(\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2] - (\partial_x u_h)^4 - (\partial_y u_h)^4 - (\partial_z u_h)^4}{|\nabla u_h|^4} \right] \\
&= 4\epsilon_0\bar{\epsilon} \frac{\partial_z u_h}{|\nabla u_h|^2} \left[\frac{[\partial_z u_h]^2 [(\partial_x u_h)^2 + (\partial_y u_h)^2] - (\partial_x u_h)^4 - (\partial_y u_h)^4}{|\nabla u_h|^4} \right]
\end{aligned}$$

B.5.2. Calculation for $\frac{\partial(|\nabla u_h|^2)}{\partial u_j}$, $\frac{\partial(|\nabla u_h|^4)}{\partial u_j}$ and $\frac{\partial(|\nabla u_h|^6)}{\partial u_j}$

$$\begin{aligned}
\text{(B.9)} \quad \frac{\partial(|\nabla u_h|^2)}{\partial u_j} &= \frac{\partial}{\partial u_j} ((\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2) \\
&= 2((\partial_x u_h)(\partial_x \phi_j) + (\partial_y u_h)(\partial_y \phi_j) + (\partial_z u_h)(\partial_z \phi_j))
\end{aligned}$$

$$\begin{aligned}
\text{(B.10)} \quad \frac{\partial(|\nabla u_h|^4)}{\partial u_j} &= \frac{\partial}{\partial u_j} ((\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2)^2 \\
&= 2((\partial_x u_h)^2 + (\partial_y u_h)^2 + (\partial_z u_h)^2) \frac{\partial|\nabla u_h|^2}{\partial u_j} \\
&= 2|\nabla u_h|^2 \frac{\partial(|\nabla u_h|^2)}{\partial u_j}
\end{aligned}$$

$$\text{(B.11)} \quad \frac{\partial(|\nabla u_h|^6)}{\partial u_j} = 3|\nabla u_h|^4 \frac{\partial(|\nabla u_h|^2)}{\partial u_j}$$

B.5.3. Calculation for $\frac{\partial \alpha}{\partial u_j}$

$\frac{\partial \alpha}{\partial u_j}$ can be written as a vector where its components α_x , α_y and α_z correspond to the numerators of $\frac{\partial \epsilon}{\partial(\partial_x u_h)}$, $\frac{\partial \epsilon}{\partial(\partial_y u_h)}$ and $\frac{\partial \epsilon}{\partial(\partial_z u_h)}$ in Equation B.8 in Section B.5.1.

$$\text{(B.12)} \quad \frac{\partial \alpha}{\partial u_j} = \left(\frac{\partial \alpha_x}{\partial u_j}, \frac{\partial \alpha_y}{\partial u_j}, \frac{\partial \alpha_z}{\partial u_j} \right)$$

Using product rule:

$$\begin{aligned}
\frac{\partial \alpha_x}{\partial u_j} &= \frac{\partial}{\partial u_j} ((\partial_x u_h)^3 (\partial_y u_h)^2 + (\partial_x u_h)^3 (\partial_z u_h)^2 - (\partial_x u_h) (\partial_y u_h)^4 - (\partial_x u_h) (\partial_z u_h)^4) \\
&= (3(\partial_x u_h)^2 (\partial_x \phi_j) (\partial_y u_h)^2 + 2(\partial_y u_h) (\partial_y \phi_j) (\partial_x u_h)^3) \\
&\quad + (3(\partial_x u_h)^2 (\partial_x \phi_j) (\partial_z u_h)^2 + 2(\partial_z u_h) (\partial_z \phi_j) (\partial_x u_h)^3) \\
&\quad - ((\partial_x \phi_j) (\partial_y u_h)^4 + 4(\partial_y u_h)^3 (\partial_y \phi_j) (\partial_x u_h)) - ((\partial_x \phi_j) (\partial_z u_h)^4 + 4(\partial_z u_h)^3 (\partial_z \phi_j) (\partial_x u_h))
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \alpha_y}{\partial u_j} &= (3(\partial_y u_h)^2 (\partial_y \phi_j) (\partial_x u_h)^2 + 2(\partial_x u_h) (\partial_x \phi_j) (\partial_y u_h)^3) \\
&\quad + (3(\partial_y u_h)^2 (\partial_y \phi_j) (\partial_z u_h)^2 + 2(\partial_z u_h) (\partial_z \phi_j) (\partial_y u_h)^3) \\
&\quad - ((\partial_y \phi_j) (\partial_x u_h)^4 + 4(\partial_x u_h)^3 (\partial_x \phi_j) (\partial_y u_h)) - ((\partial_y \phi_j) (\partial_z u_h)^4 + 4(\partial_z u_h)^3 (\partial_z \phi_j) (\partial_y u_h))
\end{aligned}$$

$$\begin{aligned}
\frac{\partial \alpha_z}{\partial u_j} &= (3(\partial_z u_h)^2 (\partial_z \phi_j) (\partial_x u_h)^2 + 2(\partial_x u_h) (\partial_x \phi_j) (\partial_z u_h)^3) \\
&\quad + (3(\partial_z u_h)^2 (\partial_z \phi_j) (\partial_y u_h)^2 + 2(\partial_y u_h) (\partial_y \phi_j) (\partial_z u_h)^3) \\
&\quad - ((\partial_z \phi_j) (\partial_x u_h)^4 + 4(\partial_x u_h)^3 (\partial_x \phi_j) (\partial_z u_h)) - ((\partial_z \phi_j) (\partial_y u_h)^4 + 4(\partial_y u_h)^3 (\partial_y \phi_j) (\partial_z u_h))
\end{aligned}$$

APPENDIX C

Phase Segmentation in Atom-Probe Tomography Using Deep Learning-Based Edge Detection

C.1. Introduction

Advances in atom-probe tomography (APT) allow three-dimensional atomic reconstruction of materials with an unparalleled spatial and atomic resolution [64, 194, 195]. Application of APT to various materials, *e.g.*, metals, ceramics, biominerals and composites, now provides atomic structure-property relations to facilitate further materials development. APT is particularly useful in studying interfacial properties of precipitates, surfaces and thin films. Once the interface is identified, the elemental distribution along the interface may be closely examined using various statistical tools, such as proximity histograms [75] and elemental mapping [196].

