

High Resolution Characterisation of Oxidation Mechanisms in Polycrystalline Nickel Based Superalloys



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Abstract

In order to withstand the demanding conditions experienced at the heart of modern jet turbine engines, nickel based superalloys must combine extreme strength with resistance to temperature-dependent degradation mechanisms such as oxidation and fatigue. This is increasingly becoming a priority, as operating temperatures continue to be pushed higher due to tighter fuel economy and emissions targets.

A new generation of high temperature, damage tolerant superalloys has been developed which balances all of these properties through careful control of composition. For further alloy development, the relationship between oxidation kinetics and alloy composition must be established. Two elements in particular have been focussed on – titanium and niobium. Both of these elements are vital for maintaining high temperature strength; however Ti has been experimentally shown to increase rates of oxidation, while Nb has been implicated in accelerating dwell fatigue crack growth.

In order to study these composition-property relationships, a family of near identical superalloys have been created with varying titanium/niobium ratio, and subsequently characterised. Oxidation kinetics were studied using thermogravimetric analysis, which confirmed the link between titanium and oxidation, while also creating oxide scales for further characterisation. A variety of high-resolution techniques have been used to analyse these oxide scales on the smallest scales, revealing the location of titanium – some was found dissolved in chromia oxide scales as expected – but much more was found segregated to grain boundaries within the oxide. Ion transport along these grain boundaries may explain the oxidation kinetics better than the lattice diffusion mechanism previously assumed.

A number of fatigue crack tips also underwent examination, in an attempt to shed light on the mechanism by which niobium encourages dwell fatigue. While no evidence could be found for this, a number of analysis techniques have been developed and refined to hopefully aid these efforts in future.

Preface

The research in this thesis has been prepared for publication as follows:

- M.T. Lapington, D.J. Crudden, R.C. Reed, M.P. Moody, P.A.J. Bagot. Characterization of Phase Chemistry and Partitioning in a Family of High-Strength Nickel-Based Superalloys. *Metallurgical and Materials Transactions A*, 49 (6), 2302-2310
- M.T. Lapington, D.J. Crudden, R.C. Reed, M.P. Moody, P.A.J. Bagot. Characterization of Oxidation Mechanisms in a Family of High-Strength Nickel-Based Superalloys. Ready for submission

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Chapter 1. Introduction

The emergence and use of nickel based superalloys is inextricably linked to the development of commercial jet engines. Global aviation is a highly competitive and growing market, with 4.1 billion passengers transported in 2017, and a projected 4.6 billion passengers estimated for 2019 [1]. With this growth in passenger numbers comes other concerns, such as climate impact and increasing fuel costs. In 2011 global aviation accounted for 12% of all transport CO₂ emissions, which corresponded to 2% of all global CO₂ emissions at that time [2]. Limits on emissions and noise pollution are being put into place, such as the Flightpath 2050 directive implemented by ACARE (Advisory Council for Aviation Research and Innovation in Europe), which aims to reduce CO₂ emissions by 50% per passenger kilometre, reduce noise by 50%, and also to reduce NO_x emissions by 80% [3]. In order to meet these tight emissions targets, while also supporting the projected increase in global aviation traffic, the efficiency of jet turbine engines must be increased. The approach to efficiency increase covered during this project centres on maximising the thermal efficiency of the jet turbine engine, by tackling some of the obstacles which prevent further increases to maximum engine operation temperatures.

1.1 Thermodynamics and Efficiency of Jet Turbine Engines

Jet engines can be modelled using a Carnot cycle, the efficiency of which can be calculated using Equation 1.1 [4]:

$$\eta = \frac{W}{Q} = 1 - \frac{T_2}{T_1} \quad (\text{Eq. 1.1})$$

where η = efficiency, W = useful work extracted, Q = heat supplied, T_1 and T_2 = internal and external temperatures respectively. Efficiency can therefore be raised by increasing the difference between T_1 and T_2 . In practice, raising T_1 is the most practical option, with the limit for T_1 being the capability of the component materials to withstand the increase in turbine entry temperature

(TET). Since the introduction of the gas turbine engine, TET has more than doubled from 700°C to 1500°C as shown in Figure 1.1 [5].

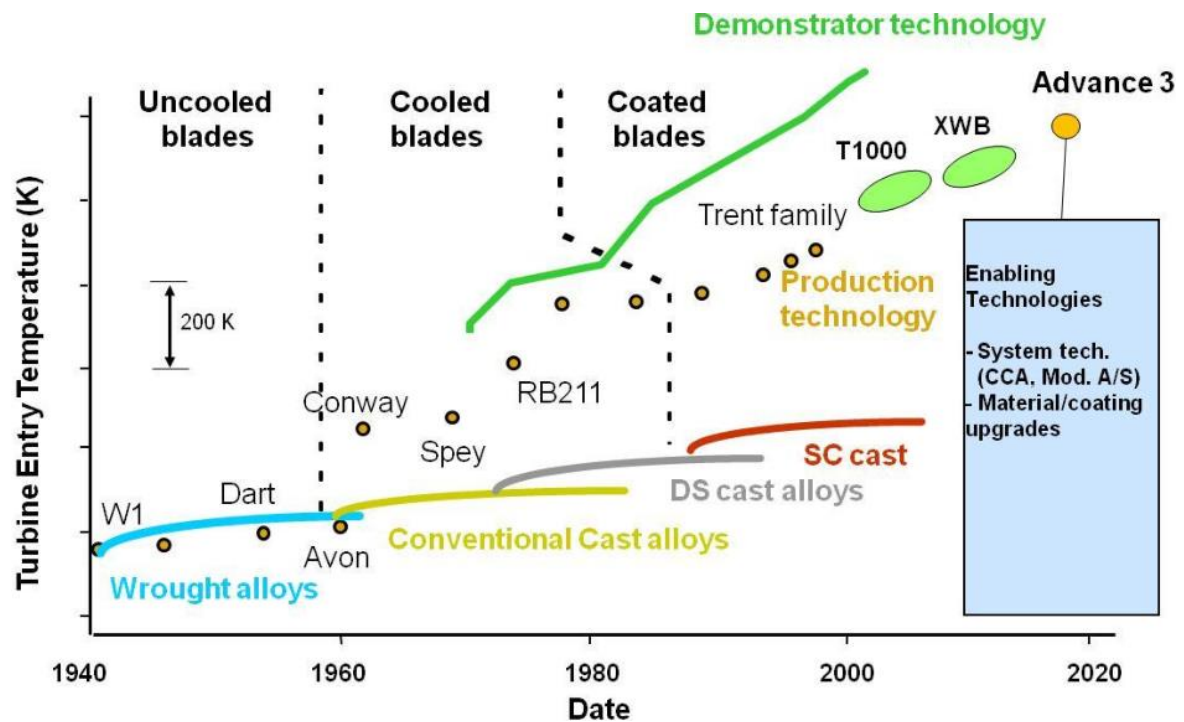


Figure 1.1 – Overview of the evolution of engine TET since 1940, compared with the material capabilities of the highest temperature components, in this case the turbine blades. The temperature capabilities of blade alloys are shown, alongside advances in coating technology. Reproduced from [6] under the Creative Commons Attribution License 4.0 (CC-BY-NC-ND).

This temperature increase has required the development of a number of enabling technologies, such as active cooling strategies and the application of thermal barrier coatings [7], which have allowed turbine blades to endure TET up to and even beyond their melting point. However not every component in the turbine section can be equally protected using these technological developments, so focus must remain on improving alloy performance.

1.2 The Jet Turbine Engine

A schematic overview of a Rolls-Royce Trent 500 is presented in Figure 1.2 a), which represents a typical commercial turbofan jet engine. It is colour coded to show the materials encountered in each section of the engine, which is mostly determined by the operating temperature of each section as shown in part b). The fan, casing, and low pressure compressor sections operate at

comparatively low temperatures, which allows the use of high specific strength materials such as titanium, aluminium, and composites to minimise weight. The high pressure compressor, combustor, and turbine sections operate in temperature regimes far beyond the safe operating window of these materials, necessitating the use of high temperature nickel based superalloys.

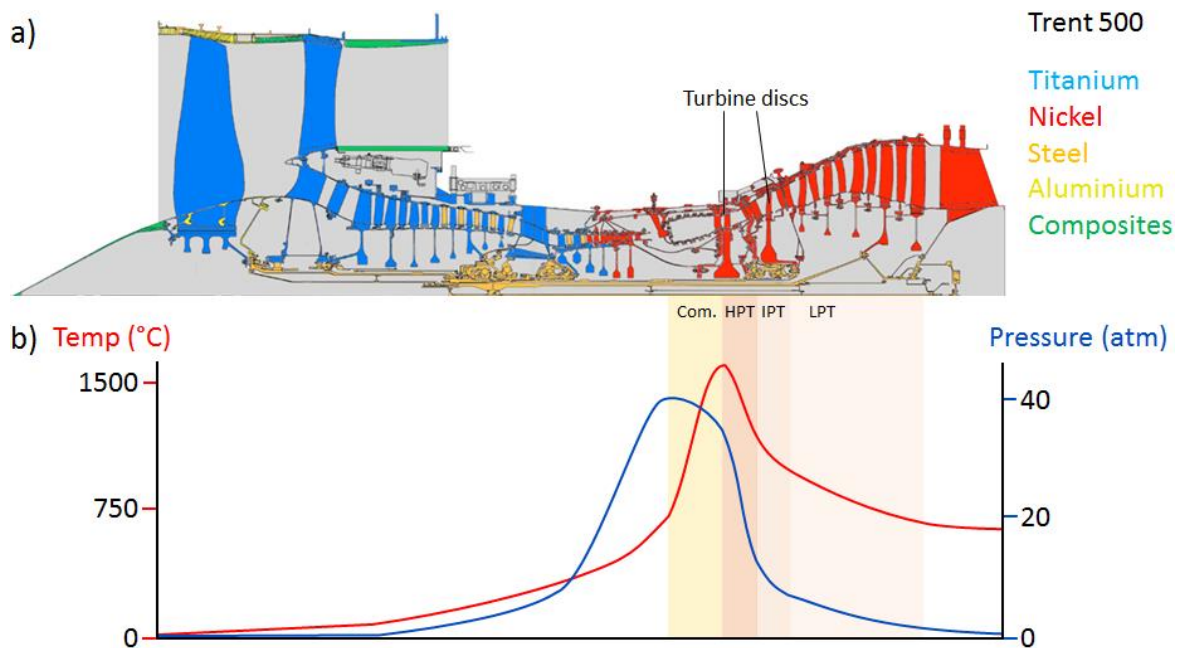


Figure 1.2 – a) Cross-sectional schematic of a Rolls-Royce Trent 500 turbofan jet engine, colour coded to show structural materials found in each section (adapted from [5], courtesy of Rolls-Royce. b) Operating temperatures and pressures found in each section, through the compressor, then high, intermediate, and low pressure turbines

The turbine assembly is responsible for much of the thrust created by a jet engine, which is achieved by capturing kinetic energy from the hot airflow immediately exiting the combustion chamber, and converting it into mechanical work to drive the front fan and compressor sections. As this hot airflow exits the combustion chamber at temperatures up to and exceeding 1500°C, the turbine section contains the components with the highest operating temperatures. Of these, the turbine blades experience the highest temperatures, as they project directly into the hot airflow. Due to the small size and processing techniques used to create turbine blades, they can be protected from these extreme temperatures using a number of approaches, including the active cooling and thermal barrier coating strategies mentioned previously.

However, these strategies can not be universally applied to other turbine components with different size or processing requirements. The turbine disc is one such component, which can measure over 84 cm in diameter [8]. This is the apparatus that holds the turbine blades while rotating at rates up to several thousand revolutions per second, leading to stresses in the disc reaching up to 1200 MPa [9]. It must therefore maintain exceptionally high strength at temperatures in excess of 800°C, while also resisting failure mechanisms such as oxidation, creep and fatigue. Discs in particular are safety-critical components, as each turbine disc is manufactured as a single monolithic entity. As disc failure is usually catastrophic to engine operation, understanding and preventing these failure mechanisms is paramount to safe engine operation.

1.3 History of Nickel Superalloy Development

Nickel based alloys began development in the 1900s, upon the discovery of their high-temperature and corrosion-resistant properties [10]. A period of rapid development occurred in the 1940s in response to growing demand for high temperature materials for the burgeoning jet engine industry, as evidenced by Figure 1.1. The first nickel based superalloy Nimonic 80 was developed during this time, which was based on empirical findings from alloys within the Ni-Cr system, and was used for uncooled turbine blades at TET up to 800°C [11].

Two concurrent paths have been followed to improve the properties and microstructure of superalloys. The first is optimisation of composition, which has resulted in progressively more complex alloys, with modern variations roughly doubling the number and amount of alloying elements present. This complexity can be seen in Table 1.1, which presents compositions of a selection of common commercially available superalloys consisting of up to 13 different elements. In the early days of superalloy development, optimisation was empirical in nature, as experimental trial-and-error methods could improve superalloy properties without requiring a

complete understanding of the underlying mechanisms. However, modern alloys have been refined to the point that further advancement of temperature capability requires a more in-depth understanding of these complex composition-property relationships.

Alloy	Cr	Co	Mo	W	Ta	Re	Nb	Al	Ti	Hf	C	B	Y	Zr	Other
<i>Conventionally Cast Alloys</i>															
Mar-M246	8.3	10.0	0.7	10.0	3.0	—	—	5.5	1.0	1.50	0.14	0.02	—	0.05	—
Rene' 80	14.0	9.5	4.0	4.0	—	—	—	3.0	5.0	—	0.17	0.02	—	0.03	—
IN-713LC	12.0	—	4.5	—	—	—	2.0	5.9	0.6	—	0.05	0.01	—	0.10	—
C1023	15.5	10.0	8.5	—	—	—	—	4.2	3.6	—	0.16	0.01	—	—	—
<i>Directionally Solidified Alloys</i>															
IN792	12.6	9.0	1.9	4.3	4.3	—	—	3.4	4.0	1.00	0.09	0.02	—	0.06	—
GTD111	14.0	9.5	1.5	3.8	2.8	—	—	3.0	4.9	—	0.10	0.01	—	—	—
<i>First-Generation Single-Crystal Alloys</i>															
PWA 1480	10.0	5.0	—	4.0	12.0	—	—	5.0	1.5	—	—	—	—	—	—
Rene' N4	9.8	7.5	1.5	6.0	4.8	—	0.5	4.2	3.5	0.15	0.05	0.00	—	—	—
CMSX-3	8.0	5.0	0.6	8.0	6.0	—	—	5.6	1.0	0.10	—	—	—	—	—
<i>Second-Generation Single-Crystal Alloys</i>															
PWA 1484	5.0	10.0	2.0	6.0	9.0	3.0	—	5.6	—	0.10	—	—	—	—	—
Rene' N5	7.0	7.5	1.5	5.0	6.5	3.0	—	6.2	—	0.15	0.05	0.00	0.01	—	—
CMSX-4	6.5	9.0	0.6	6.0	6.5	3.0	—	5.6	1.0	0.10	—	—	—	—	—
<i>Third-Generation Single-Crystal Alloys</i>															
Rene' N6	4.2	12.5	1.4	6.0	7.2	5.4	—	5.8	—	0.15	0.05	0.00	0.01	—	—
CMSX-10	2.0	3.0	0.4	5.0	8.0	6.0	0.1	5.7	0.2	0.03	—	—	—	—	—
<i>Wrought Superalloys</i>															
IN 718	19.0	—	3.0	—	—	—	5.1	0.5	0.9	—	—	0.02	—	—	18.5Fe
Rene' 41	19.0	11.0	10.0	—	—	—	—	1.5	3.1	—	0.09	0.005	—	—	—
Nimonic 80A	19.5	—	—	—	—	—	—	1.4	2.4	—	0.06	0.003	—	0.06	—
Waspaloy	19.5	13.5	4.3	—	—	—	—	1.3	3.0	—	0.08	0.006	—	—	—
Udimet 720	17.9	14.7	3.0	1.3	—	—	—	2.5	5.0	—	0.03	0.03	—	0.03	—
<i>Powder-Processed Superalloys</i>															
Rene' 95	13.0	8.0	3.5	3.5	—	—	3.5	3.5	2.5	—	0.065	0.013	—	0.05	—
Rene' 88 DT	16.0	13.0	4.0	4.0	—	—	0.7	2.1	3.7	—	0.03	0.015	—	—	—
N18	11.2	15.6	6.5	—	—	—	—	4.4	4.4	0.5	0.02	0.015	—	0.03	—
IN100	12.4	18.4	3.2	—	—	—	—	4.9	4.3	—	0.07	0.02	—	0.07	—

Table 1.1 – Comparison of a number of commercially-available superalloy compositions. Reproduced from [12] with permission of the Journal of Propulsion and Power conveyed through Copyright Clearance Center Inc.

In addition to composition, optimisation of processing routes has been the second driver behind advances to nickel based superalloys. Turbine blades in particular have undergone major changes in processing route, as they reside in the hottest sections of jet engines, and have therefore been a bottleneck to improving temperature resistance. Directionally cast (DC) blades were developed to remove grain boundaries perpendicular to the loading axis, in order to prevent the formation of voids and cavities due to creep under load [13]. Grain boundaries parallel to the loading axis are prone to sliding, so these were later removed with the development of single-crystal (SC) turbine blades [14]. Both of these techniques have provided noticeable increases to maximum operation temperature, which can be seen in Figure 1.1.

The small size and lack of isotropic strength requirements placed on turbine blades allows complex processing paths which are unavailable to turbine disc manufacture. Unlike modern turbine blades, discs tend to use polycrystalline superalloys, which have increased strength due to the Hall-Petch effect, and more isotropic properties [15]. The development of powder metallurgy (PM) techniques enable fine control over grain size [16], fine distribution of strengthening precipitates, and also prevents excessive solute segregation to the grain boundaries [17]. However, the presence of grain boundaries can also accelerate many failure mechanisms, especially at higher temperatures. They enable faster diffusion rates through the material, which can lead to the formation of creep cavitation and voids [18]. Increased diffusion additionally enables corrosion and oxidation processes, which can have knock-on effects with embrittlement and fatigue [19–21]. Due to the safety-critical nature of turbine discs, these failure mechanisms must be avoided at all costs, and have previously been the subject of extensive research in order to find safe component lifetimes. However, the lack of understanding behind the underlying mechanisms means that these lifetime estimations can be inaccurate, and require overly large and inefficient safety margins to be incorporated into the design stage. Research into the composition dependence of these failure mechanisms is needed in order to create the next generation of advanced nickel superalloys, in order to increase efficiency, prevent failures, and predict component lifetimes with more certainty.

1.4 Research Aims and Thesis Structure

This thesis follows the investigation of a group of novel nickel based superalloys, in order to assess how their resistance to various damage processes is related to composition. This first introductory chapter has covered the aims and motivations behind the project, with discussion of how jet engine efficiency can be increased and some of the obstacles that prevent this. The importance of alloy composition optimisation has been established, culminating in a brief

overview of some of the failure mechanisms that must be understood and overcome in order to achieve higher efficiencies.

Chapter 2 reviews the body of literature currently available. It first covers the physical metallurgy of nickel based superalloys, including the properties and significance of each phase present. This is followed by a more detailed look into some of the failure mechanisms that occur in these materials, and some preventative measures to inhibit them. Finally, all of these topics are combined in a discussion of the Alloys-By-Design (ABD) composition optimisation strategy, in which a family of similar alloys has been designed specifically to study some of the aforementioned composition-property relationships.

Chapter 3 details the experimental methodologies used to characterise the chemistry and microstructure of these alloys in various conditions. The equipment and techniques used to simulate several different types of environmental attack have been described, as well as the characterisation methods used to investigate the resulting damage. In particular, high-resolution microscopy and atom probe techniques have been evaluated in order to investigate to near atomic scales.

Chapter 4 describes the characterisation of the as-received ABD alloys in their pristine undamaged state, with emphasis on experimental determination of phase compositions. This allows property predictions made during the alloy design process to be evaluated, as well as the identification of any compositional changes resulting from damage mechanisms such as oxidation and fatigue.

Chapter 5 focusses on the high-temperature oxidation experiments that were performed on the ABD alloys to investigate how resistant they are to extreme temperatures, and to what extent this resistance depends on alloy composition. Post-exposure characterisations of the resulting oxide layers have been performed and analysed, which is followed by a discussion of some potential mechanisms which may explain the observed link between alloy composition and oxidation resistance.

Chapter 6 covers the characterisation of fatigue cracking that occurs at high temperatures in oxidising environments, in order to speculate on the underlying mechanisms. Crack tip characterisation has been carried out using various electron microscopy techniques, after which they were transformed into needle-shaped atom probe specimens for a more detailed characterisation.

Chapter 2. Literature Review

2.1 Physical Metallurgy of Nickel Based Superalloys

Nickel based alloys are appealing for a number of reasons:

- Nickel has a relatively high melting point of 1455°C, comparable with iron (1495°C), cobalt (1495°C), and titanium (1668°C).
- They tend to adopt a Face-Centred Cubic (FCC) crystal structure, which contains many potential slip systems. This provides high toughness and ductility, while ensuring isotropy of properties.
- The lack of allotropic phase transformations greatly reduces design complexity for components that are required to operate in a large temperature range.
- Low diffusivity ensures a greater resistance to diffusion controlled processes such as creep, oxidation and precipitate coarsening.
- Nickel can easily form solid solutions with a wide variety of elements, enabling greater scope for solid solution strengthening.

This ability to hold many alloying elements in solution offers great scope for tailoring the properties of nickel based superalloys via composition refinement. The majority of commonly added elements come from groups IV-VI of the transition metals, with a few notable exceptions. These elements are shown in their position in the periodic table provided in [Figure 2.1](#).

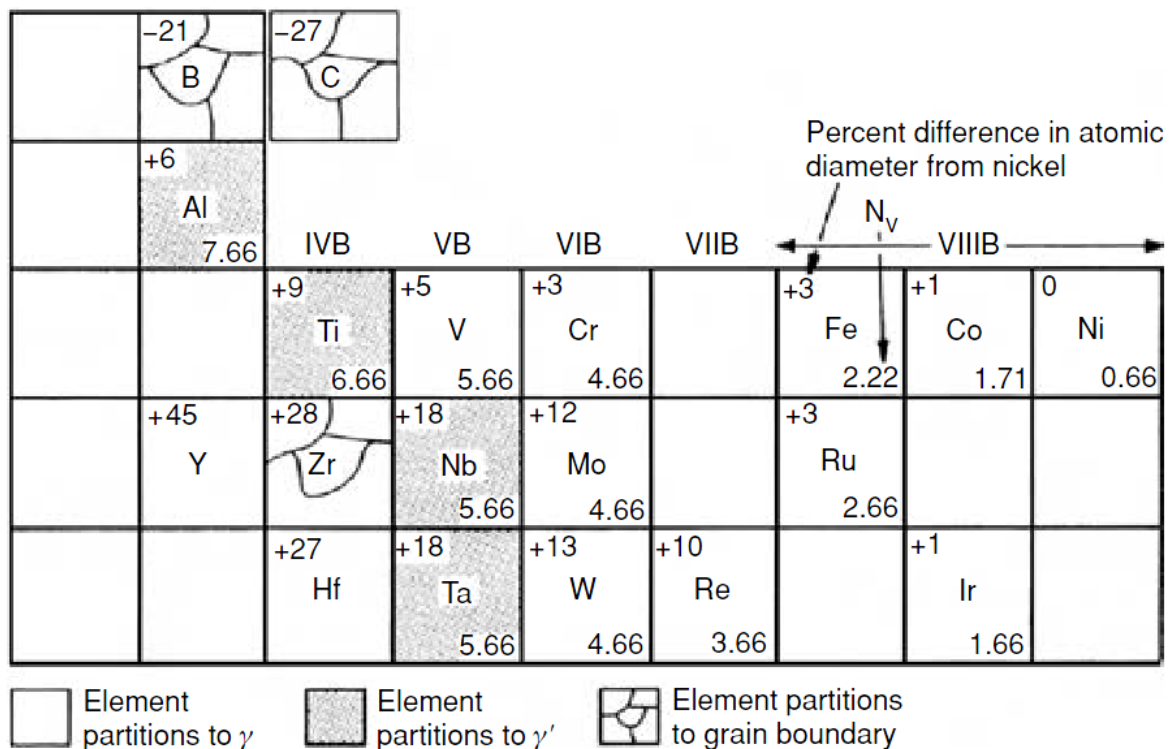


Figure 2.1 – Common superalloy additive elements in their position of the periodic table, showing phase segregation preference and atomic size difference relative to Ni. Adapted from [22] with permission of Wiley conveyed through Copyright Clearance Center Inc. Copyright © 1987 by John Wiley & Sons Inc.

Element additions are made in order to change a number of physical properties, with each element often fulfilling multiple roles. For example, cobalt is primarily added to increase processability by reducing the solvus temperature of precipitate phases [23,24]. In addition to this, Co also plays an important role in providing matrix strength via solid solution strengthening, and promoting resistance to creep by decreasing stacking fault energies [25]. Addition of elements must be made carefully however, as each new element can simultaneously affect multiple physical properties, which leads to the creation of many property tradeoffs during alloy design.

The final equilibrium microstructure is determined by alloy chemistry, with most elements tending to partition to preferred phases as outlined in Table 2.1. This partitioning behaviour can complicate discussions of alloy chemistry due to the non-uniform distribution of alloying

elements. The beneficial effects provided by a particular element may only be expressed when it resides in a certain phase, a relevant example being the increase in yield strength resulting from Ti addition [26], which only affects the γ' precipitate phase induced by Al (nominally Ni_3Al). For this reason, partitioning behaviour must be considered during characterisation of superalloys.

Element	Phase Partitioning	Effects
Al	Strong γ' former	Added to promote γ' phase – nominally Ni_3Al [27].
Ti	Strong γ' former	Also provides corrosion resistance via Al_2O_3 formation [28]. Stabilises γ' , increases γ' strength [26], carbide former [29]. High Ti/Al ratio can lead to potentially deleterious η phase (nominally Ni_3Ti) [30].
Ta	Strong γ' former	Stabilises γ' , carbide former [31].
Nb	γ' former	Stabilises γ' , increases γ' strength [32]. Large additions can form δ phase, the benefits of which are under debate [33].
Cr	Strong γ former	Increases corrosion resistance via Cr_2O_3 formation [28]. γ solid solution strengthener. Additions over 7 at.% can form deleterious σ phase [34].
Co	Strong γ former	γ solid solution strengthener. Improves processability by lowering γ' solvus [24].
W	Slight γ preference	γ solid solution strengthener and creep resistance [35].
C, B, Zr	Grain boundary	Grain boundary strengtheners [36].

Table 2.1 – Roles of some common additive elements to nickel based superalloys, with their phase partitioning preferences and effects on physical properties.

As described in Table 2.1, element additions can lead to the formation of a number of secondary phases, a selection of which are arranged in Table 2.2 with their nominal stoichiometries. These phases form in a wide variety of morphologies and microstructures, some of which are depicted in Figure 2.2 as a representative diagram. Some of these additional phases imbue superalloys with highly desired properties such as increased strength and resistance to high temperatures and creep, whereas some phases are universally detrimental. Therefore the presence and volume fractions of these phases must be carefully considered when adjusting compositions, as beneficial elements may form deleterious phases in large amounts, and vice versa.

Phase	Structure	Nominal Stoichiometry	Notes
γ (gamma)	FCC disordered	Ni solid solution	
γ' (gamma prime)	$L1_2$ ordered	Ni_3Al	
γ'' (gamma double-prime)	BCT DO_{22}	Ni_3Nb	Metastable, forms δ
MC (primary carbide)	FCC	(Nb, Ti, Ta, W)C	
δ (delta)	Orthorhombic DO_a	Ni_3Nb	Grain boundaries
η (eta)	HCP DO_{24}	Ni_3Ti	Forms from Ti-rich γ'
μ (mu)	Rhombohedral $D8_5$	$(Co, Ni, Fe)_7(Mo, W, Cr)_8$	TCP
σ (sigma)	BCT $D8_b$	$(Cr, Mo)_x(Ni, Co)_y$	TCP
Laves	Various	Various	TCP

Table 2.2 – Typical phases present in nickel based superalloys, with their crystal structures and nominal chemistries. Adapted from [29] with permission of OPA (Overseas Publishers Association) conveyed through Copyright Clearance Center Inc.

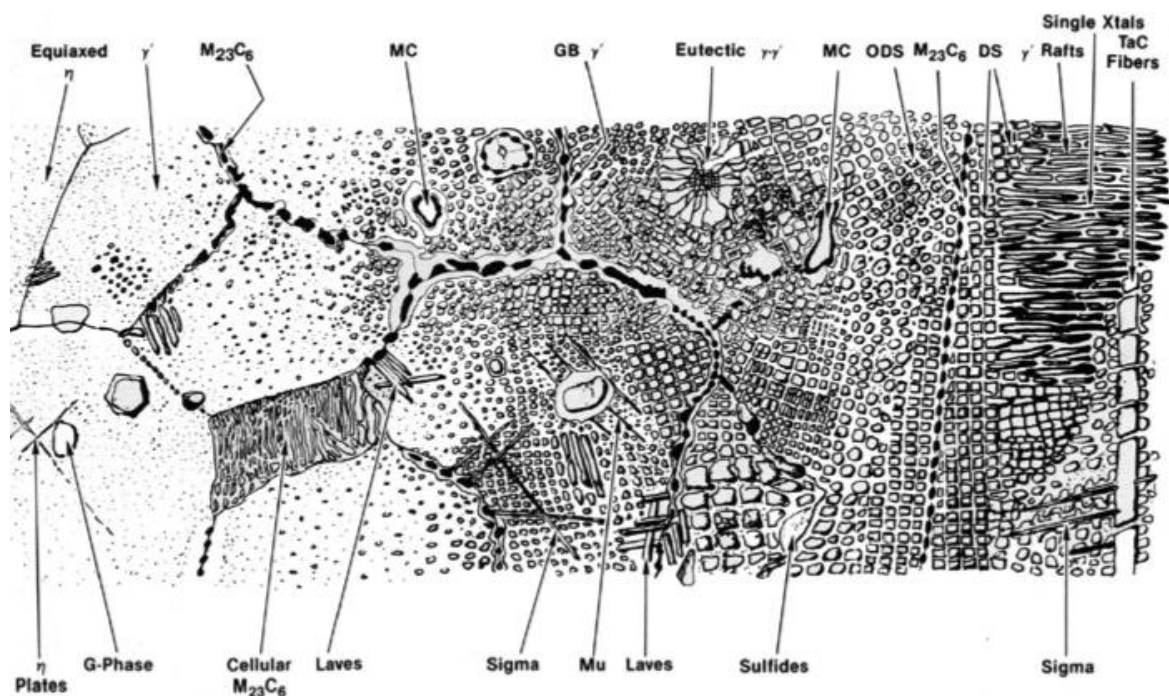


Figure 2.2 – Representative diagram illustrating the variety of phases and microstructures present in superalloys. Adapted from [22] with permission of Wiley conveyed through Copyright Clearance Center Inc. Copyright © 1987 by John Wiley & Sons Inc.

2.1.1 Gamma Phase

Pure nickel naturally assumes an austenitic face-centered cubic (FCC) structure. This contains 12 possible slip systems, which ensures high toughness and ductility compared to the more brittle body-centered cubic (BCC) and hexagonally close packed (HCP) structures, as exemplified by iron

and titanium alloys respectively [37]. The FCC structure also prevents texture effects due to the large number of inherent symmetries, leading to more isotropic properties.

In nickel based superalloys, many of the alloying additions remain in solid solution in the FCC matrix to form an unordered austenitic FCC phase referred to as gamma (γ). This comprises elements with similar atomic radius to nickel, such as chromium and cobalt, as well as the refractory elements tungsten, molybdenum, rhenium and ruthenium [5]. These elements help to increase matrix strength via solid solution strengthening [38].

2.1.2 Gamma Prime Phase

The addition of aluminium induces the formation of an intermetallic precipitate phase named gamma prime (γ'), which has a nominal composition of Ni_3Al . Unlike many other phases, the presence of γ' is actively promoted due to the beneficial effects it has on superalloy properties. This motivates the addition of titanium, tantalum and niobium, which preferentially segregate to γ' and help to stabilise it.

This phase exhibits an L1_2 crystal structure, which is the ordered counterpart of the disordered FCC structure, as shown in Figure 2.3 [15]. The ordered L1_2 structure of γ' is formed due to the preference for Ni-Al bonds over a combination of Ni-Ni and Al-Al bonds. In pure Ni_3Al , Ni atoms are located at the face centres (α sublattice) and Al atoms are located at the corners (β sublattice). These sublattices are differentiated by the number of nearest atomic neighbours. In more compositionally complex alloys, γ' partitioning elements tend to replace Al atoms in the β sublattice, while Cr and W can replace atoms on both sublattices [39]. Site occupancy of alloying additions in these two sublattices is important, as it has been shown to have an effect on γ' ductility [40].

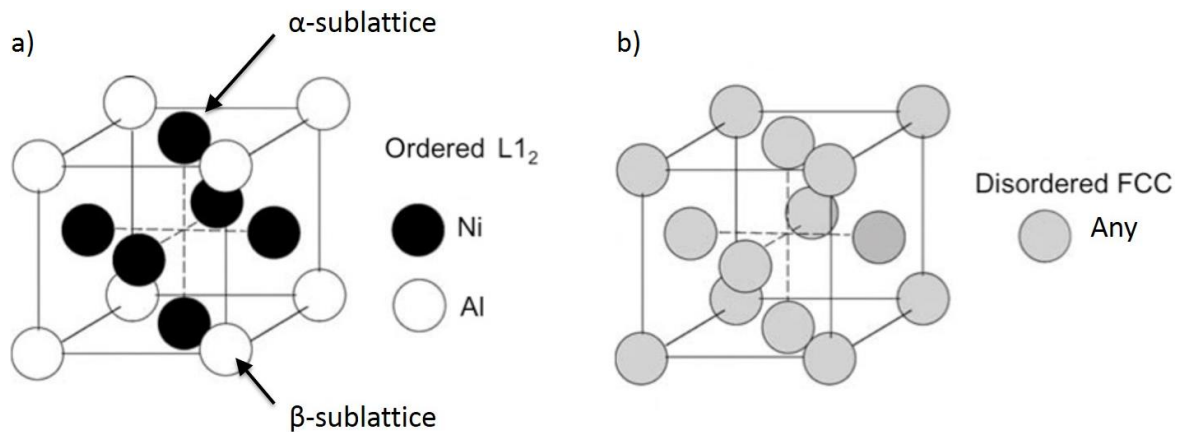


Figure 2.3 – Nickel superalloy crystal structure unit cells. a) Ordered γ' in $L1_2$ crystal structure. b) Disordered FCC γ phase. Reproduced from [5] with permission from Cambridge University Press through PLSclear. © R. C. Reed 2006.

The fact that γ and γ' phases exhibit similar crystal structures is extremely relevant as it allows the γ' precipitates to keep a fully coherent interface with the γ matrix, thus maximising the precipitate strengthening effect by reducing interfacial energy. The level of coherency between these phases is dependent on the difference in lattice parameter between them, referred to as the lattice parameter misfit. This can be controlled by altering the γ' stoichiometry [12,38].

While γ' volume fraction is largely determined by composition, the size and distribution of γ' precipitates also has a profound impact on the strengthening effect they provide, which can be controlled by the processing and heat treatment regimen used during alloy production. The γ' precipitates tend to be found in three distinct size ranges, as represented by Figure 2.4 [41]. Primary γ' precipitates (γ'_I) are by far the largest, manifesting as separate incoherent grains with size range around $1\ \mu\text{m}$. They persist through subsolvus heat treatments, and will dissolve during supersolvus treatments given enough time, so heat treatment must be carefully controlled. Grain boundary decoration of γ'_I provides an important Zener-pinning mechanism, which helps to control final γ phase grain size [42].

Finer secondary (γ'_{II}) and tertiary (γ'_{III}) precipitates can be observed in the 100 nm and 10 nm size ranges respectively, and tend to fully dissolve during both supersolvus and subsolvus heat treatments. The ageing conditions are therefore a large factor behind the size and distributions of γ'_{II} and γ'_{III} as they reprecipitate from solution [43]. Both of these precipitate generations are found within γ grains, where they provide exceptional strength at high temperatures and creep resistance [44]. The morphology of γ'_{II} and γ'_{III} precipitates is dependent on interfacial energy, which is a direct consequence of the lattice misfit parameter mentioned previously [45].

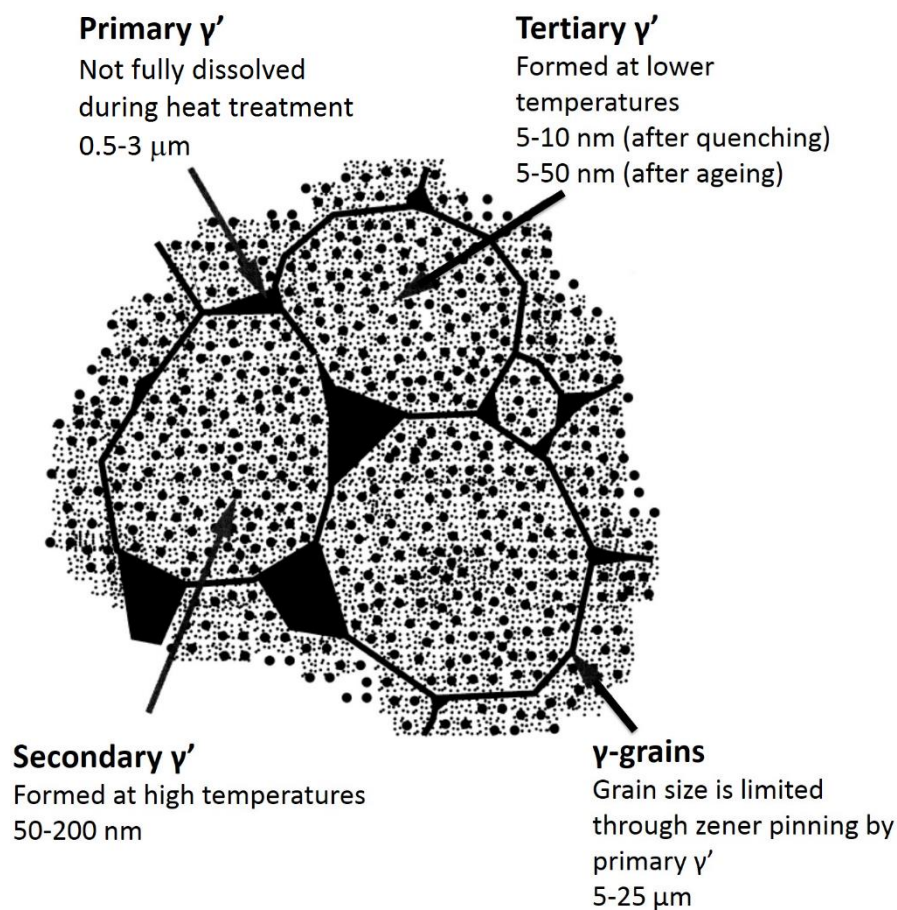


Figure 2.4 – Typical sizes and distributions of different γ' precipitate generations. Reproduced from [46] with permission from Elsevier. © 1999

The greatest proportion of strengthening in nickel based superalloys comes from the γ' phase precipitates, due to their unique interaction with dislocations. γ' is an ordered phase in which a dislocation can not simply move each atom along one site without forming undesirable Ni-Ni or

Al-Al first neighbour bonds. Instead the Burgers vector inside a γ' precipitate is twice that of a dislocation in γ phase. Any $a/2 \langle 1\bar{1}0 \rangle \{111\}$ dislocation attempting to shear this ordered structure will leave a planar crystallographic defect in its wake known as an anti-phase boundary (APB), which is comprised of undesirable first-neighbour bonds and is thus highly energetically unfavourable [32]. This leads to dislocations travelling in pairs of partial $a/2 \langle 1\bar{1}0 \rangle \{111\}$ dislocations, separated by an APB, where the second partial dislocation restores the lattice to its original state. This makes shearing of γ' precipitates very difficult, due to the competing energies of APB interface formation versus the repellent interaction of the partial dislocation stress fields. This APB fault energy is a determining factor of the yield stress of superalloys. All γ' forming elements will alter the APB energy to a certain extent, and therefore also have an effect on the strength of the γ' phase. Ta, Ti and Nb in particular have been found to increase APB energy significantly [47], so the amounts of these elements present in γ' are vital to understanding and predicting the high-temperature strength of nickel based superalloys.

These strengthening effects are best exploited by maximising the dislocation cross-section of γ' precipitates. This is determined by their volume fraction, size, and distribution, so careful control of these is vital. This can be achieved through adjustment of composition by increasing the amount of γ' forming elements (Al, Ti, Ta, Nb), as well as heat treatment and ageing processes [48].

2.1.3 Grain Boundary Phases

Grain boundaries in polycrystalline superalloys can increase tensile strength by preventing dislocation transmission, however they can also act as sites for fatigue crack progression, creep cavitation and grain boundary sliding [49]. Preferential solute segregation and phase formation at grain boundaries during heat treatment can also significantly alter superalloy properties [50].

Elements such as carbon, boron, hafnium and zirconium are added in trace amounts to strengthen grain boundaries [12]. Carbon and boron combine with reactive elements such as Ti, Cr, Mo, Nb and Ta to form carbides (of the form MC, M_6C , and $M_{23}C_6$) and borides (of the form M_3B_2 and M_5B_3), which serve several roles. These phases can strengthen polycrystalline superalloys by inhibiting dislocation movement, and reduce creep by inhibiting grain boundary sliding and cavitation [22], however the presence of grain boundary phases can be problematic as they are intrinsically brittle and can act as crack initiation sites [51]. Hafnium is often added to control the size and morphology of these carbide particles [52], while zirconium acts to prevent grain boundary sliding due to its large size misfit with nickel [26]. These elements have also been shown to exhibit gettering behaviour, as Hf and Zr has been observed scavenging embrittling elements such as S or O which have segregated to the grain boundary [53].

Grain boundaries also provide fast diffusion pathways for elements, with diffusion rates along grain boundaries being orders of magnitude higher than diffusion through the matrix [54]. This makes grain boundary chemistry and character a major consideration for corrosion and oxidation, and as such this topic is further explored in [Chapter 2.2.3](#).

2.1.4 TCP Phases

The complex chemistries of superalloys result in the formation of many additional stable or metastable precipitate phases. While some are encouraged due to their beneficial effect on properties (such as γ' and γ''), most are detrimental. Some of the most detrimental phases include the topologically close-packed (TCP) phases such as σ , δ , η , μ and Laves phases [12,29]. These tend to be brittle intermetallics with complex crystal structures and limited slip systems [55]. They also tend to be rich in refractory elements, which depletes them from the matrix, thereby reducing their solid solution strengthening effect [56].

- γ'' – Gamma double prime (Ni_3Nb) is a metastable phase with an ordered body-centered tetragonal (BCT) D_{022} structure, which transforms to the more stable δ phase over time. It is also often utilised for its precipitation hardening properties in high-Nb, high-Ti alloys [29,57].
- σ – Sigma phase $(\text{Cr},\text{Mo})_2(\text{Ni},\text{Co})$ significantly deteriorates superalloy performance, and correlates strongly with the formation of other TCP phases. This is a major limiting factor to the amount of Cr that can be added to superalloys, and therefore avoidance of σ phase formation must be balanced with maintaining adequate oxidation resistance [47].
- δ – Delta phase (Ni_3Nb) forms as incoherent ordered lamellae precipitates at grain boundaries. Problems arise due to the high mismatch in thermal expansion coefficients and low interface strength between δ and the γ - γ' matrix, which can limit fatigue life. However, some δ phase has been found to be beneficial if it can be controlled, for example in IN718 [58].
- η – Eta phase (Ni_3Ti) exists as an incoherent platelet phase that can extend across grains. It is brittle and exhibits low strength [59].
- μ – Mu phase $(\text{Co},\text{Ni},\text{Fe})_7(\text{Mo},\text{W},\text{Cr})_8$ is similar to σ , and tends to form in superalloys with high Cr, Mo, W, and Co contents. Its presence in the matrix has been found to be detrimental to rupture strength, room temperature tensile ductility, impact toughness, and corrosion resistance [60].
- Laves phases are a wide family of brittle intermetallic TCP phases formed at or near an AB_2 composition, which often assume a plate-like morphology [61].

It can be seen that many important alloying elements tend to induce TCP phase formation, especially Cr and the γ' forming elements Ti and Nb. This puts limits on the amounts that can safely be added, creating trade-offs between maintaining phase stability and other important properties such as oxidation resistance and strength.

2.2 Oxidation

Oxidation is the unavoidable result of hot reactive gasses coming into contact with metal components. Brittle oxide products consequently form on the surface, sometimes even leading to subsurface damage, which can be devastating to fatigue resistance by acting as sites for crack initiation [62]. The incorporation of alloying elements into oxide scales also leads to depletion of these elements in the underlying alloy [63], in a similar manner to the sensitisation suffered by stainless steels [64]. Despite this, oxidation is encouraged to a certain degree, as certain oxides form a protective oxygen-impermeable scale which prevents further damage due to oxygen ingress [26]. Cr and Al in particular are used for this reason due to the high thermal stability of chromia (Cr_2O_3) and alumina (Al_2O_3) oxides [65]. Turbine discs tend to utilise Cr_2O_3 scales due to their better adherence properties [66], while Al_2O_3 is preferred for the higher temperature requirements of turbine blades, due in part to the volatilisation of Cr_2O_3 to gaseous CrO_3 at temperatures approaching 1000°C [67].