Traditionally, interfaces are identified through iso-concentration surfaces constructed based on the marching cubes algorithm, which extracts an iso-concentration surface from a discrete scalar field with user-supplied concentration values [197]. The method is subjective and prone to inconsistencies due to local composition inhomogeneities. In addition, such a labor-intensive manual process prevents analyses of large amounts of APT datasets, limiting the scope of APT studies.

In this paper, we focus on identifying the interface in a precipitate-matrix system by phase segmentation. This approach holds the potential to expedite and reduce inconsistencies in the process of identifying interfaces and study of interfacial properties, and can furthermore be scaled up to high-performance computer platforms.

Segmentation is an approach used to partition two- (or three-) dimensional space into visually distinct and homogeneous regions with respect to certain properties. Segmentation is widely studied in the context of digital images, where the spatial information is represented by means of picture elements (pixels) in two-dimension and volume elements (voxels) in three dimensions. A pixel is the smallest unit of information that makes up a digital image in two-dimension; it is usually a square, and pixels are typically arranged in a two-dimensional grid. The color intensity in each pixel is represented by three channels, representing the intensities of red, blue and green (commonly referred to as RGB), respectively, and their combination uniquely defines the intensity of the pixel. The attributes of the voxel are similar to that of the pixel, except that it is in three dimensions.

Classical approaches to segmentation include those that are intensity-thresholding based, edge-detection or boundary-based, region/similarity-based, clustering-based, as well as graph-based approaches (see [198] for a detailed review). These approaches are primarily unsupervised, *i.e.*, the segmentation models are obtained from datasets consisting of image data without any explicitly labeled segments. There are also several supervised segmentation approaches that use *a priori* knowledge involving the ground truth of the segments to recognize and label the pixels in a new image according to one of the object classes on which the model is trained. This approach is usually referred to as

semantic segmentation [199], and tends to identify different objects present in an image as well as their location.

The success of deep learning approaches in surpassing the human level accuracy in tasks such as images classification [200] and language translation [201] has motivated several recent works in the field of digital image segmentation. This research has typically been focused on the semantic segmentation approach, as it has the potential to achieve complete image/scene understanding, which is a crucial aspect of computer vision. There are several applications under the umbrella of computer vision, such as autonomous transport [202] and human-computer interaction as well as other applications, such as medical image analysis [203], remote sensing [204], which have adopted semantic segmentation. One shortcoming of this approach is that it is only applicable for segmenting the objects (with a distinct shape) used in training sets.

Alternatively, edge/contour detection has also been significantly improved with deep learning approaches [205]. A supervised learning approach is used for edge detection, wherein each pixel is labeled as either edge or non-edge. This approach is slightly different from semantic segmentation, in that there are only two classes (edge and no-edge) and lesser semantic knowledge; hence this approach could be applicable for segmentation of objects with morphologies different from those in training data. In the case of APT, the precipitate shape can range from a thin slab to a complicated irregular volume; it is therefore a compelling case for the application of edge detection to segment the precipitate from the matrix.

Early deep learning approaches for edge detection used a conventional convolutional neural network (CNN) [206], while the latter approaches replaced the CNN with fully

convolutional networks (FCNs), which provide an end-to-end framework for pixel-wise label prediction [207]. The holistic nested edge detection (HED) approach [208] was subsequently proposed, which utilizes FCN along with the side outputs (model predictions at the intermediate layers of the network) and deep supervision to significantly improve the edge detection. HED was also demonstrated to achieve human level accuracy in edge detection. Several enhancements have been proposed for HED [209, 210], but it still remains the most widely used approach because of its efficiency and multi-scaling scheme to handle resolution and scale problems [205]; hence, we adopt HED for segmentation in this work.

Although the deep learning approaches have been shown to be successful in many tasks, one shortcoming is that they rely heavily on being provided with precise and abundant data to train the deep neural networks underlying the approaches. Especially for the supervised learning used for edge detection, large amounts of labeled data are required. Although labeled data are abundantly available for edge detection in natural images, it is challenging in problems such as interface detection in APT as significant time and effort are required to conduct each experiment [194] and to manually identify the iso-concentration surfaces as labeled data. We circumvent this challenge of labeled data collection for training the edge detection model by adopting transfer learning, which in general seeks to generalize a model trained on one task to another similar task. More specifically, the transfer learning approach we adopt utilizes the knowledge acquired from learning edge detection features on the source domain (natural images), which has abundant labeled data, to a target domain (APT) edge detection.

In our work, we present and demonstrate a digital image segmentation based surface extraction as an alternative to manual, and *ad hoc*, construct of iso-concentration surfaces for APT datasets. We show that our approach can transfer learnt edge detection features from natural images to segment APT reconstructions accurately and efficiently. We demonstrate the qualitative and quantitative accuracy of our approach using a synthetic data set constructed with molecular dynamics simulations, as well as experimental APT datasets of Co and Al superalloys [211].

C.2. Methodology: Segmentation of Phases

C.2.1. Holistically-Nested Edge Detection (HED)

We adopt HED, an end-to-end edge detection approach that performs image-to-image prediction (*i.e.*, takes an image as input, and outputs the prediction at each pixel) by means of a deep learning model that leverages FCN and deeply supervised nets. A FCN is similar to the regular CNN model used for classification, but the last fully connected layer is replaced by another convolution layer with a large filter size, which allows pixel-wise label prediction. Deep supervision is achieved by using the local output from each of the hidden layers (that is analogous to the final output obtained from a network truncated at the current hidden layer) and back-propagating the error not only from the final layer, but simultaneously from all the local outputs in the learning stage. The side outputs and deep supervision contribute to a significant performance gain over the patch-based CNN and simple FCN for edge detection.

The training phase of this approach aims to learn a functional mapping between the two-dimensional input image described by N pixels X_k , $k = 1, \dots, N$, where edge detection

is desired, and the corresponding ground truth binary edge map (Y_k) on all the pixels of image X_k . This map is obtained by training a neural network, which is composed of a VGGNet (a neural network consisting of 16 convolutional layers, five pooling layers and three fully-connected layers, which was proposed by the Visual Geometry Group (VGG) [212]), where the fifth pooling layer and the fully connected layers are trimmed, resulting in five stages with a total of 16 convolutional layers. The side output layer is connected to the last convolutional layer in each stage for deep-supervision.

The process of collecting APT data is expensive and time-consuming, and manually identifying the interfaces is cumbersome, labor-intensive and subjective. Hence, we adopt the transfer-learning approach in which: (1) the parameters for the trimmed VGGNet part of the network are initialized to the weights from VGGNet pre-trained on the Imagenet dataset [213]; and (2) the entire network is then trained using the Berkeley Segmentation Dataset and Benchmark (BSDS 500) [214] dataset (composed of 200 training, 100 validation, and 200 testing images) containing a wide variety of natural scenes with at least one discernable object (*e.g.* birds, animals, etc.). Each image in the dataset has been manually annotated to obtain the ground truth contours. This training approach is similar to the procedure for edge prediction in natural images outlined by Xie and Tu (2015) [208]. Figure C.1 shows an example of the image and the contours from the BSD dataset.

C.2.2. Orthogonal Volumetric Segmentation

The neural network trained using the procedure mentioned in the previous section is then used to perform segmentation on a three-dimensional APT dataset.

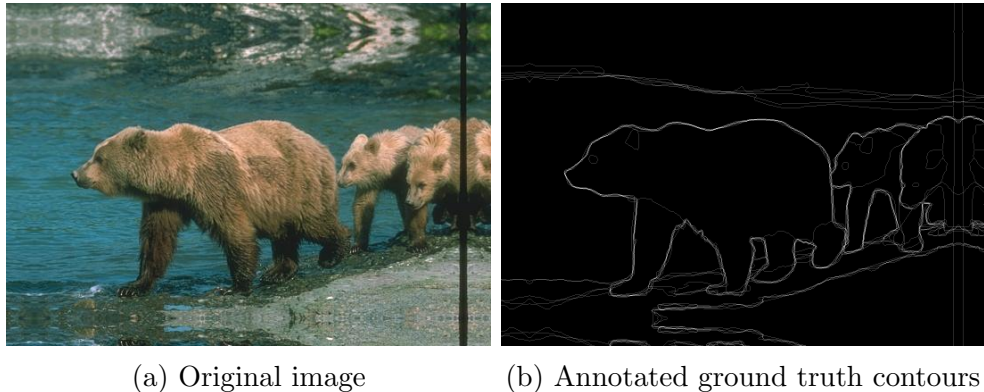


Figure C.1. Sample training image from BSDS 500 dataset

Before segmentation, the data have to be prepared and processed into a suitable format. The datasets obtained from APT consist of the spatial coordinates of each atom, as well as a label for their chemical identity. These data are transformed into a regular 3D grid of atomic concentrations, where the grid is obtained by partitioning the 3D space into a series of voxels, and the concentration is calculated for a given chemical species on each voxel based on its relative atomic fraction with respect to the other species. This grid along with the concentrations is herein referred to as the **concentration space**. The concentration values range between $[0, 1]$, hence they can be converted into grayscale images with a single intensity channel, and subsequently replicate these intensity values into three channels corresponding to RGB of each voxel. The segmentation approach can then be applied to the **concentration space** and its associated RGB voxels.

We propose to segment the **concentration space** by extracting 2D slices in each of the three orthogonal directions and detecting the edges using the HED model trained on natural images. Once the edges are obtained on each of the image slices in the three orthogonal directions, a 3D edge detection map for each slice direction is obtained by stacking all the 2D edges in that direction. Then all the three 3D edge detection maps are

merged into one by taking a union of all the voxels detected to have edges. Since there are only two phases in the APT datasets studied herein, the obtained edge detection map in 3D serves as the interfacial surface between the two phases. However, we note that the thickness of this surface depends on the thickness of the edges delineating the two surfaces. If the edges are thicker and extend to more than one voxel, there could be two surfaces, one on either side of the edge. This, however, is still acceptable as it only shifts the proximity histograms described in the next section by a small distance from the interface, and hence do not have significant effects on the interface properties calculations.

C.2.3. Proximity Histogram Calculation

The 3D point cloud data from the APT results consisting of the atomic positions and elemental identities; when combined with the edge-detected surface, a one-dimensional plot that represents the change in the relative concentration of the chemical species as a function of the distance from the surface is obtained. This plot is referred to as the proximity histogram or *proxigram*, and is acquired following the procedure outlined in Hellman et. al.(2000) [75], except that the iso-concentration surface is herein replaced by the interfacial surface obtained by edge detection. Algorithm 1 outlines the approach used to obtain the *proxigrams*.

C.3. Data Acquisition and Preparation

C.3.1. Synthetic data set for validation and verification

To create a verifiable test case, a synthetic sample with a known concentration was created using a molecular dynamics (MD) approach—an atomistic simulation method, where the

Algorithm 1 *Proxigram* calculation

- 1: Obtain the edge detected surface
 - 2: Triangulate the surface to obtain mesh and corresponding elemental surface normals
 - 3: **for** $i = 1$ to number of elements **do**
 - 4: Calculate the distance of each atom with elemental identity i from the surface
 - 5: $Hist_i \leftarrow$ Obtain histogram of the distances using a bin width B
 - 6: $Hist_{all} \leftarrow$ Repeat the histogram calculation using atoms from all elements
 - 7: **for** $i = 1$ to number of elements **do**
 - 8: $Proxigram_i = Hist_i / Hist_{all}$
-

motion of atoms is modeled using Newton’s laws of motion. In these simulations, the forces between atoms are modeled using empirical forcefield equations, and motion is created using various time integration schemes. The synthetic sample was first created by inserting two different amorphous mixtures of Al and Co into a box at opposite ends. The two phases were bridged with an amorphous interface, whose mixture was initially a linear gradient of 5Å. Once the initial structure was generated it was then heated under molecular dynamics using the LAMMPS software package[215]. This was done at a constant temperature of 2000 K for 100 picoseconds of simulation time in order to smooth out the interface. The Embedded Atom potential by Mishin *et al.* was used for the inter-atomic forces[216]. The MD synthetic structure contains one layer with an 80/20 Co to Al mixture and a second layer with a 50/50 mixture. The total number of atoms from all the elements, Co and Al, was 16,000, and the dimensions of the volume enclosing them are $1000 \times 100 \times 100 \text{ Å}^3$.