2.2.1 Thermodynamics of Oxidation Reactions

Determining which oxidation products will form for a particular alloy requires an understanding of the underlying equilibrium thermodynamics. The oxidation of a pure metal M with oxygen is described by the following reaction:



By taking the activities of both the metal and oxide as unity, then the minimum oxygen partial pressure at which the oxide and metal coexist ($P_{O_2}^{M/MO_2}$) is given by:

$$P_{O_2}^{M/MO_2} = \exp\left(\frac{\Delta G_0}{RT}\right) \quad (\text{Eq. 2.2})$$

Where ΔG_0 is the standard free energy of formation, R is the gas constant, T is temperature, and P_{O_2} is the partial pressure of oxygen. This equation allows calculation of the partial pressure of oxygen required to form oxides of various metals. The high thermal stability of these oxides is the

result of the large reduction in Gibbs free energy resulting from their formation, which provides the thermodynamic driving force for oxidation. The free energy of formation (ΔG_0) of a selection of metal oxides is plotted against temperature, as depicted in an Ellingham-Richardson diagram shown in Figure 2.5.

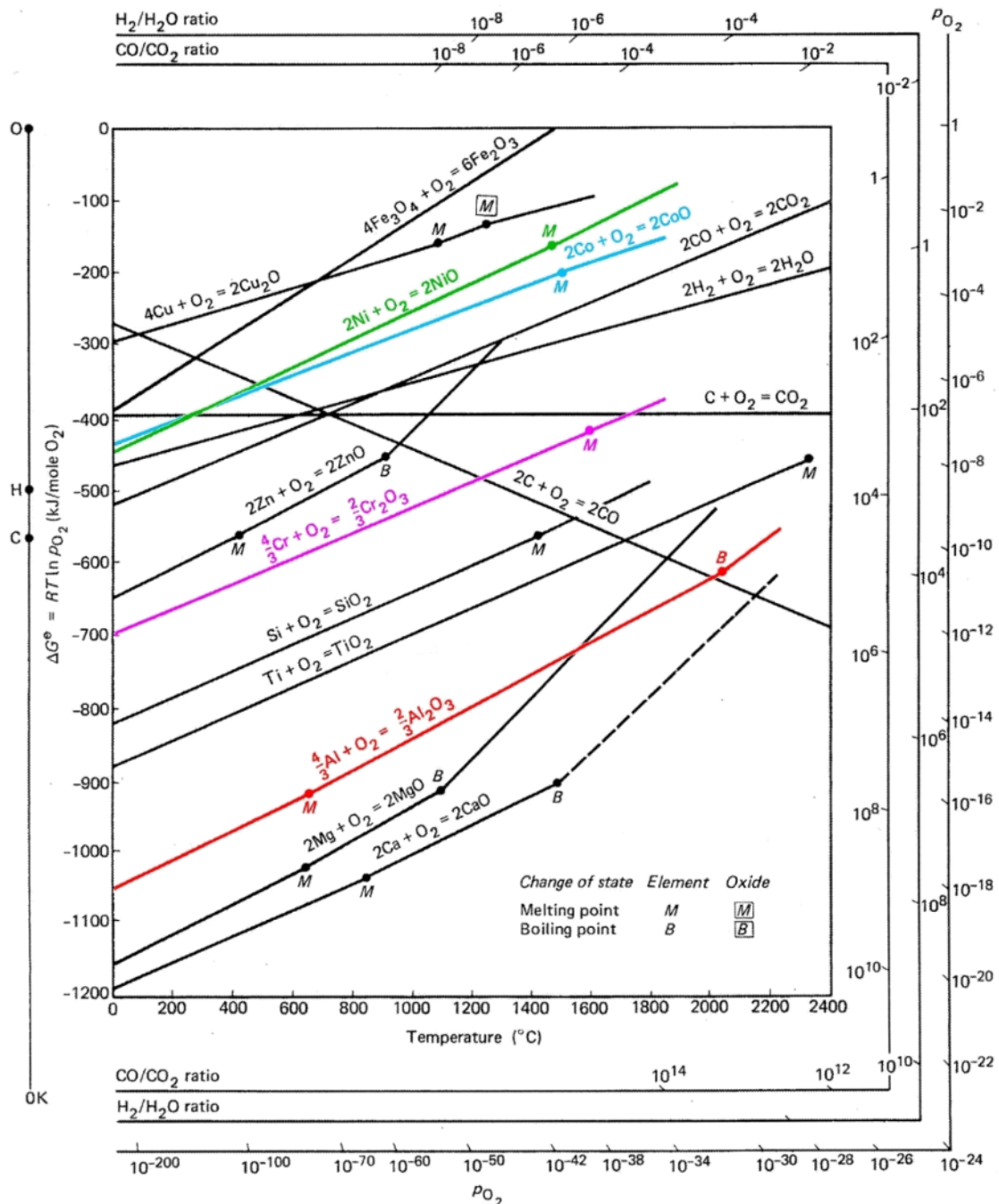


Figure 2.5 – Ellingham-Richardson diagram, showing the standard free energy of formation for a selection of oxides against temperature. From this, the P_{O_2} can be used to predict the oxide layered structure. Adapted from [68] with permission from Cambridge University Press through PLSclear. © N Birks and G H Meier 1983.

The comparative stability of these oxide products can be derived from this graph, with the more stable oxides appearing lower on the graph due to their ability to form at lower P_{O_2} . It can be seen that the stability, and therefore likelihood of formation of these oxides is directly correlated to the temperature and P_{O_2} . Some insights can be gleaned from this graph, as the relative P_{O_2} required for oxide formation can be used to estimate the order of the layered microstructure often observed in nickel superalloy oxide scales. However, this prediction is based on systems at thermodynamic equilibrium, and neglects to take into account kinetics, meaning that in practice many alloys show scale compositions different from those predicted by the Ellingham diagram. In addition, it also must be noted that this two-dimensional graph becomes less accurate as compositions become more complex, due to the additional degrees of freedom of the underlying Gibbs energy phase diagrams [69].

2.2.2 Oxide Scale Formation in Multicomponent Superalloys

After a protective oxide layer has formed, kinetics become a major factor, as further oxide growth occurs via diffusion of elements through the scale. According to the Wagner theory of high temperature oxidation [70], the rate at which mass is gained due to oxide growth tends to follow a parabolic law as described by Equation 2.3 [68]:

$$(\Delta m)^2 = K_p t \quad (\text{Eq. 2.3})$$

where Δm = specific mass change, K_p = parabolic rate constant and t = time. This parabolic law applies when ion transport across the oxide scale becomes the rate-limiting process, and implies that scale thickening will accompany a reduction in oxide growth rate. For practical purposes, the parabolic rate constant provides a consistent measure for comparing oxidation kinetics between alloys with different compositions.

Composition plays a large role in determining oxidation properties, due to competition between Al, Cr, and other reactive elements for available oxygen. Giggins and Pettit examined the Ni-Cr binary system in great detail, observing the effect that varying the Cr percentage of an alloy has on oxidation rate, as represented by the parabolic rate constant K_p , as shown in Figure 2.6 [71].

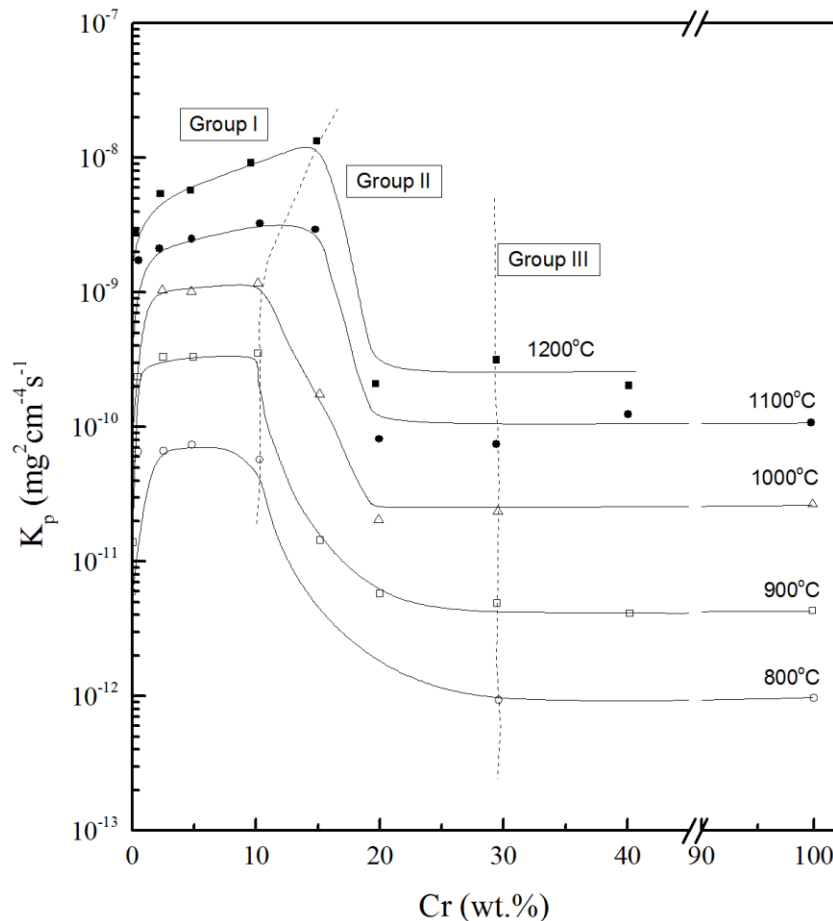


Figure 2.6 – Composition dependence for parabolic rate constant for the oxidation of model Ni-Cr alloys between 800°C and 1200°C. Reproduced from [71] with permission from Springer © 1969.

From Figure 2.6 it can be seen that oxidation resistance reaches a maximum value at about 30 wt.% Cr, which poses a dilemma, as Cr levels in this range promote formation of deleterious TCP phases such as σ [72]. However the presence of other alloying elements can not only encourage dense Cr_2O_3 formation at lower Cr at.% levels, but also form dense oxides of their own. Further work by Giggins and Pettit on ternary Ni-Cr-Al alloys showed that Al addition in the right amounts could reduce the amount of Cr required to form a continuous, protective chromia scale [73].

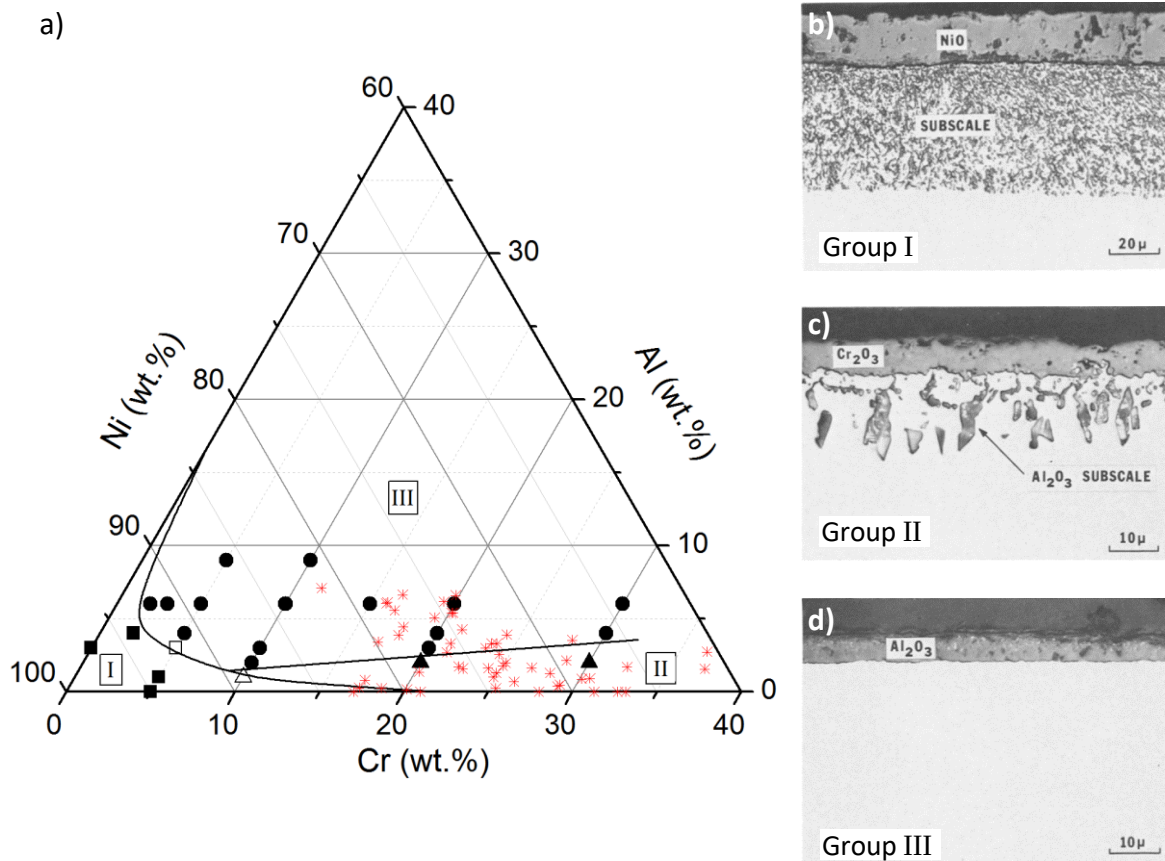


Figure 2.7 – a) Composition limits of group I-III oxidation mechanisms at 1000°C in 0.1 atm O₂, as determined by marked alloy compositions (■=group I, ▲=group II, ●=group III) from [73]. Red data points (*) correspond to compositions of some commercially-available turbine disc alloys [74]. b-d) Typical oxide chemistry and morphologies formed by group I-III superalloys at 1000°C [73]. Reproduced with permission of the Journal of the Electrochemical Society, conveyed through Copyright Clearance Center Inc. Red data points from part a) reproduced with permission from the copyright holder D Crudden © 2014.

The group I-III superalloys referred to in Figure 2.7 a) represent the three distinct oxide scale formation mechanisms observed in ternary Ni-Cr-Al alloys. An oxide scale from a Group I alloy is shown in part b). These alloys are low in Cr and Al, with oxide scales comprised of a large external NiO scale with Cr₂O₃, Al₂O₃, and Ni(Cr,Al)₂O₄ spinel subscales. Part c) shows a Group II high-Cr, low-Al alloy, which form an external Cr₂O₃ scale with Al₂O₃ subscale. Group III alloys are shown in part d), which are high in Al and only form an external Al₂O₃ scale, with no traces of internal scales.

Modern turbine disc alloys tend to be designed with compositions which favour group II oxide scales, as the thick external chromia scale reduces oxygen diffusion into the alloy. The slight Al addition slows the oxidation kinetics, helping the chromia scale to form a dense, continuous layer [75], while also resulting in the presence of a dispersed Al_2O_3 subscale. Modern superalloys contain many more than three components however, many of which are highly reactive [75]. Reaction products have been found to include Cr_2O_3 , Al_2O_3 , TiO_2 , Ta_2O_5 , Nb_2O_5 and WO_3 , as well as spinel phases such as NiCr_2O_4 , NiAl_2O_4 , NiTa_2O_6 and NiWO_4 among others [76].

Titanium in particular has been shown to have a detrimental effect on the protective nature of chromia scales. Experiments by Nagai and Okabayashi show that titanium additions increase mass gain rate during thermogravimetric analysis (TGA), which is a good indicator of increased oxidation rate [77]. It has been known for some time that chromia will dissolve Ti. Experiments by Foss et al. [63] showed evidence of TiO_2 particles formed on the outer surface of chromia scales, indicating diffusion of Ti through the chromia scale. Use of an ^{18}O marker to track the sequence of oxidation implied that outward diffusion of Ti occurred after the formation of the chromia scale.

However despite the indicated increase in oxidation rates, addition of Ti is vital for increasing γ' precipitate strength, so the trade-off between increased strength and the detrimental effects on oxidation resistance must be carefully considered. Rather than reducing the Ti content of these superalloys, a more productive approach may be to investigate the exact mechanisms by which titanium addition increases oxidation rates.

2.2.3 Oxidation Mechanisms of High-Strength Polycrystalline Superalloys

A possible mechanism for the exacerbation of oxidation rates by titanium was proposed by Nagai and Okabayashi [77], which suggests that Ti dopants create additional cation vacancies due to the higher valency of Ti^{4+} compared to Cr^{3+} ions. These additional vacancies are theorised to increase

the diffusion rates of ions through the otherwise impermeable oxide layer, leading to increased mass gain due to oxidation. This is backed up by the observation of subsurface TiN particles by Chen et al. [75], and Taylor et al. [78]. However, this bulk diffusion mechanism is based on the Wagner model of oxidation, which assumes thermodynamic equilibrium throughout the oxide scale, combined with negligible deviations from oxide stoichiometry [68]. Both of these assumptions can break down in the complex multilayered nanocrystalline oxide layers that form on nickel based superalloys [79].

In addition to the lattice diffusion described above, diffusion also occurs along short-circuit defects such as oxide grain boundaries and dislocations, often at rates that are orders of magnitude faster [21]. Thermodynamic predictions tend to break down when considering oxidation at these defects, where rapid diffusion and non-equilibrium positioning of constituent atoms can lead to preferential oxidation [80]. This has been verified by the observations of thick oxide ridges located directly above grain boundaries by Cruchley et al. [81], and Chen et al. [75]. These short-circuit diffusion paths through grain boundaries and defects, combined with complex local chemistries means that oxide formation at grain boundaries is incredibly difficult to predict and model, making safe fatigue lifetime estimation challenging.

Grain boundaries also act as nucleation points for elemental segregation and chemically complex phases [50]. The carbides and borides that form here tend to be comprised of large amounts of reactive elements such as Cr, Ti and Nb. Ti-rich MC and Cr-rich $M_{23}C_6$ carbides have been observed at the grain boundaries of Waspaloy by Chen et al. [75]. Oxidation of $Cr_{23}C_6$ has been shown to form brittle oxide films at grain boundaries, which reduces oxidation resistance by depleting available Cr [82], and can induce brittle fracture [53]. A number of Nb-containing species including NbC carbides have also been directly observed in several studies [54,83–85], and these have been known to reduce fatigue resistance via the formation of brittle Nb_2O_5 . This

oxide can be particularly detrimental to grain boundary fracture toughness, as the oxidation of grain boundary NbC carbides to Nb₂O₅ oxide involves a negative transformation strain, leading to tensile forces at the crack tip and spontaneous oxide cracking [86]. This is the opposite of most other oxides, which tend to undergo a volume increase during transformation, creating compressive stresses which result in a transformation toughening effect.

A few studies have noted increased segregation of Nb to the grain boundaries in IN718, which is a high-Nb alloy that is primarily strengthened by the nominally Ni₃Nb γ'' phase. Carpenter et al. gave three plausible explanations for increased levels of intergranular Nb [87]. Two of the mechanisms involve the precipitation of either NbC carbides or δ phase (Ni₃Nb), while the other mechanism involves segregation of elemental Nb to grain boundaries during heat treatment [88]. Regardless of the exact mechanism, addition of Nb to superalloys imposes another trade-off: Fatigue resistance vs strength and oxidation resistance. Further research into the underlying mechanism is required before composition optimisation of Nb levels can be achieved.

2.3 Dwell Fatigue

Some of the major limiting factors to current superalloy development involve overcoming failure mechanisms such as fatigue, creep, yield and oxidation. Fatigue accounts for the vast majority of all in-service failures in polycrystalline disc alloys due to mechanical causes, and is a major determining factor in predicting component lifetimes. It can cause component failure at stresses far below the material yield stress, which must be accounted for during component design.

At low temperatures, the failure mode of most structural components is either yield or fatigue. These have been studied extensively, and are fairly well understood and managed, with yield stress tolerances routinely accounted for during the component design stage. Fatigue is also manageable at room temperature, with cracks propagating in an easily predictable cycle-

dependent manner where loading time and cycle frequency do not affect crack propagation rates [18]. An oxygen-containing environment at low temperature does increase fatigue crack growth rates, but still in a time-independent manner [89]. These fatigue cracks tend to travel in a transgranular manner, easily identifiable from their striations.

However at high temperature the rates of many failure mechanisms are vastly accelerated. The yield strength of nickel superalloys is highly dependent on the microstructure, which can change significantly with temperature. Examples of phenomena that can influence yield strength include grain growth, γ' coarsening and dynamic carbide precipitation at grain boundaries [90]. A number of additional time and frequency dependent fatigue mechanisms occur at higher temperatures, which severely increase fatigue crack growth rates by up to three orders of magnitude [84,87]. This time-dependence is highly influenced by the time spent at full load, referred to as the dwell period [62]. Gas turbine engine components typically experience high temperatures, long dwell times and low cyclic frequency. This greatly increases the amount of time for environmental effects to influence conditions at the fatigue crack tip, leading to an increase in time-dependent fatigue behaviour. Increased rates of diffusion, combined with more energetic kinetics, result in acceleration of creep and oxidation processes. Both of these affect conditions at fatigue crack tips, which can have subsequent effects on crack growth rates (both beneficial and detrimental).

2.3.1 Environmental Effects

Dwell fatigue cracking is characterised by distinctive intergranular crack paths, indicating that degradation of grain boundaries may be occurring. Dwell fatigue crack growth behaviour has been widely reported to be environmentally sensitive, with crack growth rates increased by three orders of magnitude in air compared to vacuum or inert gaseous environments [87]. Multiple studies on IN718 support the conclusion that crack growth is due to environmental degradation [91–93], one of which is shown in Figure 2.8.

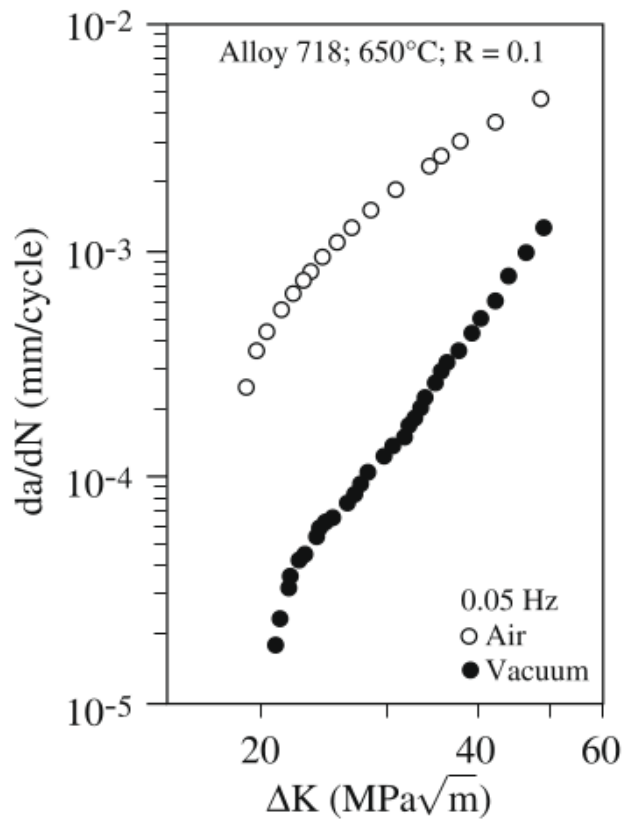


Figure 2.8 – Comparison of fatigue crack growth rates in IN718 in air and vacuum at 650°C. Reproduced from [91] with permission from Materials Science and Engineering A with permission from Elsevier © 1992.

2.3.2 Dwell Fatigue Mechanisms

Environmental attack is typically associated with oxygen and other embrittling elements such as sulfur, hydrogen or chlorine [15,43]. It is postulated that the presence of these elements causes weakening of grain boundaries, and accelerates the growth rates of fatigue cracks that follow them. The exact mechanism by which this happens is currently under debate, with two separate mechanisms claiming to account for this environmental degradation; Dynamic embrittlement (DE) and stress-assisted grain boundary oxidation (SAGBO). Both mechanisms invoke embrittlement of grain boundaries caused by oxygen ingress, but the method of embrittlement differs in each case.

2.3.2.1 Dynamic Embrittlement (DE)

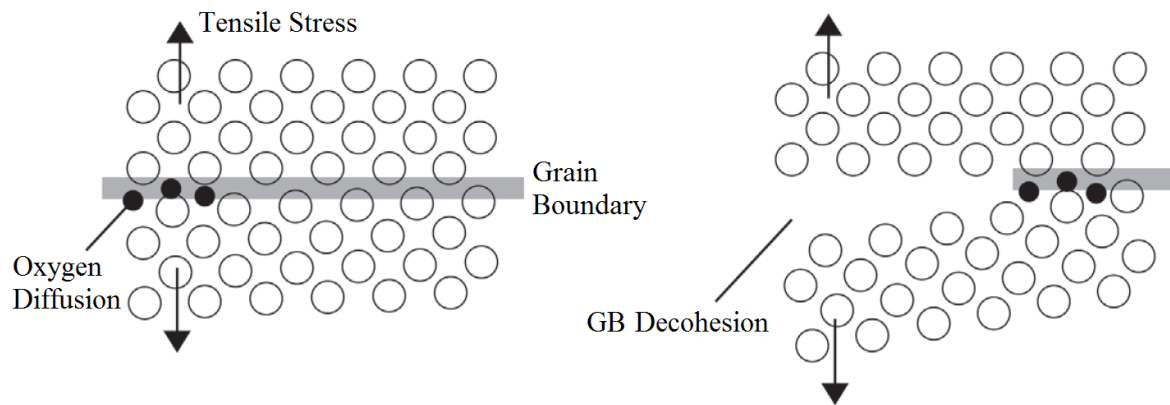


Figure 2.9 – Schematic representation of the dynamic embrittlement mechanism. Reproduced from [94] under the Creative Commons Attribution License 4.0 (CC-BY-NC).

The dynamic embrittlement mechanism was first conceived by Liu and White in the 1980s to describe oxygen adsorption ahead of a moving crack tip in pure Ni_3Al at high temperatures [92]. Evidence was observed for oxygen diffusion ahead of the crack tip, leading to a decohesion of the preceding grain boundary. This is similar to the effect of sulphur embrittlement as seen in alloy steels as studied by Shin and McMahon [95], where a surface-adsorbed embrittling element diffuses down grain boundaries due to the influence of high tensile stresses at the crack tip, leading to local grain boundary decohesion and crack growth.

An alternative DE mechanism has been put forward by McLean [96], whereby oxygen diffusion can not only reduce intergranular cohesion, but also lower the boundary interfacial energy, promoting the nucleation of smaller sized cavities. Hayes et al. performed quantitative SEM on stress-rupture fracture surfaces, and argue that clear evidence of intergranular cavity growth and coalescence was observed as the result of DE [97]. An important observation to make is that DE does not require a pre-existing crack tip oxide in order to explain the increase in crack growth rates. Studies carried out on oxygen-embrittled IN718 by Pfaendtner and McMahon [92], and by Krupp [49,93], all showed fracture surfaces lacking in oxides, therefore concluding that DE must be the operative mechanism [85].

Further evidence for DE was provided by Krupp et al. performing interrupted crack experiments, where the P_{O_2} was reduced as quickly as possible by evacuating oxygen from the test chamber [94]. Fatigue cracking immediately reverted to a time-independent nature, and was shown to restart as soon as oxygen was reintroduced. It was argued that this immediate restarting of time-dependent crack propagation would not give enough time for vacancies to form or SAGBO to occur. No evidence for GB oxidation was found during analysis of the fracture surfaces. These results have been replicated by Zhao et al. [98]. Further experiments were carried out with regards to quench-cracking of René 95, where it was again argued that oxygen-induced fatigue cracking began in a timeframe too fast for oxides to form [99].

DE so far has mostly been investigated via comparison of modelling predictions with observed evidence of oxide-free surfaces. As such, there currently exists little experimental verification of long-range oxygen diffusion down grain boundaries.

2.3.2.2 Stress-Assisted Grain Boundary Oxidation (SAGBO)

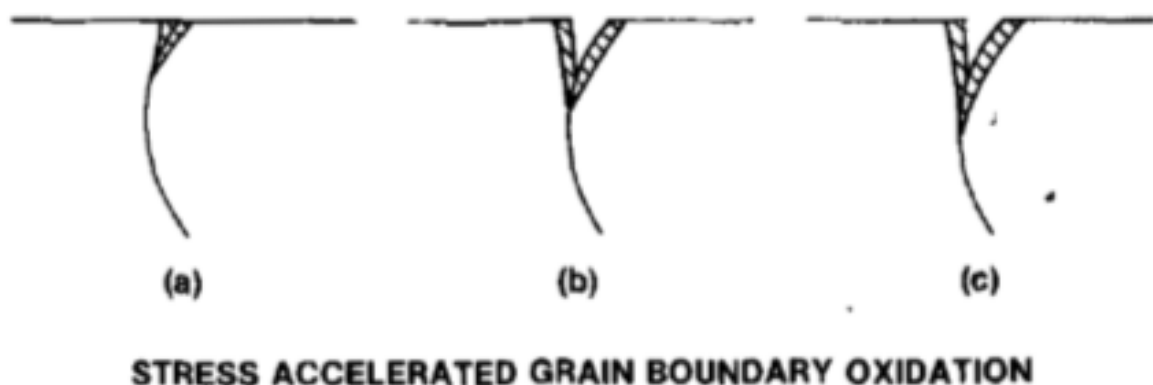


Figure 2.10 – Schematic representation of the SAGBO mechanism. Reproduced from [53] with permission from Taylor and Francis.

The alternative SAGBO mechanism was proposed by Smith et al. [100] to explain oxygen-assisted cracking in the Fe-Ni base superalloy IN903 [53]. It involves the local formation of a wedge shaped

oxide down a grain boundary preceding a crack tip, as depicted in [Figure 2.10](#). This leads to a cycle whereby the brittle oxide partially fractures, allowing further oxide penetration through this region to form oxide in front of the crack tip. It differs from DE in that oxide intrusions down grain boundaries exist ahead of the crack tip, rather than in its wake.

A major advantage of SAGBO is that the free energy reduction for oxide formation is much larger than that of grain boundary decoherence [\[101,102\]](#). This means that the SAGBO mechanism should be more thermodynamically favourable than DE, but of course this disregards the kinetics of oxidation and oxygen diffusion. The time required for oxides to grow has been used in arguments against SAGBO by Zhao et al. [\[98\]](#), and Krupp et al. [\[99\]](#) as mentioned above, however TEM observations by Kitaguchi et al. have shown that crack tips propagating at rates up to 6 $\mu\text{m/s}$ still retained a 1.5 μm long intergranular oxide intrusion ahead of them [\[103\]](#). Many other experiments have also verified the presence of oxides directly at the crack tip using high resolution imaging techniques such as SEM, TEM and atom probe tomography (APT) [\[101,103–107\]](#). Of these, both Hörnqvist et al. and Kitaguchi et al. observed no evidence of long-range oxygen diffusion down the grain boundary ahead of the crack tip.

The oxides that form along grain boundaries are highly dependent on local chemistry. Preferential oxidation of Nb, Ti, Al and Cr have been observed in IN718 using X-ray photoelectron spectroscopy (XPS) after sustained-load fatigue tests carried out at 700°C [\[84\]](#). As has been previously discussed, Nb oxides have been implicated in reducing dwell fatigue resistance in IN718 [\[108\]](#).

Andrieu et al. performed fatigue experiments on IN718 in a range of environments at temperatures of 650°C [\[109\]](#). TEM analysis of the oxides on the fracture surface were deemed to suggest a two-stage oxidation process. First, a porous spinel oxide $\text{Ni(Fe,Cr)}_2\text{O}_4$ forms, which

lowers the P_{O_2} until the formation of chromia becomes more thermodynamically favourable (as determined by the Ellingham-Richardson diagram depicted in [Figure 2.5](#)). This dense impermeable Cr_2O_3 layer forms at the metal-oxide interface, which reduces the P_{O_2} and governs the kinetics of further oxide growth, by reducing the diffusion of oxygen through to the crack tip.

2.3.3 Fatigue Mechanism Discussion

The exact mechanism behind oxygen-induced dwell fatigue cracking is currently the subject of much debate. Part of the problem is that distinguishing between the two mechanisms is not trivial, due to the multitude of variables. There are innumerable parameters which could affect the failure mode, including but not limited to: temperature range, dwell time, alloy composition, oxygen partial pressure, grain boundary chemistry, grain boundary orientation, precipitate distribution, crack tip stress intensity, and many more. This complexity is only added to by the fact that these variables are all co-dependent. It is also conceivable that both mechanisms may be operating at the same time but in different locations. Grain boundary topology can vary, which could lead to variations in P_{O_2} . High P_{O_2} could feasibly lead to oxidation, while low P_{O_2} may lead to decoherence. Alternately, the strength of grain boundaries may be a factor, with stronger boundaries avoiding decoherence long enough for oxidation to take place.

Identifying the mechanism at work is important, as the oxidation kinetics differ between models. Methods for preventing dwell fatigue also differ depending on the mechanism - SAGBO could feasibly be prevented by adjusting the grain boundary chemistry to promote protective and impermeable oxides such as Cr_2O_3 , while preventing the formation of Nb_2O_5 . DE is more likely to be avoided by engineering grain boundaries to prevent oxygen diffusion, utilising grain boundary phases to inhibit or capture diffused oxygen. Both of these approaches will require further examination of the role of elements in oxidation and grain boundary phase precipitation.

With this in mind, there are some things which are known for certain. Oxidation plays a large role in enabling dwell fatigue through environmental embrittlement. Ti has been shown to be detrimental to oxidation resistance, and the role of Nb oxides in fatigue behaviour is also firmly established. It follows therefore that a useful approach could involve a systematic set of studies, to determine how Ti and Nb composition affect oxidation and dwell fatigue crack behaviour. High-resolution characterisation would be required in order to provide intimate detail of the structure and chemistry of crack tips, including oxides and the preceding grain boundaries. The small concentrations of embrittling elements will require techniques with high elemental sensitivity, and analysis of the complex morphologies of crack tip oxides is facilitated by techniques offering 3D visualisation capabilities.

2.4 Optimisation of Alloy Composition

2.4.1 Design Tradeoffs

Optimisation of superalloy composition is complicated by the many trade-offs that exist. Yield strength, phase stability and resistance to failure mechanisms all impose constraints on the type and amount of alloying elements which can be added. Maximisation of yield strength is used as an example here, as it remains a major reason behind the widespread use of superalloys in turbine engines. The total γ' volume fraction plays a vital role in high temperature strength and creep resistance, which can be increased through additions of γ' formers such as Ti, Ta and Nb. However all of these elements are also implicated in TCP phase formation, with Ti forming η , Nb forming δ , and Ta encouraging carbide formation [29]. In addition, Ti is highly detrimental to oxidation resistance [77], Nb reduces fatigue resistance [110], and heavy refractory elements such as Ta increase the cost and density of alloys. In addition, high γ' volume fractions can increase susceptibility to environmentally related cracking [103]. Elements in the γ matrix are also subject to design limitations, with increasing Cr concentrations linked to the formation of σ

phase, despite its key role in providing oxidation resistance via formation of protective Cr_2O_3 barrier layers.

It is clear that the large number of variables involved in superalloy composition render large-scale experimental testing inefficient, expensive and time-consuming. A historical example of this can be found in the development of the alloy N18, which was designed as a blend of René 95 and Astroloy, in order to combine their high strength and fatigue resistance respectively [111]. This led to the creation of 47 potential candidate compositions, from which the final composition was selected for further evaluation [112]. Exploration of this broad compositional design space can be assisted by using in-silico modelling and optimisation techniques, in order to increase the speed and reduce the cost of alloy development.

2.4.2 Alloys-By-Design Methodology

A number of computational methods have previously been developed in order to model physical properties, in order to optimise compositions [113–116]. This project focusses on the Alloys-By-Design (ABD) process developed by Reed et al. for the optimisation of single crystal turbine blade alloys [117], and further refined for use on polycrystalline turbine blade alloys by Crudden et al. [47]. The ABD process involves establishing composition-property relationships across a broad compositional space, virtually modelling and testing millions of compositions. This allows the regions within this design space which best satisfy the given design constraints to be precisely targeted.

A number of design constraints have been identified, using a variety of methods:

- Equilibrium phase fractions have been determined via Thermo-Calc coupled with both TTNi8 and TCNi8 databases [118]. This informs yield strength estimations based on γ' volume fraction, as well as phase stability estimations based on σ volume fraction.
- The strengthening effects of γ' based on the compositionally-dependent APB energy have been estimated using an Ising model to interpret Thermo-Calc site preference data.
- Yield strength has been estimated through the use of a Bayesian artificial neural network, trained on a database of 125 current superalloy compositions (56 commercial, 69 prototype) from papers, patents and data sheets (listed in [74]).
- Oxidation and corrosion resistance has been estimated via calculation of the activity of chromia (a_{Cr}) via Thermo-Calc, which is inversely proportional to the parabolic rate constant K_p .
- Creep performance has been estimated, using diffusion equations to calculate the rates of dislocation unpinning from pinned configurations.
- Density and cost can be calculated directly from alloy composition.

A visual representation of some of these constraints is shown in Figure 2.11, in which three key tradeoffs relating to the additions of Cr, Mo and W have been balanced against each other. A key consideration is phase stability, in particular the avoidance of σ phase formation. This phase can form when Cr concentrations are high, which limits how much can be added to impart oxidation resistance. In addition, W and Mo also promote σ phase, which constrains creep resistance and strength. This graph demonstrates how design decisions can be assisted, by showing to what extent the tradeoffs between phase stability, strength and resistance to both creep and oxidation can be optimised through slight reductions to both Cr wt.% and (W+Mo) wt.%.

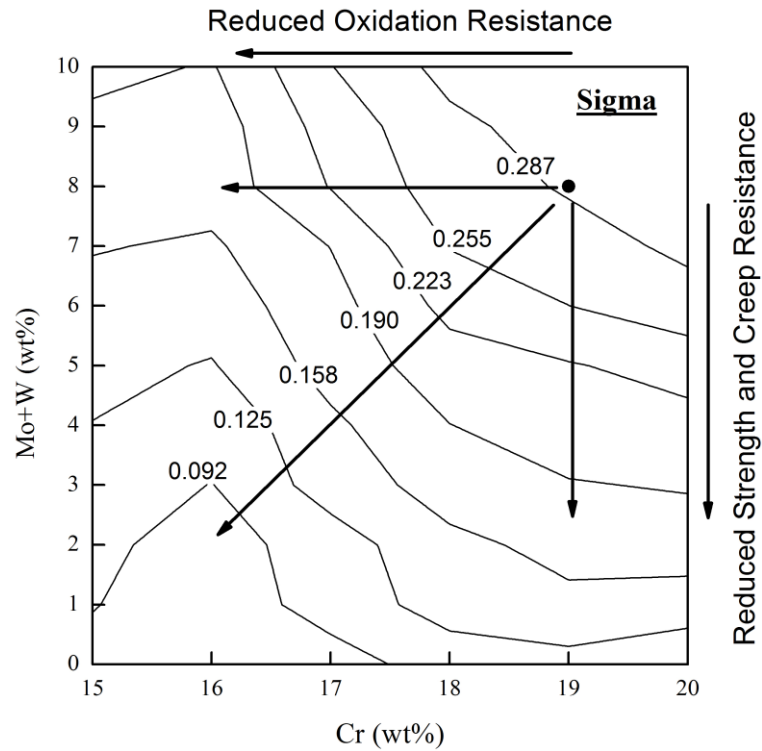


Figure 2.11 – A visual representation showing how the Alloys-by-Design method can be used to balance multiple design tradeoffs, allowing more informed optimisation of compositions. Reproduced from [47] with permission from Springer © 2012.

This particular set of tradeoffs between Cr, Mo and W additions, and their effects on strength, phase stability and oxidation and creep resistance became the rationale behind the first generation of ABD alloys (ABD-1 to ABD-3). The following chapters investigate the second generation of ABD alloys, which focusses on optimising resistance to oxidation and fatigue.

Chapter 3. Experimental Procedure

This chapter describes the experimental methodology used during the production of a family of model nickel-based superalloys, with compositions isolated using the Alloys-by-Design process as described in [Chapter 2.4.2](#). It also explains the equipment and procedures used to characterise the chemistry and microstructure of these alloys in varying conditions. The techniques used to simulate several different types of environmental attack have been described, as well as the characterisation methods used to investigate the resulting damage.

3.1 Materials

3.1.1 ABD Alloy Composition

The Alloys-by-Design process described in [Chapter 2.4.2](#) has been followed in order to narrow down the optimal composition range for polycrystalline nickel-based superalloys designed for use in next-generation Rolls-Royce turbine discs. The composition of the current generation alloy RR1000 was used as a starting point, which is currently one of Rolls-Royce's most technologically advanced turbine disc materials [\[74\]](#). The goal of the first iteration of the ABD process was to develop three alloys that could operate at a temperature of 800°C (50°C higher than RR1000), while maintaining similar yield strength, phase stability, and resistance to high temperature damage, as previously depicted in [Figure 2.11 \[74\]](#). These first three alloys were designed to investigate the effects of varying Cr, W and Mo concentrations on the aforementioned properties, and were designated ABD-1, ABD-2 and ABD-3. Of these, ABD-2 was found to best satisfy the property requirements, and was chosen as a candidate alloy for this project.

In order to test the suitability of niobium as a potential constituent, whilst also investigating some long-standing questions regarding the relationship between oxidation kinetics and titanium, the

ABD-2 alloy chemistry was modified to produce a family of near-identical and easily-comparable model alloys. This required the use of identical processing paths and unchanged compositions, except for the systematic replacement of titanium with niobium. These elements were chosen for substitution as they have previously been shown to have a comparable effect on important requirements such as yield strength [32] and γ' precipitate phase volume fractions [119], which is further investigated in Chapter 4. The nominal and measured compositions for this generation of ABD superalloys, designated ABD-4, 5, and 6, are given in Table 3.1.

	Alloy	Ni	Cr	Co	W	Al	Ti	Ta	Nb	C	B	Zr	Fe	Si
ABD-2	Target	49.2	18.7	18.2	0.9	8.0	4.1	0.6	0.0	0.13	0.08	0.04	-	-
	Measured	48.5	18.9	18.5	1.0	7.9	4.3	0.7	0.0	0.13	0.05	0.04	0.00	0.00
ABD-4	Target	49.3	18.7	18.2	0.9	8.0	3.6	0.6	0.4	0.13	0.08	0.04	-	-
	Measured	48.5	18.6	18.6	0.9	7.9	4.0	0.6	0.4	0.14	0.10	0.04	0.00	0.04
ABD-5	Target	49.3	18.7	18.2	0.9	8.0	3.2	0.6	0.8	0.13	0.08	0.04	-	-
	Measured	49.4	18.6	18.3	0.9	7.6	3.3	0.6	0.8	0.14	0.11	0.04	0.03	0.06
ABD-6	Target	49.3	18.7	18.2	0.9	8.0	2.8	0.6	1.2	0.13	0.08	0.04	-	-
	Measured	48.1	18.9	18.8	0.9	8.1	2.9	0.6	1.2	0.12	0.11	0.04	0.03	0.06

Table 3.1 – Target and measured compositions (at. %) of ABD series superalloys investigated in this study. Compositions were kept as similar as possible, with the exception of Ti and Nb (as highlighted). Composition measurements made using the spectroscopy techniques of X-ray fluorescence, combustion infra-red and inductively coupled plasma-optical emission. Reproduced from [119] under the Creative Commons Attribution License 4.0 (CC-BY).

3.1.2 ABD Alloy Processing Route

These alloys were produced using a powder metallurgy process, as their high alloying content and resulting γ' precipitate volume fraction could otherwise lead to segregation issues during more traditional cast and wrought processing routes [16]. The powders were manufactured by ATI powder metals using a laboratory-scale version of their powder metallurgy process, in which a melt produced via Vacuum Inducting Melting (VIM) is atomised then solidifies into fine metallic particles with diameters ranging between 30-300 μm . This helps to limit elemental segregation, as well as lowering the resultant grain size [9]. Powders are then screened for size and

consolidated via Hot Isostatic Pressing (HIP) at 100 MPa and 1107°C. The compacts undergo isothermal forging into pancakes at a temperature of 1100°C and a rate of 0.2 min⁻¹ [120], similar to those shown in Figure 3.1.



Figure 3.1 – Final pancake forgings created for the previous generation of ABD alloys (ABD-1:3). They measure approximately 110mm in diameter. Reproduced from [74] with permission from the copyright holder D Crudden © 2014.

A two stage super-solvus heat treatment process was carried out, as represented in Figure 3.2.

Stage one consisted of γ' solutionising at a temperature of 1170°C for 2 hours, which is 30°C above the γ' solvus temperature as determined by Thermo-Calc [74], followed by a controlled quench to 1050°C at 1°C s⁻¹. Stage two involved ageing at 850°C for 4 hours, which is 50°C above the nominal alloy operation temperature.

The as-manufactured compositions of each alloy were analysed by Rolls-Royce plc using a combination of spectroscopy techniques, including X-ray fluorescence (XRF), combustion infrared, and inductively coupled plasma optical emission spectroscopy (ICP-OES). The measured compositions differed only slightly from the nominal values, which was deemed within acceptable limits, as is further discussed in Chapter 4. The final as-manufactured alloy composition values were used to perform all subsequent Thermo-Calc and lever-rule calculations.

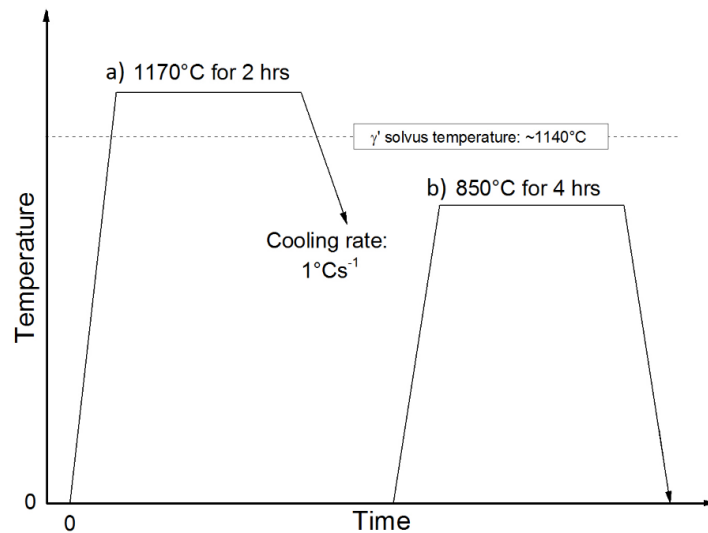


Figure 3.2 – Heat treatment processing route for ABD series nickel-based superalloys. a) Stage one γ' solutionising. b) Stage two ageing. Reproduced from [74] with permission from the copyright holder D Crudden © 2014.