Similarly, a layered synthetic structure with the composition of a Co-based superalloy (see below) was generated using Cameca’s IVAS analysis code. To more closely emulate the structure obtained from APT, where atomic positions deviate from the perfect crystalline lattice due to uncertainties from the field-induced evaporation process [63], the

IVAS synthetic dataset was artificially introduced with a random spatial deviation from the theoretical atomic sites.

C.3.2. APT dataset

Cobalt and aluminum superalloys were used as model materials for experimental APT datasets. The Co-based superalloy used herein is a ternary alloy with 8.8 at.% Al and 7.3 at.% of W. Coherent precipitates of the γ' -phase ($L1_2$) are formed in the γ -phase (fcc) matrix with concentration differences in the two phases following the bulk thermodynamic potentials. These concentration differences lead to concentration changes across interfaces that can be used to identify them. The Al superalloy study herein is an Al-Er-Sc-Zr-Si alloy that is strengthened by ordered ($L1_2$) coherent $Al_3(Er,Sc,Zr)$ precipitates and has a concentration of 0.005 at% Er, 0.02 at% Sc, 0.07 at% Zr and 0.06 at% Si.

Atom-probe tomograms of the alloys were obtained by preparing nanotips and analyzing them using a Cameca's local-electrode atom-probe (LEAP) 4000X-Si equipped with picosecond ultraviolet laser. During the pulsed laser illumination, surface atoms are evaporated toward a two-dimensional position sensitive detector, thus constructing three-dimensional atomic tomograms of the specimens. Along with the time-of-flight measurements, the mass-to-charge ratio of the atoms can be determined, providing chemical information for each individual atoms. The experimental procedures and tomogram reconstruction conditions are detailed in Ref. [217]. The APT raw datasets were processed

using IVAS for mass spectra analyses and spatial reconstructions. After raw data processing, a position file that contains the reconstructed species’ spatial positions and mass-to-charge state (“m/n”) ratios was obtained. Additionally, a range file which matches an m/n ratio to a particular elements enables identification of each atomic species [63].

C.4. Results and Discussion

C.4.1. Segmentation

We evaluate the effectiveness and quantitative fidelity of the proposed supervised edge detection and transfer learning based digital image segmentation approach using three different interface modalities: (1) layered interface, in which the precipitate and matrix are two different layers separated by a thin interface; (2) isolated interface, in which the precipitate is an ellipsoid embedded in the matrix; and (3) interconnected interface, which is a general case where the precipitate phase exhibits an irregular morphology. The layered interface structures examined herein are synthetic and were generated using molecular dynamics simulations or using IVAS software. The isolated and interconnected precipitates APT data sets were obtained experimentally.

C.4.1.1. Layered structures. A synthetic layer structure was generated using the molecular dynamics approach outlined in Section C.3.1. **Concentration space** was obtained for the Co atoms with a voxel size chosen as $2 \times 2 \times 2 \text{ \AA}^3$. In this particular case, there was no interface component in the X-direction, so only the slices in the Y- and Z-directions are used. A 2D slice in the Y-direction and the corresponding image showing the edge detection map (indicated in white) is shown in Figure C.2a. The edge detection map correctly identified the interface between the top and bottom regions. A similar

exercise on a slice in the Z-direction is shown in Figure C.2b, where the interface was also captured appropriately by the edge detection map. Merging the 2D edge detection map from slices in Y- and Z- direction produces the surface separating the top and bottom regions as shown in Figure C.2c.

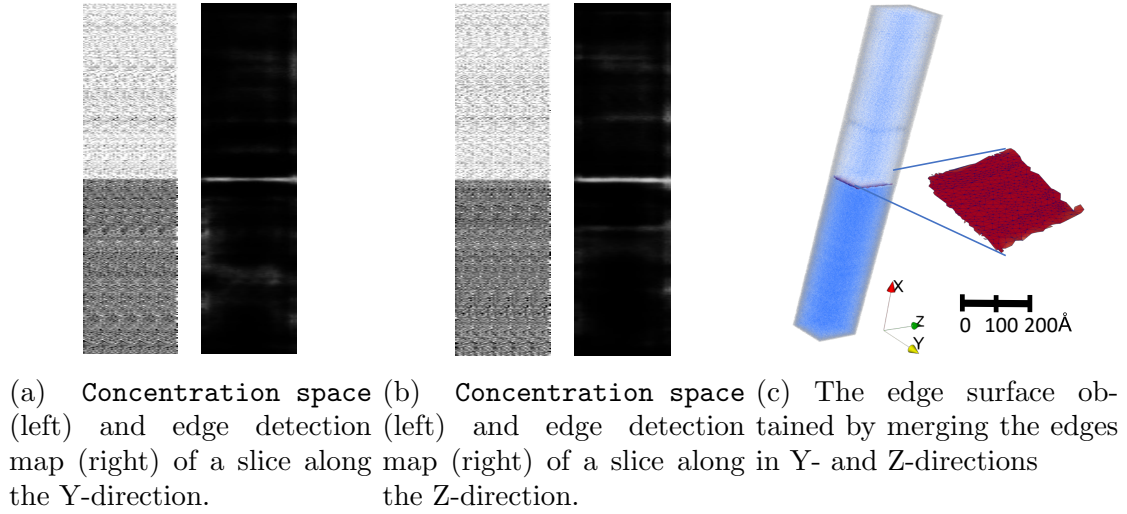


Figure C.2. Two- and three-dimensional edge detection map in a synthetic Co-Al alloy generated from MD simulation.