3.2 Environmental Testing

Turbine discs operate in extremely harsh environmental conditions, resistance to which is an important driver for superalloy design and optimisation. Jet turbine engine components are subjected to extreme temperatures which can exacerbate the rates of damage mechanisms such as corrosion, creep, and dwell fatigue crack growth [15]. It is very difficult to perform in-situ measurements for all of these damage processes simultaneously, especially as many of these processes exhibit complex interactions with one another. Therefore, a select few of these environmental factors have been replicated, in order to simplify the models and reduce the number of environmental variables. The focus on optimisation of titanium and niobium levels has informed the types of damage process chosen for investigation, which are isothermal oxidation and dwell fatigue crack growth.

3.2.1 Thermo-Gravimetric Analysis

Oxidation is an easily replicatable and measurable damage process that is of critical importance due to its influence on other damage-causing processes. It can also be significantly affected by

slight changes in composition, especially when considering more reactive elements [77]. The rate of oxidation was measured for these alloys by using thermo-gravimetric analysis (TGA) to record the weight gain due to the growth of oxide over time, which also allows the kinetics of the oxidation reactions to be determined. The constant measurement of sample weight without the requirement to remove and cool samples has significant advantages over traditional furnace experiments, where spalled oxide material may be lost during handling.

Sample Preparation

The heat-treated pancake forgings mentioned in [Chapter 3.1.2](#) were sectioned into more conveniently-sized pieces using an electro-discharge machining (EDM) wire erosion method. Smaller TGA samples of 10 mm² cross-sectional area and 1 mm thickness were cut from these using a Buehler Isomet 5000 slow saw. These TGA samples underwent surface preparation according to Rolls-Royce recommended practice, which prescribed grinding to a 1200 grit finish using successively finer grades of silicon carbide grit paper, followed by ultrasonic cleaning in an isopropyl alcohol bath. Initial sample masses were measured using a microbalance with $\pm 10 \mu\text{g}$ resolution, and total surface areas were calculated via micrometer, with a geometric factor applied to account for the bevelled edges.

Equipment

The oxidation resistance of these alloys was evaluated using a Netzsch Jupiter F1 TGA, as represented by a schematic diagram in [Figure 3.3](#). This equipment essentially consists of a sample carrier attached to a mass balance inside a vertical tube furnace. Gas flow can be controlled through the furnace and around the surrounding sheath to prevent atmospheric contamination. Polished samples are suspended from the sample carrier using Pt wire, around which the furnace tube is lowered. This equipment allows measurement of weight changes as small as $\pm 25 \text{ ng}$, in a variety of atmospheric environments, and at temperatures up to 2000°C.

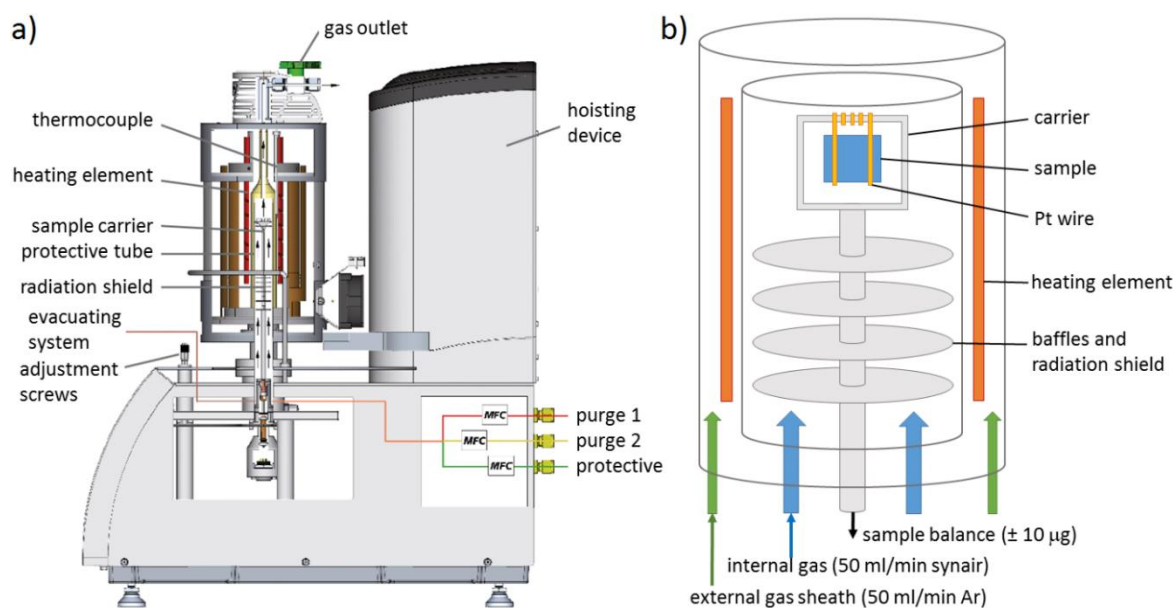


Figure 3.3 – a) Schematic of the Netzsch 449 F1 Jupiter used in this project. b) A generalised schematic of this particular equipment, simplified to the most essential components.

A calibration run with no loaded sample is required, in order to counteract the measured weight fluctuations caused by buoyancy effects due to gas density and temperature changes. The lower thermal mass of the apparatus without a loaded sample could possibly lead to quicker heating rates, but the samples have a small enough mass that this was deemed acceptable.

Experimental Conditions

The experiment consists of four stages, with samples beginning at room temperature in an atmosphere of argon gas. During stage one, the temperature is ramped up to 800°C at $20^{\circ}\text{C min}^{-1}$ maintaining an argon atmosphere to prevent early oxidation. This is followed in stage two with a 10 minute hold in argon at 800°C to allow the temperature to stabilise. Stage three involves an isothermal hold for 100 hours in an atmosphere of dry lab air (80% N_2 , 20% O_2), during which the sample weight is measured and recorded once per second. The equipment and sample are brought back down to room temperature in stage four.

Analysis

Data are captured from the TGA using Netzsch Proteus software. Raw unprocessed data were exported as a .csv file for further analysis and visualisation using Microsoft Excel. This involves subtracting the calibration run, converting weight gain into specific weight gain (gain per unit surface area) and repositioning the graph origin to the beginning of stage three. The calibration time/temperature curves have been smoothed, in order to remove perturbations caused by external vibrations during analysis.

Post-Experiment Sample Preparation

Both oxidised and unoxidised samples were mounted to SEM stubs using conductive silver epoxy for surface SEM and FIB characterisation, an example of which is shown in [Figure 3.4 b\)](#). The oxidised samples were bisected using a Buehler Isomet low speed saw, with one half remaining on the stub for FIB analysis, while the other half underwent cold mounting in low-viscosity low-shrinkage Struers epoxy resin for cross-sectional EDX analyses, as shown in [Figure 3.4 c\)](#).

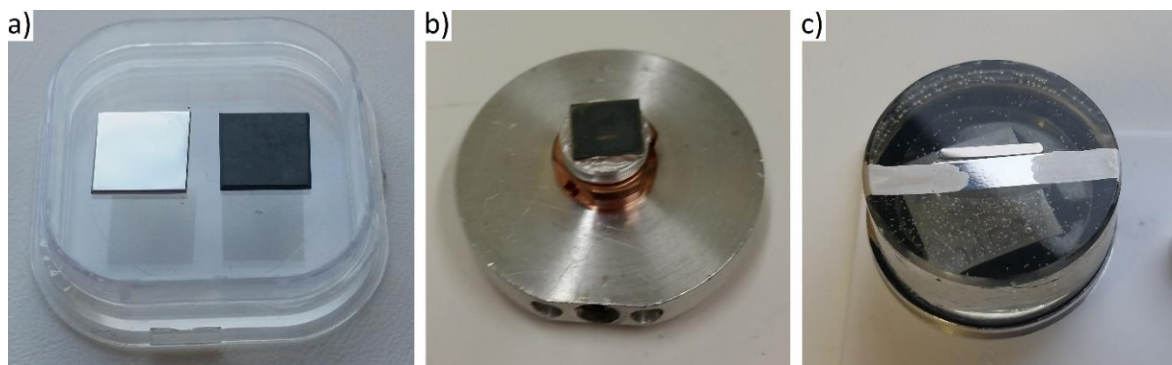


Figure 3.4 – TGA sample preparation. a) Pre-exposure (left) and post-exposure (right) TGA samples. b) Oxidised TGA sample epoxy mounted to SEM stub, in sample holder for FIB-SEM analysis. c) Mounted and polished cross-section sample ready for EDX analysis.

3.2.2 Electro-Thermal Mechanical Testing

Accurate fatigue lifetime estimation is vital during the production and evaluation of turbine discs, as they are machined from large monolithic forgings for which crack growth could be potentially catastrophic. The majority of fatigue research focusses on cyclic fatigue, but attention to dwell

fatigue is beginning to assume greater importance as operating temperatures increase – dwell fatigue has previously been shown to be highly dependent on environmental conditions [91]. The ABD alloys produced during this project provide a highly relevant sample set for studying dwell fatigue, as the influence of niobium at fatigue crack tips is of considerable interest [87,88,108]. Electro-thermal mechanical testing (ETMT) can be used to replicate some conditions experienced in-service, by utilising tensile and cyclic fatigue testing at high temperatures in extreme environments. Specimen heating is achieved by passing a direct current through the specimen, which experiences an increase in temperature at the thinner waist section due to electrical resistance.

All sample preparation and ETMT operation was performed by André Németh at the Begbroke Science Park, representing the High Performance Alloys for Extreme Environments group at Oxford University.

Sample Preparation

Miniaturised tensile specimens with a cross-section of $1 \times 1 \text{ mm}^2$, sample length of 40 mm, and gauge length of 14 mm were produced using wire-based electrical discharge machining (EDM). Specimen surfaces were ground to 1200 grit using successively finer grades of silicon carbide paper to create an even surface finish free of any recast from the EDM process. These were modified for fatigue crack growth experiments by machining a circular notch on one side to a depth of $150 \text{ }\mu\text{m}$.

Equipment

Tensile and fatigue properties were measured using a 5 kN Instron electro-thermal mechanical testing (ETMT) machine. This equipment essentially consists of a high tensile load frame similar to those found in tensile testing rigs, in which samples are heated to high temperatures using

resistance heating caused by a direct current passed through the specimen. This all occurs inside an environmental test chamber in which the atmosphere is carefully controlled.

In order to accurately measure the temperature at the thinnest point of the sample where strain is localised, a K-type thermocouple was welded to the central portion of the specimen gauge.

Tests were performed at a constant strain rate at a setpoint of $1 \times 10^{-4} \text{ s}^{-1}$, which was measured using a linear variable displacement transformer (LVDT). Strain measurements were performed using digital image correlation (DIC) of a thermal paint pattern applied to the central 5 mm of the specimen gauge. This was monitored using an Imetrium DIC software package operating at 1 Hz, which for this sample geometry gives real time strain measurement with a displacement resolution of $0.1 \text{ } \mu\text{m}$. This allowed the tensile stress to be immediately removed when crack growth was detected, so that cracking could be interrupted and total sample failure averted.

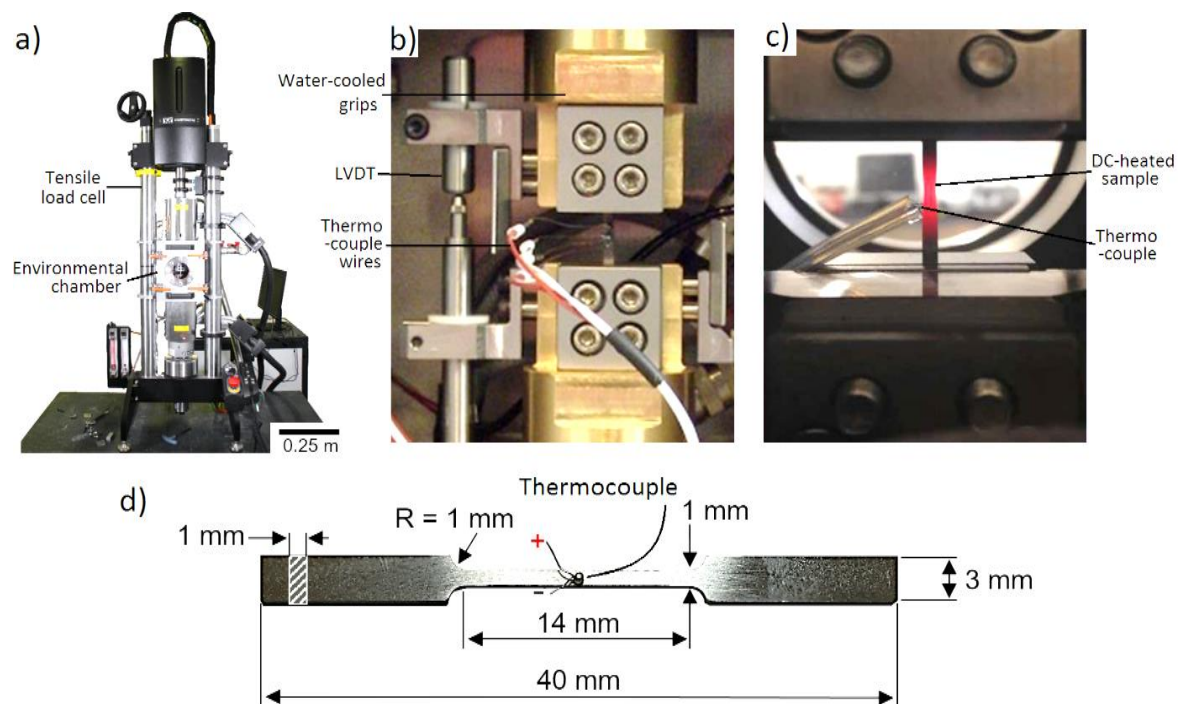


Figure 3.5 – a) Overview of main structural components of the ETMT system. b) Inside the environmental test chamber, including sample, LVDT, and thermocouple. c) View obtained during operation showing DC heating of sample. d) Sample specifications. All adapted from [121] with permission from the copyright holder A Németh © 2017.

Experimental Conditions

An initial crack was created by applying low-cycle fatigue conditions (R-ratio of 0.1 and a 2 Hz sinusoidal cycling waveform) to the notched samples at room temperature, up to a maximum stress level of 95 % total yield strength (σ_y). The gauge length extension (L_0-L_f) was monitored using DIC to track a thermal paint pattern applied to the central 5 mm of the specimen where the temperature and deformation are uniform. These pre-cracked test pieces were subjected to a tensile test with a constant extension rate of $0.5 \mu\text{m s}^{-1}$ at 700°C in air, causing the environmentally-assisted growth of the crack. Tests were interrupted as soon as crack growth was detected, by unloading and simultaneously reducing the temperature to ambient with a cooling rate close to 100°C s^{-1} .

3.3 Scanning Electron Microscopy

Scanning electron microscopy (SEM) techniques can quickly and easily reveal important information about a wide range of samples with minimal sample preparation required. A variety of SEM techniques were employed to characterise a range of properties of the ABD alloys, from evaluation of microstructural properties such as the γ' volume fraction of unoxidised metal and damage profiles through oxidised samples, to elemental distributions through oxide scales and fatigue crack tips. As electron microscopes are a standard piece of characterisation equipment, the principles by which they operate have not been explained here.

3.3.1 Surface SEM

Electron microscopy was used to characterise properties of the ABD alloys such as grain size, and γ' precipitate characteristics such as morphology and size distributions. Compositionally unique precipitate phases could be differentiated using the inlens secondary electron detector, in which lower atomic number elements show up with higher contrast, allowing aluminium-rich γ' and

grain boundary carbides to be easily identified. Magnifications of 20,000 $\times$ could be reached, allowing individual γ' precipitates with sizes down to about 20 nm diameter to be resolved.

Sample Preparation

Metallographic samples for SEM analysis were sectioned into 10 mm² squares using a Buehler Isomet 5000 slow saw with a diamond cutting wheel, and attached to SEM stubs using conductive silver epoxy. These surfaces were ground using successively finer grades of SiC grit paper, followed by mirror polishing using diamond suspension and 0.06 μ m COL-K colloidal silica. No etching was performed, as any deviation from a flat plane would invalidate the Delesse-Rosiwal conditions which allow the assumption that precipitate cross-sectional area fraction equals precipitate volume fraction [122].

Equipment & Experimental Conditions

A Zeiss Nvision 40 FIB-SEM was used to capture SEM images using a 5 kV beam current and a 30 μ m aperture. This low electron beam current minimises the electron interaction depth, which enhances resolution and γ - γ' phase contrast. A magnification of 500 $\times$ was used to capture grain size information, while a higher magnification of 20,000 $\times$ was required to characterise the largest tertiary γ'_{III} precipitates. The inlens secondary electron detector was used to enhance the visual contrast between γ and γ' phases.

Analysis

Post-processing and analysis was performed on the resultant micrographs using the ImageJ software suite. The 500 $\times$ micrographs were prepared for grain size analyses by converting them to 8-bit greyscale images, maximising grain contrast, and applying a 'despeckle' filter to reduce noise. An initial grain size estimate was performed using the 'Linear Intercept Method', in which a number of randomly-oriented lines are overlaid and the average number of grain boundary

crossings per unit length is tabulated, as visualised in [Figure 3.6 a\)](#). The relationship between intercept length and grain diameter is not exceptionally well-defined [\[123\]](#), but the values are at least internally consistent which allows comparison between alloys.

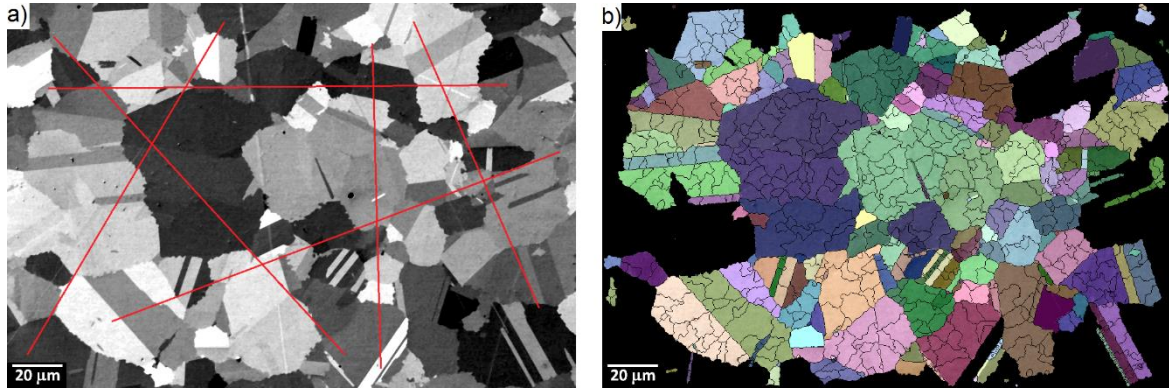


Figure 3.6 – Two methods for grain size determination from a 500× micrograph from alloy ABD-2. a) Linear intercept performed using standardised overlay template consisting of 6 randomly-oriented lines. b) Morphological segmentation tool (including microdomains and blacked-out border regions).

A more thorough grain size analysis was performed using the morphological segmentation tool from the MorphoLibJ plugin [\[124\]](#). The ‘object image’ option was selected, using a gradient radius value of two, and tolerance value between 10 and 16 decided on a per-image basis. This creates a domain map with matching grain boundaries, although the domains are much smaller than the relevant grain. Domains within the same grain are merged together, then all domains in contact with the edge of the micrograph are removed, resulting in a domain map as shown in [Figure 3.6 b\)](#). This could then be analysed using ImageJ, providing a tabulated output of many measured properties such as; grain area, perimeter length, and grain circularity.

Precipitate distributions were extracted from the 20,000× micrographs using the inbuilt ImageJ particle analysis tool. This process is displayed in [Figure 3.7](#). Part [a\)](#) shows cropping and contrast enhancement, after which a thresholding technique was used to differentiate the lighter γ' precipitates from the darker γ matrix as shown in part [b\)](#). These thresholded images were processed using a watershed algorithm, which separates closely packed or touching precipitates.

A small number of clover-leaf shaped precipitates were unintentionally split during this process, an example of which is denoted by label 1 in part c), which may lead to a perceived increase in number density and a reduction in average precipitate size. Conversely some precipitates remained agglomerated, an example of which is denoted by label 2 in part c), which may lead to a lower count of larger precipitate sizes. It is unknown to what extent these two effects change the observed size distributions.

The ImageJ particle analysis tool was used to calculate cross-sectional particle areas (A), which were converted into equivalent particle diameters (d) using the equation $d = 2\sqrt{A/\pi}$.

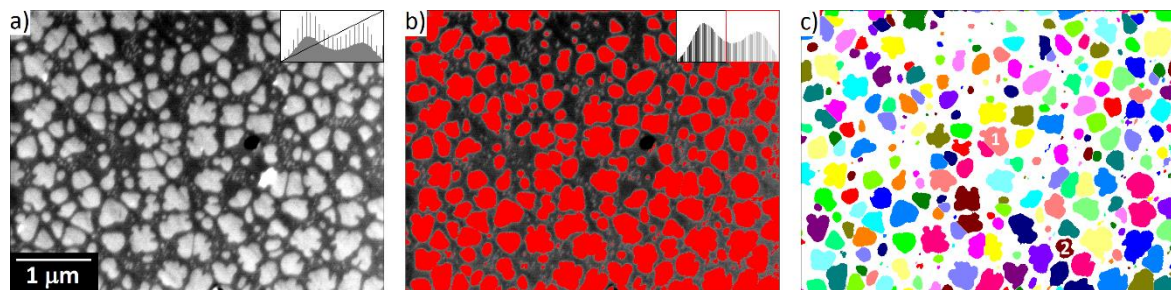


Figure 3.7 – a) Alloy ABD-2 SEM micrograph using inlens detector at 20,000× magnification, with contrast maximisation inset. γ' precipitates appear as lighter regions in the darker γ matrix. b) SEM micrograph after thresholding of 8-bit greyscale intensity values. Precipitates shown in red are defined by intensity values within the red box of inset histogram. c) Final identified and separated precipitate areas used to estimate γ' size distribution and volume fraction.

3.3.2 Focussed Ion Beam Microscopy

Microscale cross-sections through a material can be cut and analysed using a focussed ion beam (FIB) system in a combination FIB-SEM instrument. This uses an accelerated ion beam (30 kV Ga^+) focussed on a preselected region to remove material, in order to cut trenches and polish cross-sections. A dual-beam FIB-SEM allows these polished cross-sections to be observed during the milling process. Minimal sample preparation is required for this, with samples only requiring mounting to an SEM stub using conductive silver epoxy for handling. Because neither coating nor mounting in another medium are required, this limits any obstruction of microstructural features

or sample contamination. FIB-SEM was used in this instance to study the surface and sub-surface oxidation damage.

Equipment & Experimental Conditions

A Zeiss Nvision 40 dual beam FIB-SEM was used to study the oxidised surface of samples produced via TGA. Once a site of interest was identified, trenches were cut through the oxide layers by focussing a 30 kV Ga⁺ ion beam with a current of 3 nA on a 60 µm x 10 µm region, until the trench was 10 µm deep. A lower ion current of 700 pA was used after this to limit Ga⁺ ion damage to the trench edges. The exposed cross-sectional surface was then polished using a rastered 30 kV 300 pA beam to give a smooth surface while avoiding the beam curtaining effects that often result from density variations present within the oxide layer.

During FIB milling, the surface was kept under constant observation with the SEM column at 5 kV accelerating voltage using a 120 µm aperture. A 36° tilt correction was applied to the resultant SEM cross-sectional micrographs, due to the 54° angle between the SEM and FIB columns – These orientations are demonstrated in a schematic diagram of the FIB-SEM instrument shown in [Figure 3.8](#). Final micrographs were obtained using both the SE2 detector to record surface features, and the Inlens secondary electron detector for increased phase contrast.

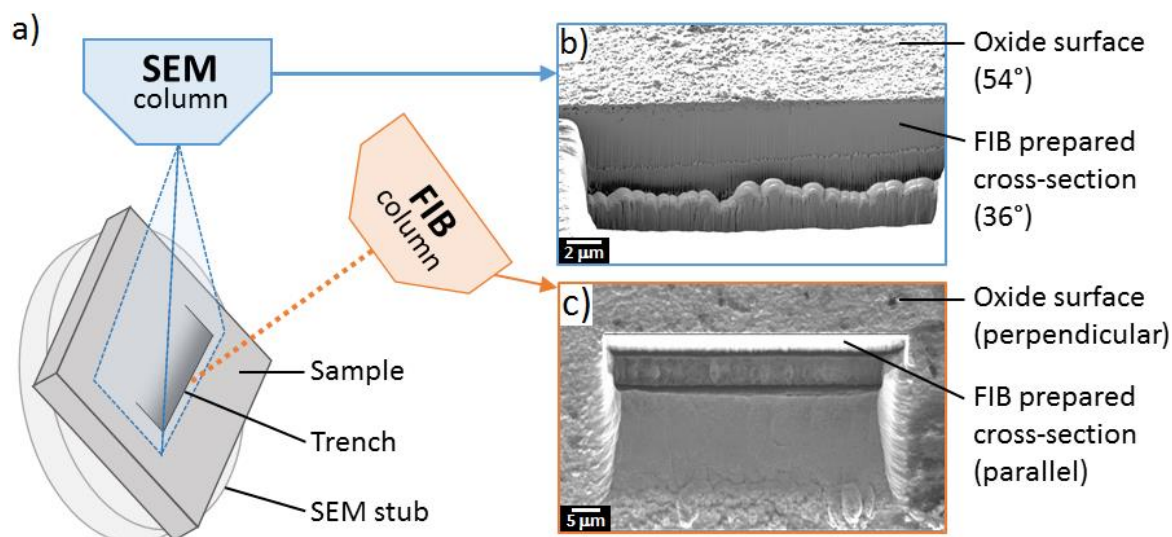


Figure 3.8 – a) Schematic of sample mounted to SEM stub during FIB-SEM, showing orientations of oxide surface and FIB-milled trench relative to the respective view column. b) View observed from SEM column. c) View observed from FIB column.

3.3.3 Cross-Sectional EDX

Energy-Dispersive X-ray spectroscopy (EDX) measures the energies of X-rays emitted by electrons in atoms in the sample after excitation from an electron beam. These electrons are excited to a higher energy state, then revert to a lower energy state while emitting surplus energy as an X-ray photon. These emitted X-rays have characteristic wavelengths as determined by the elemental identity of the atom, allowing a compositional map to be built up over the micrograph. This allows the composition of both metal and oxides to be analysed, as well as any elemental segregation to features within these layers. Two different methods were used to perform EDX analyses; Traditional cross-sectional EDX analysis on mounted and polished samples, as well as FIB-EDX characterisation similar to that described in [Chapter 3.3.2](#).

Sample Preparation

Oxidised TGA samples were bisected using a Buehler Isomet low speed saw, so that a vertical cross-section through the oxide layer was exposed. One half of the sample underwent mounting to an SEM stub using conductive silver epoxy for FIB-EDX characterisation as described previously.

The other half was prepared for more traditional cross-sectional analyses by cold mounting in low-viscosity, low-shrinkage epoxy resin, followed by grinding to a mirror polish using a combination of SiC grit paper, diamond suspension, and 0.06 μm COL-K colloidal silica. Thin strips of silver dag were applied between the sample surface and SEM stub to limit image drift caused by sample charging from the electron beam.

Equipment & Experimental Conditions

The more conventional cross-sectional EDX was performed in a Zeiss Merlin SEM-EDX fitted with an Oxford Instruments Xmax 150 EDX detector, using a 150 pA beam current at 10 kV. This voltage was chosen to give high-resolution images while also activating enough principal emission lines to avoid peak overlaps such as the Cr $L\alpha$ / O $K\alpha$ overlap at 0.55 keV. Magnifications of 10,000 $\times$ were used. Despite the application of silver dag, some image drift caused by sample charging was encountered, which limited the scanning time to a maximum of five minutes.

FIB-EDX characterisation was performed using a Zeiss Crossbeam 540 fitted with an Oxford Instruments XmaxN 150 EDX detector. These samples were not pre-sectioned, with an intact oxide layer perpendicular to the FIB gun. To prevent Ga^+ ion damage to the oxide surface, a protective W layer was deposited. Cross-sectional trenches were cut using a 30 kV Ga^+ ion beam, with current reducing from 3 nA to 300 pA during the final polishing stages to remove FIB damage. Trench edges were polished by rastering a 30 kV, 300 pA beam across them. EDX analysis was again carried out using a 10 kV SEM gun voltage to differentiate the Cr and O signals, although the beam current was increased to 250 pA.

Analysis

All EDX micrographs and spectroscopic data were analyzed in the Oxford Instruments Aztec 3.3 nanoanalysis software suite.

3.3.4 Fatigue Crack Characterisation

As discussed in [Chapter 3.2.2](#), attention to dwell fatigue crack growth assumes greater importance as engine operating temperatures continue to increase. The exact mechanism by which dwell fatigue crack growth is related to crack tip oxidation remains unresolved, but has been investigated using high-resolution characterisation techniques on fatigue crack tips manufactured using ETMT. Dwell fatigue cracks are known to progress along grain boundaries [\[49,53\]](#), so two different forms of diffraction-based electron microscopy methods were used to highlight the grain boundaries preceding from the very tips of fatigue cracks. Grains could be differentiated by measuring the diffraction patterns resulting from the interaction between electrons and crystalline lattice structures.

Electron back-scatter diffraction (EBSD) analysis was used to calculate the relative orientations of separate grains so that grain boundaries could be easily identified on polished cross-sections before further sample preparation was carried out. Transmission Kikuchi diffraction (TKD) is a related technique with increased resolution that requires samples thin enough to be electron transparent, which equates to around 200 nm for pure Ni. Both TKD and EDX analysis were carried out on thin lamella with sub-200 nm thickness, and needle-shaped specimens with sub-100 nm tip diameter for APT, in order to identify oxidised grain boundaries and crack tips.

Sample Preparation

The miniaturised ETMT tensile specimens that had previously undergone fatigue crack growth in [Chapter 3.2.2](#) were mounted by André Németh in conductive black resin, encased in a steel tube, and attached to a SEM stub for handling purposes. These were ground and polished using successively finer grades of SiC grit paper, diamond suspension and 0.06 µm COL-K colloidal silica, after which they were ready for surface EBSD and EDX analysis in a FIB-SEM. The thin lamella required for TKD and EDX analysis were created from these polished samples using FIB techniques

described in the following section. The copper tomography posts used for mounting crack-tip liftout bars onto were ultrasonically cleaned in isopropyl alcohol, and the tip was flattened in the FIB using a 30 kV, 26 nA ion beam.

Equipment & Experimental Conditions

A Zeiss Crossbeam 540 FIB-SEM was used for all sample preparation, as well as EDX, EBSD and TKD analyses using an XmaxN 150 EDX detector and a NordlysMax 3 EBSD detector, both by Oxford Instruments.

Polished ETMT crack-tip samples first underwent SEM, EDX and EBSD analyses to locate and identify crack tips in order to determine whether they are primary or secondary crack tips. The following Pt protection, liftout, and mounting process is shown in [Figure 3.9 a](#)). Once a suitable crack tip was identified and higher-resolution micrographs obtained, they were protected from further ion damage using electron-beam Pt deposition to create a small fiducial dot directly at the crack tip. A thicker Pt layer was then deposited using a 30 kV, 150 pA Ga⁺ ion beam to cover the entire 3 µm by 10 µm region of interest, oriented along the crack and preceding grain boundary. This area was extracted from the sample using a fairly standard liftout procedure [\[125,126\]](#), consisting of trench cutting along the top (grain boundary side) and each side of the Pt-protected region using a 30 kv 3 nA beam. Undercut trenches were cut at 30° to the sample surface to liberate the liftout bar from the sample. An Omniprobe micromanipulator was Pt welded to the top (grain boundary side) of the liftout bar, after which the final trench was cut at the bottom (crack side) of the sample, allowing removal of the liftout bar and manipulator. The sample was then replaced with a Cu tomography post, which was mounted horizontally to align with the liftout bar as shown in [Figure 3.9 b](#)).

The liftout was mounted to the Cu tomography post using a modification of the techniques created by Lotharukpong et al., Meisnar et al., and Kruska et al. [127–129], which help to avoid some of the inherent limitations of creating a strong butt joint between dissimilar materials on the micro-scale. This technique involves depositing a layer of Pt around the base of the liftout, followed by the cutting and backfilling of reinforcement ‘keys’ through the base of the liftout and into the tomography post below.

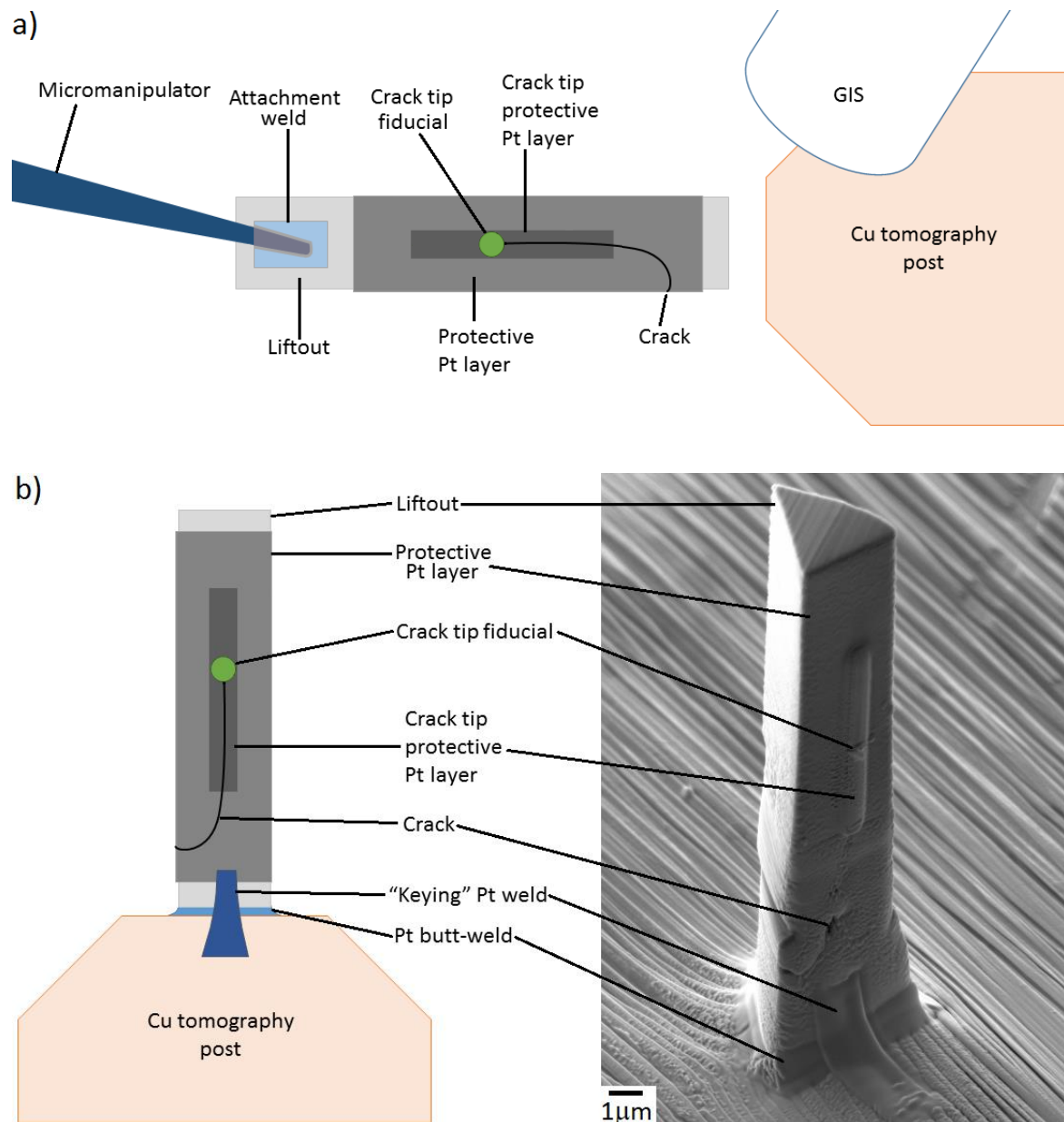


Figure 3.9 – a) Top-down schematic of crack tip liftout, and orientation compared to copper tomography post and gas injection system (GIS). b) Welding method used to join liftout to tomography post.

Once firmly affixed to the tomography post, the liftout was aligned perpendicular to the FIB column (54° stage tilt), so that the top side of the liftout with the protective Pt layer and fiducial were aligned facing the SEM column, as shown in Figure 3.10. The sample was thinned to a lamella with sub-200 nm thickness aligned parallel to the top surface. This was achieved by milling away the bottom side of the liftout and the Pt protective strip using a 30 kV, 300 pA ion beam. The lamella underwent EDX analysis at 54° stage tilt, then TKD analysis using the EBSD detector at 70° stage tilt.

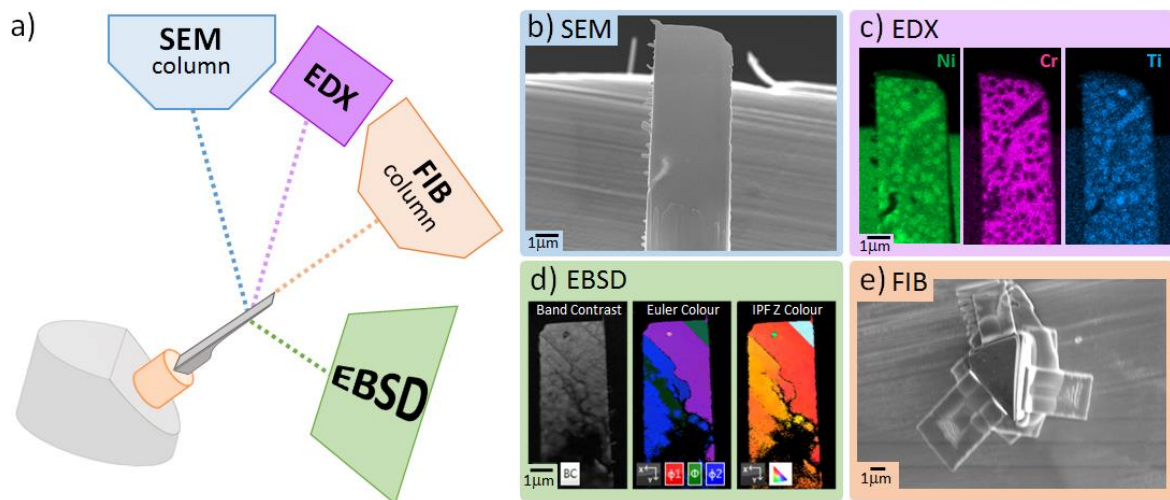


Figure 3.10 – a) Schematic of crack tip lamella sample mounted to a Cu tomography post in a +45° pretilt holder. Both SEM and FIB columns are shown in their relative positions, as well as both EDX and EBSD detectors. b) to e) show representations from each respective view.

Analysis

All EDX micrographs and spectroscopic data, as well as EBSD and TKD diffraction data, were analyzed in the Oxford Instruments Aztec 3.3 nanoanalysis software suite.

3.4 Atom Probe Tomography

Atom Probe Tomography (APT) is a three-dimensional characterisation technique which can determine the position and elemental identity of millions of individual atoms within a sample. This makes it uniquely suited to the study of sub-nanometre-scale composition and microstructure. Tomographic techniques have an advantage over plane and projection based

methods such as SEM, EDX and TEM in that the full 3D structure of samples can be analysed, which is invaluable when studying complex nanoscale 3D features such as tertiary γ'_{III} precipitates, grain boundaries and fatigue crack tips. The small size of these features and need for accurate chemistry determination requires a quantitative analysis technique with high spatial resolution and elemental sensitivity.

It also has advantages over these electron microscopy based techniques in that chemical identity is determined via time-of-flight mass spectra analysis, which gives APT a similar detection efficiency across all elements [130]. This is ideal for studying oxides due to the importance of identifying and locating elements with low atomic number such as carbon, nitrogen and oxygen. The chemical sensitivity of APT also compares favourably against most EM techniques, with APT having the ability to detect concentrations of elements up to tens of ppm, such as elemental segregation found at grain boundaries, fatigue crack tips and nanometre-sized precipitates [131].

3.4.1 Equipment

Atom probe tomography involves the controlled atom-by-atom evaporation of ions from a needle-shaped specimen via field evaporation, a schematic diagram of which is shown in [Figure 3.11](#). This requires an intense electric field to be created around the sample via the application of a large standing voltage between the sample and a local ring electrode. The field is increased further by carefully controlling sample geometry to form a needle shape with extremely small tip radius, typically less than 100 nm, which can be derived using [Equation 3.1](#);

$$F = \frac{V}{k_f R} \quad (\text{Eq. 3.1})$$

where F is the electric field generated at the apex of a tip of curvature R , V is the applied voltage and k_f is the field reduction factor required due to the non-spherical tip geometry. This standing DC voltage field is deliberately kept just below the field value required for ion evaporation, upon which an additional energy pulse is superimposed to overcome the activation barrier for

evaporation. Measuring the time between this pulse and a detection event allows time-of-flight information for each ion to be recorded. The additional energy pulse can take the form of either a small voltage spike to temporarily increase the electric field, or a laser pulse to provide extra thermal energy to the sample. This laser pulsing allows running of fragile and poorly conducting samples such as oxides or crack tips, by reducing the voltage at which evaporation events can take place, consequently reducing the probability of sample fracture.

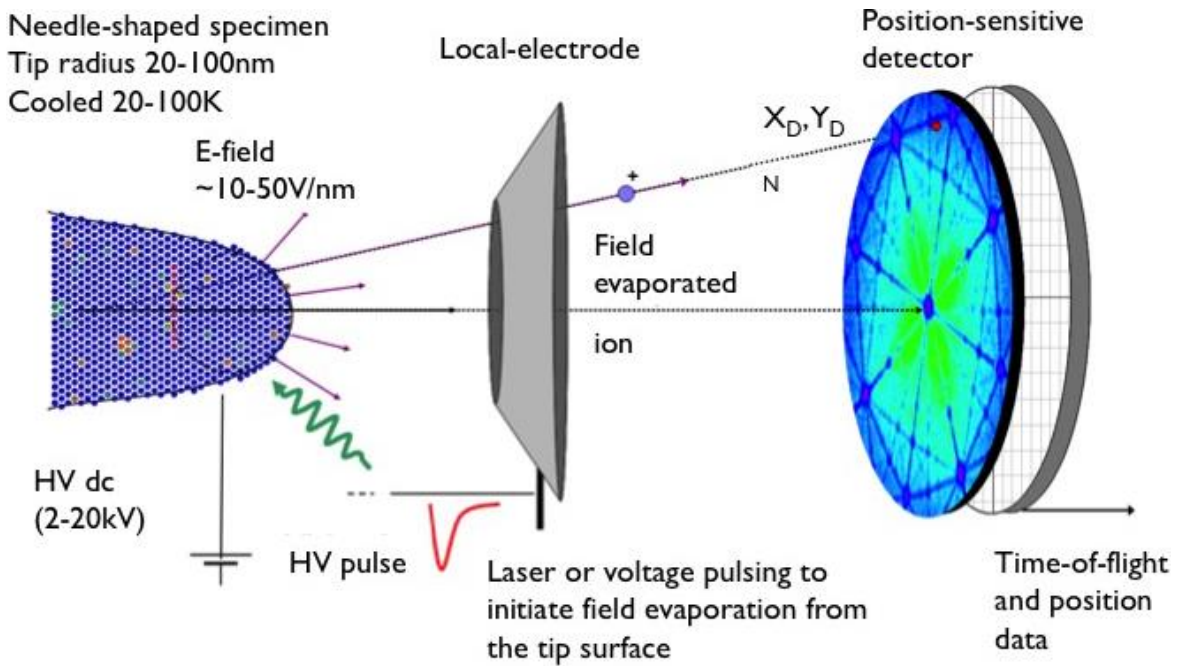


Figure 3.11 – Schematic diagram showing the operating principles of the local electrode atom probe (LEAP). Reproduced from [132] with permission from Cambridge University Press.

After an ion evaporates, it is accelerated by the standing voltage field towards the position-sensitive detector, which records both position and time-of-flight information for each ion. The time-of-flight between voltage pulse and detection event enables mass-to-charge to be calculated for each ion using Equation 3.2;

$$\frac{m}{n} \approx 2eV \left(\frac{t_{\text{flight}}}{L} \right)^2 \quad (\text{Eq. 3.2})$$

where $\frac{m}{n}$ is mass-to-charge-state ratio, e is the electron charge, V is voltage, t_{flight} is the time of flight, and L is the flight length between sample and detector. Spatial information from the

position sensitive detector allows the position of each ion within the sample to be calculated using a reverse-projection algorithm, which is built up into a 3D point cloud reconstruction of all the detected atoms within the sample.

3.4.2 Sample Preparation

3.4.2.1 Electropolishing

This sample preparation technique is a quick, cheap and straightforward method for creating needle-shaped specimens through the use of electrochemical polishing. A sample tip created this way usually contains a randomly-selected region, so it was used during [Chapter 4](#) to analyse bulk metallic samples where no site-specific information was required.

Sample blanks of 20 mm × 0.5 mm × 0.5 mm were cut from bulk superalloy using a Buehler Isomet 5000 slow saw. These matchsticks were shaped using a two-stage electropolishing process, involving the passing of a current through the sample whilst immersed in a conductive liquid electrolyte, as depicted in [Figure 3.12](#). With the sample acting as an anode, charge is carried through the apparatus via the dissolution of sample atoms as ions, to be re-deposited on a gold cathode. Careful control of current and voltage is required to prevent etching or pitting, and the use of a thin electrolyte layer combined with oscillation of the sample gives control over sample shaping.

The first stage involves removal of material from the middle of the sample blank to create two needle-shaped samples. This is performed by oscillating the blank through a thin electrolyte layer consisting of 25% perchloric acid solution (in acetic acid), which floats above an inert and insulating Galden™ layer. After some experimentation, a voltage of 16 V was found to dissolve material at the smoothest rate. The second stage uses the same principles in a different

configuration, with the electrolyte suspended within a metal loop forming the cathode. The blank was oscillated horizontally through this loop under an optical microscope, to ensure much finer control over final tip radius. The electrolyte used here was a 2% perchloric acid solution (in butoxyethanol) at a voltage of 10 V. For ease of handling, the sharpened needles were crimped inside 0.8 mm diameter copper tubes between the first and second electropolishing stages.

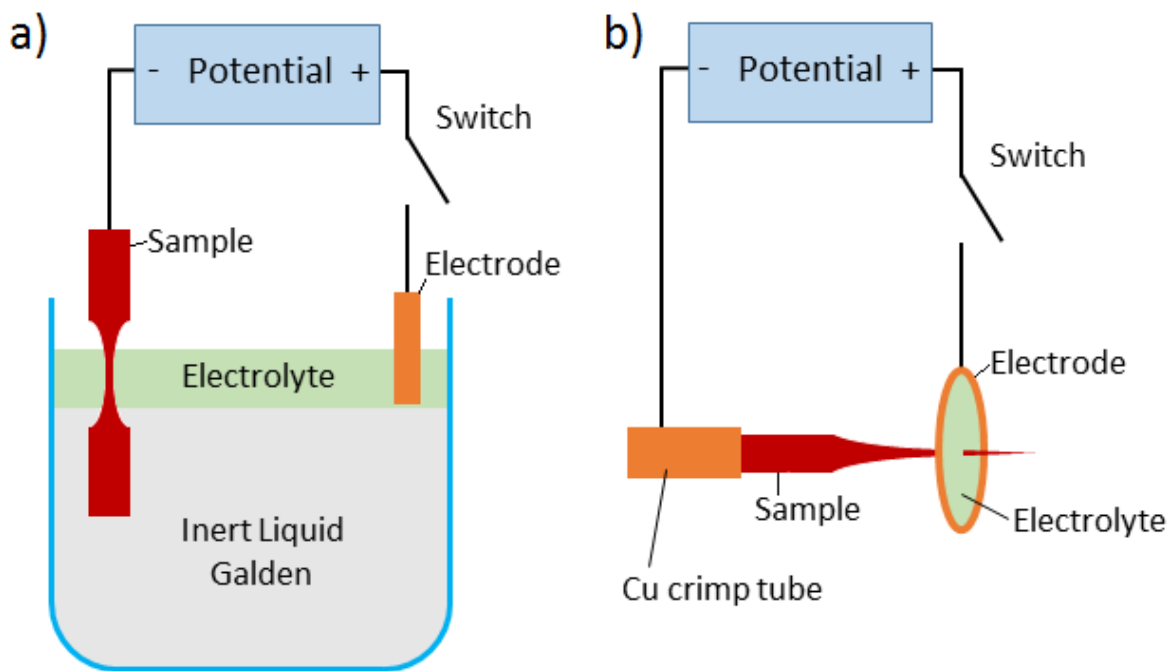


Figure 3.12 – Schematic of dual-stage electropolishing apparatus. a) Stage 1: Needle creation and rough polishing. b) Stage 2: Final polishing and tip shaping.

3.4.2.2 FIB Coupon Liftouts

Site-specific APT samples were created using a standard FIB liftout technique [125,126], in which the region of interest is extracted from the sample and mounted onto an array of pre-sharpened silicon tips as shown in Figure 3.13. This allows a small region of interest to be turned into multiple atom probe tips without having to mill away a large amount of the sample, which was ideal for the analysis of oxide layers covered in Chapter 5.

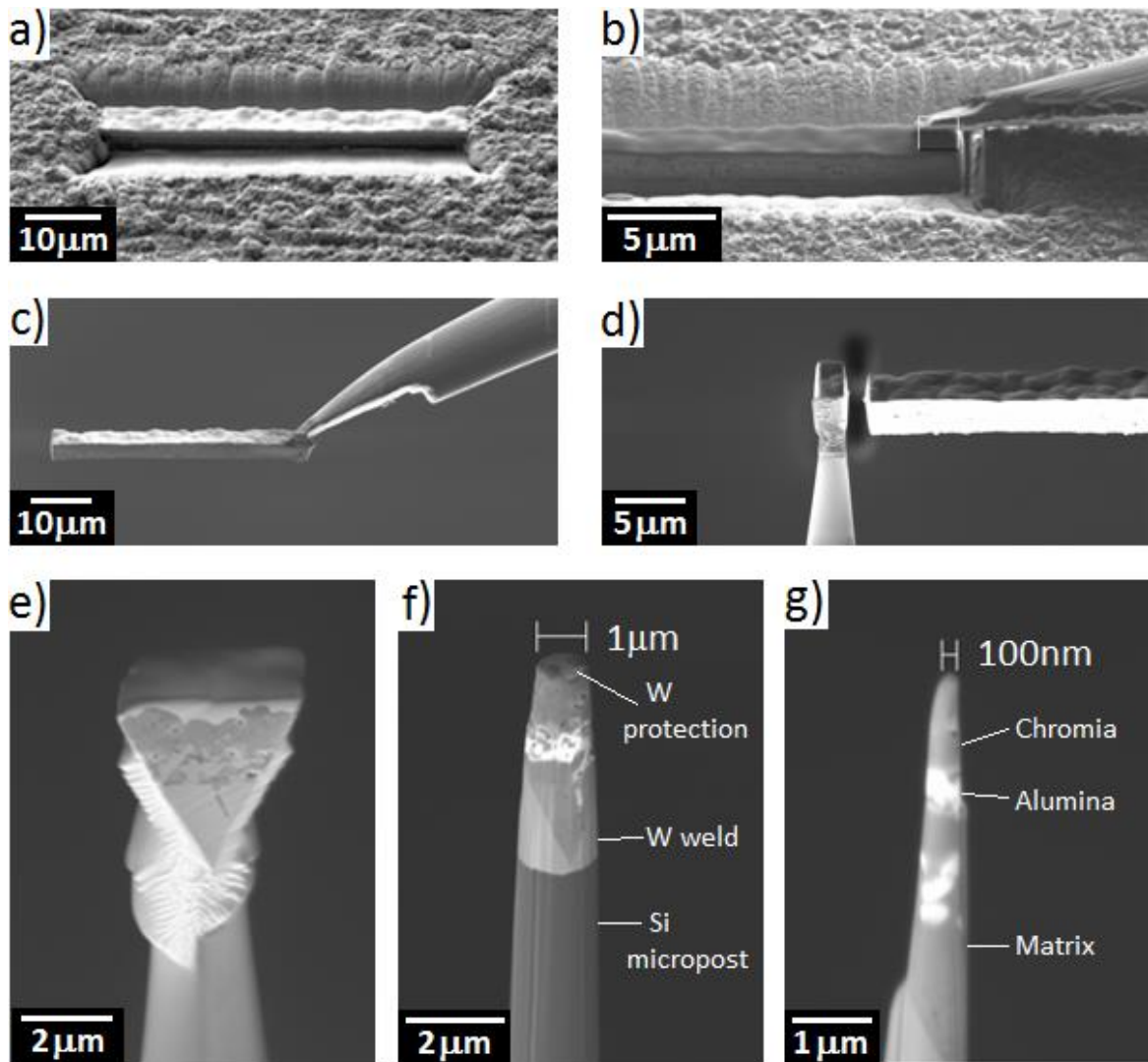


Figure 3.13 – FIB needle creation: a) Oxide layer + W protected liftout bar. b) Welding onto Kleindiek micromanipulator c) Liftout extraction. d) Attachment to silicon micropost. e) to g) Annular milling and final tip with labelled oxide regions.

In this case, regions of oxide above grain boundaries were identified during FIB cross-sectioning, and were protected from surface ion damage by the deposition of a $50\ \mu\text{m} \times 3\ \mu\text{m}$ rectangle of tungsten. Trenches were then cut along the sides of this rectangle, first perpendicular to the surface using a 30 kV, 3 nA beam, then at a 30° angle using a 30 kV, 1.5 nA beam to remove material beneath the protected region and create a liftout bar, as in [Figure 3.13 a](#)). Extraction of the liftout bar was achieved by touching a Kleindiek micromanipulator to the liftout surface, welding it in place using deposited tungsten, then snipping the other side of the liftout from the sample using a rastered 30 kV, 700 pA Ga^+ ion beam as in parts [b-c](#)). At this point, the rest of the

oxidised TGA sample could be removed from the FIB, and replaced with a coupon containing a silicon micropost array, allowing the creation of many individual atom probe tips from a single liftout.

Individual tips were created by tungsten welding the end of the liftout bar to a single silicon micropost, then separating this welded section and repeating until running out of either silicon microposts or the liftout bar as in part [d](#)). Each post containing a wedge of sample then underwent several annular milling steps to thin each tip down to a sub-100 nm tip diameter, as shown in parts [e-g](#)). These steps started off using a 30 kV, 300 pA ion beam, slowly reducing down to 30 kV, 150 pA as the tips approached 500 μm width, followed by a final polishing step via a 5 kV, 250 pA imaging mill.

The sample was oriented so that the full microstructural cross-section could be viewed throughout all of these steps, as demonstrated in part [e](#)). Micrographs were captured throughout the milling process so that depth estimates of the tip below the oxide surface could be made.

3.4.2.3 FIB Crack Tip Liftouts

Atom probe needles were created from the crack tip liftouts mounted on Cu tomography posts as previously described in [Chapter 3.3.4](#). These had already been sharpened down to thin lamella (of sub-200 nm thickness) to enable TKD analysis, so they were already primed to create a thin 100 nm tip diameter needle. Once a crack tip had been precisely located and characterised the redundant material at the sides of the lamella were removed, followed by the annular milling technique previously covered, as shown in [Figure 3.14](#). Samples were periodically analysed using both TKD and EDX to make sure that both the crack tip grain boundary and crack tip oxides remained within the sample.

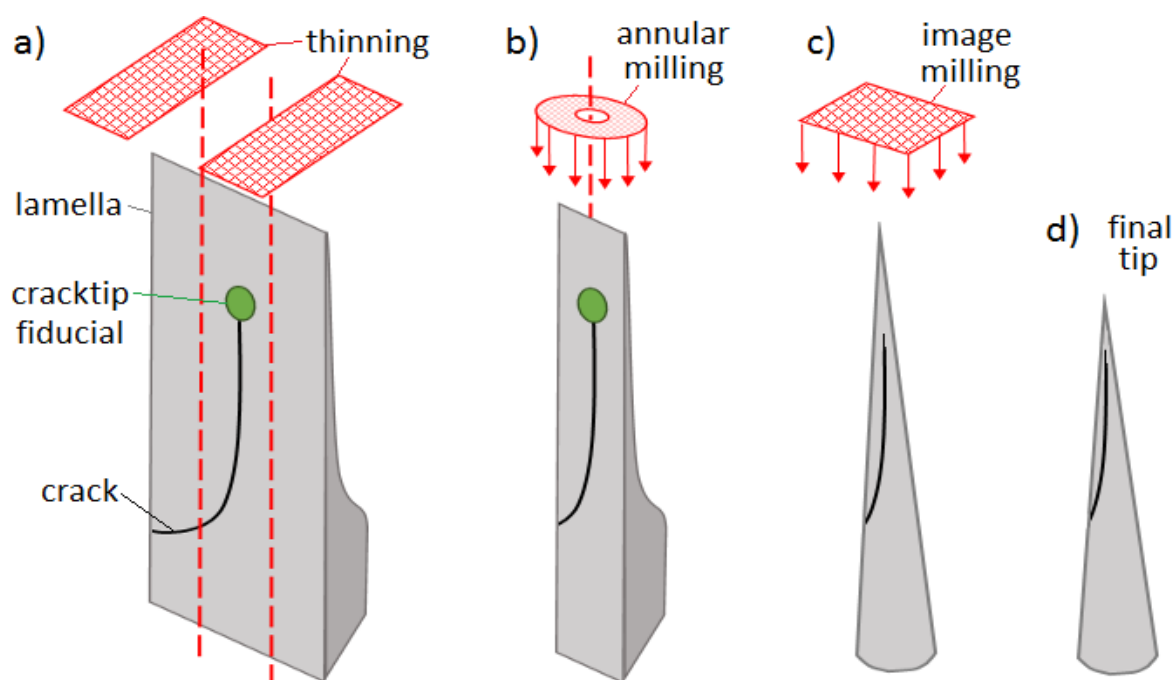


Figure 3.14 – Preparation of APT needle from TKD lamella a) Thinning lamella and centring region of interest (ROI). b) Annular milling around ROI to create circular needle. c) Imaging mill to remove material from top, leaving ROI within 300-400 nm of tip. d) Final APT tip.

3.4.3 Experimental Conditions

Several parameters can be adjusted before and during an APT experiment to optimise data collection and quality, and to prevent the fracture of delicate samples. An example of the tradeoff between data quality and sample integrity involves setting the sample base temperature, in which noise reduction and mass resolution are optimised using lower temperatures, while sample integrity is maximised at higher temperatures. All experiments performed in this thesis used a stage temperature of 50 or 55 K unless otherwise stated.

The majority of additional parameters involve the pulsing technique used to overcome the ion evaporation energy barrier, either by increasing the electric field during voltage pulsing, or through the addition of thermal energy via a laser pulse. All APT experiments performed during this project made use of laser-assisted evaporation, which differed slightly between the two atom probes used. A LEAP 3000X HR contains a green 532 nm wavelength laser, and was used to analyse the unoxidised specimens examined in [Chapter 4](#), as well as three of the oxidised samples

analysed in [Chapter 5](#). These samples were run at 50 K using a pulse frequency of 200 MHz with a laser energy of 0.5 nJ. All of the other oxidised samples and crack tip samples experiments performed in [Chapters 5 and 6](#) were examined using a LEAP 5000HR containing a 355 nm UV-wavelength laser. Oxide samples were run at 50 K using a laser energy of 50 pJ and a variable pulse frequency, which was optimised to top out the mass spectrum at 250 Da. Crack tip samples were run using varying conditions, optimised for valuable and fragile specimens by increasing sample base temperature and laser pulse energy.

While the voltage required to induce ion evaporation is mostly set by sample geometry, fine control of the voltage setpoint allows on-the-fly adjustment of the target evaporation rate, defined as the number of detection events per hundred pulses.

3.4.4 Data Analysis

All APT data have been reconstructed and analysed using the Cameca IVAS software suite. IVAS version 3.6.12 was used for all unoxidised samples in [Chapter 4](#), and IVAS version 3.8.0 was used for all oxide and crack tip samples in [Chapters 5 and 6](#). In addition, the freely-available APTtools [\[133\]](#) and AtomProbeLab [\[134\]](#) software suites were used for further rangefile and mass spectrum analyses.

The two-dimensional detector event histogram and time-of-flight information are turned into a fully realised three dimensional model via a multi-step reconstruction process. First, a back projection model is used to trace each detected ion back along the electric field lines to a point on the surface of a virtual sample [\[135,136\]](#). Each ion has X and Y co-ordinates which are calculated directly via back projection from the position sensitive detector, while the Z depth co-ordinate is calculated by incrementally advancing the virtual sample surface as each atomic layer is built up over time. A geometry correction is also applied to the time of flight data, in order to transfer

from the pseudo-stereographic projection of detector space into the standard (X,Y,Z) Cartesian co-ordinates of sample space.

After reconstruction, the dataset consists of a three-dimensional point cloud, with each point representing an ion with a specific mass-to-charge value measured in Daltons (Da). Peaks in this mass-to-charge spectrum are assigned to particular ionic species in a process called ranging. An example of a ranged reconstruction is shown in [Figure 3.15 a](#)), in which each element and its associated oxides are represented by a different colour. This allows easy visual identification of regions with different composition throughout the dataset. The ranging process itself is shown in [Figure 3.15 b](#)).

For simple metallic samples such as those found in [Chapter 4](#), most of the mass-to-charge peaks belong to elemental isotopes with a particular charge. The peak heights of each isotope of an element have a signature pattern determined by their relative isotopic abundance, which helps to establish peak identity and highlight possible peak overlaps. Both IVAS and AtomProbeLab software suites contain deconvolution algorithms to help separate peak overlaps into their constituent components [\[134,135\]](#).

For samples with a large amount of strongly-bonded phases, such as the oxides and carbides found in [Chapters 5 and 6](#), complex ionic species containing multiple elements are commonly detected. This makes ranging more difficult by vastly increasing the number of possible combinations of species. The mass-to-charge spectrum shown in [Figure 3.15 b](#)) is a particularly difficult one to analyse, demonstrating the large number of complex ionic species and overlapping peaks that can be present. The APTtools program `weights.exe` helps in this regard, by calculating all of the combinations of selected elements that can combine to give a certain mass-to-charge peak value [\[133\]](#).

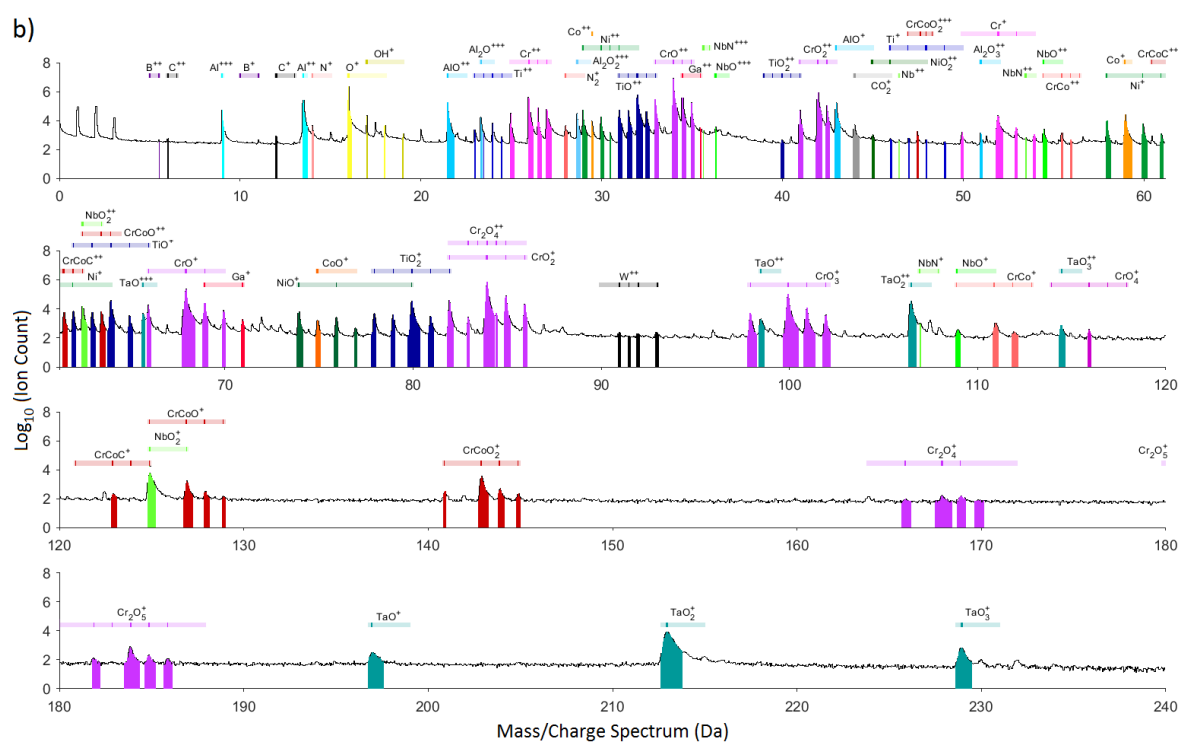
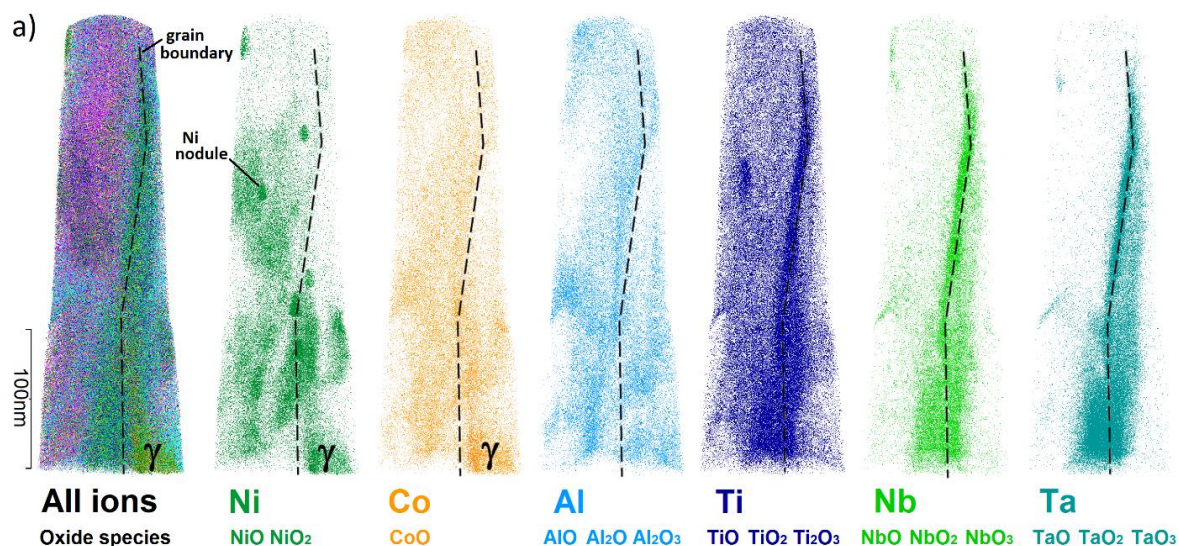


Figure 3.15 – a) A reconstruction from the chromia oxide layer formed on Alloy ABD-6 after TGA exposure at 800° for 100 hours, showing an oxide grain boundary enriched in Ti, Nb and Ta.

b) The corresponding mass/charge spectrum after processing in AtomProbeLab [134], with peaks coloured according to their ranged identity. The bars above each peak show the location of ranged ionic species, which helps to indicate potential overlaps.

Chapter 4. Phase Chemistry and Partitioning

This chapter describes the characterisation of the as-received ABD alloys with varying Ti:Nb ratio that were created prior to this project, following the alloys-by-design methodology outlined in [Chapter 2.4.2](#), and the composition and processing routes described in [Chapter 3.1](#). These experiments were carried out to investigate the character of these alloys in their pristine state, and to establish a baseline for comparison against later investigations into the damaged condition resulting from oxidation and fatigue.

4.1 Introduction

The physical properties of nickel-based superalloys are heavily influenced by their compositions, and the volume fractions of each phase present [\[46\]](#). These properties have been experimentally measured and compared against values predicted using Thermo-Calc, in order to verify and improve the models used during the alloy design process. Particular attention has been paid to the character of the γ' precipitate phase, which plays a major role in the high temperature strength of nickel-based superalloys [\[12\]](#). The volume fraction and size distribution of γ' precipitates are of great importance due to the dislocation-inhibiting mechanism by which γ' increases the strength of superalloys at high temperatures [\[15\]](#). These characteristics have been directly measured using the surface SEM techniques described in [Chapter 3.3.1](#), and indirect volume fraction measurements were subsequently calculated using γ' phase composition measurements. This requires high-resolution techniques due to the extremely small 20-50 nm size scale of the smallest tertiary γ'_{III} precipitates. Phase composition information also provides an insight into how each constituent element partitions, which is important when considering strengthening mechanisms that require particular element-phase configurations, e.g.: solid solution strengthening provided by W and Mo in the γ matrix phase [\[75\]](#), and the increase of anti-

phase boundary energy resulting from the presence of Ti and Nb in γ' precipitate phases [137,138].

There are two ultimate goals of this chapter. The first involves performing comparisons between the ABD alloys, to discern whether there are any microstructural or compositional effects caused by the replacement of Ti with Nb. The second involves comparing experimentally-derived alloy characteristics with the predictions made by Thermo-Calc, in order to assess the predictive accuracy of the Alloys-By-Design process, and provide useful feedback for model improvements.

4.2 Microstructural SEM Analysis

In order to characterise both the grain structure and the γ' precipitate distribution, SEM analysis was performed on samples polished using the methodology described in [Chapter 3.3.1](#).

Micrographs were taken from each of the studied alloys at two magnifications, with 500 $\times$ micrographs used for grain size analysis, and 20,000 $\times$ micrographs for secondary and tertiary γ' precipitate analysis. A representative selection of some of these micrographs are presented in [Figure 4.1](#).

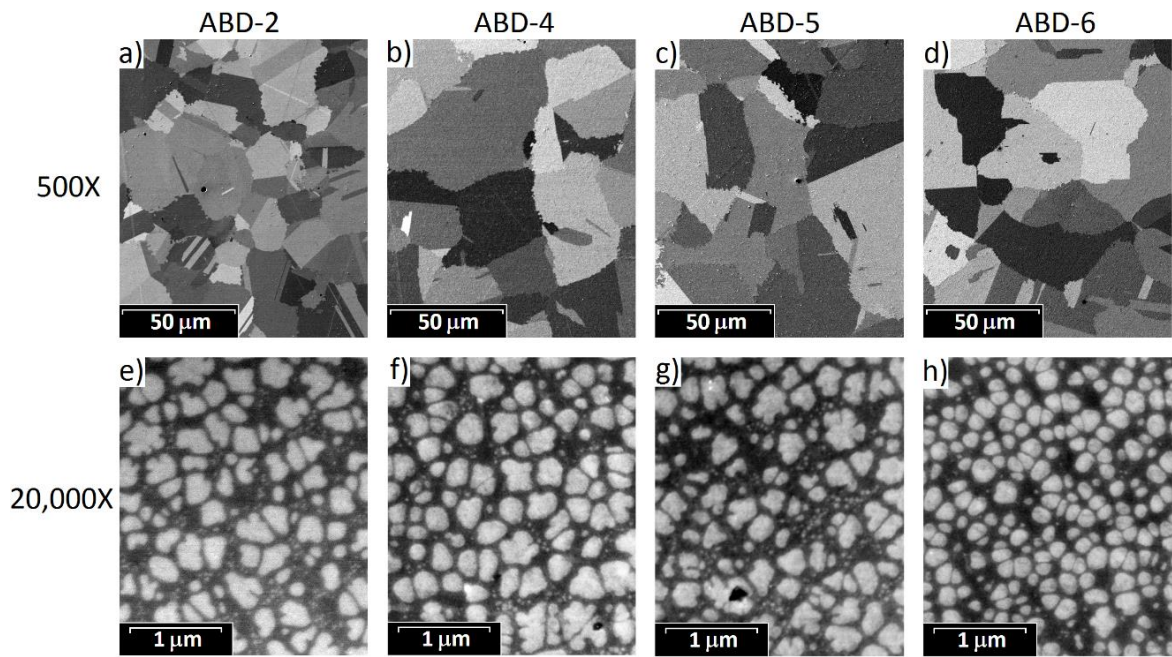


Figure 4.1 – SEM micrographs taken from polished samples of ABD alloys at two different magnifications. Parts a) to d) use a magnification of 500× for grain size analysis. Parts e) to h) use a magnification of 20,000× for γ' precipitate size analysis.

4.2.1 SEM Grain Size Analysis

Grains could be identified and distinguished in these micrographs due to their differing contrast under the electron beam, which was fortunate as there was no provision for performing a more comprehensive EBSD analysis during the early stages of the project. Upon initial visual inspection, many twin boundaries were observed, likely formed as the result of a stress-induced transformation during heat treatment [139]. Twin boundaries were regarded as grain boundaries for the purpose of this characterisation, as they are comparable in terms of physical properties such as yield strength [140] and fatigue crack propagation [141]. Grain boundaries were also observed to be serrated, with no additional phases or precipitates observed at this magnification. This was anticipated as carbides or borides are likely too small to see, and few large intergranular primary γ' are expected to persist through the two hour super-solvus heat treatment.

Grain sizes were measured from the SEM images using two methods as described in Chapter 3.3.1. The linear intercept method is the quicker and easier to apply of the two, for which six

randomly-oriented lines were analysed to give average one-dimensional intercept lengths of 48, 84, 94 and 94 μm for alloys ABD-2, 4, 5 and 6 respectively. The relationship between intercept length and grain diameter is not exceptionally well-defined [123], but the values are at least internally consistent, showing a correlation between grain size and increasing Nb:Ti ratio.

A more thorough analysis was performed in ImageJ [142], using the morphological segmentation tool available in the MorphoLibJ plugin [124], which measured and presented tabulated grain area data. This was converted to an effective grain diameter using the formula: $d = 2 \sqrt{(a/\pi)}$, where d = effective grain diameter and a = grain area, resulting in average grain diameters of 9, 10, 10 and 12 μm for alloys ABD-2, 4, 5, and 6 respectively. These are much smaller than the design target of 32-45 μm (7-6 ASTM) as specified in the patent relating to these alloys [143], which may be due to the effect of noise in the datasets, or the effect of twins decreasing the grain size. Comparing values across alloys also indicates a correlation between grain size and Nb:Ti ratio. The observed distribution of grain diameters has been plotted as a histogram with a 2 μm bin size in Figure 4.2, in which the shift towards higher grain sizes can be seen in the higher Nb alloys.

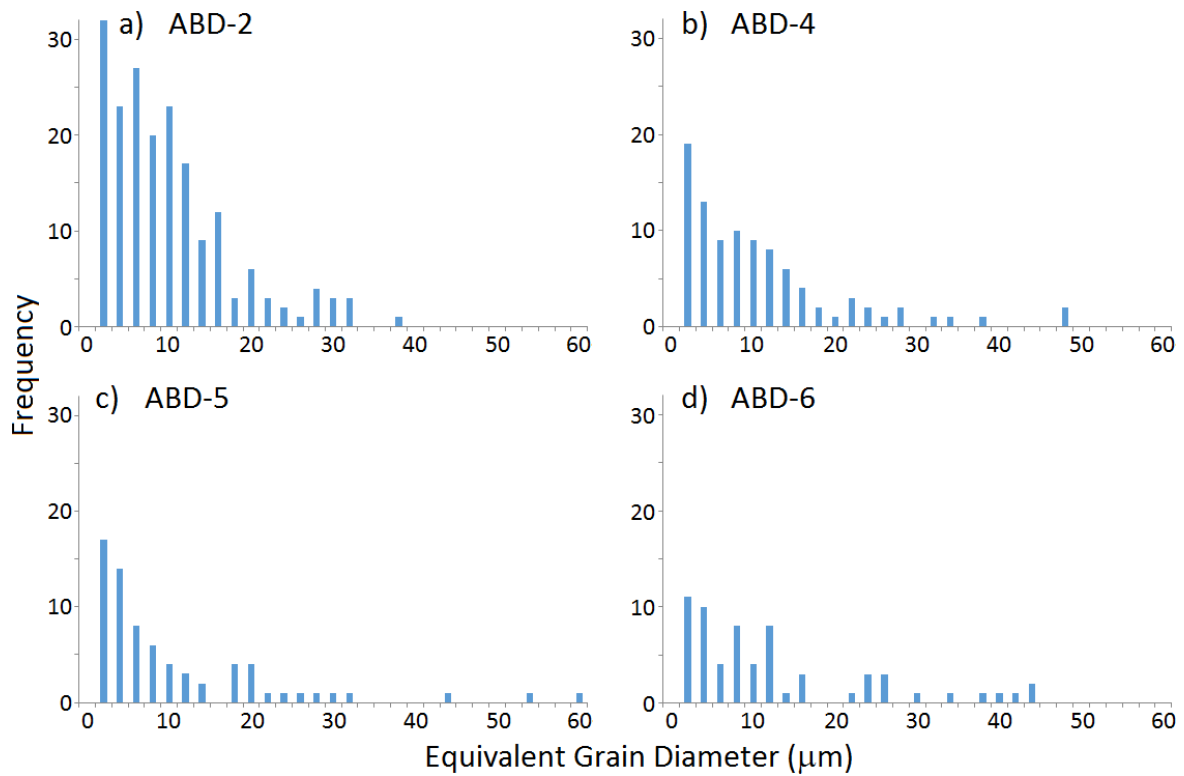


Figure 4.2 – Images a) to d) show equivalent grain diameter distribution histograms from alloys ABD-2, 4, 5 and 6 respectively. Histograms have been generated using a 2 μm bin size.

4.2.2 SEM γ' Precipitate Analysis

SEM micrographs used for γ' precipitate analysis were taken from intragranular regions to avoid misidentification of other grain boundary phases as γ' , and also as very little primary γ' was expected to persist through the two hour super-solvus heat treatment. At a magnification of 20,000 $\times$ secondary and tertiary γ' precipitates could easily be identified as lighter regions within the darker γ matrix. The secondary γ'_{II} precipitates showed some variation in morphology from spheroid, to cubic, to the clover-leaf shaped 'octodendritic' [144]. One notable exception to this can be seen in the high-Nb alloy ABD-6, which consists solely of secondary γ'_{II} precipitates in a much narrower size range with a spheroidal morphology as shown in Figure 4.1 h). The morphology of tertiary γ'_{III} precipitates is more difficult to identify as their sub-50 nm size range is at the low resolution limit, but appear to be spheroid.

A more thorough analysis was carried out in ImageJ, using the inbuilt particle analysis tool to determine the γ' cross-sectional area fraction and size distribution, following the methodology described in [Chapter 3.3.1](#). The small size of many of the tertiary γ'_{III} precipitates lead to significant amounts of noise during the ImageJ particle analysis, which was mitigated somewhat by discounting precipitates with an area less than 300 nm² (equivalent diameter 19.5 nm), which represents any precipitate covering less than nine pixels of the SEM micrograph at 20,000 $\times$ magnification. Precipitate volume fraction was found by summing individual precipitate areas to find the total γ' cross-sectional area fraction for each micrograph. According to Delesse and Rosiwal [122], volume fraction can be estimated to equal cross-sectional area as long as the analysis plane is flat. Three micrographs were generated for each alloy, resulting in mean average γ' volume fraction measurements of 48 %, 48 %, 43 % and 47 % for Alloys ABD-2, 4, 5, and 6 respectively (as summarised in [Table 4.2](#) in [Chapter 4.4.2](#)).

The size distribution histograms for γ' precipitates are shown in [Figure 4.3](#), which are summed over three micrographs from each alloy by grouping into 20 nm bin increments. The three low-Nb alloys; ABD-2, 4, and 5, all show peaks around 40 nm equivalent diameter, which correspond to the smallest tertiary γ'_{III} precipitates not discounted as noise. Secondary γ'_{II} precipitates appear to have a bimodal size distribution with precipitates in ABD-2, 4 and 5 averaging 140 nm or 260 nm diameter. The outlier here is the high-Nb alloy ABD-6, with very few tertiary γ'_{III} precipitates and a unimodal secondary γ'_{II} distribution peak centered around 180 nm.

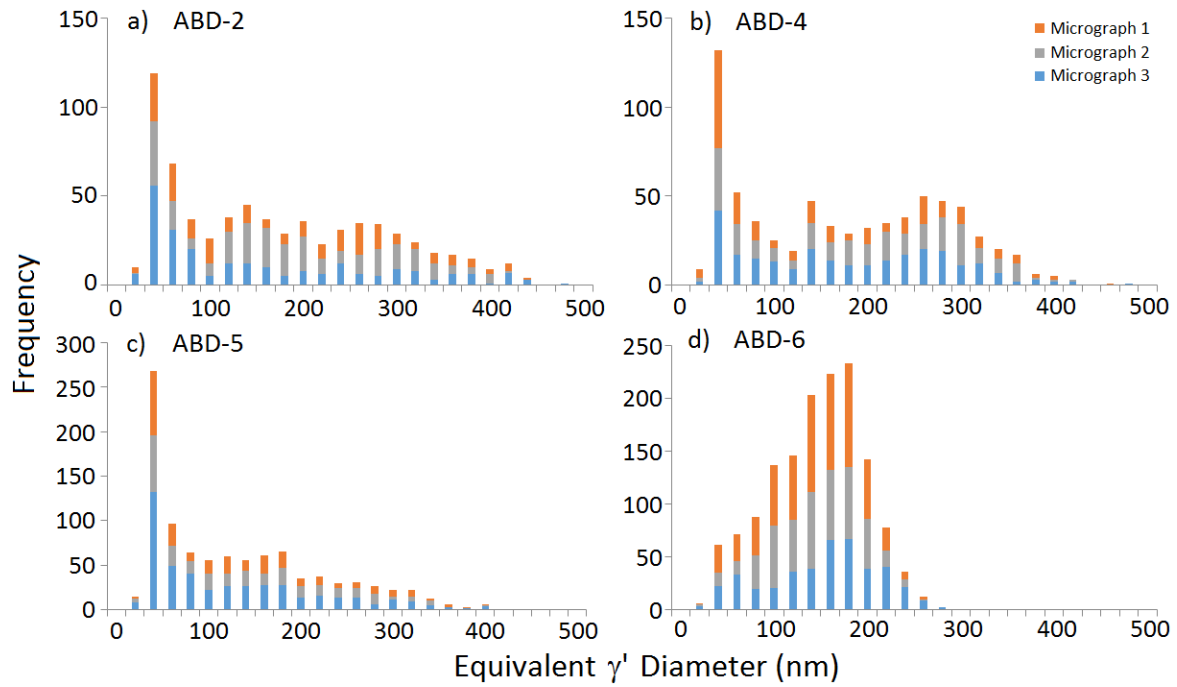


Figure 4.3 – Images a) to d) show equivalent γ' precipitate diameter distribution histograms summed over three separate SEM micrographs from alloys ABD-2, 4, 5 and 6 respectively. Histograms have been grouped using a 20 nm bin size.

4.3 Atom Probe Tomography

Using the methodology described in [Chapter 3.4](#), a total of eight successful atom probe experiments were performed, consisting of two specimens per alloy. The subsequent reconstructions varied in size from 26 to 105 million ions, all of which are shown in [Figure 4.4](#). These reconstructions share the same scale, to further allow comparison between them. During the ion ranging step, colour ranges were carefully chosen to aid visual identification, with γ matrix partitioning elements such as Cr and Co represented using red, pink and orange, while γ' precipitate partitioning elements such as Al, Ti and Nb are coloured using blue and green. The precipitate phases are immediately apparent due to the change in colour, resulting from a change of phase composition.

In these APT reconstructions, the γ' precipitate phase can be observed assuming a wide variety of sizes and morphologies; ranging from tiny spherical tertiary γ'_{III} on the scale of 20 nm, up to the

large clover-leaf shaped ‘octodendritic’ secondary γ'_{II} of at least 300 nm length shown in [Figure 4.4 f](#)). Also present are a few intrinsic and extrinsic sample features; An example of an intrinsic feature is the blue region at the bottom of part [f](#)), which is highly enriched in boron and likely to be a grain boundary boride. The most obvious examples of extrinsic features are the yellow regions at the top of reconstructions [e](#)) and [g](#)), which mostly consist of Cr, Co and Ni oxides that have formed along the γ - γ' interface. This is unlikely to be elemental or diffused oxygen, as a range of complex oxygen-containing ionic species were detected.

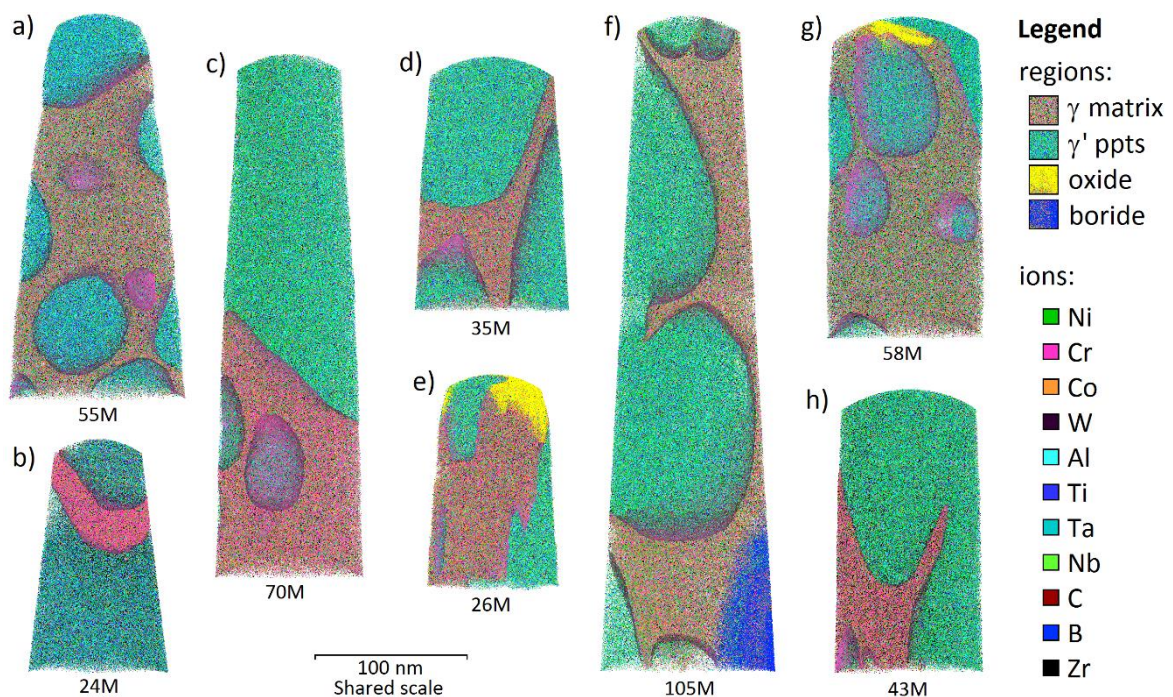


Figure 4.4 – All eight reconstructions from unoxidised ABD alloys, labelled with total ion count beneath. The wide variety of γ' precipitate sizes and morphologies can be seen, including large octodendritic γ'_{II} + small spheroid γ'_{III} . A 22.5 at.% Cr isosurface is also shown in each reconstruction, as used to define phase boundaries. Alloy ABD-2 is shown in parts a) and b), ABD-4 in c) and d), ABD-5 in e) and f), ABD-6 in g) and h).

[Figure 4.5](#) consists of a single 20 nm thick slice clipped from a reconstruction of the ABD-5 alloy (the same as shown in [Figure 4.4 f](#)). Each element has been displayed individually in part [a](#)) in order to highlight their phase preference. All elements appear to partition as expected; Ni occurs throughout the sample with a 2:1 $\gamma':\gamma$ ratio, while Al, Ta, Ti and Nb all partition to γ' precipitates,

and Cr and Co partition to the γ matrix. W only appears to show a very slight preference for the γ matrix. These visual appraisals are qualitative – A full quantitative analysis of phase chemistry and partitioning has been carried out in [Chapter 4.3.1](#).

Another subtle feature of [Figure 4.5 a\)](#) involves the distribution of the ions. The γ - γ' interface in particular appears to show a discontinuity; ions which partition to the γ matrix appear to have a sharp, well-defined interface, while ions which partition to the γ' precipitate show a more diffuse interface. This is most evident in the Ni atom map, as Ni appears in both phases. An ion density analysis was carried out for this reconstruction as shown in [Figure 4.5 b\)](#), with regions of higher density shown in red and low density shown in blue. It can be seen that the highest ionic densities occur on the matrix side of the γ - γ' interface, while the lowest densities occur on the precipitate side of the interface. This disparity is likely to be an artefact caused by ion trajectory aberrations, likely to be induced by the higher electric field required to evaporate the γ' precipitates [\[145\]](#).