Similarly, a synthetic structure of a Co-based superalloy generated using IVAS is shown in Figure C.3. The synthetic structure contains a layer of γ' (L1₂) precipitate and a layer of γ (f.c.c.) matrix. This dataset contains additional spatial variations compared to the MD structure. As in the previous case, 2D slices were only generated in the Y- and Z- directions to obtain the edge detected surfaces. A slice in the Y-direction and the corresponding edge detection map is shown in Figure C.3a, and corresponding images for a slice in the Z-direction are displayed in Figure C.3b. The total number of atoms from all the elements Co, Al and W was 1,983,127, with the dimensions of the enclosing volume being $41 \times 51 \times 51$ nm³. **Concentration space** was obtained for the Co atoms

with a voxel size chosen as $1 \times 1 \times 1 \text{ nm}^3$. We note that, unlike the previous case, the detected edges are thicker and we observe secondary edges on the side (Figure C.3a). The thickness of the edges is a consequence of the uncertainty in the boundary between the top and bottom layers as well as the HED edge detection algorithm itself, which tends to produce thicker edges [218]. Alternative edge detection approaches such as the Crisp Edge Detection (CED) [218] could be used to alleviate this situation and decrease the thickness of the edges. The consequence of a thicker edge is only that we would obtain two surfaces, one at the top and other at the bottom as displayed in Figure C.3. This, however, does not affect the accuracy of the *proxigram* because it only shifts the *proxigram* by a small distance from the interface (See Section C.4.2 for a discussion on the *proxigrams* obtained). The secondary edges detected on the side could be removed by preprocessing the 2D slices to remove the empty volume.

C.4.1.2. Isolated Phase. To further validate the effectiveness of the implemented segmentation method, an experimental APT dataset of a L1_2 strengthened Al-Er-Sc-Zr-Si superalloy is used. The interface exhibits a more complex morphology with the precipitate having an ellipsoidal morphology.

The total number of atoms from all the elements, Al, Er, Sc, Zr and Si, is 668,388 with the dimensions of the enclosing volume being $29.5 \times 23.5 \times 22.5 \text{ nm}^3$. **Concentration space** is obtained for the Al atoms with a voxel size chosen as $0.5 \times 0.5 \times 0.5 \text{ nm}^3$. For the APT tomogram with a three-dimensional varying morphology, the 2D slices have to be extracted in each of the three orthogonal directions to reconstruct accurately the precipitate geometry. The 2D slices and the corresponding edge detection map in X-, Y-, Z-direction are shown in Figures C.4a, C.4b, C.4c, respectively. The morphology of

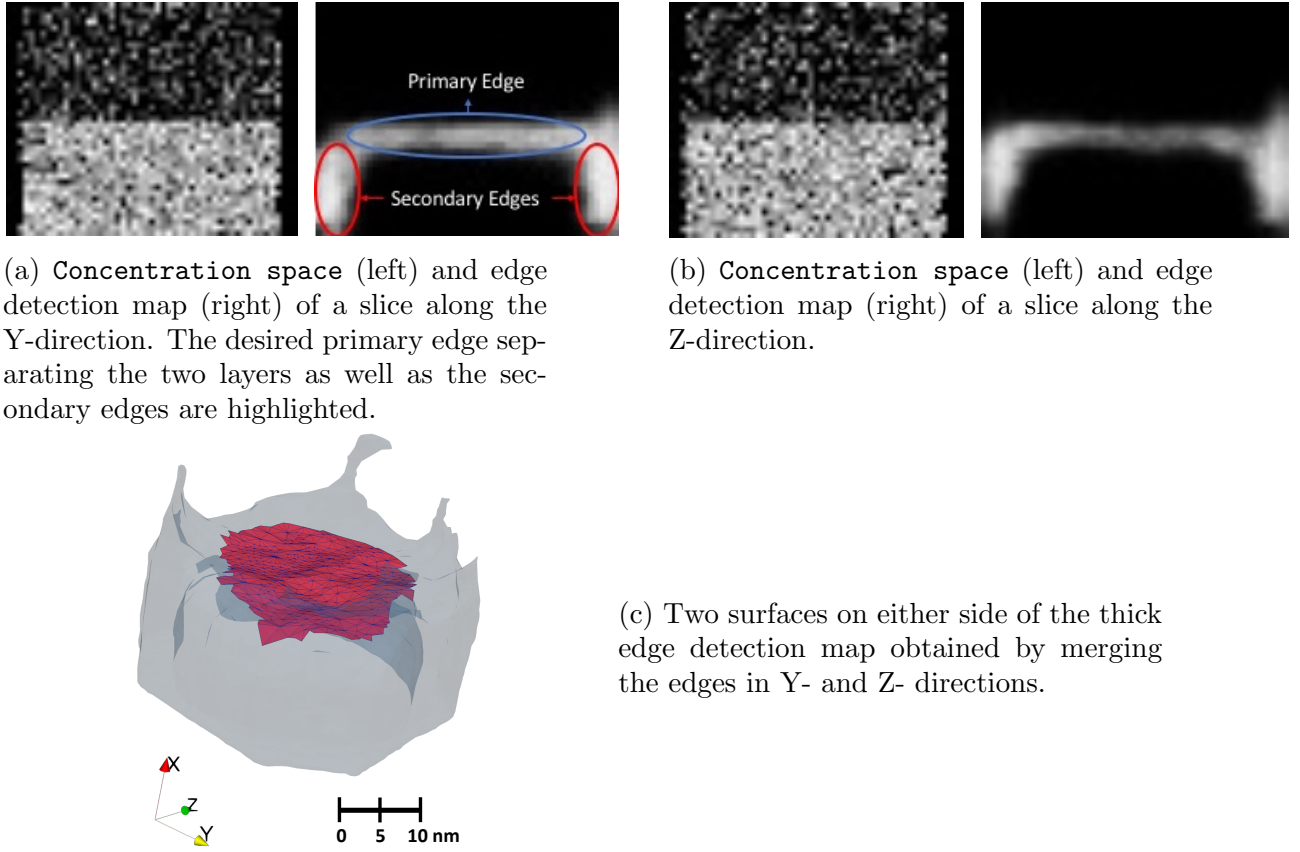


Figure C.3. Two- and three-dimensional edge detection map in synthetic Co-Al-W alloy generated using IVAS.

the precipitate has been accurately retrieved as seen in the edge detection map obtained on a 2D slice in each of the three orthogonal directions, and the fully reconstructed 3D surface obtained from fusing all slices in three directions (Figure C.4d). We observe the thick edges in the experimental APT dataset as well. The ability to capture accurately the interface in the Al superalloy, which contains tens of percents of alloying elements (Si, Sc, Zr and Er), signifies the interface identifying capability of the HED method.