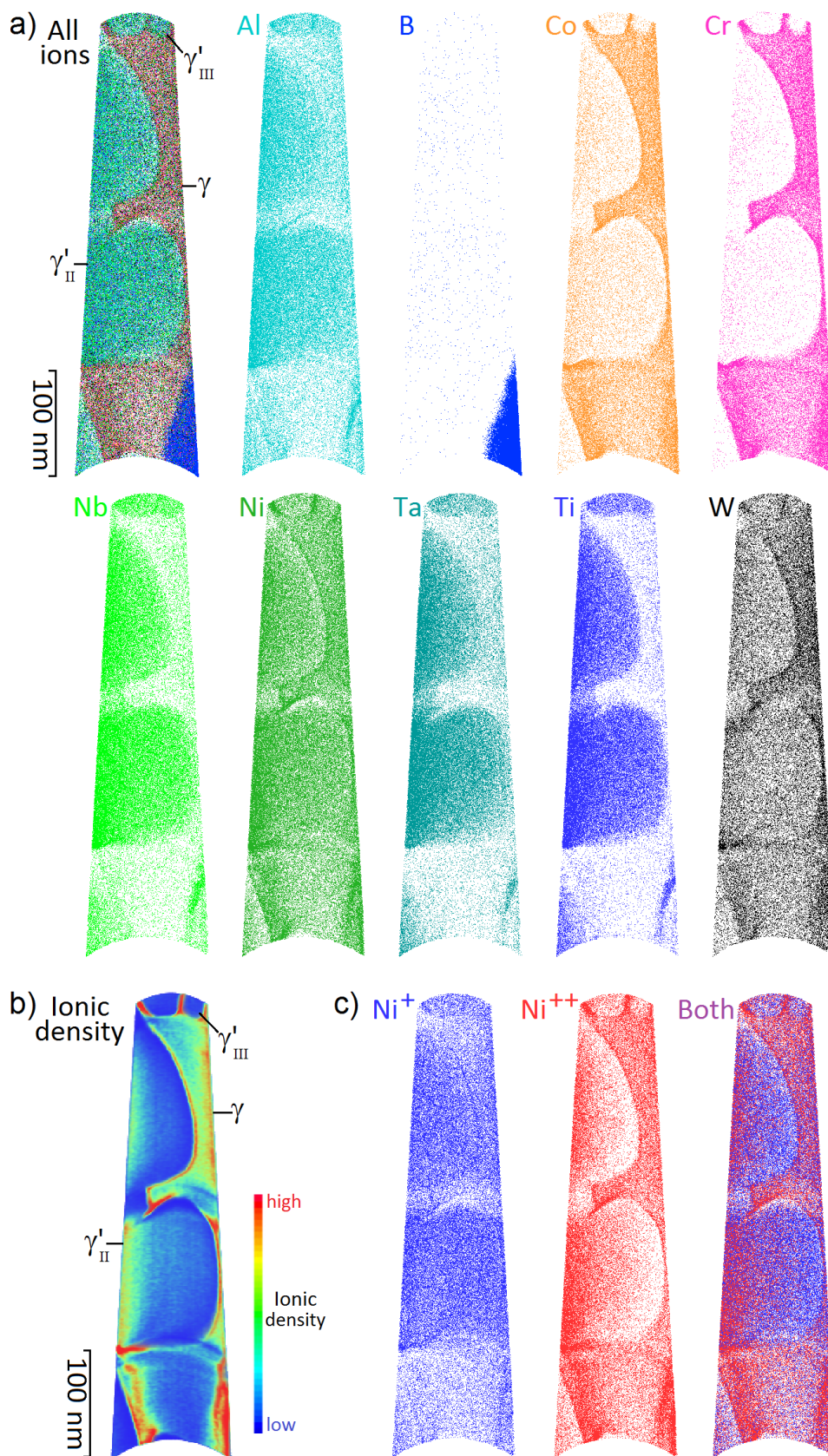


Figure 4.5 – All atom maps are from a 20 nm thick slice from a reconstruction of the ABD-5 alloy.
a) Individual elements separated to highlight elemental partitioning to different phases.
b) Ionic density map showing higher apparent density of ions at γ - γ' interface, likely resulting from trajectory aberrations. c) All Ni ions, separated into individual charge states.

The increase in field required to evaporate γ' precipitates can also cause the charge state of evaporated ions to change in different regions of the reconstruction, as shown in [Figure 4.5 c](#)). Ni ions are observed as doubly-charged Ni^{++} ions on the γ' precipitate side of the boundary, and singly-charged Ni^+ on the matrix side. Ordinarily this is not an issue as both charge states would be ranged as the same ionic species, but problems may ensue if peaks from one charge state are misranged or involved in an overlap.

4.3.1 Phase Compositions

Defining a discrete phase boundary makes performing phase composition analysis much easier, although care must be taken as fully two-dimensional phase boundaries are a useful abstraction rather than a physical reality, even in the coherent γ - γ' interface found in Ni-based superalloys. What inevitably occurs in atom probe reconstructions is a boundary region with mixed composition, especially where one phase requires a higher evaporation field thus leading to the trajectory aberrations mentioned previously [\[146\]](#).

To define a useful all-purpose γ - γ' interface, a region of interest was created across the interface of a γ' precipitate, along which an elemental concentration profile was plotted as shown in [Figure 4.6 a](#)). It was decided that the interface could be most precisely defined using the element with the strongest partitioning behaviour at the steepest point of the concentration profile. Using these criteria the γ - γ' phase boundary was defined by a 22.5 at.% chromium isoconcentration surface. A concentration profile was calculated as a function of the distance to this isosurface, also known as a proximity histogram (or 'proxigram' [\[147\]](#)), which is shown in [Figure 4.6 b](#)).

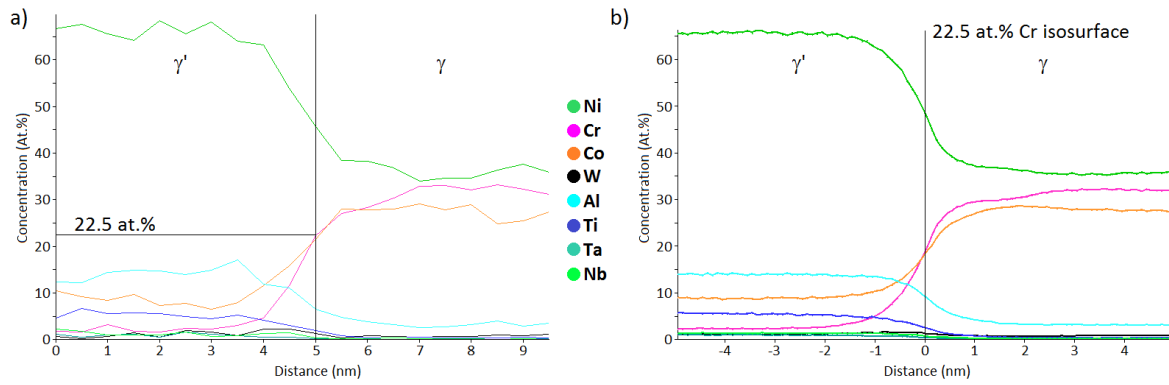


Figure 4.6 – a) 1D concentration profile used to define γ - γ' interface, used to inform the creation of a 22.5 at.% Cr isosurface. b) Proxigram created across the previously defined isosurface.

4.3.1.1 Individual γ' precipitates: Composition Vs Size

Due to the importance of γ' composition and size distributions, the study of size-composition relationships in γ' precipitates is an active area of research [148–151]. The larger secondary γ'_{II} are the initial precipitates to form after heat treatment, while the cooling material is still rich in solute. Smaller tertiary γ'_{III} form afterwards when the material is less solute-rich, so a change in composition between the γ' generations would be anticipated. With precipitate composition as the main focus, the γ - γ' interface for compositional measurement was defined using a 7 at.% Cr isosurface in order to reduce the amount of γ matrix material included within the outer shell of the precipitates. Minimizing the amount of surrounding matrix in this measurement is important, as the surface area-to-volume ratio is another size-dependent variable which could mask any size-composition relationships. As the matrix cannot entirely be removed using an isosurface, a slight slope in the size-composition graph is expected in any elements that show a phase preference due to the surface area-to-volume relationship.

Another potential source of error lies in the small scale of APT analysis, which means that only tertiary γ'_{III} precipitates are small enough to reside entirely within the reconstruction volume, and Many secondary γ'_{II} precipitates are not fully encapsulated within the reconstruction. An attempt was made early in the analysis to estimate the proportion of each precipitate captured and scale

accordingly, but this is a highly subjective judgment which would likely replace one source of error with another.

The resulting γ' precipitate compositions are shown in [Figure 4.7](#), in which the concentrations of each element present in a precipitate are plotted against the total ion count of that precipitate on a logarithmic scale. Points marked with a solid circle represent tertiary γ'_{III} precipitates fully encapsulated within the dataset, of which there were only four across all eight reconstructions. Points marked with a cross represent all other precipitates which do not contain the total ion count, and must be analysed accordingly. Ti and Nb γ' compositions have been separated per alloy, as these are the only two elements to change in the nominal alloy compositions.

The four fully encapsulated precipitates do show some slight trends with changing Ti:Nb ratio, such as Cr and Co which are both γ matrix partitioning elements but appear at slightly increased concentration in larger precipitates. This is the opposite trend that would be expected if the only source of these elements is the γ -enriched shell, indicating that another mechanism may be at work. For most elements, the data from non-encapsulated precipitates appears to follow the same trends, despite the fact that they are likely to be misrepresentative of the true precipitate ion count. Interestingly, the non-encapsulated data from W and Ta both appear to show a slight correlation with precipitate size, with W showing a positive correlation and Ta showing a negative correlation. However, the lack of a trend in the four trusted data points means that no conclusions have been drawn from this.

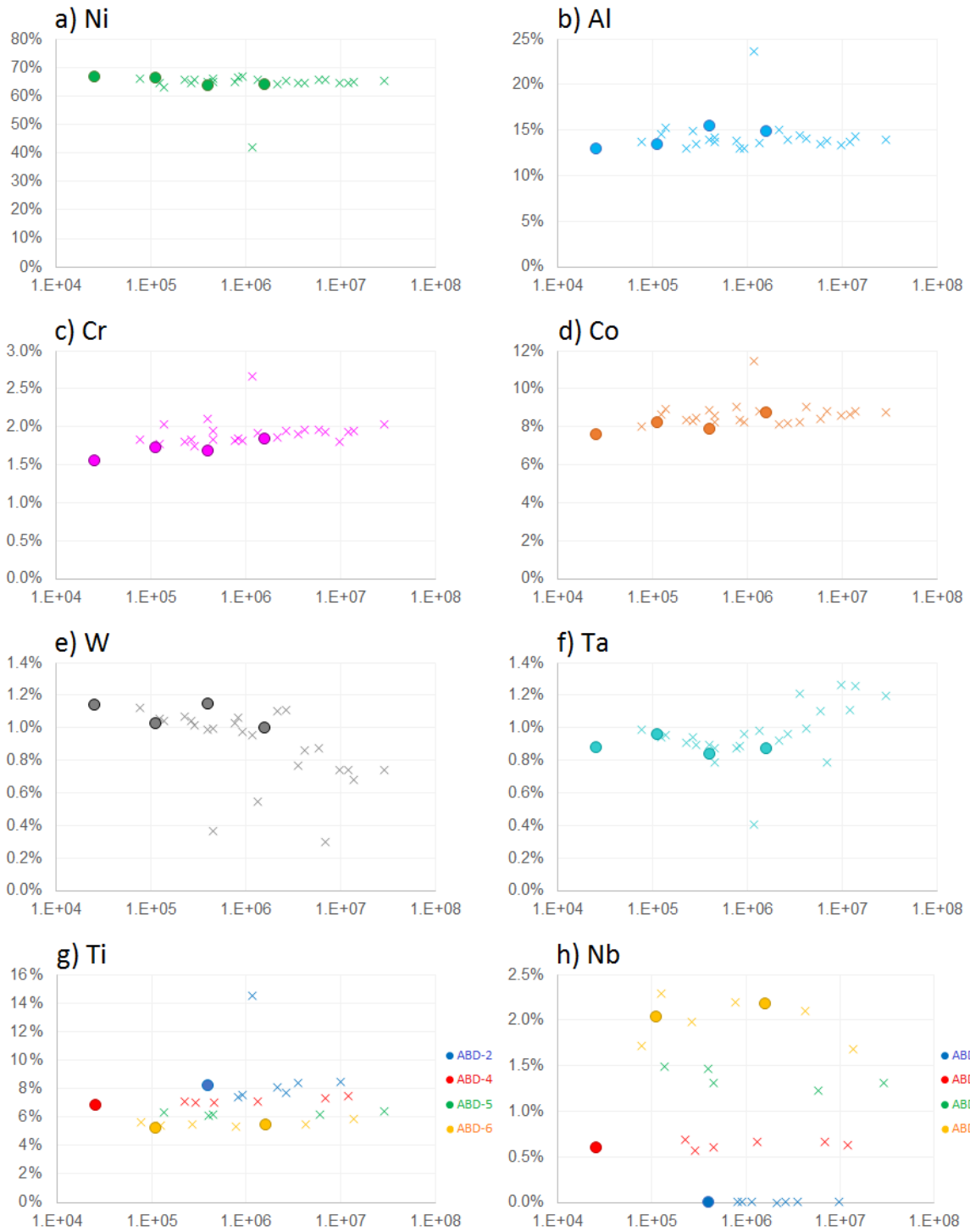


Figure 4.7 – Element concentration present in γ' precipitates, plotted as a function of precipitate ion count. Fully encapsulated tertiary γ'_{III} precipitates marked with ●, and all other precipitates marked with *. Parts g) and h) differentiate alloys due to the change in nominal Ti and Nb concentrations.

4.3.1.2 Total Average Phase Compositions

As the precipitate compositions displayed only a slight correlation with size, a weighted average could be calculated using a combination of secondary and tertiary γ' precipitates. Matrix compositions were also averaged from several regions of interest per dataset. The average phase compositions from both reconstructions from each alloy are presented below in Table 4.1, and plotted in Figures 4.8 and 4.9. All compositions were calculated using a 10 nm × 10 nm × 10 nm region of interest located far from any γ - γ' interfaces to avoid any deviations resulting from segregation or reconstruction artefacts.

Alloy/sample	Phase	Ni	Cr	Co	W	Al	Ti	Ta	Nb
ABD-2	Total	41.9	26.3	21.7	1.0	5.8	2.4	0.3	0.0
	a γ	33.7	35.2	26.3	0.9	2.8	0.4	0.0	0.0
	γ'	64.3	2.0	8.4	1.0	14.6	8.0	1.0	0.0
	Total	56.8	8.3	12.7	0.7	11.9	7.3	1.0	0.0
	b γ	31.7	35.7	28.1	0.6	2.1	0.3	0.2	0.0
	γ'	66.3	1.8	8.7	0.5	12.6	8.3	1.3	0.0
ABD-4	Total	45.6	22.2	20.6	1.0	6.6	2.8	0.4	0.3
	a γ	34.7	33.5	27.2	1.0	2.5	0.4	0.1	0.1
	γ'	65.0	2.1	8.9	0.9	14.0	6.9	1.0	0.6
	Total	51.2	16.3	16.5	0.8	8.9	4.5	0.7	0.4
	b γ	33.7	34.2	26.8	1.2	3.0	0.5	0.1	0.1
	γ'	65.5	1.9	8.6	0.9	13.2	7.1	1.0	0.6
ABD-5	Total	46.8	21.3	19.4	0.8	6.6	2.5	0.4	0.5
	a γ	36.9	32.4	25.8	1.1	2.6	0.3	0.1	0.1
	γ'	65.2	2.0	8.6	0.9	13.7	6.1	1.1	1.3
	Total	48.1	19.7	19.4	0.7	7.5	2.9	0.5	0.7
	b γ	36.3	32.3	27.0	0.7	2.5	0.4	0.1	0.2
	γ'	64.9	2.2	8.6	0.9	13.9	6.3	1.1	1.3
ABD-6	Total	40.0	28.4	23.1	0.9	4.9	1.3	0.2	0.6
	a γ	34.7	34.2	26.1	1.1	2.5	0.3	0.1	0.3
	γ'	64.5	2.0	8.9	0.9	14.3	5.4	1.0	2.1
	Total	54.1	13.8	15.0	0.8	10.2	3.9	0.8	1.2
	b γ	32.8	36.0	25.8	1.1	2.7	0.3	0.1	0.2
	γ'	64.8	2.1	8.8	0.5	14.3	6.0	1.3	1.6

Table 4.1 – Total and average phase compositions (at.%) observed via APT for major alloying elements in ABD series superalloys. Grain boundary segregating elements such as Zr, B and C have been omitted due to the lack of grain boundaries in reconstructions.

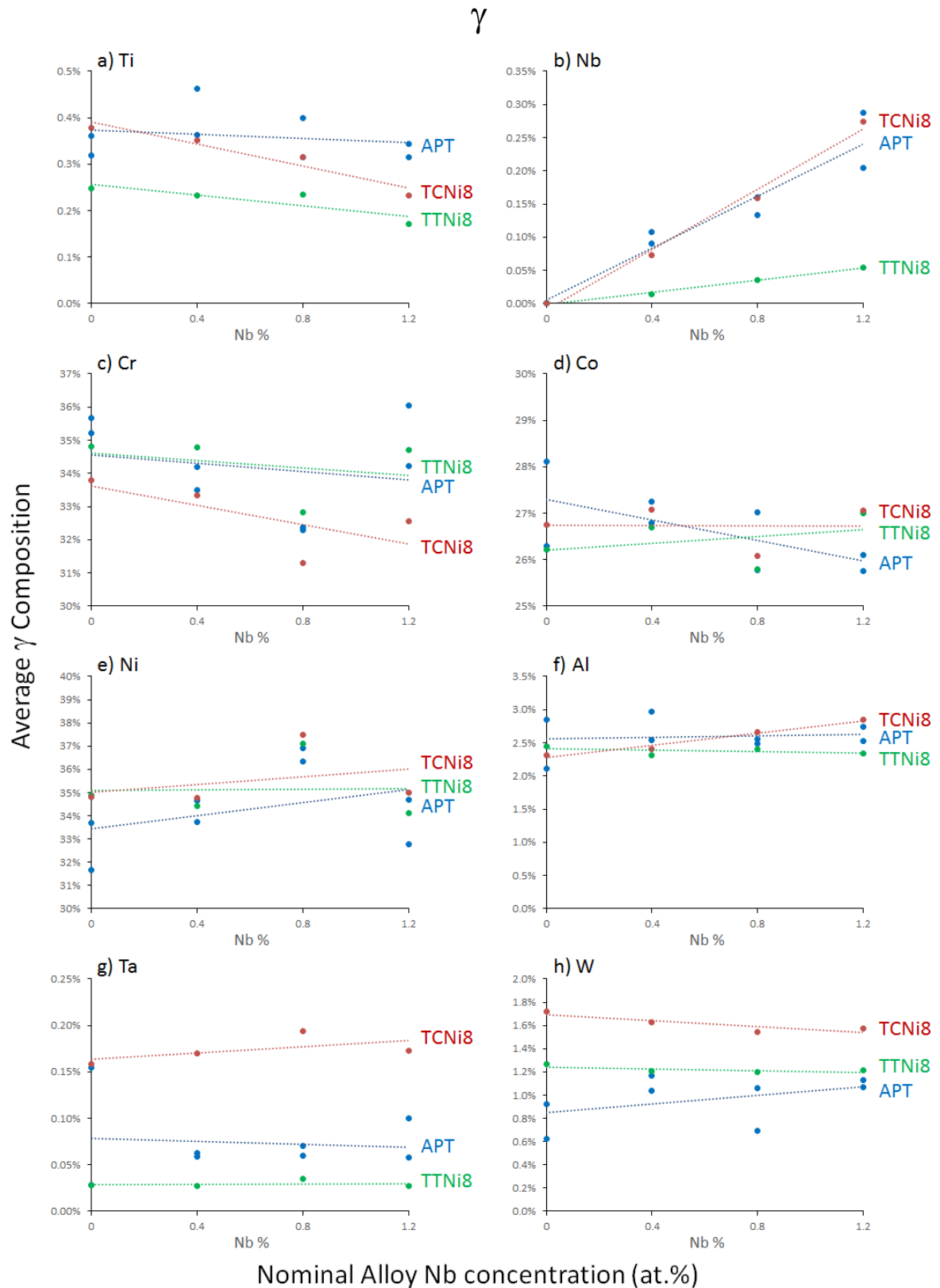


Figure 4.8 – Gamma phase compositions (in at.%) observed via APT for major alloying elements in ABD series superalloys, plotted against Nb nominal alloy composition (in blue). Also plotted are gamma phase compositions predicted using Thermo-Calc based on two databases: TCNi8 (in red) and TTNi8 (in blue).

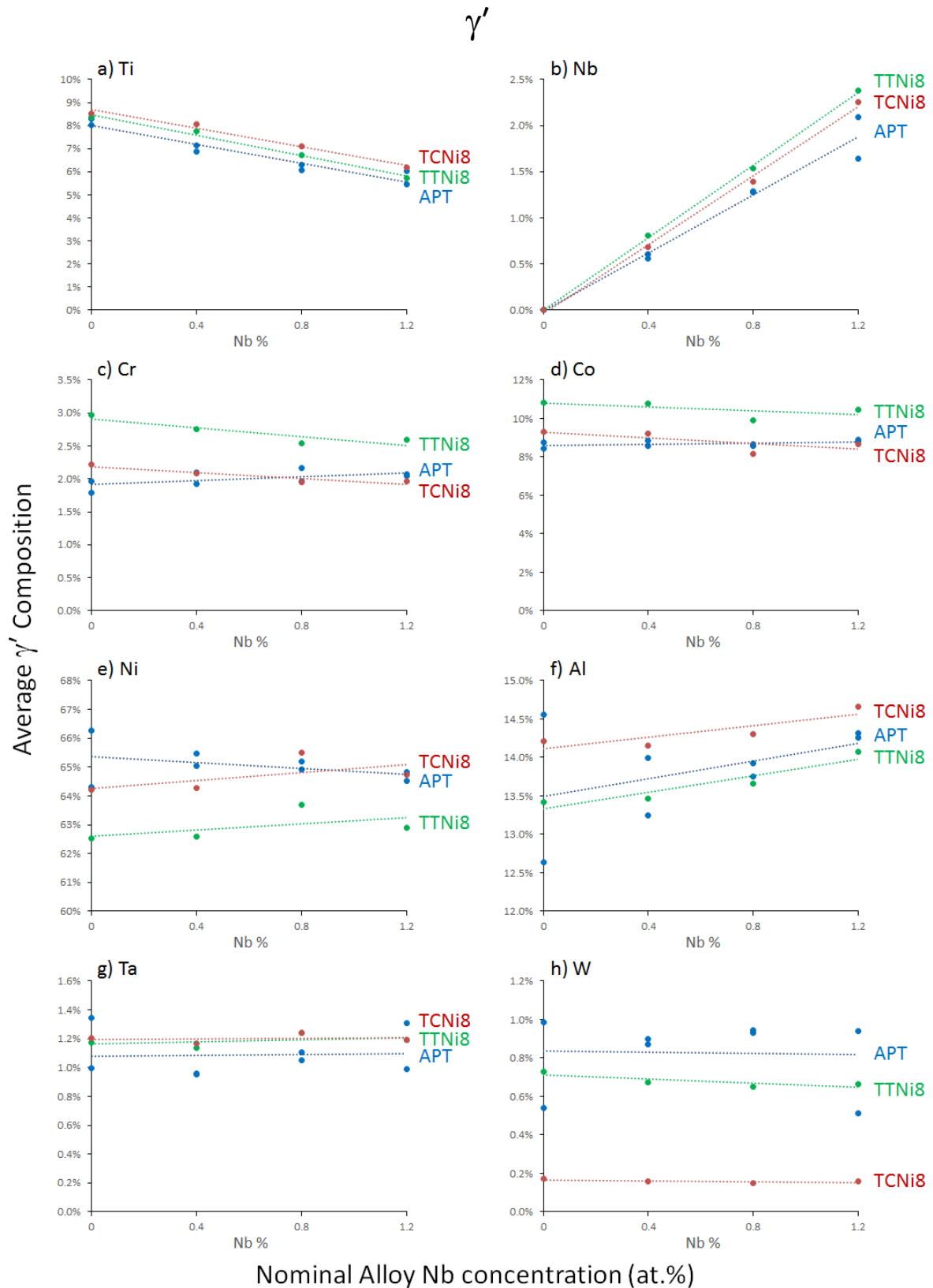


Figure 4.9 – Gamma prime phase compositions (in at.%) observed via APT for major alloying elements in ABD series superalloys, plotted against Nb nominal alloy composition (in blue). Also plotted are gamma prime phase compositions predicted using Thermo-Calc based on two databases: TCNi8 (in red) and TTNi8 (in blue).

4.3.1.3 Phase Partitioning

Experimental observations of composition allow direct comparisons to be made between alloys, or between an alloy and its thermodynamically predicted properties, but cannot easily be used as a metric of material properties. One method of transforming composition data into a more useful metric is the partitioning coefficient ($K^{\gamma'/\gamma}$), which is defined as the average concentration of a particular element in the γ' precipitates divided by the average concentration of that element in the γ matrix. Consequently, high $K^{\gamma'/\gamma}$ values indicate that this element partitions strongly to γ' , while elements with near-zero $K^{\gamma'/\gamma}$ partition strongly to γ . Figure 4.10 shows the partitioning coefficients of all major constituent elements across the four alloys, with $K^{\gamma'/\gamma}$ values calculated using APT measurements shown in blue, compared against values Thermo-Calc predictions made using two separate databases (TCNi8 in red, TTNi8 in green) with the as-manufactured alloy compositions.

Partitioning

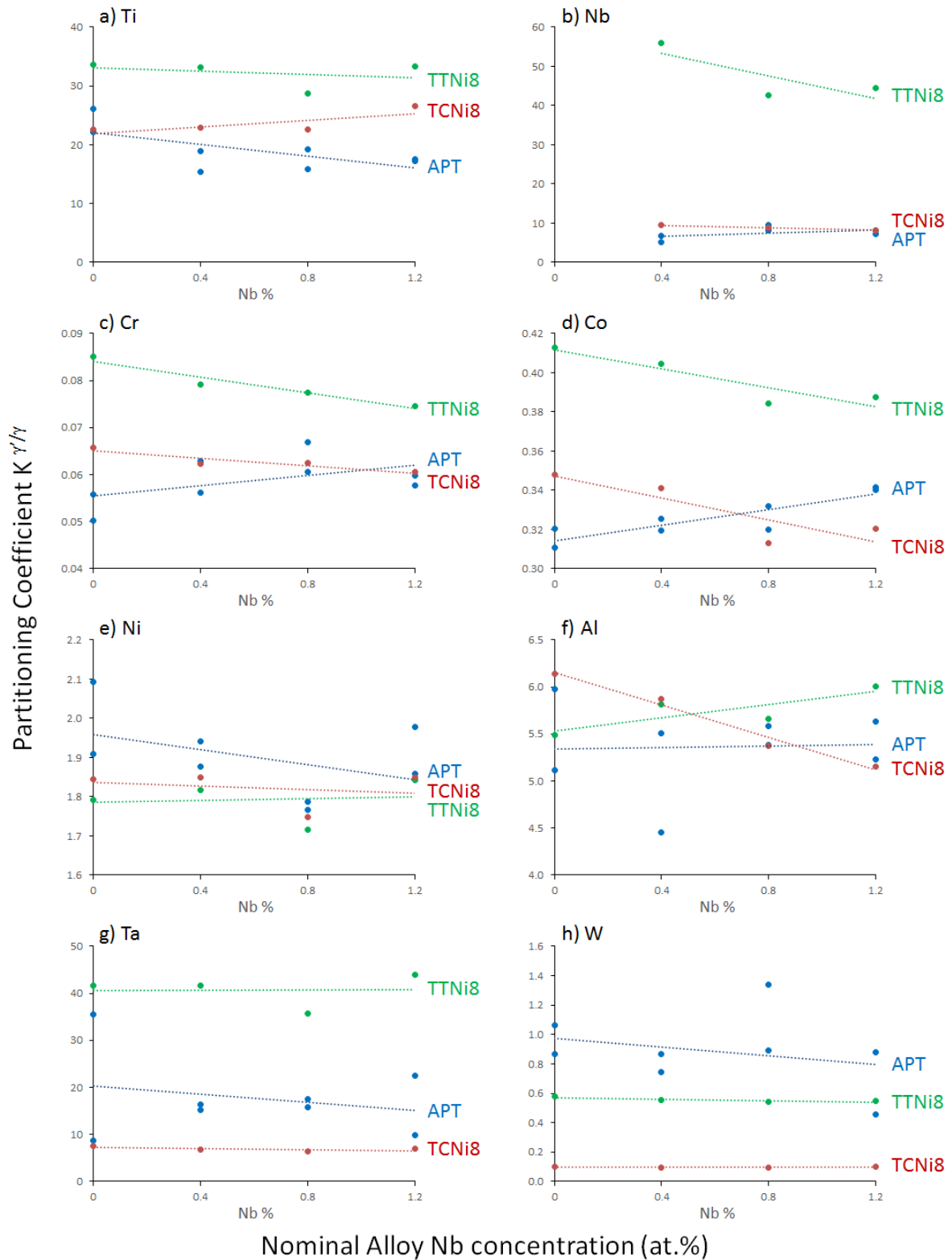


Figure 4.10 – Partitioning coefficients of all major constituent elements as a function of Nb at.%, representing the four alloys studied. APT data are represented in blue, with Thermo-Calc made using TTNi8 and TCNi8 databases shown in green and red.

A number of general trends can be discerned in these graphs. First is that the predictions made using the two databases give different predictions of partitioning behaviour, especially in the case of Nb and Ta which show over a factor of four difference between the two databases. On the whole, it seems that the TCNi8 database gives values which are numerically closer to observed APT measurements, although often show an opposite trend with increasing Nb at.%. The spread between the two APT measurements tends to be less than the spread between the two Thermo-Calc databases. Another point of interest is that observed APT partitioning values for Ti, Nb, Cr, Co and Al tend to lie on the lower end of the range of Thermo-Calc $K^{\gamma'/\gamma}$ values, indicating that they are more prevalent in the γ matrix than thermodynamic predictions would suggest. This trend is counteracted by Ni and W, which partition to γ' precipitates more than predicted, with W showing $K^{\gamma'/\gamma}$ values around 1 indicating no partitioning preference. Ta is the only element to sit directly between the two Thermo-Calc predictions. These complex behaviours are further discussed in [Chapter 4.4.3](#).

Determination of phase chemistries allows an estimate of the γ' volume fraction $\phi_{\gamma'}$ to be made using a derivation of the lever rule as written in [Equation 4.1](#). [152]:

$$C_n = \phi_{\gamma'} C_{\gamma'} + (1 - \phi_{\gamma'}) C_{\gamma} \quad (\text{Eq. 4.1})$$

where C_n is the concentration of an element present in the nominal alloy composition, and C_{γ} and $C_{\gamma'}$ are the concentrations measured in the γ and γ' phases respectively. The γ' volume fraction can be estimated by plotting $C_n - C_{\gamma}$ versus $C_{\gamma'} - C_{\gamma}$ for each element, and measuring the gradient of the best fit line, as shown in [Figure 4.11](#). Partitioning characteristics for each element can also be determined from this figure, with γ' forming elements located in the top right quadrant and γ formers in the bottom left. Elements centred about the origin have been magnified in inset [b](#)). Most elements fall directly on the line of best fit, as the total composition is simply the sum of the γ and γ' phase contributions. Exceptions to this include C, B, and Zr which

are all known to segregate to grain boundaries, and W which has been observed segregating to γ - γ' interfaces (which is explored further in [Chapter 4.4.4](#)).

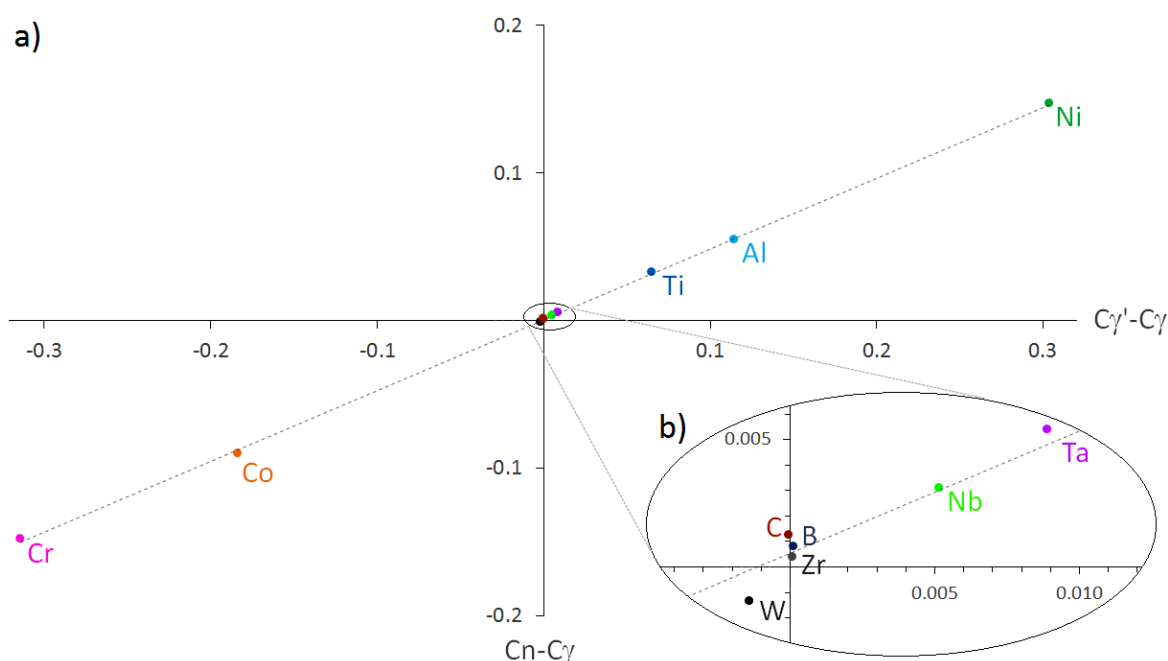


Figure 4.11 – a) Lever rule derivation plot for the ABD-4 alloy. The line of best fit gradient equates to γ' volume fraction (48 % in this case). b) Inset view of the elements centered about the origin.

4.3.2 Interface chemistry

The interesting behaviour of certain elements in proxigrams, as well as the γ' size-composition dependence of W and Ta, warranted investigation of γ - γ' interfaces for potential indications of segregation. The proxigram shown in [Figure 4.12](#) was created over a 10 nm region crossing the interface in the ABD-5 alloy, separated into major (below 5 at.% nominal) and minor (above 5 at.% nominal) constituent elements. Enrichment of W at the γ - γ' interface was observed in this proxigram, which is a feature seen consistently in reconstructions from these alloys. Additionally, many other elements appear to have a 2 nm wide transition region between γ and γ' phase compositions. Following the concentration profiles for Ti and Ta from γ matrix into the γ' precipitates, equilibrium γ' concentrations are not reached until several nanometres into the precipitates. Another trend can be seen in the other direction travelling into the γ matrix, where the concentrations of Ni, Cr and Co level off 1 nm from the interface to form a small 'plateau'.

Then at 3 nm from the interface the concentrations of Ni and Co drop a few percent, while Cr rises a few percent, before equilibrium matrix composition is reached 3 nm from the interface. This was initially dismissed as an peculiarity of this particular γ - γ' interface, but has been seen in other reconstructions during these experiments and also by Antonov et al. [146].

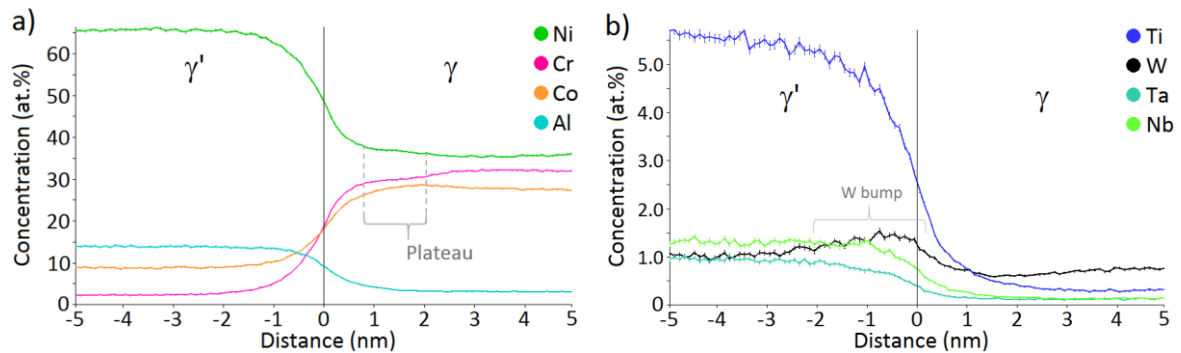


Figure 4.12 – Proxigrams showing concentration profiles across a secondary γ' - γ interface defined by a 22.5 at.% Cr isosurface in the ABD-5 alloy. Graphs a) and b) show major (above 5 at.%) and minor (below 5 at.%) constituents respectively.

A reconstruction containing multiple tertiary γ'_{III} from the ABD-2 alloy is depicted in Figure 4.13.

Part a) consists of a 10 nm thick slice through the reconstruction, overlaid with a 22.5 at.% Cr isosurface in pink and a 1.8 at.% W isosurface in black. The Cr isosurface has been previously established to define the interface between γ and γ' phases, and the W isosurface shows that the highest concentration of W lies directly at this interface. One γ' precipitate has been chosen for an in-depth γ - γ' interface analysis, which is outlined in the red square. Part b) consists of a proxigram formed using the 22.5 at.% Cr isosurface, in which the W segregation at the interface can clearly be seen. Ta has also been included as a visual phase indicator due to its partitioning preference for γ' . Parts c) and d) both consist of one-dimensional concentration profiles formed along 60 nm x 10 nm x 10 nm regions of interest across the precipitate. The horizontal profile in part c) shows defined W peaks at locations assumed to be γ - γ' interfaces judging by the Ta concentration. The vertical profile in part d) shows a well-defined W peak where the top interface is, and a poorly-defined bottom interface.

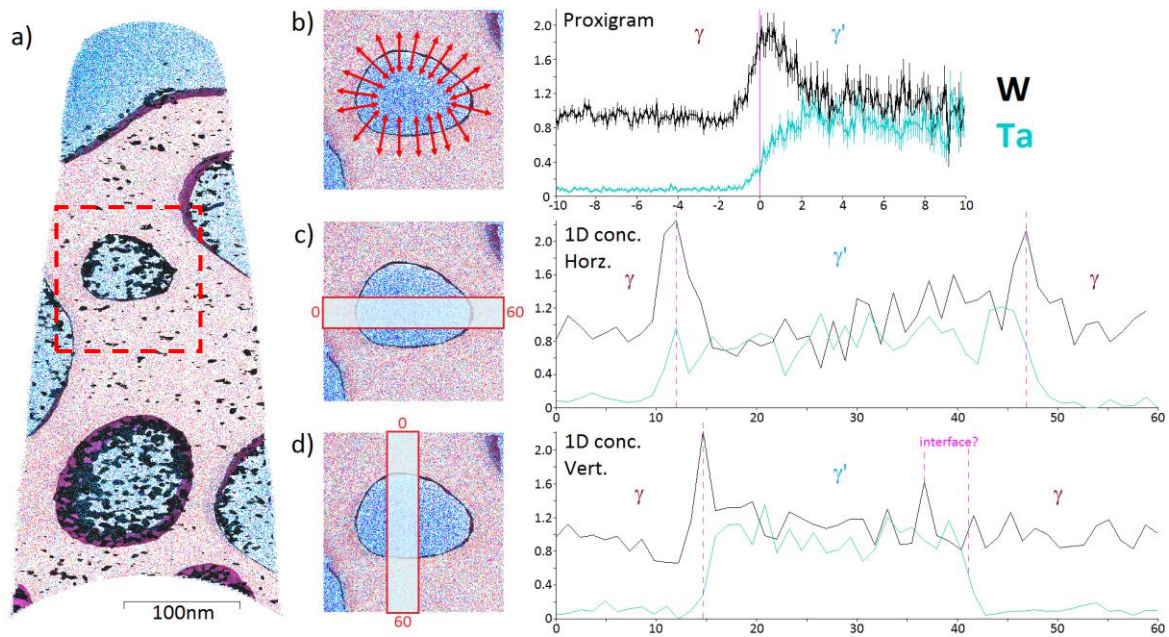


Figure 4.13 – a) 10 nm slice of ABD-2 reconstruction with 22.5 at.% Cr and 1.8 at.% W isosurfaces.
b) Proxigram formed across Cr isosurface (labelled in pink), showing W pile-up at interface.
c) 1D concentration profile formed horizontally across a γ' precipitate. W pile-up easy to identify.
d) Vertical 1D concentration profile with less pronounced W pile-up.

4.4 Discussion

4.4.1 Grain Structure

Grain size was observed to show a correlation with increasing Nb:Ti ratio, which matches similar observations made by Németh et al. on alloys ABD-2, ABD-4 and ABD-6 [120]. That study utilised EBSD to analyse grain size distributions, finding average sizes of $18.5 \pm 1.5 \mu\text{m}$ for alloy ABD-2, $24 \pm 2.5 \mu\text{m}$ for ABD-4 and $45 \pm 9.7 \mu\text{m}$ for ABD-6. It was postulated by the authors that this grain size increase in the higher-Nb alloys may be the result of a change in MC carbide chemistry. These carbides are critical to limiting grain growth via a Zener pinning mechanism [153], and their temperature stability is known to be composition-dependent [22]. Note was made of the stabilizing effect that has Ti has on MC carbides, however Nb and Ta have both been shown to have much stronger stabilisation properties [154,155], which sheds doubt on this theory. Ultimately the cause of this correlation between grain size and Nb:Ti ratio is currently unknown.

The composition of carbides present in these alloys was further investigated by Collins et al. [156] via XRD analysis, resulting in a small but identifiable diffraction peak which could only be explained by the presence of TiC carbides, ruling out substantial volume fractions of other phases such as NbC or TaC.

4.4.2 γ' Precipitate Microstructure

Precipitation of γ' phase is perhaps the most crucial strengthening mechanism in nickel based superalloys, for which the precipitate volume fraction and size distribution are important considerations. The concentrations of γ' -forming elements (Al, Ti, Nb and Ta) in these alloys were chosen so that the microstructure would consist of 50 % γ' phase by volume, which was implemented using thermodynamic predictions made by Thermo-Calc using both TTNi8 and TCNi8 databases at the 850°C aging temperature [143]. These thermodynamically predicted values, along with the experimentally-determined γ' volume fractions obtained in APT via lever rule derivation and SEM observations, can be found in Table 4.2.

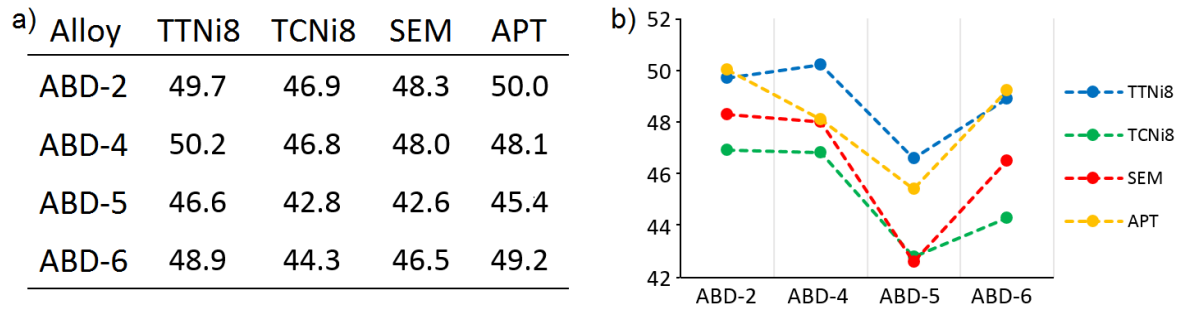


Table 4.2 – a) γ' volume percentages predicted using two different thermodynamic models TTNi8 and TCNi8, compared against observations made via SEM and APT. b) Visualisation of part a).

The two sets of experimentally-derived values agree to within 3% of each other, with SEM tending to produce values a few percent lower than APT. This shortfall may result from the discounting of smaller tertiary γ'_{III} as noise during ImageJ analysis, or possibly blurring of γ - γ' interfaces during thresholding. Both sets of experimentally-observed γ' volume fraction values

tend to lie between the two Thermo-Calc predictions, with TTNi8 predicting volume fractions at the higher end of the observed values, and TCNi8 predicting values at the lower end. This echoes a similar trend seen in the partitioning results, in which the TTNi8 database consistently estimates $K^{\gamma'/\gamma}$ at the higher end of observed values for most elements, which could hypothetically increase the predicted γ' volume fraction. In contrast, the TCNi8 database predicts values at the lower range for γ' volume fraction. Another observed trend is a depletion of γ' volume fraction for alloy ABD-5 among both experimental techniques and the two thermodynamic databases. It is tempting to attribute this lower γ' volume fraction to the slight Al deficit seen in the as-manufactured compositions in [Table 3.1](#) (7.6 at.% measured versus 8.0 at.% target), which could lead to a reduction in the nominally Ni₃Al γ' phase. It must be noted, however, that the difference in γ' volume fraction is an order of magnitude larger than the Al compositional deficit, so no direct causal link can be firmly established.

The size distribution of γ' precipitates observed during this study was estimated purely from SEM images, as APT datasets are too small to fully encapsulate the larger primary and secondary γ' generations as seen in [Figure 4.4](#). No primary γ'_I was observed at grain boundaries during SEM analysis, which matches expectations as these alloys are designed to be coarse-grained, using a two hour super-solvus heat treatment to dissolve the majority of boundary-pinning primary γ'_I thus allowing grain growth. Both secondary γ'_{II} and tertiary γ'_{III} were observed during this study, as shown in APT reconstructions in [Figure 4.4](#), or in SEM images in [Figure 4.2](#). The γ' size distributions observed during SEM analysis are shown in [Figure 4.3](#), which for most alloys suggests a bimodal distribution of secondary γ'_{II} of around 200 nm, and a unimodal distribution of sub-50 nm tertiary γ'_{III} . These size ranges were not observed to be composition-dependent in Alloys ABD-2, 4 and 5. Alloy ABD-6 showed anomalous behaviour which is further discussed below.

The observed distributions are in agreement with results from Hisazawa et al. [157], who performed SEM image analysis on alloys ABD-2, ABD-4 and ABD-6. A small amount of residual primary γ'_I was observed, combined with secondary γ'_{II} in a size range around 200 nm and tertiary γ'_{III} with a sub-50 nm size range. It was noted that there was no size-composition dependence in the as-received condition, although a difference in tertiary γ'_{III} size distribution was observed between the alloys after additional heat treatments, with the higher Nb alloys showing increased rates of tertiary γ'_{III} growth. Németh et al. also performed SEM image analysis on the same three alloys, observing a composition-independent distribution of 230 nm secondary γ'_{II} and 40 nm tertiary γ'_{III} [120]. Primary γ'_I was noted to be absent. Both of these studies provide γ' size distributions that appear to agree with the results presented here. However, caution must be advised when comparing these results as they both employ etchants to dissolve the γ matrix in order to emphasize the remaining γ' precipitates. This can be misrepresentative of true γ' size distributions due to the loss of smaller γ' and over-representation of larger γ' , which is acknowledged by Hisazawa et al.

The only discrepancy observed during this experiment involves the high-Nb ABD-6 alloy, which was observed to have a unimodal size distribution with little differentiation between secondary and tertiary precipitates, as seen via SEM in Figure 4.1 and as a size distribution in Figure 4.3. The shape of secondary γ'_{II} was also observed to be much more spheroidal in ABD-6 than in the other alloys. Both of these observations do not match the APT data obtained from alloy ABD-6, in which both regular tertiary γ'_{III} were seen in Figure 4.4 g), as well as octodendritic γ'_{II} in Figure 4.4 h). The abnormal precipitate distributions were also not observed by either Hisazawa et al. or Németh et al., which leads to the conclusion that this is likely to be an idiosyncrasy of this particular sample. Three separate micrographs from different areas of the analysis plane all show this same discrepancy however, which implies that the analyzed section of this alloy does indeed deviate from other observed samples. The observed unimodal distribution combined with the change to a

more spherical morphology indicates this region of the alloy is likely to have experienced higher rates of growth than nucleation during heat treatment [158], possibly due to its position within the forging experiencing a faster cooling rate [41].

The octodendritic or “clover-leaf” morphology observed in the secondary γ'_{II} is also of interest. These γ'_{II} can be seen in Figure 4.14, which shows an SEM micrograph of alloy ABD-2 containing γ'_{II} in various stages of splitting. Spheroid and cubic γ'_{II} can be seen, as well as octodendritic, doublet and octet configurations. These morphologies are also seen in SEM images from three other papers which characterise these alloys; Németh et al. and Collins et al. make no comment on these morphologies, while Hisazawa et al. note a combination of granular and “flower-like” secondary γ'_{II} . These “flower-like” γ'_{II} are observed to form dents along the sides, which are likely the result of the early stages of splitting. These morphological changes were hypothesized to be the result of cyclic directional coarsening, caused by elastic interactions between precipitates. However an alternative explanation was provided by Antonov et al. [146], in which the critical size for morphological change is derived based on elastic strain caused by lattice misfit. Given the lattice misfit of a precipitate, predictions could be made of the size at which a spherical precipitate transitions to a cube, or cube to a doublet, or cube to an octet. These critical sizes for splitting were found to be at least double the size of observed split particles, indicating that elastic strains caused by lattice misfit are not the only phenomenon that leads to splitting. Compositional changes at γ - γ' interfaces resulting from solute rejection were also indicated to encourage splitting by significantly increasing lattice misfit. This is discussed further and compared with other observations of γ - γ' interface chemistry in Chapter 4.4.4.

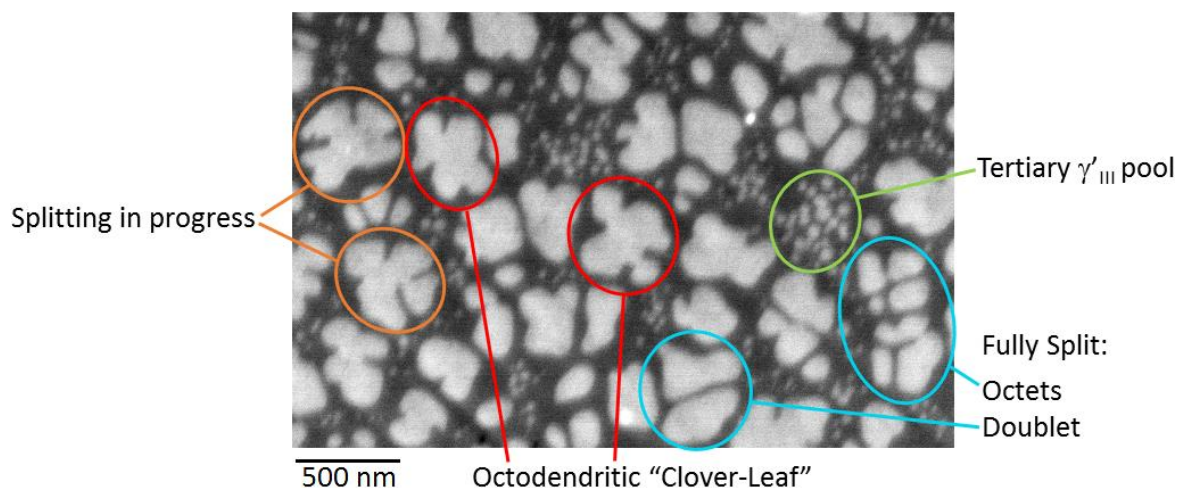


Figure 4.14 – 20,000× micrograph of alloy ABD-2 showing secondary γ'_{II} precipitates in various stages of splitting, from initial octodendritic shape to doublet and octet configurations. Pools of tertiary γ'_{III} are also visible.

4.4.3 Phase Chemistry & Partitioning

Control of alloy composition is critical to ensuring a good balance of properties within both the matrix and precipitates. The alloy design goal underpinning the creation of this generation of ABD alloys is to assess whether Ti can be partially replaced by Nb, without significantly changing the alloy properties. This is further described in the patent for these alloys (where these alloys are referred to using the designations T2, T4, T5 and T6) [143]. Both Ti and Nb promote high-temperature strength by increasing APB energy in the γ' phase, but this effect is lessened if they preferentially partition to another phase. In the compositions studied here, the only phases present aside from γ' are the γ matrix, or possibly grain boundary carbides (such as the TiC seen by Collins et al. [156]). If Ti or Nb additions were substantially increased, a variety of other phases could be formed, including but not limited to η (Ni_3Ti) [59], γ'' (Ni_3Nb) [57], or δ (Ni_3Nb) phases [58]. Cr, Co and W fulfil similar roles in the matrix by providing oxidation and creep resistance, but over-addition can lead to the formation of undesirable topologically close-packed (TCP) phases such as σ ($\text{Cr},\text{Mo})_x(\text{Ni},\text{Co})_y$ or μ ($\text{Co},\text{Ni})_7(\text{Cr},\text{W})_8$ [29]. These other phases have mostly been ruled out by compositional limitations imposed during the previous iteration of the ABD alloys, so the focus for this generation of ABD alloys involves how changes in Ti:Nb ratio affect elemental

partitioning between γ and γ' . This is examined in [Figure 4.10](#), in which it can be seen that the experimentally-derived partitioning coefficient of Nb is much smaller than that of Ti, meaning that a 1:1 replacement of Ti with Nb could lead to lower concentrations of APB energy-enhancing elements in the γ' precipitates. This raises the issue of whether the calculated high-temperature strengthening effect of Nb is weighted to account for this drop in precipitate Nb concentration. The addition of Nb also appears to affect the partitioning coefficients of other elements – most notably Ti which partitions to γ' less as nominal alloy Nb concentration increases, potentially affecting APB energy even further. A similar trend is observed among Cr and Co, which both show increased partitioning to γ' precipitates as nominal alloy Nb content increases. Ni also appears to show a reduced $K^{\gamma'/\gamma}$ value with increasing Nb, but the abnormally low $K^{\gamma'/\gamma}$ values shown by alloy ABD-5 may be skewing the data here. When phases are looked at individually, these changes to elemental partitioning imply that a simple 1:1 swap of Ti for Nb may lead to potential strength decreases, which may help to explain the small drop in yield strength seen by Németh et al. [\[120\]](#). However, Nb is known to also be a potent γ phase solid solution strengthener, which may counteract this loss of strength somewhat.

The experimentally-derived $K^{\gamma'/\gamma}$ values have also been compared against values predicted by Thermo-Calc using the two databases TTNi8 (Thermo-Tech) and TCNi8 (ThermoCalc). There is a larger spread between the two Thermo-Calc predictions than between the two APT datasets, especially when looking at Ta and Nb, both of which show at least a factor of four difference between the predicted $K^{\gamma'/\gamma}$ values. As mentioned previously, the TCNi8 database tends to produce predictions which are numerically closer than TTNi8 to the experimentally observed values, although often showing an opposite trend with increasing Nb at.%. However, when compared to the experimental results both Thermo-Calc databases tend to underestimate $K^{\gamma'/\gamma}$ values for Ni and W, while overestimating $K^{\gamma'/\gamma}$ values for Ti, Nb and Cr. As Ti and Nb are required to partition to γ' to provide strengthening benefits, the overestimates of partitioning behaviour

may lead to successive overestimation of precipitate strength. This mirrors similar findings relating to thermodynamic predictions of Nb partitioning by Antonov et al. [159] and Miller et al. [160], who noted that overestimation of Nb γ' partitioning can lead to inflated strength predictions. These discrepancies may be due to the assumption of thermodynamic equilibrium which is never reached due to material inhomogeneities, or possibly some unaccounted for kinetics and diffusion [160].

4.4.4 Interface Chemistry

One of the unexpected results from this experiment was the discovery of W enrichment at γ - γ' interfaces. The first indication came from the Lever rule plots used to calculate γ' volume fraction (an example of which is shown in Figure 4.11), where the plotted positions of C, W, and Ta data points do not lie directly on the best fit line, indicating that they partition to regions other than γ or γ' . This discrepancy was almost dismissed, as W and Ta are both known to form carbides [60]. However the presence of a W 'bump' at tertiary γ'_{III} interfaces observed during proxigram creation (as shown in Figure 4.12), as well as the strange size-composition dependence of Ta and W (as shown in Figure 4.7) warranted a more detailed investigation of interface regions.

Figure 4.13 shows proxigrams and 1D concentration profiles of W and Ta across a γ - γ' interface. The proxigram shows a thin shell of W-enriched material surrounding the γ'_{III} precipitates, which echoes results published by Amouyal et al. in two alloys: ME-9 alloy [38] and a single crystal directionally-solidified superalloy [161]. It is unknown if this behaviour is due to preferential segregation, or rejection of W during γ' formation. The shape of the W concentration profile over the γ - γ' interface is similar to the 'bow-wave' profile seen by Warren et al. for Re in single-crystal RR3000, which was attributed to diffusion-limited rejection of solute [162]. This could also apply to W, which has been shown by Karunaratne et al. to have a similar, but slightly larger interdiffusion coefficient to Re through γ phase [163]. The fact that the 1D concentration profiles

in these perpendicular directions do not agree with each other is also of interest. The horizontal profile is consistent with the proxigram, showing W segregation at the interface, while the vertical profile only shows a consistent W peak at the top interface. The lack of a W peak at the bottom interface could be explained as a delayed evaporation artefact. The difference seen between crystallographic directions also shares a similarity with results from Amouyal et al. [161], who see a directionality of W segregation in secondary γ'_{II} based on changing interfacial energy, although this was only seen in the larger cubic γ'_{II} precipitates rather than small spheroid γ'_{III} .

No segregation behaviour was observed for Ta, in fact the concentration profile for both Ta and Ti showed a slight depletion around the outer shell of the γ'_{III} precipitate before reaching a plateau 5 nm into the precipitate. A similar effect was observed for Ti, Ta and Hf by Bagot et al. during APT analysis of the RR1000 alloy [164], where it was attributed to the large lattice misfits for these elements as estimated using Vegard's Law [5]. As discussed previously in Chapter 4.4.2, Antonov et al. [146] also observed interesting composition deviations at γ - γ' interfaces, where W, B and Mo were seen at elevated levels at the interface, while Ta was shown to exhibit the same outer-shell depletion and plateau as observed here.

Cr concentration profiles were also found to be non-uniform heading into the γ matrix phase, showing a trend of rising to a plateau concentration of roughly 30 at.%, before rising another 2-4 at.% a few nanometres from the interface. This trend was repeated across 29 of the 32 γ - γ' interfaces analysed during this project. No conclusions were made regarding the Cr and Co plateau during the previous publication of these data, which was instead attributed to a field-induced artefact [119]. Citing this plateau, Antonov et al. argue that this is likely due to a transient phase caused by the rejection of solute caused by growing γ' [146]. As γ'_{II} form at higher temperatures where the solubility of Cr and Co is also higher, a subsequent cooling to a lower temperature should leave Cr and Co super-saturated in γ' . This could either diffuse out to form

the observed Cr and Co plateau, or lead to the formation of secondary γ clusters in the form of dendrites along the sides of precipitates, which are theorised to lead to precipitate splitting.

4.5 Conclusions

The overall microstructure changes very little between the alloys, mostly agreeing with thermodynamic predictions. Grain size has been shown to correlate with Nb:Ti ratio, which is consistent with research conducted by Németh et al. on the same ABD alloys [120]. These authors claimed that this correlation between grain size and Nb:Ti ratio may be caused by a change in composition of grain boundary MC carbides, leading to dissolution at high temperatures. This is challenged by research by Sun et al. [154] and Qin et al. [155], which shows that NbC is more stable at temperature than TiC carbides, so this correlation of grain size with Nb:Ti ratio is likely to be caused by a different mechanism. Ultimately this loss of Hall-Petch strength is not enough to cause concern, as grain size can be easily modified by adjusting the heat treatment regime. However, this behaviour should at least be acknowledged during alloy development.

The intragranular microstructure consisted of secondary γ'_{II} and tertiary γ'_{III} phase precipitates, with secondary γ'_{II} in a bimodal distribution. The γ' size distributions show little to no correlation with alloy composition, and the unimodal ABD-6 is most likely an anomaly judging by the results from complementary studies by Németh et al. [120], Collins et al. [156], and Hisazawa et al. [157]. Experimentally observed γ' volume fractions also displayed little correlation with Ti:Nb ratio, although a strong dependence was seen with Al composition, as demonstrated by the slight dip in γ' volume fraction of ABD-5 which was experimentally measured to be Al-deficient in Table 3.1.

Thermo-Calc predictions of γ' volume fraction tended to line up well with APT measurements as seen in Table 4.2. Here, TTNi8 is shown to systematically over-predict γ' volume fraction when compared to experimental observations, while TCNi8 under-predicts. No changes to models are

required here, although the over-prediction of γ' volume fraction by TTNi8 is discussed further in a following point.

The compositions of secondary and tertiary γ' precipitates were measured through the use of APT. Most elements showed very little size-composition relationship in these precipitates, with the exception of W and Ta. W concentration showed a strong negative correlation with precipitate size, leading to a 'shell-effect'. This is linked to the discovery of W-enrichment at γ - γ' interfaces, likely due to diffusion-limited pileup caused by rejection from growing precipitates. Ta showed the opposite trend, which is linked to the observation of Ta concentrations not reaching equilibrium until several nm into γ' precipitates, leading to a corresponding 'anti-shell' effect. These observations do not seem to affect total γ' volume fraction or distribution, so are not immediately relevant to physical property considerations.

The observed partitioning characteristics for each element match up well with literature, and with Thermo-Calc predictions made using the TCNi8 database. However, TTNi8 vastly overestimates partitioning coefficients for five of the eight major alloying elements, including Ti, Nb and Ta which are vital for increasing precipitate strength. Nb in particular is predicted by TTNi8 to partition to γ' four times more strongly than TCNi8 and experimental observations. The over-prediction of partitioning coefficients may also lead to the over-prediction of γ' volume fraction, as seen in [Table 4.2](#). Any strength predictions made using just this database are likely to be artificially inflated, especially when investigating Nb where the discrepancy is significant.

Chapter 5. Oxidation Mechanisms

This chapter focusses on the high-temperature oxidation experiments that were performed on the second generation of ABD alloys to investigate how resistant they are to the extreme environments found in jet turbine engines, and to what extent this resistance depends on alloy composition. Post-exposure characterisation of the resulting oxide layers has been carried out using a variety of high-resolution techniques such as APT and EDX. An analysis of these results follows, incorporating a discussion of some potential mechanisms which could potentially be responsible for the observed link between alloy composition and oxidation resistance.

5.1 Introduction

Resistance to temperature-dependent degradation mechanisms such as oxidation and fatigue is increasingly becoming a priority, as operating temperatures of jet turbine engines are continually pushed higher due to tighter fuel economy and emissions targets [165]. Higher temperature regimes have been shown to increase the kinetics of oxidation reactions, while also enabling oxidation related fatigue processes for which the mechanisms are currently poorly understood [85,109,166].

To design and optimise the next generation of polycrystalline turbine disc alloys, the relationship between oxidation and alloy composition must be established. Previous studies on nickel based alloys have observed a link between titanium additions and increased oxidation rates [75,77,78,81,167,168], however the high chemical complexity of these alloys makes direct comparisons problematic. This generation of ABD alloys were designed specifically to investigate the composition dependence of oxidation resistance, by systematically replacing Ti with Nb while keeping manufacturing routes and compositions otherwise identical [143]. These two elements were chosen for substitution as they both partition to γ' phase precipitates [119], where they

impart strength at high temperatures by increasing anti-phase boundary energy [32], as previously discussed in Chapter 2.1.2. Nb is also a frequently-used addition to many in-service alloys, which has been shown to have little effect on oxidation rates [169], making it a prime substitution candidate. However, Nb has also previously been shown to be detrimental to dwell fatigue performance [88,98], which restricts the amount of Ti that can be directly substituted out.

The mechanism by which Ti increases the kinetics of oxidation is a matter of ongoing research. The underlying thermodynamics that provide a driving force have been previously covered in Chapter 2.2, as well as much of the current understanding in the field regarding the deleterious effect of Ti. Several previous studies into these phenomena have used energy-dispersed X-ray spectroscopy (EDX) [62,75,78,81,167–170] and electron-probe micro-analysis (EPMA) [77,171] to characterise the distribution of elements through oxide layers. Many of these studies have observed dissolution of Ti into chromia scales, combined with the formation of discrete TiO₂ particles at the oxide-air and oxide-metal interfaces. These phenomena have been linked to the observed titanium-oxidation relationship via two proposed mechanisms; the first depends on increased ion transport rates through the chromia lattice via the creation of cation vacancies [77,81,167,172,173], while the second mechanism involves fast short-circuit ion diffusion along dislocations or grain boundaries [7,174].

To investigate the viability of these mechanisms, it is critically important to precisely locate where Ti and other potentially detrimental trace elements segregate to within the oxide layers. EDX analysis has been carried out to benchmark these alloys against results obtained from previous studies, and further high-resolution characterisation has been performed with APT using the techniques and methods explained in Chapter 3. APT in particular is extremely well suited to study the composition and microstructure of the nanoscale features present in oxide scales, due to its excellent chemical sensitivity (up to tens of ppm) and mass resolving power. This allows

detection of small amounts of trace elements which segregate to grain boundaries and tertiary γ'_{III} precipitates, while also being able to visualise the complex microstructures in three dimensions.

5.2 Oxidation Kinetics

The oxidation kinetics of the four ABD-series alloys were evaluated by performing a TGA experiment, which involved measuring the change in specific mass (Δm) during a 100 hour exposure at a temperature of 800°C using the methodology described in [Chapter 3.2.1](#). The specific mass gain data were processed using the Netzsch Proteus software, which involved performing a background correction and recalibrating mass measurements to the beginning of oxidation. When plotted against time, all alloys displayed specific mass gain rates which followed a parabolic growth law in agreement with the Wagner theory of diffusion-controlled oxidation [\[68,70\]](#). The parabolic rate constant K_p has been determined using [Equation 5.1](#):

$$(\Delta m)^n = K_p t \quad \text{Eq. 5.1}$$

Where Δm is the specific mass change ($\text{kg}\cdot\text{m}^{-2}$), t is exposure time (s), and K_p is the parabolic rate constant ($\text{kg}^2\text{m}^{-4}\text{s}^{-1}$). A power law exponent of $n = 2$ has been assumed based on the parabolic behaviour of previously obtained data captured at 800°C [\[81,175\]](#). With [Equation 5.1](#) in mind, the specific mass gain data were squared and replotted against time in [Figure 5.1](#). K_p values can be estimated using the gradient of the linear fit, allowing the oxidation kinetics to be compared between the alloys. A clear correlation between higher Ti concentration (in at.%) and increasing oxidation rates can be seen, with measured K_p values (in units of $\text{kg}^2\text{m}^{-4}\text{s}^{-1}$) ranging from a maximum of 7.5×10^{-12} for the high-Ti alloy ABD-2, down to 1.5×10^{-12} for the low-Ti alloy ABD-6. This range of K_p values is comparable to values obtained between 750°C and 850°C in a variety of other nickel based superalloys [\[75,78,81,94,170,175,176\]](#).

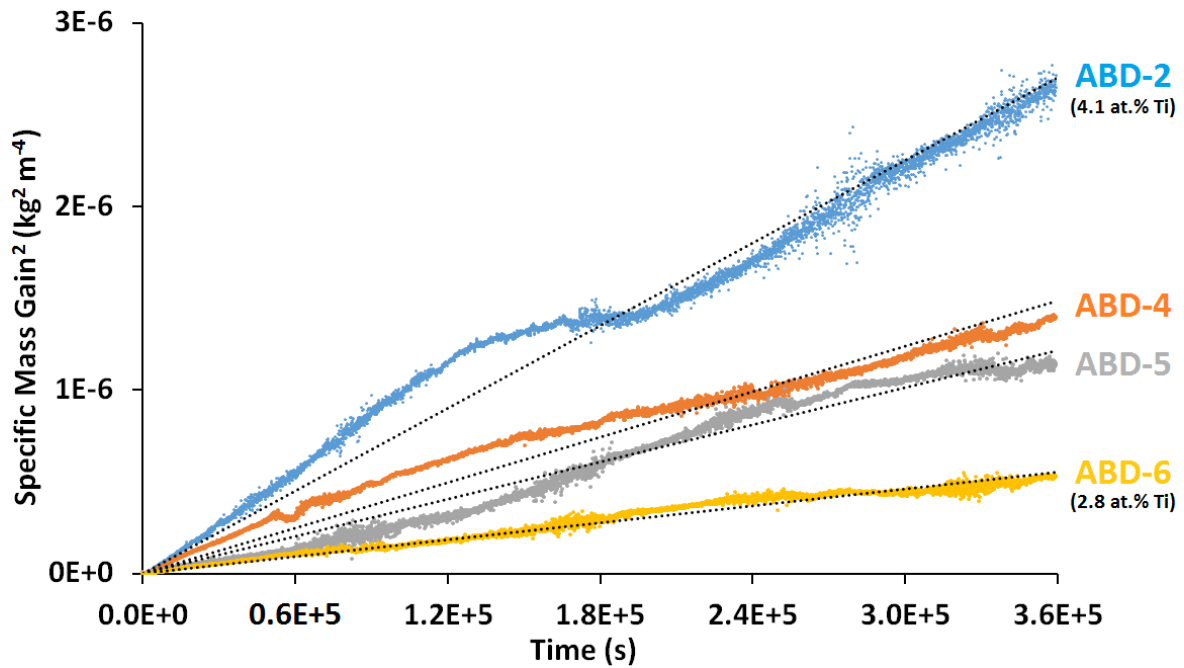


Figure 5.1 – Thermo-gravimetric analysis plot of specific mass gain squared over time, used to quantify oxidation kinetics via estimation of the parabolic rate constant (K_p) from the gradient of lines of best fit.

Specific mass gain measurements can be a useful tool for quantifying oxidation kinetics, but they fail to take into account the character and morphologies of the oxides formed. This includes features such as the presence of other phases or oxidised grain boundaries, which can have disproportionate effects on physical properties including scale adherence and fatigue lifetime.

5.3 Oxide Layer Morphology

Oxide scales in multi-component alloys exhibit complex morphologies, which form as the result of a number of competing oxidation mechanisms. The thermodynamic forces that drive these reactions are very similar however, which allows for some predictions based on theory to be made. The theories behind these thermodynamic driving forces, kinetics and mechanisms have been previously described in [Chapter 2.2](#), while this current chapter focusses more on experimental observations.

One thermodynamic prediction that influences microstructure involves how the oxide layers order themselves from oxide-air to oxide-metal interfaces, in an order based on their Gibbsian free energy of formation ΔG_0 at a particular oxygen partial pressure (P_{O_2}). Oxide layer order can be predicted using an Ellingham-Richardson diagram as shown in [Figure 2.5 \[177\]](#), which indicates that more stable oxides with lower ΔG_0 (such as Al_2O_3) are able to form at the lower P_{O_2} found in deeper oxide layers near the oxide-metal interface. This behaviour has been investigated by Giggins and Petit for the ternary Ni-Cr-Al alloy system [\[73\]](#), in which alloys with varying Ni:Cr:Al ratio have been categorised into groups according to their composition and the resulting morphology of their oxides. The chromia-forming nickel based superalloys investigated in this study oxidise in the same manner as Group II alloys - the designation given to alloys which tend to form a bilayer oxide consisting of a protective external chromia (Cr_2O_3) scale, in addition to an internal alumina (Al_2O_3) subscale consisting of either a continuous layer or individual alumina islands. While the ABD alloys are more compositionally complex than model ternary alloys, the strong oxide-forming properties and significant concentrations of Al and Cr suggest that the oxides formed by the ABD alloys are likely to follow this basic template. Even small compositional changes can lead to significant variations in oxide scale morphology and chemistry however, and the difference in oxidation kinetics between the ABD alloys hints at some change in oxidation behaviour. For this reason, the oxide scales formed during TGA analysis were characterised using a variety of cross-sectional analysis techniques.

To study oxide morphology, FIB-SEM cross sections were prepared through oxide scales, which were analysed according to the techniques described in [Chapter 3.3.2](#). A pair of example cross-sectional micrographs taken through oxides formed on the high-Ti alloy ABD-2 and the low-Ti alloy ABD-6 are shown in [Figure 5.2](#), alongside schematic diagrams labelling the major microstructural features present. The layers of alumina and chromia can be distinguished from one another by their differing contrast, which allows the variation in distribution and morphology

to be seen. The lower-Ti alloy ABD-6 tends to exhibit uniform continuous chromia scales and discontinuous but evenly distributed internal alumina islands, which is consistent with thermodynamic predictions and the previous kinetics results. Conversely, the oxide scale formed by the high-Ti alloy ABD-2 displays significant variation in uniformity. At its thickest point, the oxide consists of large external chromia deposits, above deep alumina intrusions which progress down along grain boundaries several microns into the matrix. At its thinnest points, the oxide scale measures only 100 nm. This difference in oxide morphology between the alloys, and some potential mechanisms that may cause it, are discussed further in [Chapter 5.5.1](#).

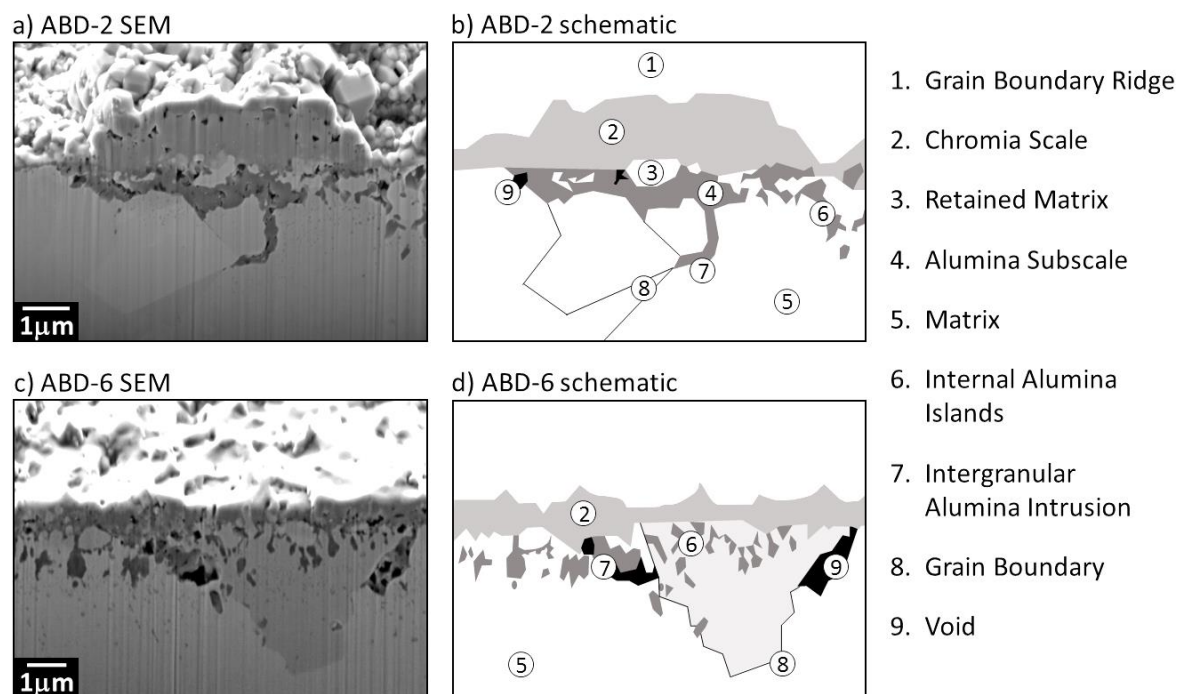


Figure 5.2 – 5,000× magnification FIB-SEM cross sections through oxide scales formed from high-Ti alloy ABD-2 (a) and low-Ti alloy ABD-6 (c) at 800°C over 100 hours. These micrographs are represented by schematic diagrams labelling the major features observed (b,d).

Another characterisation technique capable of analysing oxide cross-sections is EDX spectroscopy. This technique can locate and quantify elemental distributions throughout oxide scales, which makes it useful for finding smaller concentrations of dissolved elements in chromia and alumina, as well as identifying other regions such as carbides, nitrides, or other oxides. EDX analysis was performed on a pair of microscopes using the methodologies described in [Chapter 3.3.3](#), an

example of which is shown in Figure 5.3. The resulting micrographs and separate element maps corroborate all of the features previously characterised by SEM, such as the layering of external chromia and internal alumina, and the difference in layer uniformity observed between the high and low-Ti ABD alloys.

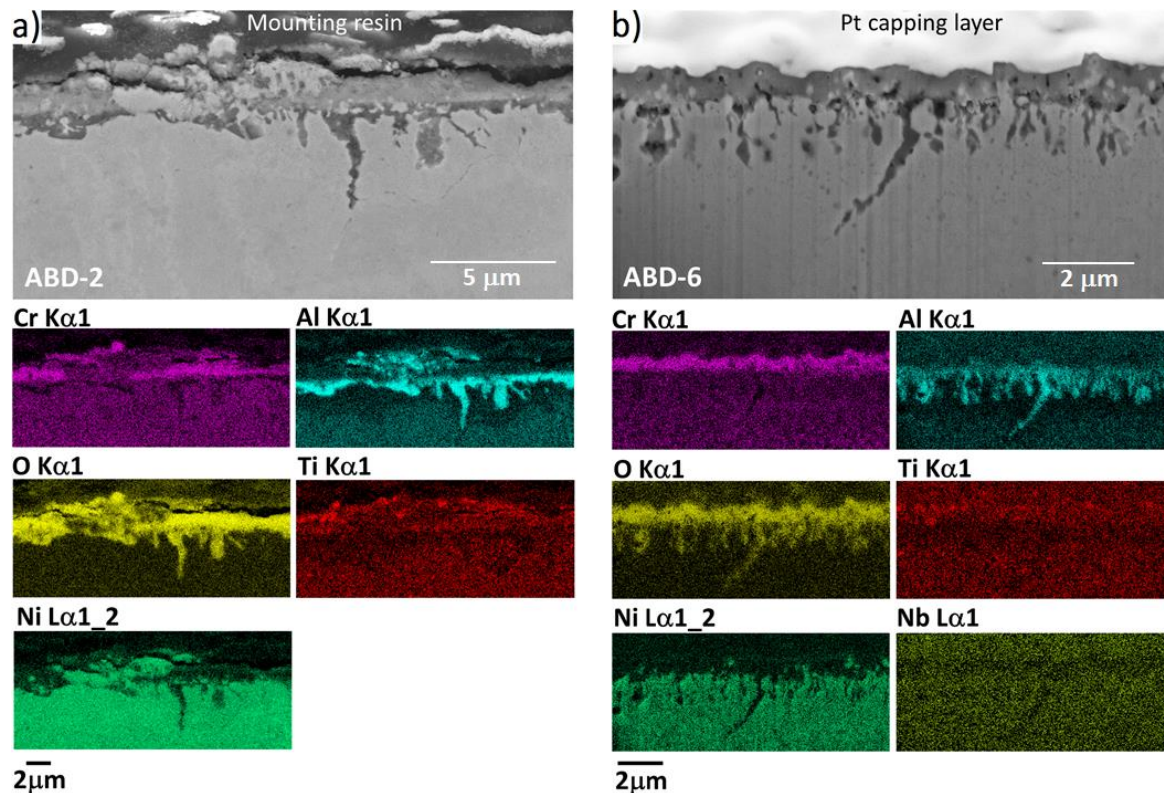


Figure 5.3 – 5,000× magnifications of SEM cross-sectional micrographs, and individual EDX element maps obtained at 10 kV for the high-Ti alloy ABD-2 and the low-Ti alloy ABD-6.

The distribution of Ti in these oxide layers is of particular interest for this generation of ABD alloys. In both the high-Ti alloy ABD-2 and low-Ti alloy ABD-6, Ti was detected to be present within the oxide layers. It is predominantly concentrated in particles both within the chromia layer and at the oxide-air interface, most likely in the form of rutile TiO_2 which has been previously reported [63,75,81]. The other element of particular interest is Nb, which is entirely absent from ABD-2, and present in alloy ABD-6 at a nominal concentration of 2.8 at.%. Unfortunately the Nb map for alloy ABD-6 is quite noisy, which is could possibly be caused by a spectral overlap between Nb and Pt present in the capping layer, as both Nb $L\alpha$ and Pt M X-ray

emission lines occur in the vicinity of 2.1 keV. Despite this, a faint shadow can be seen corresponding to the location of the oxide layers, which implies that Nb may be absent from the oxide, and is only detected in appreciable quantities in the γ matrix.

A number of other features were identified in the EDX element maps. Depletion of Cr and Al was observed in the γ matrix directly below the scale, likely caused by leeching from the matrix during the formation of oxide layers. Some regions of unoxidised γ phase matrix were also observed to be trapped between layers of oxides.

5.4 APT Oxide Analysis

In order to examine the elemental distributions and microstructure of oxide layers at the sub-nanometre scale, APT was carried out on samples obtained from site-specific FIB liftouts. These were carefully prepared from a range of depths through the oxide scale using the methods and techniques described in [Chapter 3.4.2.2](#). A total of 23 successful atom probe tips from within the oxide layers were reconstructed and analyzed, with reconstructions varying in size from 5 million to 164 million ions and the resultant oxide mass spectra including between 87 to 135 individual peaks. For comparison, the reconstructions of the unoxidised superalloy samples analysed in [Chapter 4.3](#) displayed mass spectra consisting of between 65 and 95 individual peaks. While the absolute number of mass spectra peaks is only slightly larger in the oxide reconstructions, the addition of many complex ionic species vastly increases the difficulty of identifying these peaks during the ranging process. The identity of these complex ionic species was also found to vary significantly between datasets, which rendered the previous method of applying and modifying a master range file unsuitable, necessitating the creation of new systematic ranging protocols.

5.4.1 Peak Identification and Ranging

Accurate composition determination requires careful identification of peaks in the mass spectra. For reconstructions of unoxidised superalloys, these peaks could mostly be associated to monoatomic ionic species containing individual ions of metallic elements. A number of peak overlaps were identified, such as that between ^{50}Cr and ^{50}Ti , which could be deconvoluted using the native IVAS software. The oxide mass spectra shared many of these monoatomic metallic ion peaks, with the addition of a significant number of complex ionic species. With few exceptions these complex species consisted of a combination of metal and non-metal atoms, such as oxides, carbides and nitrides. The majority of these were metal oxides of the form M_xO_y , with the most common species consisting of Cr_2O_3 and its associated fragments; CrO , CrO_2 and CrO_3 . The exceptions included species such as OH , H_2O , CO_2 et cetera.

To aid identification of these complex ions, a database of complex ionic masses was created. This contained various configurations of metal ions present in the nominal alloy composition, combined with oxygen, nitrogen and carbon. The maximum number of atoms per complex were limited to $2(\text{metal}) + 5(\text{non-metal})$, and charge states were limited to $3+$. The mass-to-charge ratios of these complexes were calculated using the major isotope of each element present, then listed in ascending order similar to that found in Appendix J of Gault et al. [136], which allowed identification of peaks relating to some of the more obscure complex ions such as NbN or TaO_3 . This database was frequently referred to when ranging unidentified peaks, in addition to the APTtools software suite [133] which is an automated tool that follows a similar algorithm.

Overlaps

Another problem encountered during ranging involves the identification of peaks which contain contributions from multiple ionic species with overlapping mass-to-charge-state ratio values,

which are hereby referred to as ‘overlap peaks’. The relative contributions of the different ionic species to an overlap peak can be estimated using a deconvolution algorithm, which is based on the assumption of natural isotopic abundances and adjacent non-overlapping peaks [135]. This is a probabilistic technique that allows composition measurement accuracy to be maintained, but cannot definitively determine the spatial distribution of the component ionic species.

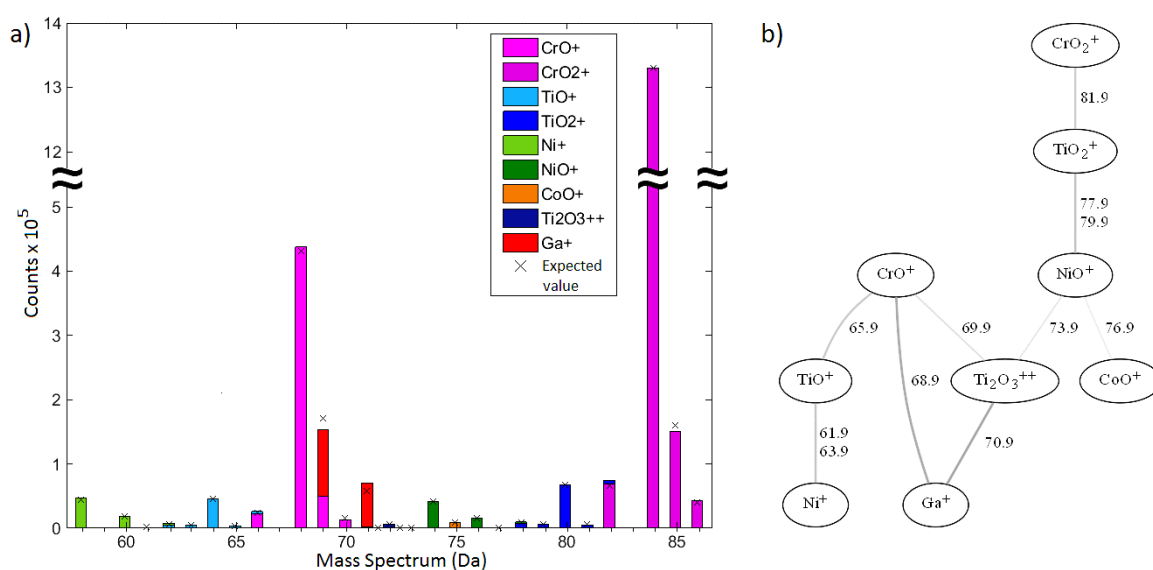


Figure 5.4 – a) A mass-spectrum segment taken from a reconstruction from the oxide layer of alloy ABD-2, after application of the peak deconvolution algorithm included in the AtomProbeLab software suite. b) Network graph for ionic species overlaps between 62 Da and 82 Da.

An example of peak overlap deconvolution is shown in Figure 5.4, using the algorithms provided by the AtomProbeLab software suite [134]. Part a) consists of a segment of the mass spectrum which has undergone deconvolution, with peak contributions displayed as stacked bars representing different ionic species. The crosses represent the expected peak height calculated from isotopic abundances and concentrations of the species ranged, which can be seen to closely match the observed peak heights. Part b) shows a diagram which depicts the ionic species which occur between 62 Da to 82 Da in part a), along with their network of overlapping peaks.

Global and Local Composition Analysis

Some modifications were made to the ranging protocol used previously in [Chapter 4.3](#) during analysis of unoxidised material, due to a number of complications that were magnified by the increased complexity of the oxide mass-spectra:

1. The identity of mass-spectra peaks varies significantly between datasets, which rendered the previous technique of applying and modifying a master range file unsuitable.
2. The amount of context-dependent peak information increases. This includes identifying neighbouring peaks for isotope and overlap determination, as well as contributions from monoisotopic species.
3. Accurate compositions are required – both globally over the entire dataset, and locally when analysing features such as grain boundaries or other phases. These require different range optimisation strategies.

All three of these potential problems could be mitigated by systematically creating a pair of ranges from scratch for each reconstruction. One set of ranges were optimised to maximise global compositional accuracy via the use of peak deconvolution, which is predominantly used in [Chapter 5.4.2](#). The other set of ranges were optimised to retain as much local information of ionic distributions as possible, which is used to investigate the composition of features such as grain boundaries and retained phases in [Chapter 5.4.3](#).

The steps involved in creating both sets of ranges are summarised below:

1. The reconstructions are initially ranged using a pre-existing master range file, which is used to estimate the global composition.
2. The ionic species ranged this way are decomposed into their respective elements, which are listed in descending concentration order.

3. An exception is made for monoisotopic elements such as Al, Co and Nb, which are placed at the front of the list. These monoisotopic species are given precedence as they are required 'a priori' information for the deconvolution algorithms.
4. Ionic species are then ranged in list order, beginning with monoisotopic species, then in decreasing order of concentration.
5. A time-economizing measure was applied during ranging, in which all ionic species sharing a common metallic element (Cr, CrO, CrO₂ ...) were ranged concurrently.

At this point, ranges used to determine global composition via a deconvolution algorithm were considered complete. The ranges for determining local compositions required another two steps:

6. A deconvolution algorithm was used to highlight peaks containing overlaps.
7. These overlaps were split into the relative contributions from each ionic species, which were then tabulated, as presented in [Table 5.1](#).

Overlap Peak	Precedence		Likely		Other	
27 Da	Al ⁺	13.8%	Cr ⁺⁺	86.2%	Ni ⁺⁺ 0.26% O ₂ ⁺ 0.92%	
32 Da	O ₂ ⁺	24.7%	TiO ⁺⁺	75.0%		
33 Da	CrO ⁺⁺	92.9%	TiO ⁺⁺	6.2%		
35 Da	Al ₂ O ⁺⁺	0.0%	CrO ⁺⁺	100.0%	Ti ₂ O ₃ ⁺⁺ 0.15% NiO ⁺ 0.22% W ⁺⁺ 0.0%	
43 Da	AlO ⁺	22.2%	CrO ₂ ⁺⁺	77.8%		
69 Da	Ga ⁺	6.4%	CrO ⁺	93.6%		
70 Da	Al ₂ O ⁺	14.6%	CrO ⁺	85.3%		
75 Da	CoO ⁺	99.8%	Cr ₂ O ₃ ⁺⁺	0.0%		
86 Da	Al ₂ O ₂ ⁺	2.2%	CrO ₂ ⁺	97.8%		
93 Da	Nb ⁺	100.0%	Cr ₂ O ₅ ⁺⁺	0.0%		
102 Da	Al ₂ O ₃ ⁺	2.0%	CrO ₃ ⁺	98.0%		

Table 5.1 – Contributions from different ionic species to overlapping peaks, in a reconstruction from Alloy ABD-6 as shown in Figure 5.6 j). Species with largest peak contributions highlighted.

The global composition ranges identify peaks according to the 'Precedence' column, which consists of ions ordered towards the front of the ranging list, either due to being present at a larger concentration, or containing a monoisotopic element. This means that monoisotopic species are less likely to be omitted, and accurate peak contributions can be calculated using a

global deconvolution algorithm, which should (in theory) distribute peak contributions accordingly.

The local composition ranges identify peaks according to the ionic species highlighted in yellow, which were determined to make the largest contribution to the overlapping peak. Often this came from the 'Likely' column, which contains the largest contributor to that peak, although sometimes the ionic species given precedence happened to also contribute most to the peak. This is intended to maintain as much local ionic distribution information as possible, at the potential cost of global composition accuracy.

Despite these systematic peak ranging protocols, a number of unidentified peaks remained. These were tabulated together using a custom MATLAB script, which allowed the identification of any unidentified peaks shared across multiple datasets. Peaks identified using this technique include an $\text{Al}_2\text{O}^{+++}$ peak at 23.3 Da, and $\text{Al}_2\text{O}_2^{+++}$ at 28.6 Da. The rest of the unidentified peaks were analysed using the APTtools software suite to identify potential ionic species, which suggested the likely presence of a number of CrCo complex ions including CrCo, CrCoO, CrCoO₂ and CrCoC. It is possible that these complex species containing ⁵⁹Co could in actuality be based on ²⁷Al¹⁶O¹⁶O species, which occur at the same mass-charge values. Traditional deconvolution algorithms based on isotopic abundance struggle with monoisotopic elements such as Co and Al. The presence of O in AlO₂ could potentially allow deconvolution, but the low 0.2% abundance of ¹⁸O would be unlikely to show above the background. The decision was made to range these as CrCo complexes because no other CrAl species were observed, and also because of the shared partitioning behaviour of Cr and Co.

An example mass spectrum ranged to optimise local compositions is shown in [Figure 5.5](#), from a grain boundary reconstruction of alloy ABD-6. This was plotted using AtomProbeLab, with identification labels representing the mass-charge range of ionic species above the spectrum.

5.4.2 Baseline Chromia Composition Analysis

Once the ranging strategies were codified, a number of reconstructions were selected to investigate whether the baseline chromia composition changes across the alloys. The selection criteria required these datasets to predominantly consist of chromia, avoiding grain boundaries or large phases which might affect the baseline composition. Any non-chromia phases remaining were removed as best as possible, although some grain boundaries remained. The 12 selected chromia reconstructions are shown in [Figure 5.6](#), consisting of three samples for each of the four ABD alloys.