C.4.1.3. Interconnected Phases. Figure C.5 shows the three-dimensional reconstruction of the entire APT nanotip from a Co-based superalloy [211]. The narrow γ matrix

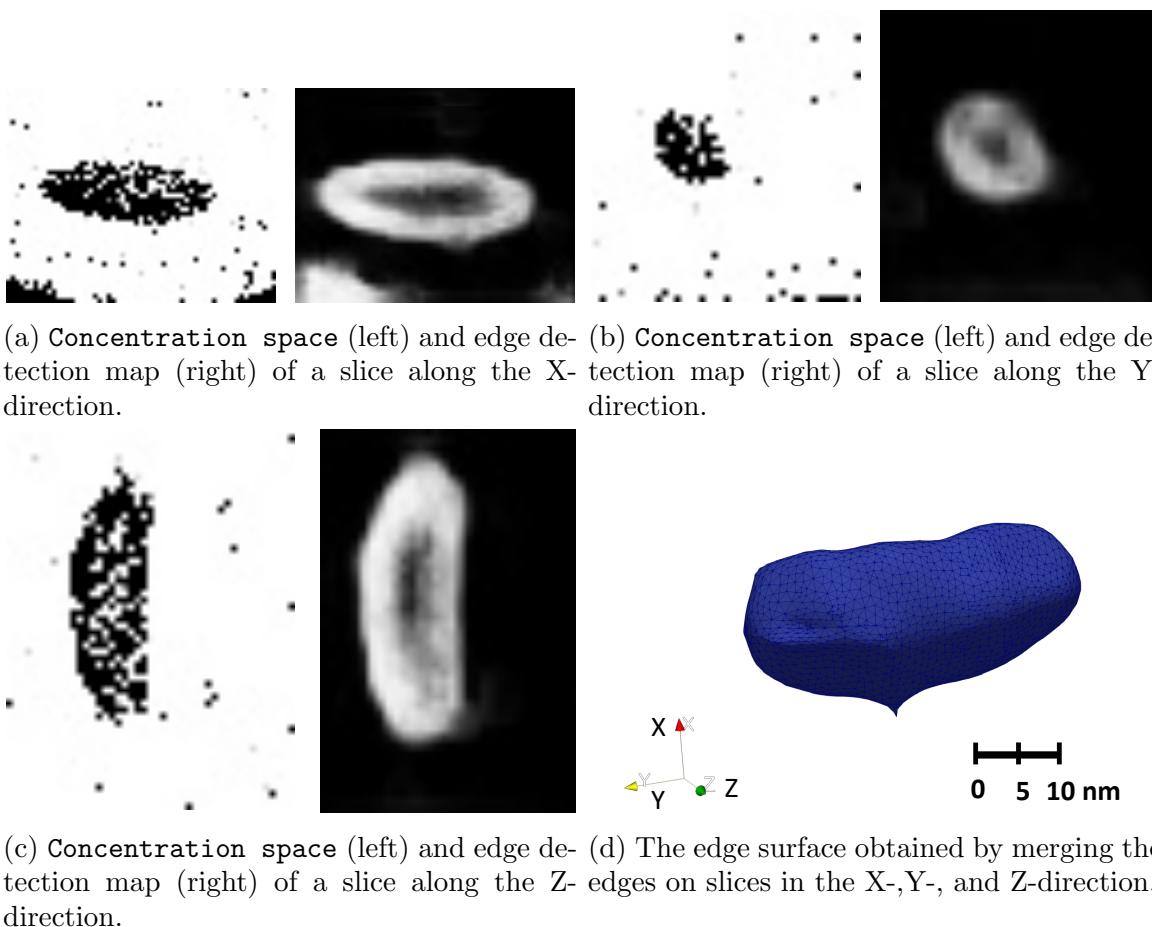


Figure C.4. Two- and three-dimensional edge detection map in the experimentally obtained APT data set from an $L1_2$ -strengthened Al-Si-Sc-Er superalloy.

channel and the inter-connectivity of the γ' from precipitate coalescence result in an overall complex interfacial structure.

This is the most general case in which the precipitate is irregular and distributed throughout the examining volume. The total number of atoms from all the elements, Co, Al and W, is 19,104,918 with the dimensions of the enclosing volume being $112 \times 90.5 \times 90.5 \text{ nm}^3$. The **concentration space** is obtained for the Co atoms with a voxel size

chosen as $0.5 \times 0.5 \times 0.5 \text{ nm}^3$. A 2D slice of the **concentration space** in the X-direction and the corresponding edges detected are shown in Figure C.5a, where it can be seen that the edge detection approach accurately identifies and segments the γ matrix phase from the γ' precipitate phase. A 2D slice in Y-, Z-direction and their corresponding edge detection map is shown in Figure C.5b and C.5c, respectively. The full 3D representation of the surface delineating the γ and γ' phases that is obtained by fusing the information from the 2D slices in the three orthogonal directions is shown in Figure C.5d.

A qualitative comparison of the **concentration space** and the edge detection maps on each slice show that the location of the matrix/precipitate interface is fairly well captured by the edges. In order to make a quantitative comparison, we obtain the iso-concentration surface using IVAS, by carefully tuning the Co concentration until the precipitate and matrix interface is captured. The obtained iso-concentration surface corresponds to a Co concentration of 0.855 and the detected surface corresponds to this concentration is shown in Figure C.6a. Using the HED approach, for the identical 2D slice, a histogram of the Co concentration at the HED detected edge is shown in Figure C.6b and has a peak at $\text{Co} = 0.87$, which agrees well with the iso-concentration surface obtained via IVAS. Thus, validating the interface detected using the HED method against the ubiquitous iso-concentration surface approach.

C.4.2. *Proxigram* Estimation

Interfacial properties of a material are frequently extracted by fitting various models to the *proxigram* composition profile. For example, sigmoid functions are well suited to model a symmetric interface [219, 220] while manual thresholding more accurately extracts the

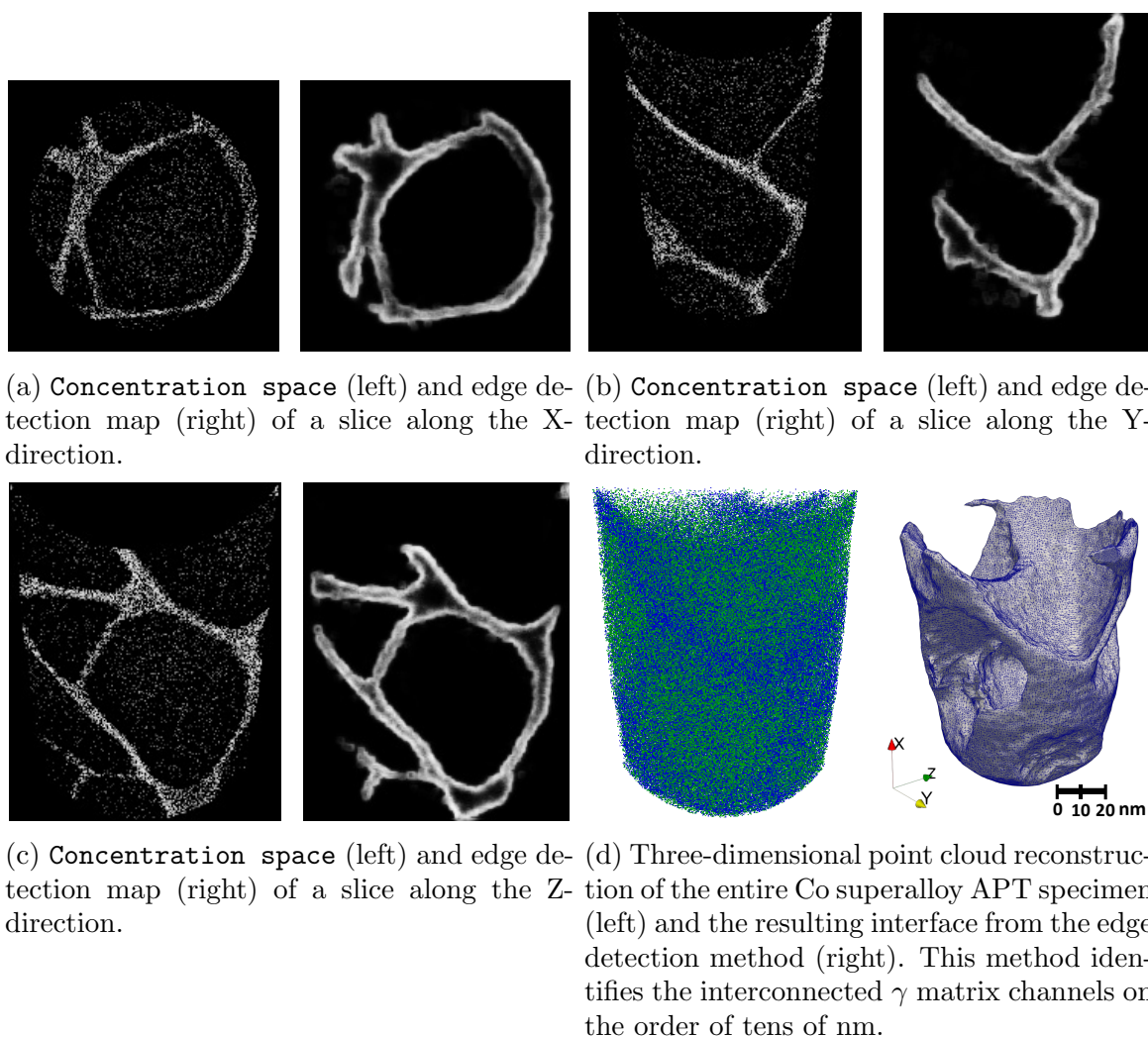


Figure C.5. Two- and three-dimensional edge detection map of the experimentally obtained APT data set from a Co-based superalloy.

properties of an asymmetric interface [221]. The accuracy of interfacial properties impacts derivative material properties, such as interfacial free energy. Specifically, interfacial free energy is dependent on the mean precipitate radius and the supersaturation of each element in the system, which APT datasets aptly capture these properties. However, any interface identification or analysis requires determining the interface location through an

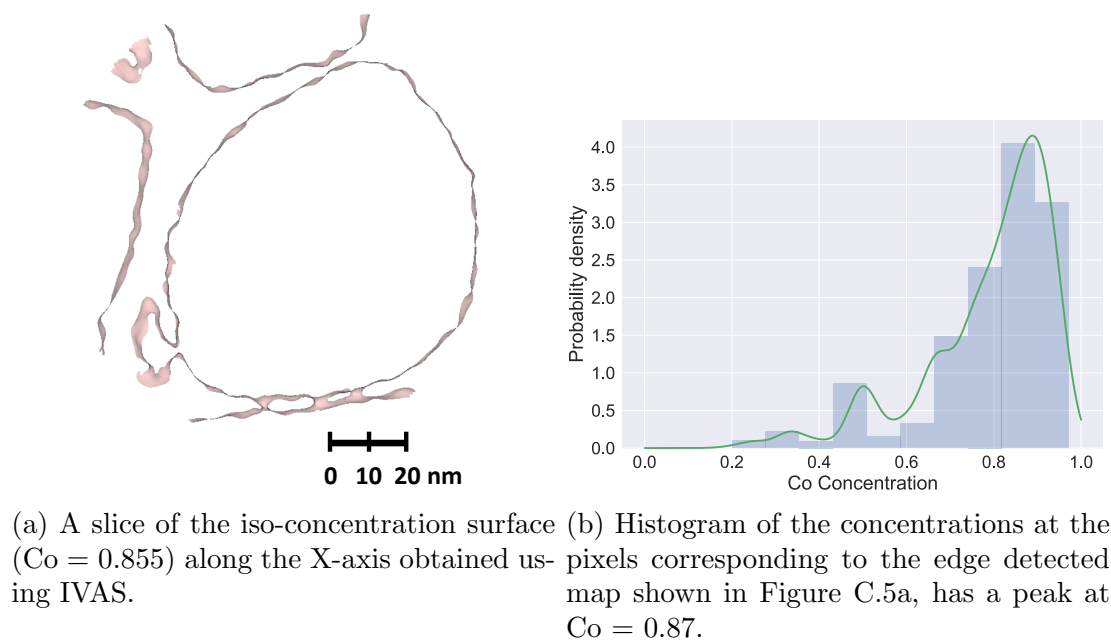


Figure C.6. Comparison of iso-concentration interface generated using IVAS software and the HED generated interfaces.