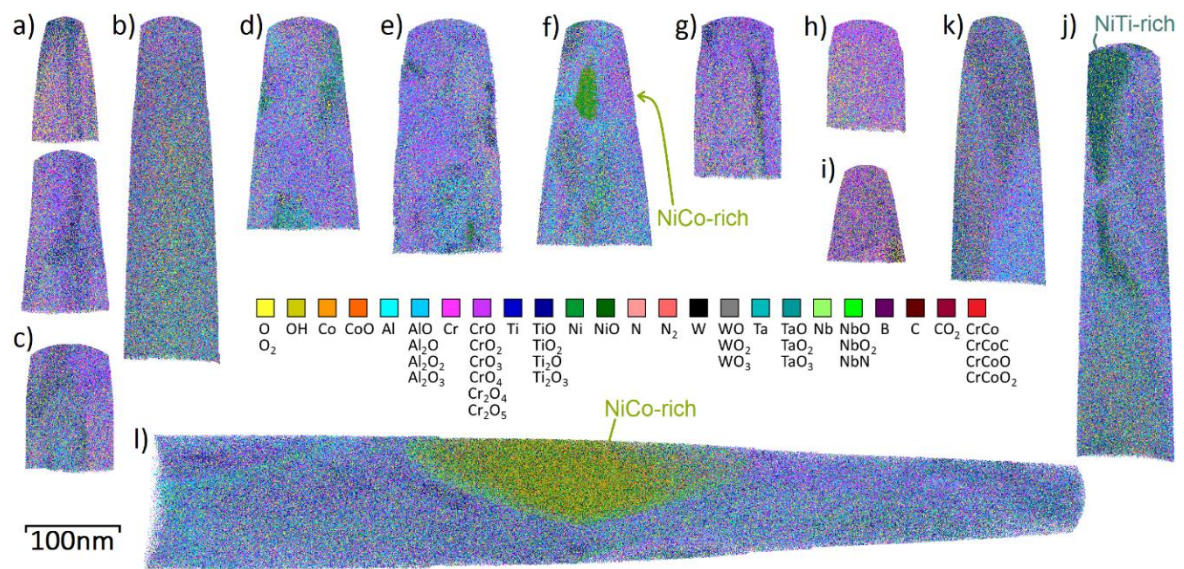


Figure 5.6 – The twelve reconstructions selected to investigate variance in chromia composition. ABD-2 represented by a, b, and c. ABD-4 by d, e, and f. ABD-5 by g, h, and i. ABD-6 by j, k, and l. All reconstructions use identical scale and ion species colour legend.

Using the global composition ranges, the twelve chromia reconstructions were analysed to identify any precipitates, retained matrix or other non-chromia phases. Many NiCo-rich retained γ phase particles were identified, such as the prominent light green regions seen in [Figure 5.6](#) parts [f](#)) and [l](#)). Part [j](#)) contains two NiTi-rich regions which appear in dark green at the top of the reconstruction. All of these regions were removed from the reconstructions by isolating and extracting them using 5 at.% Ni isosurfaces. Variations in chromia composition can be seen in almost all of the datasets, with Al-rich regions appearing as lighter blue and Ti-rich sections

appearing as navy blue. Some grain boundaries can be also observed passing through reconstructions, as shown by the lighter lines in [Figure 5.6 part l\)](#), and by the darker lines in parts [a\)](#) and [g\)](#). Due to their two dimensional form and relatively low levels of segregation, they could not be removed using an isosurface in the same manner as other phases. As such, the final chromia compositions do contain some of these segregants as part of the average.

Average chromia compositions were calculated after the removal of other phases by re-applying the deconvolution algorithm, followed by decomposing all complex ionic species into their component elements. The resultant dataset compositions are shown in [Figure 5.7](#). Part [a\)](#) consists of a stacked bar chart representing the elemental composition of all 12 datasets, from which it appears that the majority of chromia datasets consist almost entirely of stoichiometric Cr_2O_3 , with the addition of between 2-12 at.% of trace elements. In [Figure 5.7 b\)](#), Cr and O have been removed to isolate the trace element concentrations. As Ti concentration is of particular interest, it has been displayed separately in [Figure 5.7 c\)](#). In addition, the nominal Ti at.% present in the alloys are represented by a red line. It can be seen that the amount of dissolved Ti in these chromia reconstructions varies from 1-6 at.%, with little correlation to the nominal Ti at.% measured in the as-received alloys.

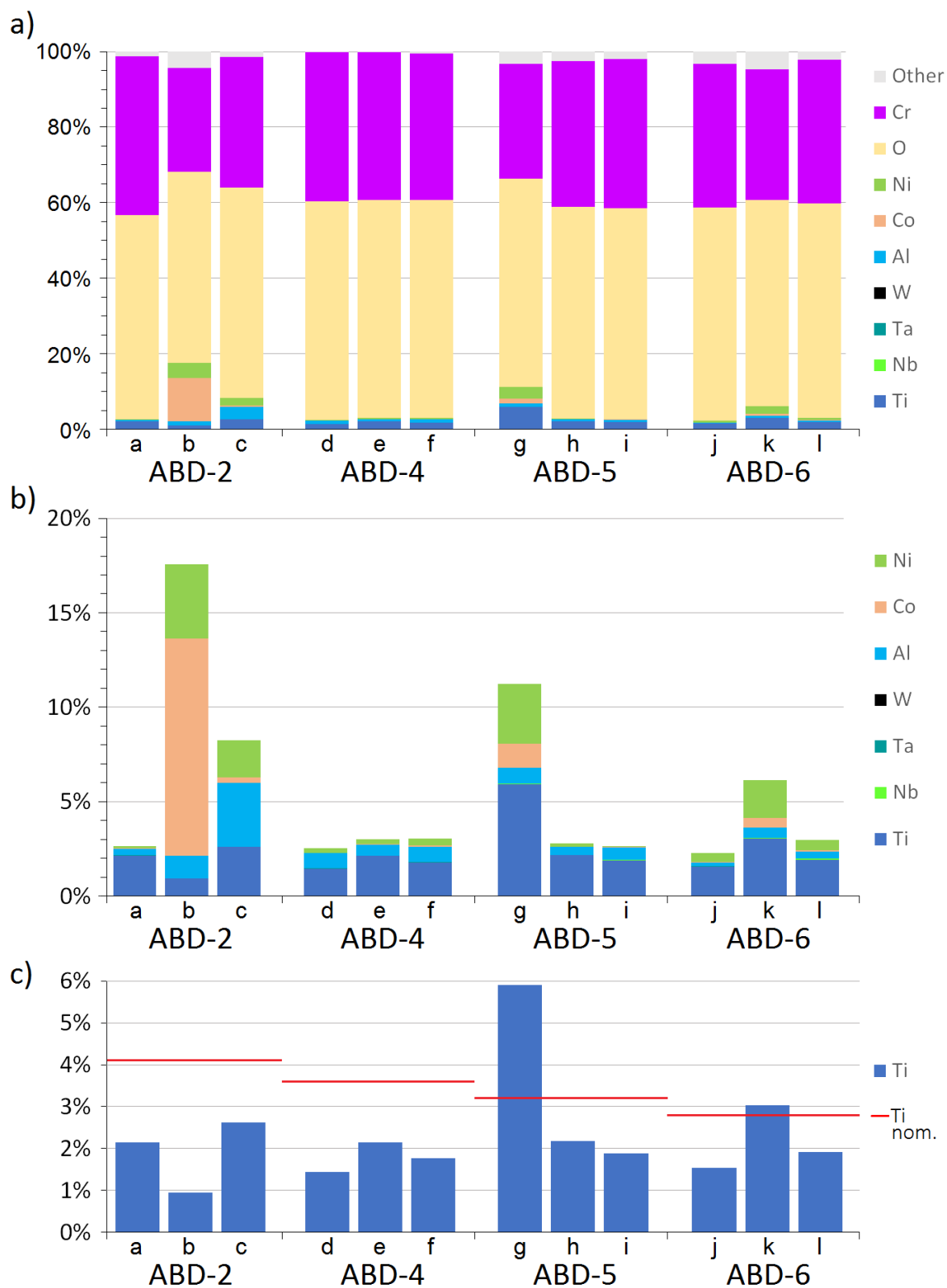


Figure 5.7 – a) Deconvoluted chromia compositions for 12 APT reconstructions across all four ABD alloys. b) After removal of Cr and O to isolate trace element concentrations. c) Nominal alloy Ti concentrations (in at.%) as measured by ICP-OES, compared with Ti (in at.%) measured in chromia.

5.4.3 Localised Chromia Feature Analysis

Some of the reconstructions selected for chromia composition analysis contained regions which were enriched in other elements, with frequent occurrences of NiCo-rich retained γ and regions with increased Ti segregation. Many other datasets were obtained which contain microstructural features with much higher concentrations of locally-segregated elements, such as grain boundaries within the chromia layer and regions of Cr-depleted γ matrix or Ti-rich nitrides. This made these particular datasets unsuitable for determining average chromia compositions, although they did warrant further investigation individually. The three-dimensional nature of atom probe datasets allows these complex features to be studied with more microstructural context than projection-based analysis methods, although care must be taken when investigating variations in local chemistry due to the tradeoff between global and local composition accuracy as previously discussed in [Chapter 5.4.1](#). In the visual representations of reconstructions that follow, the local composition ranges have been used, which allocate peaks to the ionic species with the largest peak contribution.

[Figure 5.8](#) shows a reconstruction obtained from the ABD-5 alloy, which appears to contain a grain boundary with a large amount of elemental segregation. The reconstruction has been split into separate atom maps for each element, and ionic species containing that element, presented individually to highlight segregation behaviour. Cr and Cr-containing ionic species have been excluded as they are distributed fairly uniformly throughout the sample. A grain boundary can be seen edge-on, showing enrichment of the γ' precipitate phase forming elements Ti, Nb and Ta to the interface. A small region of NiCo-rich retained γ phase was observed at the bottom of the feature, and some discrete Ni-rich nodules were also observed on the 10-20 nm scale.

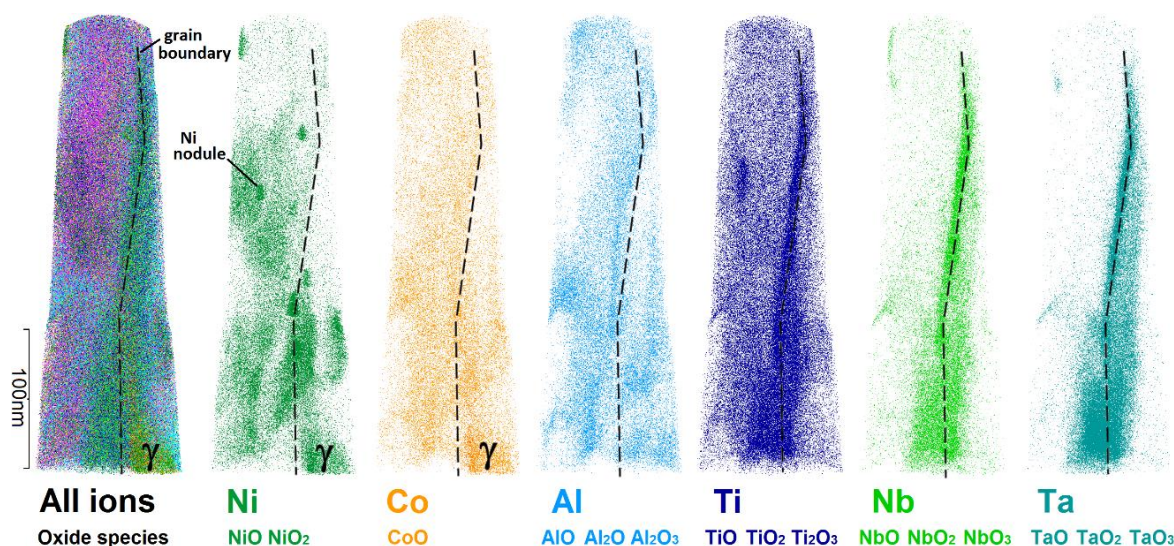


Figure 5.8 – Atom maps of an oxide grain boundary in the ABD-5 alloy, separated into individual maps showing a selection of elements and their associated oxide species detected in the APT experiment.

This trend of grain boundary enrichment of γ' precipitate forming elements was observed across multiple datasets. [Figure 5.9 a\)](#) shows a grain boundary reconstruction from the Nb-free ABD-2 alloy. Elemental segregation to the grain boundary has been further analysed by creating a $60 \text{ nm} \times 10 \text{ nm} \times 10 \text{ nm}$ region of interest perpendicular to the grain boundary and calculating a 1D concentration profile along it using the AtomProbeLab software suite [\[134\]](#), as shown in part [b\)](#). Currently, this is the only software capable of peak deconvolution of the data as it is sampled along 1D concentration profiles, which helps to mitigate the tradeoff between global and local compositional accuracy. The ability to deconvolute local concentration distributions is critical for separating the various overlaps between Ti- and O-containing species, such as $^{48}\text{Ti}^{+++}/^{16}\text{O}^+$ at 16 Da and $^{48}\text{Ti}^{16}\text{O}^{++}/^{16}\text{O}^{16}\text{O}^+$ at 32 Da. These overlaps are a particular concern at grain boundaries, where the change in electric field required to evaporate ions could potentially cause a change in ionic charge state ratios, in particular an increase in O_2^+ at 32 Da. This can lead to an artificial increase in observed peak heights, which could be misconstrued as evidence of grain boundary segregation despite evidence towards it being a field-induced artefact. Use of deconvoluted concentration profiles provides further evidence that the measured segregation of Ti, at the

expense of Cr, is in fact genuine. It also shows that no other elements are segregating to this grain boundary. A Gibbsian interfacial excess value for Ti of 18 atoms.nm⁻² was calculated to lie at the grain boundary using a custom R script provided by Dr Benjamin Jenkins, as shown in [Figure 5.9 c\)](#) and [d\)](#). No segregation data for Ta, Nb or W could be obtained as no peaks relating to these elements were detected in this dataset.

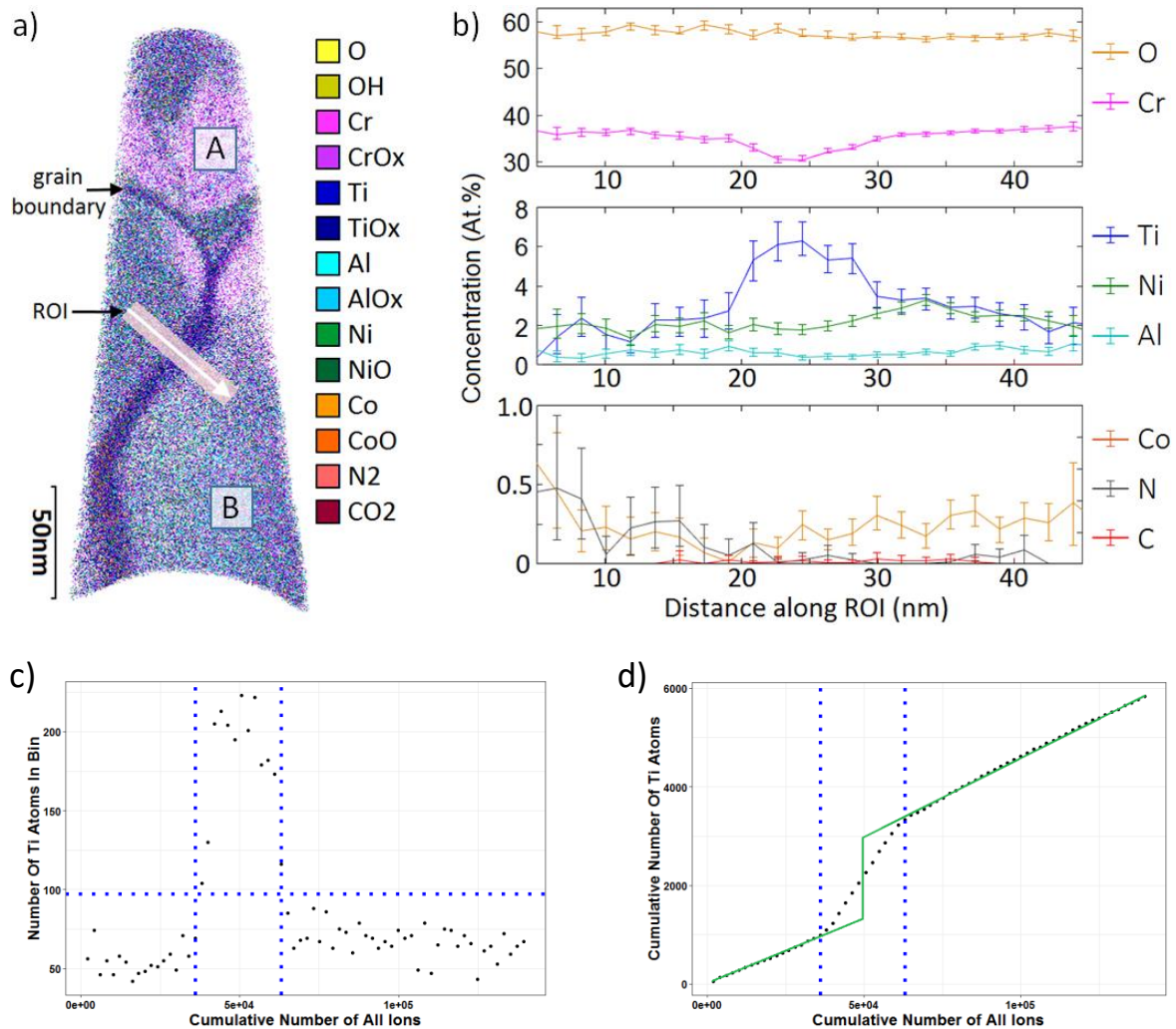


Figure 5.9 – a) A 10nm slice through a reconstruction of alloy ABD-2, containing a highly-segregated grain boundary. Regions of varying chromia composition were analysed using ROIs 'A' and 'B'. b) Deconvoluted 1D concentration profiles from a grain boundary ROI shows segregation of Ti at the expense of Cr. c) 1D distribution of Ti along ROI, used to calculate: d) Cumulative Ti profile, extrapolated to a 2D interface to calculate Gibbsian Excess values.

In addition to grain boundary segregation, the chromia also appears to vary in composition, as indicated by the colour change throughout the reconstruction. This was investigated by creating two regions of interest, as shown in [Figure 5.9 a\)](#). ROI 'A' is located in the lighter region in the

upper section of the dataset, and ROI 'B' is located in the darker blue region below. The compositions of both of these ROIs are shown below in [Table 5.2](#), and were found using the global ranging procedure, thus relying on deconvolution to maintain compositional accuracy. The obtained compositions show that ROI 'A' consists of near-stoichiometric chromia, while ROI 'B' shows enrichment of Ti, Ni, and Al at concentrations of 2.2 at.%, 1.5 at.% and 1 at.% respectively. This alloy contains 0% Nb, and neither Ta nor W were detected in this reconstruction.

	Ion Count	Al	C	Co	Cr	N	Nb	Ni	O	Ta	Ti	W
ROI A	190,829	0.13	0.02	0.01	39.6	0.04	-	0.01	58.7	-	1.23	-
ROI B	212,127	0.97	0.01	0.16	37.4	0.07	-	1.56	57.1	-	2.21	-

Table 5.2 – Compositions of ROIs 'A' and 'B' obtained from the reconstruction of the ABD-2 alloy shown in Figure 5.9 a). Compositions obtained using Global ranging procedure, allowing for deconvolution.

A similar analysis approach was carried out on a reconstruction of alloy ABD-6 as shown in [Figure 5.10](#). Local segregation of Nb, Al and Ti-containing ionic species allows the nanocrystalline oxide grain structure to be seen clearly. In addition, a large NiCo-rich retained γ particle is present, surrounded by a layer of Ni, Co and Nb oxides. Local segregation of Nb to oxide grain boundaries is clearly visible, although Gibbsian interfacial excess values were difficult to determine due to the low concentrations involved. In this case, the segregation behavior of Ti is much more subtle. Initial 1D concentration profiles obtained using the IVAS software indicated a small amount of grain boundary Ti segregation, however these were no longer apparent after repeating the analysis using AtomProbeLab software which accounted for the peak overlaps in the mass spectra. This indicates that field-induced evaporation of O_2^+ is likely occurring here rather than Ti segregation. Within the oxide grains Ti often co-segregates with Ni, which can be seen in [Figure 5.10 a\)](#) as small blue particles adjacent to the grain boundaries.

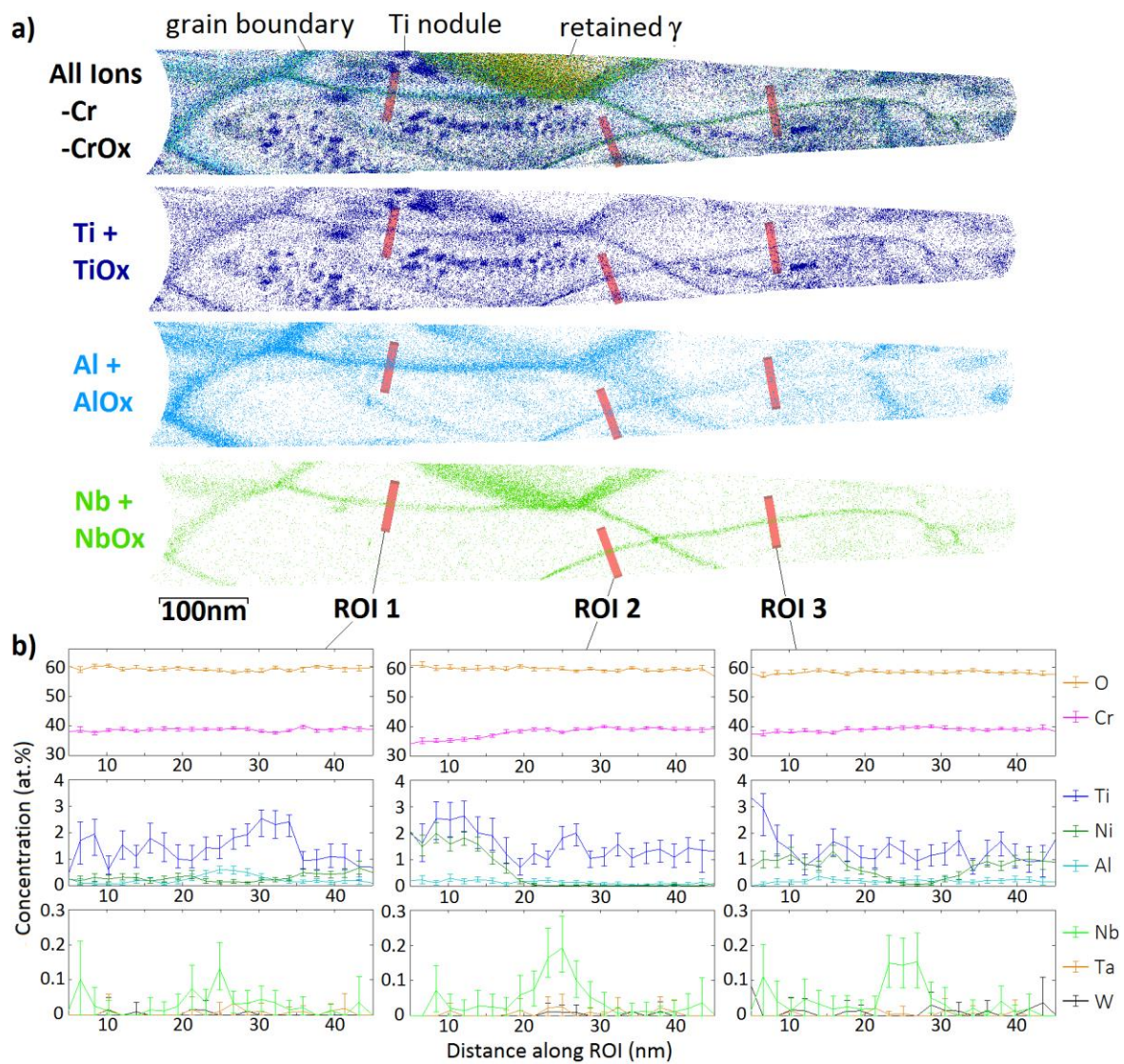


Figure 5.10 – a) A 10nm slice through chromia reconstruction of alloy ABD-6. b) Deconvoluted 1D concentration profiles across multiple ROIs created over oxide grain boundaries.

A reconstruction from the ABD-5 alloy was obtained which consisted of a large retained γ particle, in addition to a region highly enriched in the γ' forming elements Al, Ti, Ta and Nb. [Figure 5.11 a\)](#) shows the ranged reconstruction, and part [b\)](#) shows the two isosurfaces used to isolate both additional phases, which are made more prominent by only displaying 10% of the ions. The γ' element rich 'tail' shown in part [c\)](#) was extracted using a 1.5 at.% TaO₂ isosurface, as this species appeared to show the largest partitioning preference to this region. It follows the edge of the retained γ phase particle, and travels up and into the dataset following a high density surface which could possibly be a grain boundary. A relatively low concentration of TaO₂ was used to extract the particle, to maximise the number of ions included for composition analysis, but this also resulted in the inclusion of a large proportion of chromia ion species around the edge of the isosurface. The total composition of this region is included in [Table 5.3](#), with Cr, O and CrO_x species removed, revealing a large concentration of Ti-containing species in this region. Interestingly, this 'tail' region does not resemble the γ' compositions found previously in [Chapter 4](#) in [Table 4.1](#), with lower Ni and Al concentrations, combined with vastly increased Ti, Ta and Nb concentrations. Although these are all carbide forming elements, the 0.28 at.% C concentration likely rules this out.

The retained γ phase particle was extracted in part [d\)](#) using a 10 at.% Co isosurface, the composition of which is Ni and Co rich, similar to the retained γ regions seen in [Figure 5.8](#) and [Figure 5.10](#). However this also significantly deviates from the γ compositions found previously in [Chapter 4](#) in [Table 4.1](#), as this retained γ particle is heavily depleted in Cr, and contains a Ni:Co ratio which is double the nominal value.

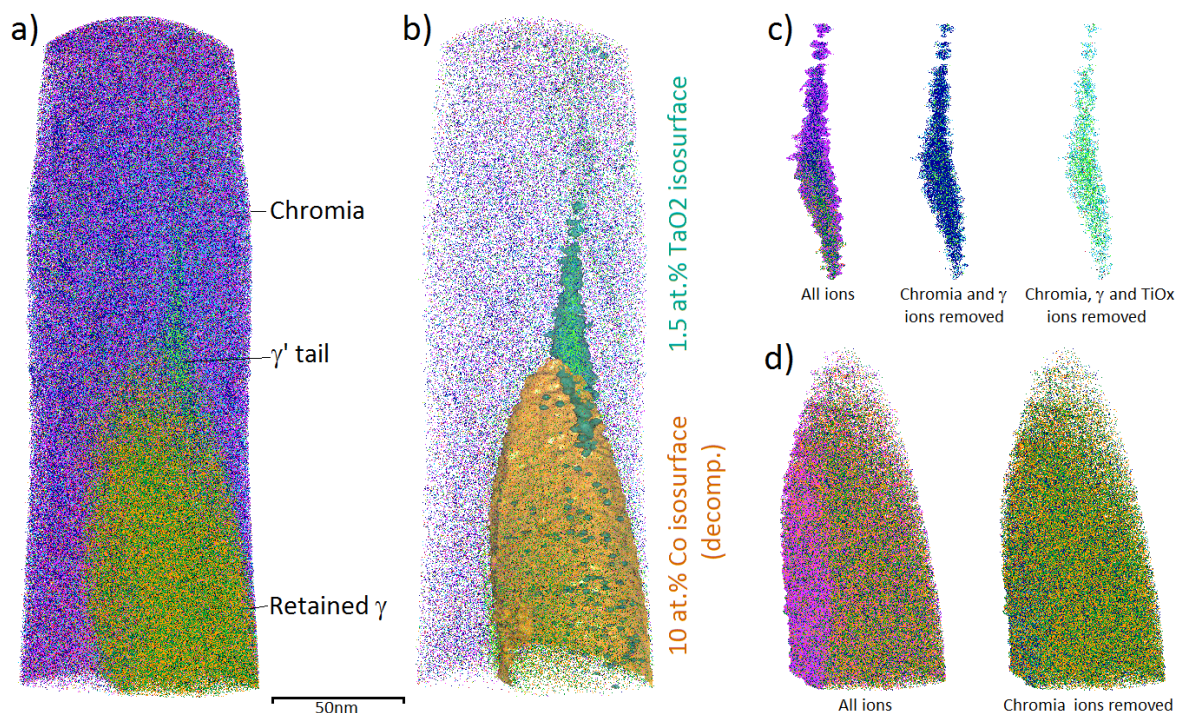


Figure 5.11 – Reconstruction from alloy ABD-5 containing a γ phase particle within the chromia layer. a) All ions shown. b) 90% of ions removed to show created isosurfaces: 1.5 at.% TaO₂ in teal, and 10 at.% Co in orange. c) Extracted TaO₂ isosurface, showing 'tail' rich in γ' -forming elements. d) Extracted Co isosurface, showing retained γ phase particle.

	Ion Count	Al	C	Co	Cr	N	Nb	Ni	O	Ta	Ti	W
Total	30347045	1.89	0.04	1.19	35.87	0.04	0.07	2.24	54.10	0.01	3.65	0.03
Chromia	27564491	1.96	0.04	0.20	37.10	0.04	0.04	0.06	56.13	0.01	3.67	0.00
γ' 'tail'	96780	1.53	0.06	1.21	25.08	0.07	1.50	2.71	54.83	1.41	11.11	0.03
γ' -Cr -O	19396	7.64	0.28	6.02	-	0.37	7.50	13.52	-	7.06	55.49	0.17
Retained γ	1085811	0.30	0.02	23.74	8.19	0.18	0.29	51.30	9.27	0.01	2.96	0.77

Table 5.3 – Phase compositions (at.%) from reconstruction of alloy ABD-5 as shown in Figure 5.11. Phases determined using shown isosurfaces, with compositions from γ' 'tail' both including and omitting chromia species

5.4.4 Alumina Oxide Layer

Three additional datasets were also obtained from the deepest depth within the oxide layer, which intersects the alumina-metal interface. One of these datasets obtained from the high-Nb ABD-6 alloy is shown in [Figure 5.12](#), which also contains a number of isoconcentration surfaces used to define phase boundaries, and a region of interest created across the alumina-metal

interface. The oxide morphology present in this reconstruction shows that this alumina region has intruded the γ matrix, and is not present as a continuous subscale.

The chemistry across the alumina-matrix phase boundary was analyzed using a set of one-dimensional concentration profiles. For clarity, these have been separated into high and low-concentration decomposed elemental distributions, as well as non-decomposed ionic distributions for a selection of oxide species. A 10 nm thick oxide region rich in Nb, Ni, Ta and Co oxides can be seen lying directly at the alumina-gamma interface, of which a large proportion are Nb-rich as seen in part [b](#)).

A composition analysis of the phases present is also shown in [Table 5.4](#), which includes both regions of retained γ matrix extracted using a 40 at.% Ni isoconcentration surface, the alumina extracted using a 30 at.% Al isosurface, and a number of Ti, Ni and Nb-rich nitrides extracted using an 8 at.% Ti isosurface. This reveals near-stoichiometric alumina, a chromium-depleted matrix, and a number of Ti, Nb and Ni-rich nitride particles. Eight of these nitride particles were found across the two ABD-6 alumina-metal interface reconstructions, all of a similar composition. No nitride particles were observed in the high-Ti ABD-4 alumina-metal interface reconstruction.

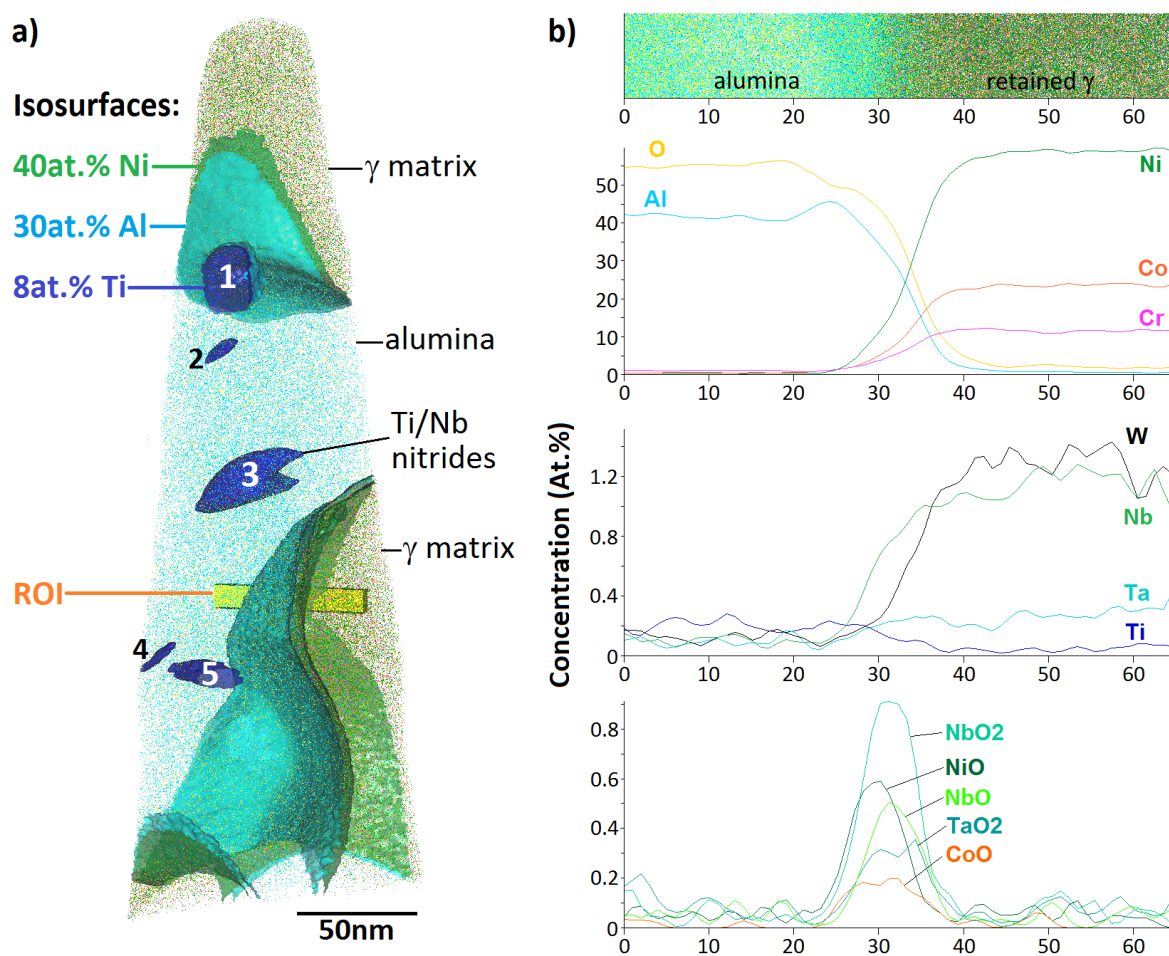


Figure 5.12 – a) Reconstruction of an alumina-metal interface from alloy ABD-6 including isosurfaces used to determine phase compositions. b) A region of interest created over the alumina-metal interface showing elemental distributions and oxides at the interface.

	Ion Count	Al	B	C	Co	Cr	N	Nb	Ni	O	Ta	Ti	W
Retained γ	23,977,358	1.97	0.00	0.02	23.37	12.39	0.15	1.23	55.96	3.20	0.21	0.54	0.97
Alumina	52,935,252	43.61	0.01	0.02	0.86	0.72	0.15	0.07	0.56	53.23	0.01	0.74	0.01
Nitride AVG	409,204	6.72	0.01	0.30	0.14	2.34	19.92	4.81	11.20	21.91	0.41	32.10	0.14

Nitride 1	110,060	6.61	0.00	0.40	0.09	2.22	19.93	3.29	11.48	21.96	0.42	33.45	0.15
Nitride 2	9,084	8.18	0.00	0.19	0.09	2.04	18.08	4.11	10.74	24.77	0.43	31.14	0.22
Nitride 3	245,995	6.59	0.00	0.25	0.16	1.88	20.01	5.46	11.47	21.42	0.34	32.27	0.15
Nitride 4	13,148	7.95	0.05	0.29	0.26	3.39	18.37	5.92	8.70	24.77	0.74	29.41	0.15
Nitride 5	30,916	7.25	0.02	0.32	0.17	6.10	20.39	4.77	9.33	23.49	0.80	27.28	0.08

Table 5.4 – Phase compositions (at.%) from reconstruction of alloy ABD-6 as shown in Figure 5.12. Phases determined using shown isosurfaces. Individual nitride compositions also included.

5.5 Discussion

5.5.1 Compositional Effects on Oxide morphology

The most obvious external sign of changing oxidation properties between the alloys can be seen in the SEM and EDX cross-sectional micrographs shown in [Figures 5.2](#) and [5.3](#). These both show that the oxide scales formed on the low titanium alloy ABD-6 are comprised of a uniform continuous outer chromia layer with evenly-dispersed internal alumina islands, while the high-Ti alloy ABD-2 forms a more irregular external chromia scale, often above deep internal alumina intrusions that progress along grain boundaries. As the alloys and oxidation conditions were designed to remove as many external variables as possible, this change in oxide morphology can be attributed to the varying Ti:Nb ratio. This composition-dependent morphology has a number of implications, perhaps the most relevant of which for industrial applications is that oxidation kinetics alone may not be an adequate indicator for determining oxidation damage, as grain boundary intrusions have been shown to act as potential fatigue crack initiation sites. Cruchley et al. [\[81\]](#) and Karabela et al. [\[62\]](#) have previously arrived at similar conclusions with respect to oxidation damage. One potential upside of these deep alumina intrusions has been presented by Whittle et al. [\[178\]](#), which theorise that these intrusions can act as ‘keys’ to help prevent oxide spallation and maintain scale integrity.

Another implication of a change in oxide morphology is a potential change in the location of ion transport. Localised areas of increased oxide formation implies that ion transport may be accelerated or hindered in particular regions. The appearance of thicker oxide ridges above grain boundaries has been previously reported by Chen et al. [\[75\]](#) in a number of commercially-available alloys, as well as Taylor et al. [\[78\]](#) and Cruchley et al. [\[81\]](#) in RR1000, which is plausible considering that grain boundaries within the metal are known to act as short-circuit diffusion paths. The fact that these grain boundary ridges appear more pronounced in the higher-Ti alloys

in this study indicate that the dominant ion transport mechanism may change with composition, although whether this is solely due to a change in Ti or Nb concentration is unknown. The addition of Nb has been previously shown by Weng et al. [169] to change the oxide scales to a smoother morphology in a family of model alloys, although the alloys in this study contain less Ti and more Nb, both at 2.0 at.%.

The formation and characterisation of subscale nitride particles containing Ti, Nb and Ta is also noteworthy. Their location beneath the alumina scale, where the oxygen partial pressure is low, is expected as nitride formation requires a reducing environment [75]. Taylor et al. [78] and Chen et al. [75] have also confirmed the presence of subsurface titanium nitrides using TEM and WDS, however the high-resolution APT characterisation shown in Figure 5.12 and Table 5.4 reveals additional details about their shape and composition.

5.5.2 Relationship between Composition and Kinetics

Oxidation kinetics have been found to vary with composition as measured by thermo-gravimetric analysis (TGA), which supports previous studies investigating the role of increasing titanium concentration on oxidation kinetics [75,77,168]. Figure 5.1 shows that the mass gain due to oxide growth follows a parabolic path, which according to Wagner et al. [70] implies that the rate-limiting step for oxide growth is ion diffusion through a continually thickening scale. It is likely that these two phenomena are connected, with Ti concentration directly affecting rates of ion diffusion through the scale.

Chromia is known to be a p-type semiconductor at high oxygen partial pressures ($P_{O_2} > 10^{-5}$ atm) [179], where the main charge carriers are electron holes and chromium vacancies. One of the more frequently cited mechanisms for creating chromium vacancies was originally proposed by

Callister et al. [180] by way of a high-valence cation doping mechanism. This involves the creation of cation vacancies during TiO_2 dissolution in Cr_2O_3 , as described by Equation 5.2 [172]:



where $\text{Ti}_{\text{Cr}}^{\bullet}$ is a Ti atom with one effective positive charge on a Cr lattice site, and V_{Cr}''' is a cation vacancy with three effective negative charges. In order to maintain charge neutrality, the aliovalent substitution of 4 Cr^{3+} ions with 3 Ti^{4+} ions on Cr lattice sites requires the creation of an additional cation vacancy, as depicted in Figure 5.13. It is these additional cation vacancies which are implicated in the increased rates of cation-diffusion through chromia.

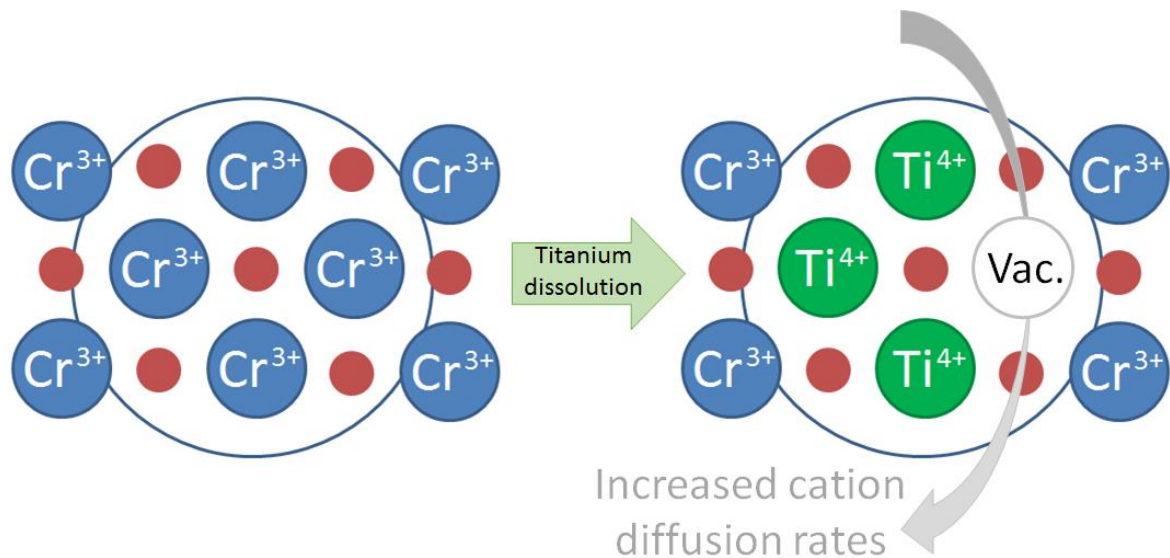


Figure 5.13 – Depiction of the mechanism by which titanium dissolution in chromia causes aliovalent substitution of 4 Cr^{3+} ions with 3 Ti^{4+} , with the additional vacancy required in order to maintain electrical neutrality aiding cation diffusion rates.

Experiments by Atkinson et al. [172] and Blacklocks et al. [173] have verified this cation vacancy mechanism in pure α -chromia doped with Ti by utilizing X-ray diffraction (XRD), density and electrical conductivity measurements combined with computer simulation of defect energies. However it must be acknowledged that pure lab-grown α -chromia is likely to exhibit a different microstructure to that of thermally-grown oxides in complex superalloys. This mechanism has also been investigated in more complex superalloys, such as in experiments performed on INCOLOY 800H by Grübmeier et al. [171] involving XRD and X-ray Absorption Spectroscopy (XAS).

These have also shown Ti^{4+} ions and vacancies to be located within the chromia lattice. However, this lattice diffusion mechanism alone cannot explain the increase in oxidation kinetics displayed by these alloys, as the Ti concentration dissolved in the chromia as measured by APT appears to show no correlation with the nominal alloy Ti concentrations (Figure 5.7 c) nor their associated kinetics (Figure 5.1). This implies that the mechanism does not solely depend on defect density.

One interesting potential mechanism that fits with the observations in this study involves an increase in cation diffusion out of the metal along oxide grain boundaries. The variation in oxide morphology displayed in Figure 5.2 has already hinted at a potential shift in preferred cation transport pathway to the grain boundaries.

5.5.3 Impact of Titanium Segregation on Potential Oxidation Mechanism

Grain boundaries are widely known to be short-circuit diffusion pathways, especially in nanocrystalline materials with a high grain boundary cross-section to volume ratio. Diffusion simulations carried out by Pedrazzini et al. [181] suggest that grain boundaries are likely to form the main outwards diffusion path for Ti ions. Manipulation of grain boundary chemistry via deliberate addition of certain reactive elements which alter their diffusion characteristics is a well-established field of research, known as the Reactive Element Effect [178,182–185]. Many superalloys already incorporate elements such as Y, Hf, La and Zr which preferentially segregate to oxide grain boundaries, where they improve scale adhesion by acting as sulphur-getters, and also reduce oxidation rates by inhibiting cation transport [186]. Ti repeatedly appears as an outlier in this regard, as it has been shown to segregate to chromia grain boundaries and accelerate oxidation rather than inhibit it. The fact that Nb has also been observed segregating to oxide grain boundaries (as seen in Figure 5.10) without any associated increase to oxidation rates (as seen in Figure 5.1) indicates that this effect is due to some property of Ti other than its valency.

Hence, from the data presented in this study it is reasonable to conclude that addition of Ti leads to a change in rate-limiting step in the oxidation mechanism from lattice cation diffusion to grain boundary ion diffusion. This explains why Ti segregation to grain boundaries can have such an effect on the oxidation kinetics, while also explaining the increasing size of alumina intrusions and grain boundary ridges due to increased anion flow into the metal.

5.6 Conclusions

The oxidation kinetics of the ABD alloys with varying Ti:Nb ratio were studied by performing Thermo-Gravimetric Analysis (TGA), which resulted in parabolic oxidation rate curves, indicating that the oxidation kinetics are based on ion diffusion through the oxide scale. The oxidation rates confirmed that a correlation exists between increasing titanium content and accelerated oxidation kinetics.