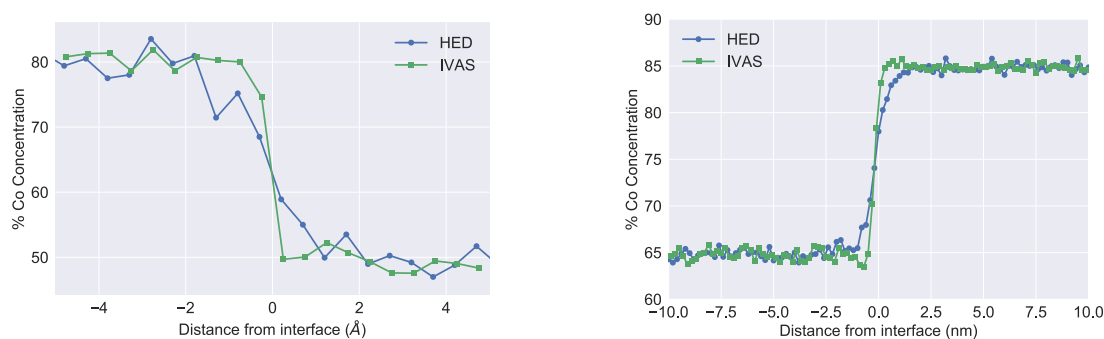


Figure C.7. *Proxigram* comparisons on the MD and IVAS generated synthetic data sets. *Proxigram* concentration profile derived from IVAS display a narrower interfacial width in comparison to the HED method.

iso-concentration analysis. Using the HED approach described herein, interface detection

is performed through compositional contrast rather than an arbitrarily defined concentration value. Therefore, the HED is agnostic with respect to models of an interface, both in regards to detection as well as to other properties, such as symmetric or asymmetric.

The resulting *proxigram* from the layered structure generated using MD is shown in Figure C.7a and those of the synthetic IVAS-generated data are shown in Figure C.7b. For the MD synthetic structure, as the Co concentration does not monotonically vary across the interface, adopting a spline fit and Co concentration thresholding will more accurately capture the interface properties as commonly practiced in the phase-field modelling community. Using the concentration thresholding method, the interface thickness obtained using the HED method is 2.3 Å, while that obtained from IVAS is approximately 1.3 Å. We note that the interfacial width obtained for the same dataset using the isoconcentration surface by IVAS (Figure C.7a) yields an interface thickness that is smaller than that obtained using the HED approach. The far-field concentration of Co on either side of the interface (80.2% and 50.7%) are both accurately recovered by the *proxigram* method, which provides a quantitative validation of the interface obtained using our segmentation approach. Far field concentrations are calculated by averaging the composition after the interfacial contribution has diminished.

Properties of a symmetric interface may be modeled using the following sigmoid function

$$(C.1) \quad f(x) = \frac{1}{2}(\rho_1 + \rho_2) - \frac{1}{2}(\rho_1 + \rho_2) * \tanh\left(\frac{x - a}{b}\right),$$

where ρ_1 , ρ_2 , a , and b are fitting parameters that correspond to the atomic densities of the two regions of the box, the interface position, and the interfacial thickness, respectively.

Direct measurement of the interfacial thickness of the MD dataset using Equation C.1 on time-averaged histograms of the Co positions along the interfacial direction results in an interfacial thickness of 3.8 Å, whereas fitting Equation C.1 to the HED *proxigram* results in an interfacial thickness of 4.0 Å. This comparison suggests that the HED interface is able to closely capture the interface thickness, which is important for calculating material properties that are particularly sensitive to measurement error, such as the coarsening rate constant.

We also compare the *proxigram* concentration profile obtained from the synthetic layered data generated using IVAS (Figure C.7b). In this case, we use the interfacial surface generated using HED approach as well as that obtained using IVAS. The *proxigram* concentration profiles generated from IVAS use a bin size of 0.5 nm to average local composition fluctuations. As in the earlier case, we find that the concentrations on either side of the interface are accurately obtained using both approaches. However, we find that even though the interfacial thickness is very close for both approaches, the interfacial thickness using the proposed HED approach is slightly larger than that obtained using IVAS, consistent with our observations for the synthetic MD-generated interface (Figure C.7a).

C.5. Summary and Conclusion

The ability to both rapidly and accurately identify interfaces, as well as to analyze qualitatively and quantitatively is paramount in the analyses of APT data, and also in general tomographic investigations of multi-grain solid structures [222, 223, 224, 225]. Current approaches utilizing iso-concentration surfaces in interface identification require

subjective input and may not be automated and scaled to high-performance computing to extract interfacial properties.

We have proposed and demonstrated a digital image segmentation approach to segment the precipitate and the matrix phases in superalloys, and use that to obtain the interfaces. The segmentation is accomplished using supervised edge detection to accommodate the irregularity in the morphologies of the two phases. Specifically, we utilize the hierarchically nested edge detection approach that consists of fully convolutional networks along with deep supervision. Furthermore, as the process of collecting and manually labeling the interface in the APT data for training the edge detection model can be cumbersome, labor-intensive, expensive and time-consuming, we propose a transfer learning approach to ameliorate this approach. Our approach utilizes the edge detection features learned on the natural images, which has abundant label data and transfers that knowledge towards segmentation in the atom-probe tomography data.

We demonstrated that our approach is qualitatively and quantitatively accurate by comparing the results of our approach with that of proprietary IVAS software from Cameca Instrument Inc. for synthetic and experimental APT data of two-phase systems. Our approach was able to successfully segment the two phases and identify the interfaces with different geometrical features. The identified interfaces correspond well with the qualitative visualization using 2D slices. In cases where the images are noisy and the interface is not clear, we obtain *thick* edges, which could be alleviated by using approaches such as Crisp Edge Detection [218].

The approach proposed herein demonstrates the power of machine learning techniques in the analyses of APT data. It should also be readily applicable to analysis of other

tomographic data of multi-phase or multi-grain systems, such as X-ray tomography of multi-phase systems, or transmission electron microscopy tomography. By using transfer learning the fully convolutional network can be trained in advance of experiments, and be applied in real time. This may be especially valuable in situations where rapid data analysis during the experiment may provide valuable real-time feedback to the experiment.