High-resolution characterization of microstructure and chemistry was carried out on the resultant oxide layers using cross-sectional electron microscopy techniques alongside Atom Probe Tomography, to investigate the mechanism by which Ti:Nb ratio affects oxidation kinetics. Analysis of oxide cross-sections verified that the oxide scale exists as a dual-layer of external chromia above an internal alumina subscale, as predicted based on consideration of oxygen partial pressure as a function of depth from the surface. A composition dependence was also observed, with the high-Ti alloy ABD-2 exhibiting rough, irregular chromia above deep alumina grain boundary intrusions, whereas the low-Ti alloy ABD-6 exhibited smooth external chromia and evenly-distributed internal alumina islands. Ti was qualitatively observed to preferentially segregate to the chromia layers during EDX analysis. A follow-up quantitative APT composition analysis determined the compositions of chromia scales from all ABD alloys, revealing near-stoichiometric Cr_2O_3 with up to 10 at.% impurities consisting mostly of Ti, Ni and Al. Importantly, the Ti concentration dissolved in bulk chromia does not appear to correlate with the nominal

alloy Ti concentration, and by extension the oxidation kinetics. This indicates that the rate-limiting step is not reliant on dopant levels.

Further APT analyses focussed more on oxide grain boundaries, which are known to be short-circuit diffusion pathways. 1D concentration profiles across grain boundaries, analysed to account for peak overlaps in the associated mass spectra, show high levels of segregation from the γ' -forming elements Ti, Ta and Nb, which appears to contradict the theory that lattice diffusion is the rate-limiting step for ion transport through the oxide scale. As the Ti concentration dissolved in chromia does not appear to correlate with the displayed oxidation kinetics, and large amounts of Ti were observed segregated to grain boundaries, the lattice diffusion mechanism was determined not to be the rate-limiting step for the oxidation of ABD-series alloys at 800°C over the time period of 100 hours.

Additional results were obtained during APT analyses of the alumina-metal interface, which revealed alumina layers with a composition close to stoichiometric Al_2O_3 , with much lower levels of solute elements compared to Cr_2O_3 . In addition, regions of Cr-depleted γ matrix phase and nitride particles enriched in Ti, Nb and Ni were also observed.

Chapter 6. Fatigue Crack Tip Characterisation

This chapter focusses on the characterisation of fatigue cracking that occurs at high temperatures in an oxidising environment. This was conducted through the use of an interrupted ETMT experiment on the ABD-2 alloy, as previously described in [Chapter 3.2.2](#). The post-exposure fatigue crack sample underwent an initial SEM characterisation, during which a complex fatigue crack morphology was observed, including a number of additional secondary crack tips.

The subsequent analysis of the primary crack tip and two secondary crack tips began in much the same way, with an initial investigation of the surrounding area, using SEM techniques such as the diffraction-based EBSD and TKD, as well as elemental mapping via EDX. Each crack tip has been covered individually in separate sections of [Chapter 6.3](#). Once suitable crack tip regions had been identified, an extraction and mounting procedure involving FIB-SEM techniques was carried out to transform them into the needle-shaped samples required for APT analysis, with an optional intermediate lamella step for a more detailed characterisation. The final APT analysis and results are covered in [Chapter 6.4](#), which is followed by a unified discussion section in [Chapter 6.5](#) and conclusions section in [Chapter 6.6](#).

6.1 Introduction

Turbine discs are subject to some of the most severe operating conditions experienced by any components that make up a jet turbine engine. They are required to combine the high temperature capabilities exhibited by turbine blades, in addition to the strength to withstand disc stresses up to 1200 MPa, at several thousand revolutions per second [9]. These feats must be carried out whilst resisting temperature-dependent failure mechanisms such as corrosion, creep and fatigue [187]. Fatigue cracking in particular must be carefully monitored, as turbine discs are

safety critical components made from large monolithic forgings, with no component interfaces to arrest crack propagation.

In order to accurately estimate safe component lifetime, it is vital to understand the different mechanisms that lead to fatigue crack propagation. Static and cyclic fatigue crack propagation have been the subject of extensive previous research [15,188], and as such safe lifetimes can be accurately estimated under these conditions. However another form of fatigue occurs during 'dwell' periods, during which components are kept at peak load for prolonged periods in oxidising or corrosive environments [189]. Literature regarding dwell fatigue is more limited in scope, but does show that this mechanism can be distinguished by two characteristic changes in cracking behaviour. First, dwell fatigue crack propagation rates have been shown to be time-dependent rather than cycle-dependent, which greatly complicates lifetime estimation [94]. Second, the crack path changes from transgranular to intergranular, which has been linked to the environmental degradation of grain boundaries [97]. Environmental degradation is likely to require some sort of reaction or diffusion process, the kinetics of which must therefore be taken into consideration. Kinetics are highly temperature-dependent, which suggests a possible exacerbation of dwell fatigue crack propagation rates at high temperatures. This could become an issue as turbine entry temperatures (TET) are increased to improve engine efficiency [5].

One difficulty with estimating component lifetime, with regards to dwell fatigue, is that the underlying mechanisms behind crack propagation are not yet fully understood, although a number of potential candidates have been proposed. One of the most well-supported mechanisms is stress-assisted grain boundary oxidation (SAGBO), which can be summarised as the repeated formation and cracking of brittle oxides down grain boundaries [84,87,102,109,190]. The other well-supported competing mechanism is dynamic embrittlement (DE), which can be summarised as the diffusion of embrittling species down grain boundaries ahead of the crack tip,

leading to repeated decohesion and cracking [49,53,92,191]. These two candidate mechanisms differ in the chronological order of oxide formation and crack propagation, which can be investigated and experimentally validated through the use of high-resolution characterisation techniques, in order to determine the chemistry and morphology of these crack-tip regions.

6.2 Cross-Sectional Fatigue Crack Analysis

The ETMT technique described in [Chapter 3.2.2](#) was performed on samples of alloys ABD-2 and ABD-6 by Németh et al. in order to measure strain response at 700°C. This was followed by cross-sectional EDX and STEM analyses of the primary fatigue crack tip, as published in [120]. The central notched region containing the crack was prepared for post-exposure characterisation by mounting and polishing using successively finer grades of SiC grit paper, diamond compound and colloidal silica suspension. Surface preparation was undertaken with great care, as the 1 mm depth of the mounted ETMT samples limits the amount of material available for removal.

Upon receipt of the ABD-2 crack tip sample, an initial SEM analysis was performed using a Zeiss Crossbeam 540 FIB-SEM. Micrographs were obtained of the area surrounding the crack, as shown in [Figure 6.1 b](#)), which revealed a number of features that would prove to be relevant when choosing a region of interest. A large FIB trench can be seen at the presumed location of the primary crack tip, due to previous experimentation. Due to the unknown depth of the damage zone surrounding this trench, and the thinness of the sample, it was decided that the initial investigation should be focussed on the two secondary crack tips labelled in [Figure 6.1 c](#)).

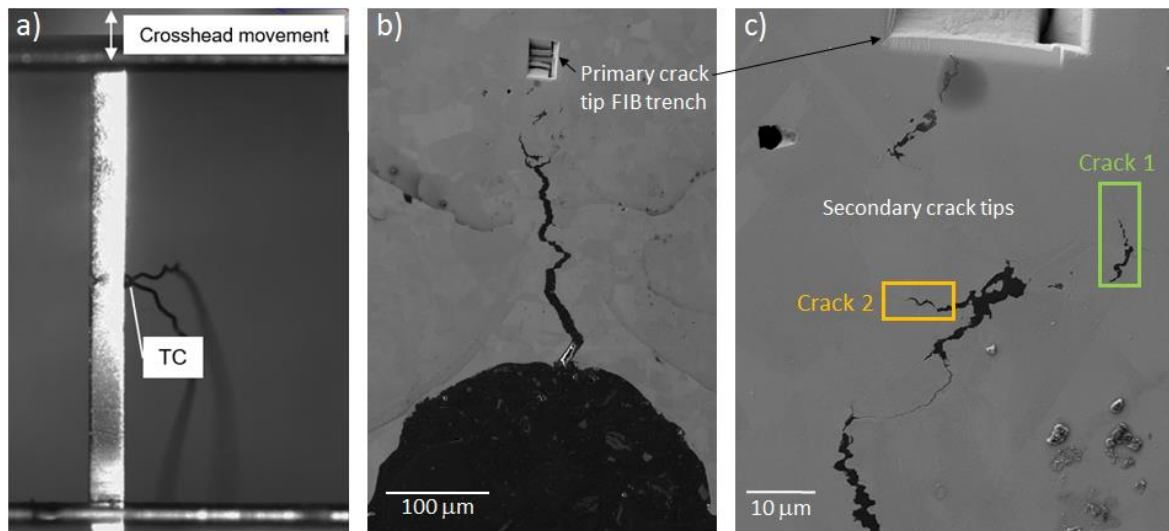


Figure 6.1 – a) ETMT sample before exposure, showing pre-cut notch and thermocouple locations (adapted from [121] with permission from the copyright holder A Németh © 2017).

b) Cross-sectional SEM analysis of polished crack tip area, including FIB trench from previous experiment [120]. c) Zoomed-in section showing secondary crack tips selected for further EDX, EBSD, and APT analysis.

SEM analyses confirm that the fatigue crack propagates along grain boundaries, in line with previous investigations into environmentally-assisted damage. The main branch of the crack extends 400 μm into the sample, and appears to be filled with mounting resin all the way to the primary crack tip. The two secondary crack tips selected for further characterisation are located between 30 to 60 μm away from the presumed location of the primary crack tip, which is close enough for environmental damage to be representative, while far enough away from the FIB trench to avoid the majority of Ga^+ ion damage. A third experiment focussed on the primary crack tip was performed after the sample underwent an additional surface grind and polish, with the aim of removing the trench and FIB-damaged region.

6.3 Individual Crack Tip Characterisation

The crack tip liftout technique used here is a modification of the techniques developed by Lotharukpong et al., Meisnar et al., and Kruska et al. [127–129], as previously detailed in Chapter 3.3.4. Further refinements were made between each experiment, in order to address and

mitigate the difficulties encountered at each step. Due to the constant adjustment of the technique and the highly sample-dependent nature of the extraction procedure, each crack tip experiment has been covered individually from initial characterisation to final APT sample.

6.3.1 Crack Tip One

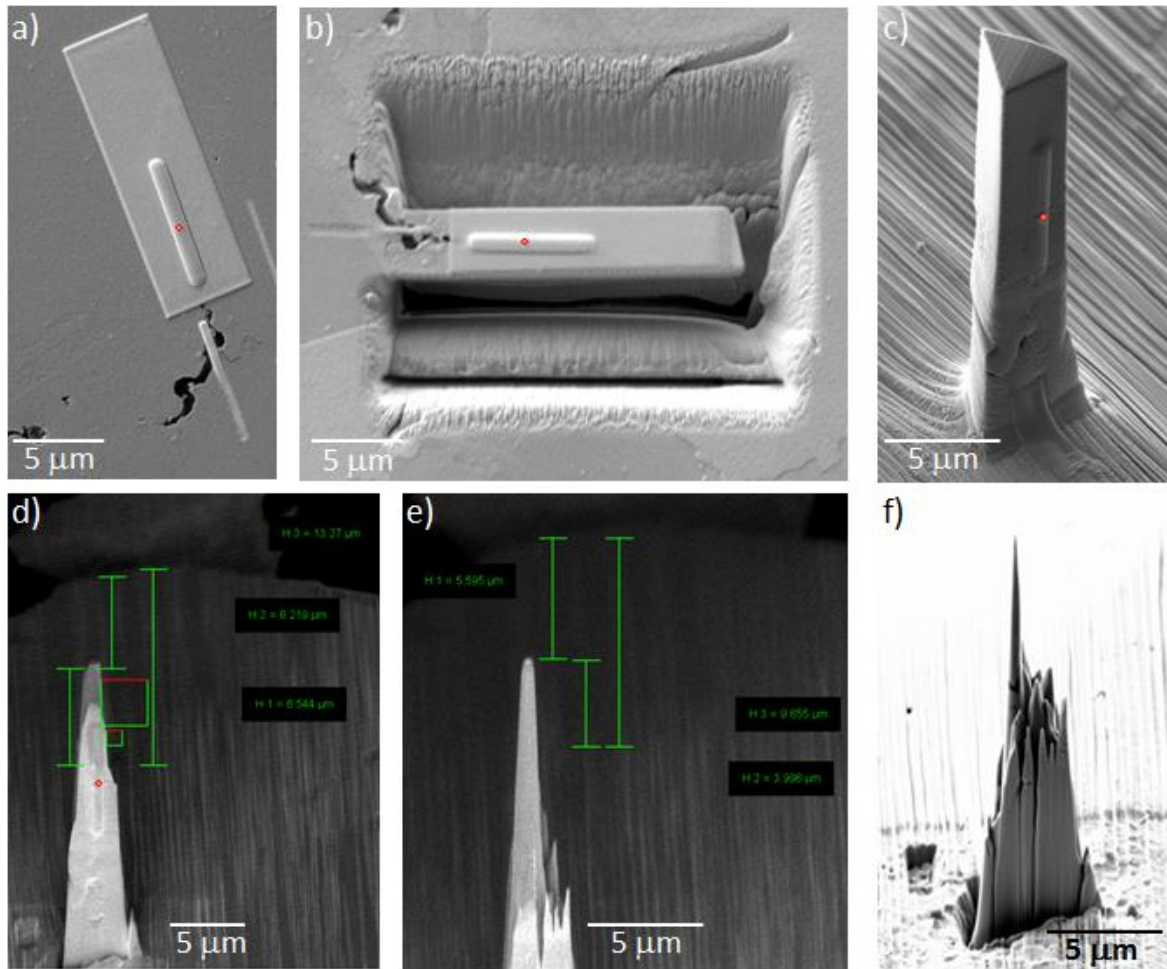


Figure 6.2 – Crack 1 liftout and mounting procedure, with crack tip fiducial highlighted in red. a) Pt deposition of protective strip and fiducial. b) Liftout undercut trenches. c) Mounted liftout on Cu tomography post. d) to f) Thinning of liftout into APT needle tip by annular milling, using fiducial spot and SmartSEM labelling as guides.

The region of interest selected for the first experiment centred around a secondary crack tip located around 25 µm from the edge of the FIB trench, as shown in [Figure 6.1 c\)](#). The crack was easily visible in SEM, and the position of the crack tip could be reasonably estimated due to the differing contrast of what were presumed to be crack tip oxides. The extraction process is

identical to that described in [Chapter 3.3.4](#), consisting of deposition of protective Pt, followed by micromanipulator liftout and mounting onto a Cu tomography post as shown in [Figure 6.2 a\) to c\)](#).

Due to the unavailability of EDX and EBSD analysis capabilities during this initial extraction procedure, the pre-liftout characterisation was limited to SEM. For this reason, the intermediate lamella thinning and characterisation step was skipped, with the mounted liftout bar sharpened directly into an APT needle as shown in [Figure 6.2 d\) to f\)](#). A layer of protective Pt was deposited on the upper surface of the mounted liftout, followed by a rough shaping mill to remove the three outer corners. After this, a fairly standard annular milling procedure was followed to create the APT tip, using the deposited Pt crack tip fiducial highlighted in red to guide the milling procedure. Additional measuring bars within the SmartSEM software were overlaid during milling, to track the crack tip location as shown in [Figure 6.2 d\) and e\)](#).

The final tip thinning and polishing steps were performed after EDX and TKD capabilities had been made available, which allowed for in-situ characterisation. SEM images and associated EDX maps were obtained at several points during the milling procedure (using a 2nA, 10kV beam), as shown in [Figure 6.3](#). This periodic observation helped to ensure that the APT sample tip contained a region of significant interest. The progression of tip shape during milling is shown by parts [a\)](#), [b\)](#), and [e\)](#), with the final tip represented by part [d\)](#). The crack can be identified in these images as darker regions, likely due to infiltration of the mounting resin, while a lighter border region between the dark resin and matrix likely indicates an oxide layer. The high contrast difference between regions meant that further TKD analysis was not deemed necessary, as the crack location was already sufficiently visible.

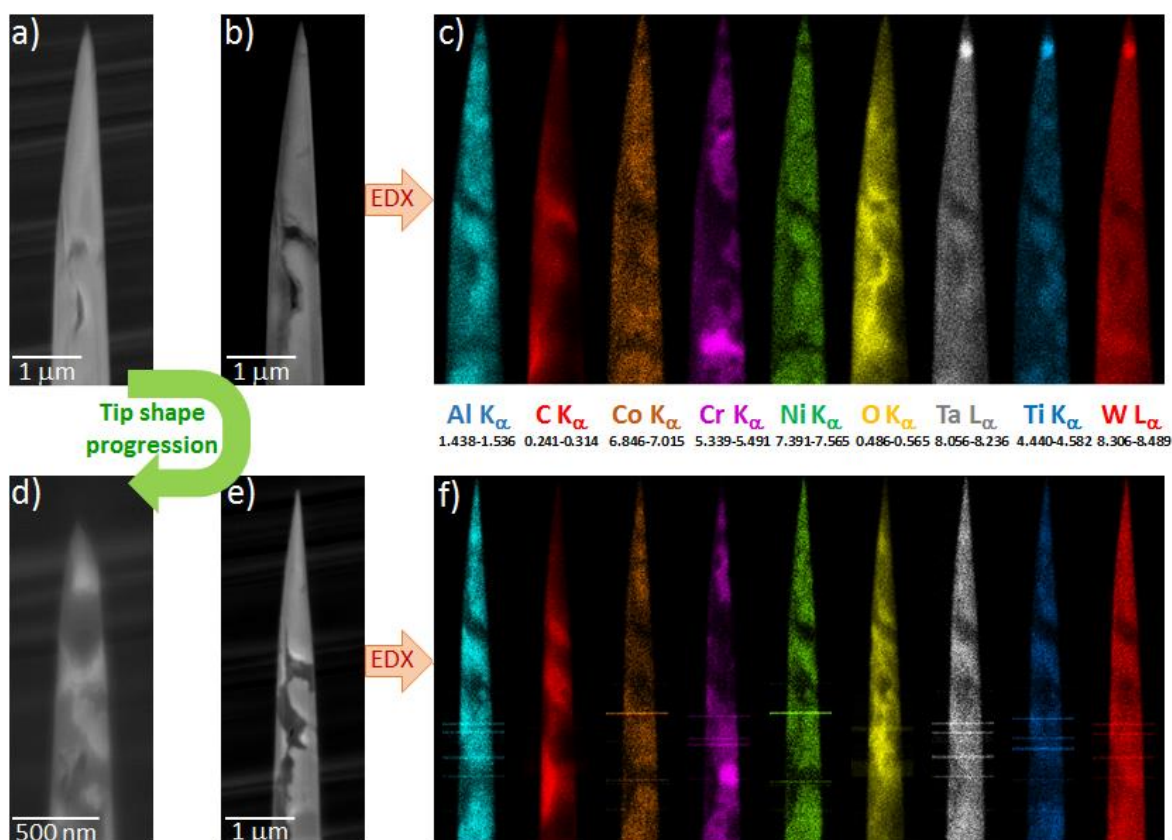


Figure 6.3 – Crack 1 APT needle thinning and characterisation. a) Initial tip. b) and c) First thinning stage and corresponding EDX maps. d) Final APT tip, showing considerable mounting resin infiltration. e) and f) Second thinning stage and corresponding EDX maps.

The EDX maps shown in Figure 6.3 c) and f) were both obtained using a 10 kV electron beam in order to activate higher energy X-ray emission lines, which was required so that peak overlaps at lower energies could be avoided. The most problematic of these overlaps involves the O K α and Cr L α emission lines around 0.55 keV, which was mitigated by mapping Cr using the higher energy K α emission line around 5.4 keV. However, the O maps based on the O K α line do still comprise some overlapping Cr signal. Despite this, the apparent location of O in these maps appears to correlate well with the lighter border regions, supporting the previous assertion that this is indeed an oxide layer. The darker region within the crack appears to be absent from all EDX maps with the exception of C, indicating that the carbon-rich mounting resin has infiltrated all the way to the crack tip. A small amount of C also appears at the top of part c) in addition to Ti, Ta and W. This is likely to be a carbide particle, as these elements are all known carbide-forming elements

[29]. In addition, a region of high Cr signal can be seen at the bottom of the micrographs, which does not appear to contain any other elements.

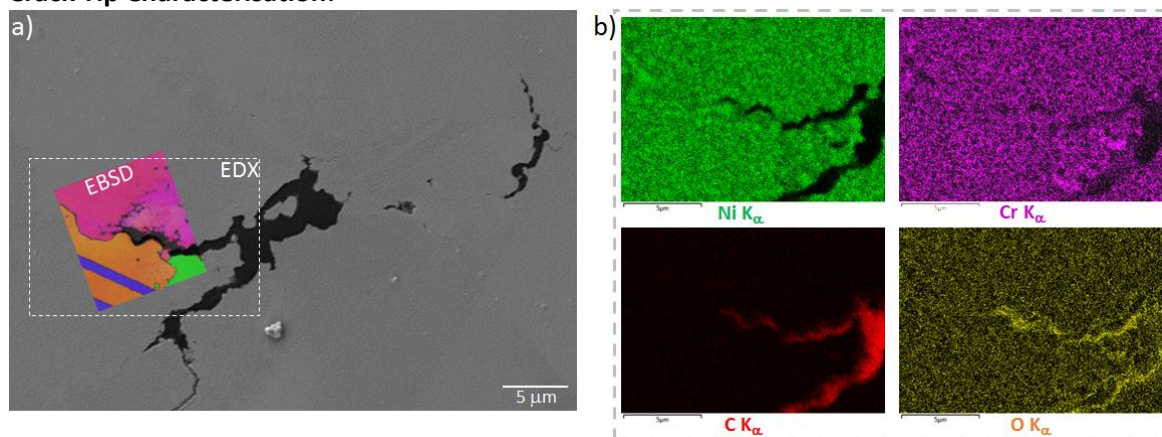
Avoiding the large resin deposits within the tip proved difficult, as the tip position can only be adjusted so much during the annular milling procedure, and the resin displayed highly inconsistent material removal rates. An SEM micrograph of the final tip shape is shown in [Figure 6.3 d](#)).

6.3.2 Crack Tip Two

Some refinements to the crack tip extraction method were made before preparing the second crack. During the previous experiment it was found that although initially locating the crack proved to be trivial, precisely locating the crack tip within the final needle was more difficult than anticipated. For this reason, a more thorough pre-liftout characterisation was carried out, utilising both EDX and EBSD techniques. EBSD was found to be particularly useful for identifying the grain boundary preceding the crack, and therefore locating the crack tip.

The entire liftout process has been displayed in [Figure 6.4](#). The pre-liftout characterisation consisting of SEM and EBSD mapping is shown in part [a](#)). This SEM image shows the locations of the first two secondary crack tips, with an inset EBSD map around the second crack tip, which confirms that the crack is travelling intergranularly. Some additional features were observed, including a dark region adjacent to the crack which is unable to be indexed in the grain above, and a number of twin boundaries in the grain below. A selection of relevant EDX maps have been chosen for display in part [b](#)), including Ni and Cr to show the presence of γ' and γ phases respectively, as well as C and O maps to demonstrate the extent of oxidation and resin infiltration along the crack. Also observed but not shown were a number of W, Ta and Ti-rich particles similar to that seen in [Figure 6.3 c](#)).

Crack Tip Characterisation:



Liftout and Mounting Procedure:

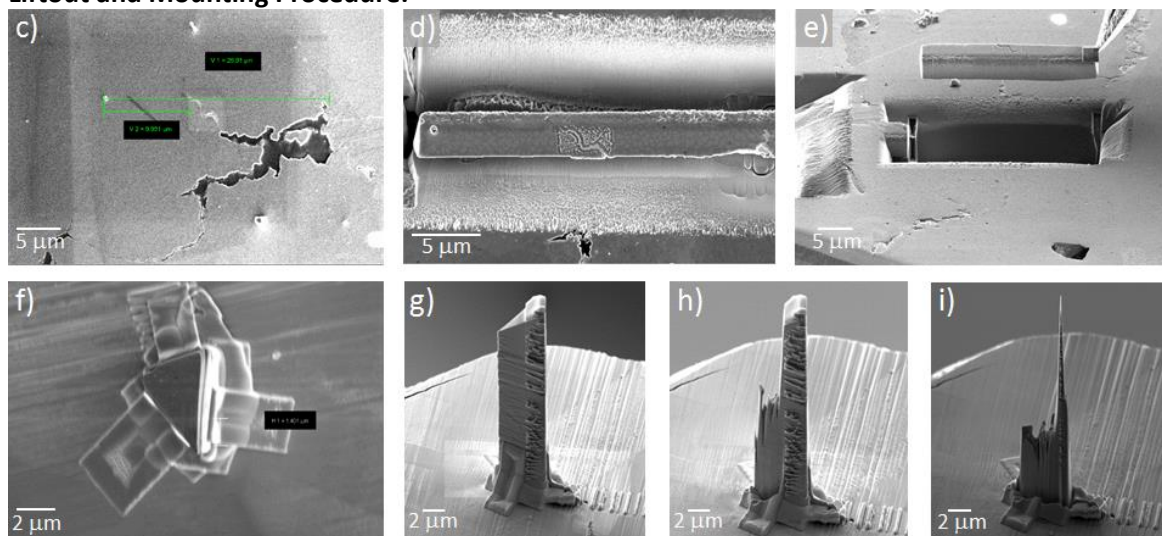


Figure 6.4 – Crack 2 pre-liftout characterisation, consisting of: a) SEM with inset EBSD map, and b) EDX maps. c) to f) covers liftout and mounting procedure. h) and i) Thinning of liftout into lamella.

The Pt protection, liftout, and mounting procedures shown in parts c) to f) were performed in a similar manner to that described during Chapter 3.3.4. However, instead of thinning directly down to an APT tip, the mounted liftout was thinned down to a lamella of sub-200 nm thickness as shown in parts g) to i). This lamella was oriented parallel to the original sample surface, so that the characterisation performed in parts a) and b) would remain valid. The thinning procedure was performed to render the lamella electron transparent, which allowed the use of the high-resolution transmission Kikuchi diffraction (TKD) technique to investigate the grain structure. Any EDX maps found would also be higher resolution due to the reduction in electron interaction volume. These techniques helped to mitigate some of the difficulties encountered during the first

liftout, such as tracking the position of the crack tip during annular milling and identifying any regions to be avoided.

The lamella characterisation and tip shaping process are shown in [Figure 6.5](#). Part [a](#)) consists of SEM, TKD and EDX micrographs of the lamella which were used to locate a region of interest to become the tip of the needle-shaped APT specimen. The preceding grain boundary can be clearly identified in the TKD analysis, as well as a round particle near the grain boundary and one of the twins seen previously in [Figure 6.4 a](#)). Interestingly, the dark region caused by a lack of indexing only exists on one side of the grain boundary. As this TKD image was obtained using a transmission EM technique, it has been reflected horizontally to better match the backscattered SEM and EDX images.

The EDX micrograph presented in [Figure 6.5 a](#)) consists of a number of element maps layered over one another, with the pink Cr map representing the γ phase, and the green Ni and blue Ti maps both representing the γ' precipitate phase. This reveals a number of large primary γ'_I phase particles directly at the grain boundary, as well as a number of secondary γ'_{II} precipitates close by. This is interesting, as it disputes claims by Németh et al. concerning γ'_{II} dissolution near crack tips acting as a possible mechanism for strength reduction close to the crack tip [\[120\]](#). Additionally a C, Ti, Ta and W-rich particle at the top of the micrograph indicates the presence of a carbide in the exact same location as the round particle seen in TKD. Maps of C and O from a square region around the crack tip are shown separately, both of which display an increase in signal intensity.

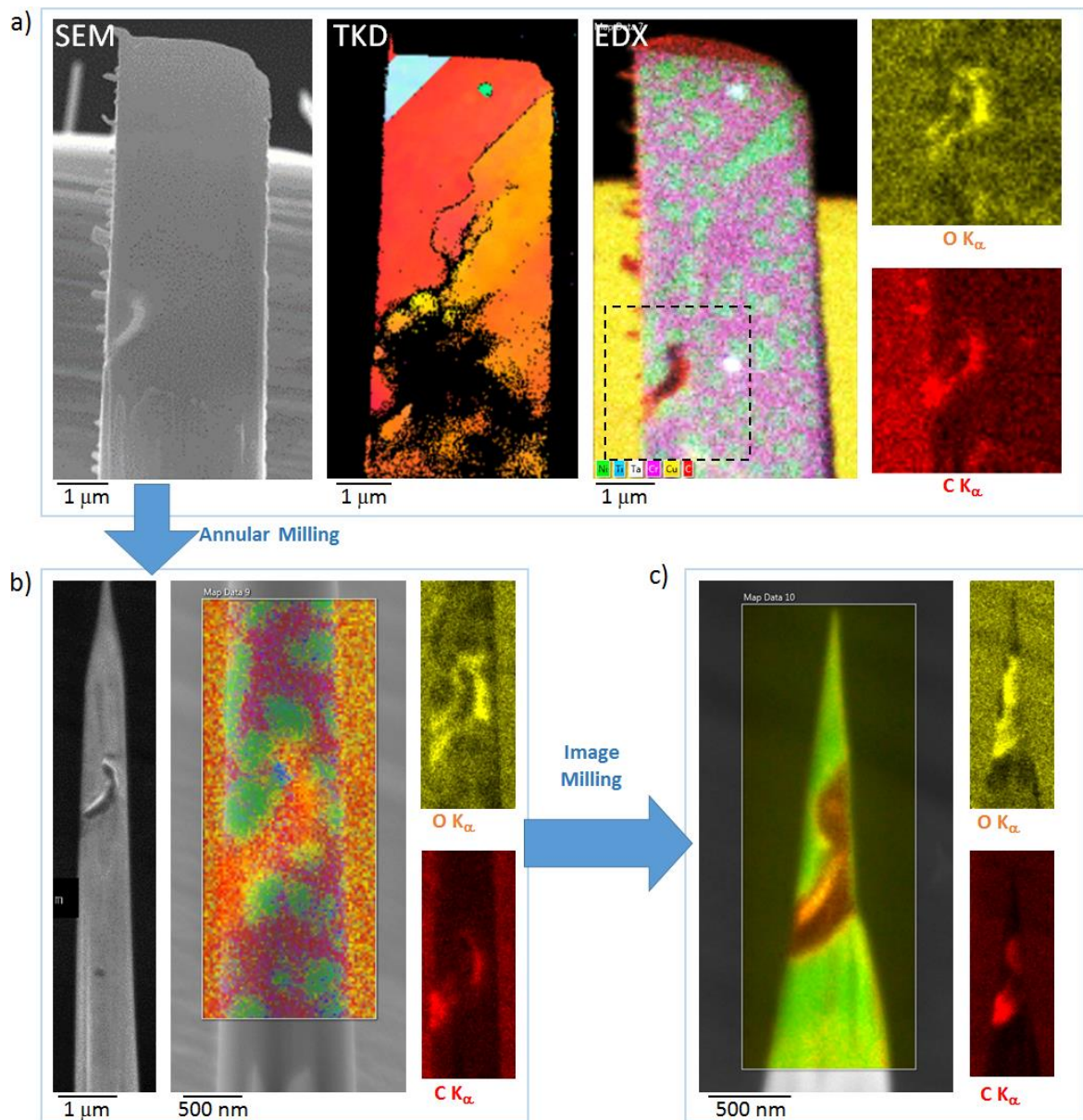


Figure 6.5 – Crack 2 liftout characterisation. a) SEM, EBSD and EDX analyses of lamella. b) SEM and EDX analysis performed during annular milling. c) SEM and EDX analysis performed on final APT tip. This was performed using a 5 kV SEM voltage, which limited EDX characterisation of Cr and Co.

After the crack tip and preceding grain boundary had been located and examined, the lamella was further milled down to an APT tip, utilising periodic EDX observations for tracking purposes as shown in Figure 6.5 parts b) and c). Similar features and phases were observed during the milling procedure, including easily visible γ and γ' phases, and a high signal from O and C within the crack. This indicated that resin has again infiltrated all the way to the crack tip, although interestingly both O and C signals appear to come from identical regions.

The final tip milling procedure was further refined based on difficulties experienced last time, so that a larger amount of matrix and oxide layer was left above the resin. This final needle tip is shown in [Figure 6.5 c](#)).

6.3.3 Crack Tip Three

The surface of the sample had been subjected to extensive FIB damage after the two previous crack tip analyses, so the surface was reground and repolished using successively finer grades of SiC grit paper, diamond solution and colloidal silica. This also removed the FIB trench that was present upon receipt of the sample, which allowed the primary crack tip to be analysed in the same manner as the two secondary crack tips. Some lessons had been learned from the previous iterations of the technique, such as the importance of depositing a thick protective layer of Pt during the liftout stage, as well as the immense utility of the intermediate lamella step.

The pre-liftout characterisation was carried out as shown in [Figure 6.6](#). Parts [a](#)) to [c](#)) show SEM micrographs of the crack tip region, progressively increasing in magnification. An important feature of the image in part [b](#)) is the dark blurring present around the crack, which is likely to be an artefact caused by charging of mounting resin that has infiltrated the crack. The micrograph in part [c](#)) features the blunt end of the crack at the top, as well as some apparent cracking down the preceding grain boundary at the bottom. It was initially unclear which region should be considered to be the crack tip, which prompted the acquisition of EDX maps for these regions, as shown in parts [d](#)) and [e](#)).

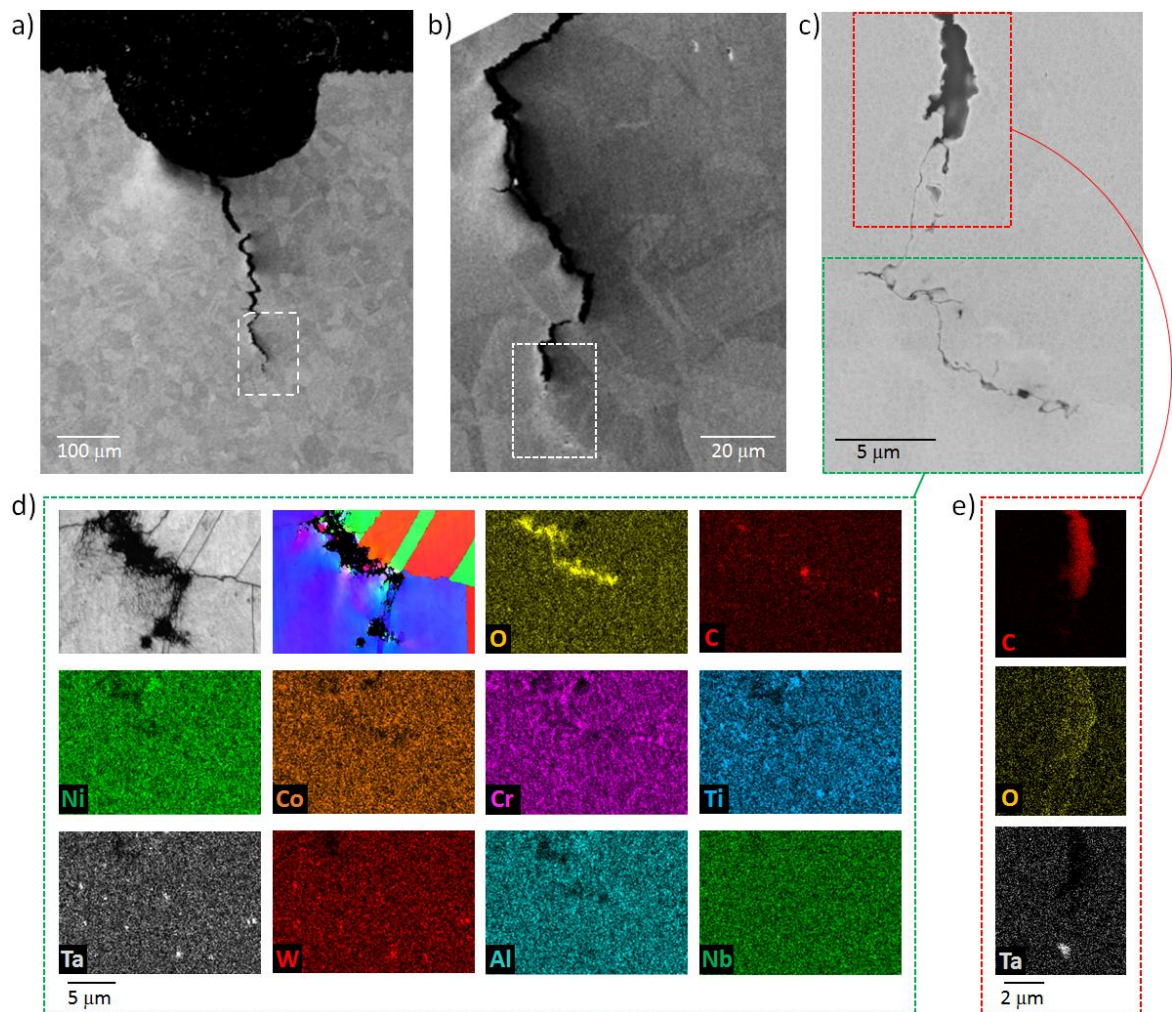


Figure 6.6 – Crack 3 pre-liftout characterisation. a) and c) Increasing magnification SEM micrographs of the primary crack tip, with two overlaid regions of interest shown in c). d) EBSD and EDX analyses of lower crack region of interest. e) EDX analysis from upper crack tip region of interest.

The first region to be analysed was located at the blunt end of the crack, as shown in part e). A Ta-rich particle can be seen, the location of which correlates with a particle visible in the SEM image in part c). Signal from C emission is prominent within the crack, likely due to the infiltration of mounting resin. The O map shows a minor increase in signal both within the blunt crack tip and down the two cracks preceding it, which could indicate oxide formation, although the Cr-O overlap means that caution should be advised when drawing conclusions. The presence of a potential O signal down the preceding grain boundary prompted further analyses of this region, which are shown in part d). These two maps show the presence of O and notable absence of C

down the cracked grain boundary. The only C present appears to be highly localised, which is likely to be caused by grain boundary carbides, but could also presumably be explained by resin present in a sub-surface crack.

Also shown in part [d\)](#) are two EBSD maps, which share some remarkable similarities to those from the second crack tip experiment as previously shown in [Figure 6.4 a\)](#). Twinning can be observed in the grain on one side of the boundary, while the other grain contains a dark unindexable region adjacent to the crack. Some residual strain also appears to be present close to this unindexable region, as evidenced by the subtle shifts in colour. An additional unindexable region can be seen descending from the oxidised grain boundary, which progresses in the same direction as crack propagation.

A region of interest around this oxidised grain boundary was selected for further analysis. [Figure 6.7 a\)](#) shows the region selected, which was protected with a thick Pt layer before commencing the liftout and mounting procedure shown in parts [b\)](#) and [c\)](#). The extent of subsurface cracking could be seen during milling of the lateral liftout trenches, which indicated that this crack was of a similar nature to those studied previously, and not merely an oxidised grain boundary. Part [d\)](#) shows the milling away of the front surface to reveal a large void, which required an immediate strategy rethink. This mounted liftout was not thinned down into a lamella, as it was unclear how much of the sample would be usable due to this void. APT samples should ideally avoid containing empty space, as this not only weakens structural integrity, but also can significantly degrade data quality through the creation of ion trajectory artefacts and secondary tips [\[136\]](#). On a positive note there was no need to worry about resin infiltration.

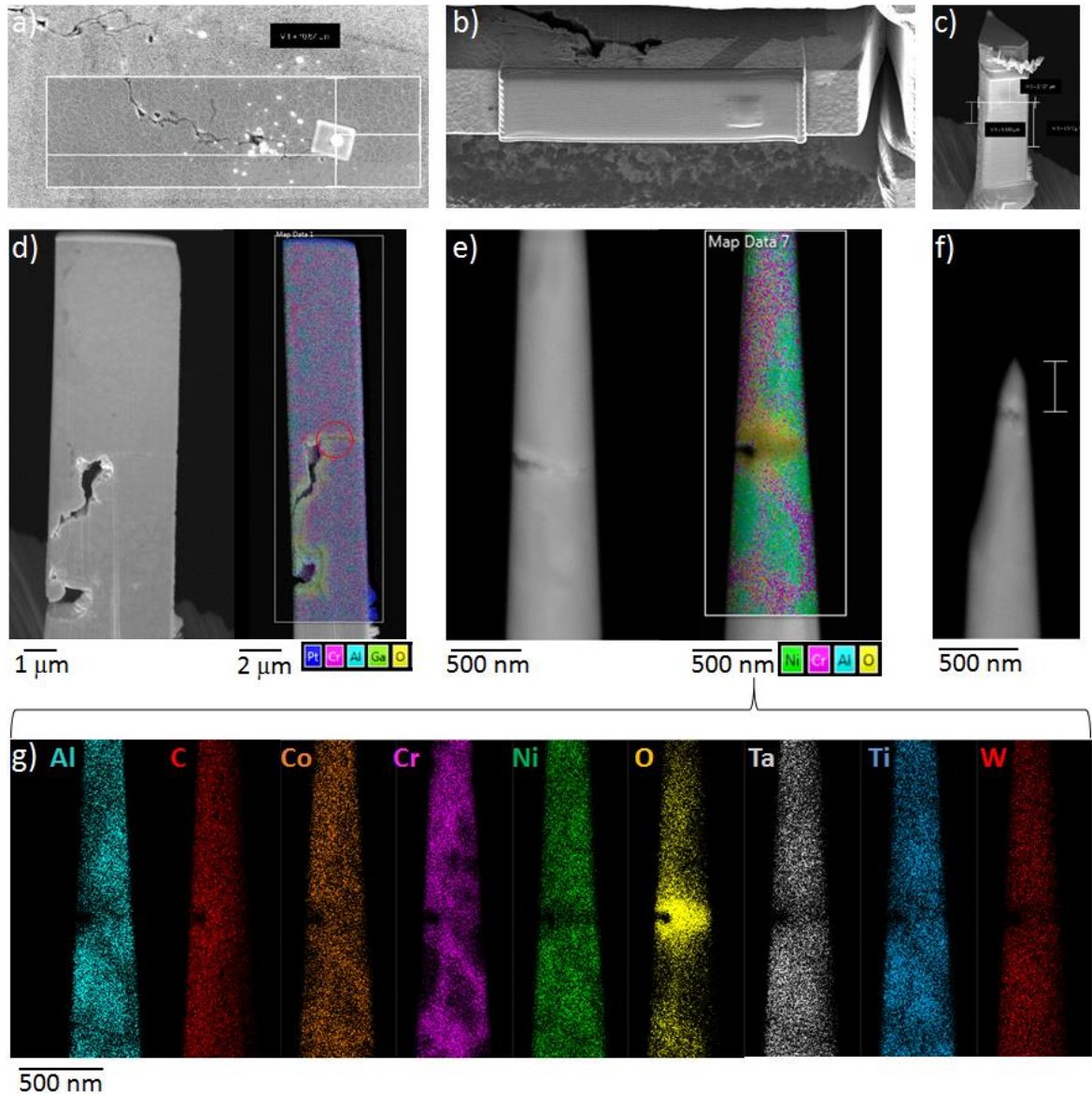


Figure 6.7 – Crack 3 liftout, mounting and sharpening procedure. a) Region of interest determined from previous characterisation. b) Liftout bar, showing sub-surface cracking. c) Mounted liftout. d) Initial FIB-polished surface showing the extent of cracking, with multiple layered EDX maps. ROI circled in red. e) Sharpened tip centred on ROI with inset layered EDX. f) Final tip SEM. g) Elemental EDX maps from part e).

An initial EDX scan of the crack surface revealed the presence of an oxidised grain boundary travelling horizontally across the mounted liftout, which would allow a tip to be created without voids. Annular milling around this region of interest lead to the creation of the needle-shaped tip shown in part e), alongside a layered EDX map with Ni, Cr, Al and O overlaid. From this, the oxygen-rich grain boundary region could be identified, as well as distinct γ and γ' phase regions.

Each elemental EDX map is shown individually in part [g](#)) below. This was then milled down into a final APT sample tip, shown in part [f](#)).

6.4 Atom Probe Tomography

Analysis of the microstructure of crack tips, and the chemistry of nanoscale oxides that form along them, requires an extremely high-resolution 3D characterisation technique with high chemical sensitivity. Atom probe tomography (APT) fits all of these criteria, although the nature of the technique means that samples containing non-conductive oxides, pre-existing flaws, and potential voids are sub-optimal for obtaining the highest levels of spatial accuracy in the resulting reconstructions.

The previous subchapters have shown that the transformation of crack tips into the needle-shaped samples required by APT is a lengthy and challenging process which absolutely necessitated the use of the various EM-based techniques covered previously: SEM, FIB, EDX and EBSD. It was fortunate that these techniques could also provide a wealth of information during the APT sample creation process. Of the three APT samples created, only one experiment resulted in the successful acquisition of data, although a post-mortem SEM analysis of the tips has identified a number of potential changes that could be made to the liftout mounting procedure to increase sample viability.

6.4.1 Crack Tip Three APT Experiment

Due to the length and extreme difficulty of the sample preparation process, the atom probe operating conditions were chosen to minimise the possibility of sample fracture. This sample was run at an elevated temperature of 60 K, using a relatively high laser pulse energy of 0.1 nJ,

combined with a low evaporation rate in an attempt to reduce the running voltage. During the experiment it was noted that the noise background was higher than anticipated, so the detection rate was increased on two separate occasions in order to improve the signal-to-noise ratio. The voltage history and evaporation rate setpoint have both been plotted in [Figure 6.8 a\)](#), from which it can be seen that the voltage history is extremely inconsistent, with constant voltage drops that are likely caused by voltage over-compensation after transient evaporation bursts. A number of other features observed in part [a\)](#) include a slight increase in slope that occurs immediately following an evaporation rate setpoint increase, marked in red, as well as a significant sudden voltage drop with no such correlation, marked in green. A sudden change in evaporation voltage like this often occurs upon reaching a horizontal interface, so it is possible that this could result from reaching the oxidised grain boundary pictured in [Figure 6.7 f\)](#). The fact that no change in evaporation rate setpoint occurred at this time means that it is unlikely to be a voltage related artefact.

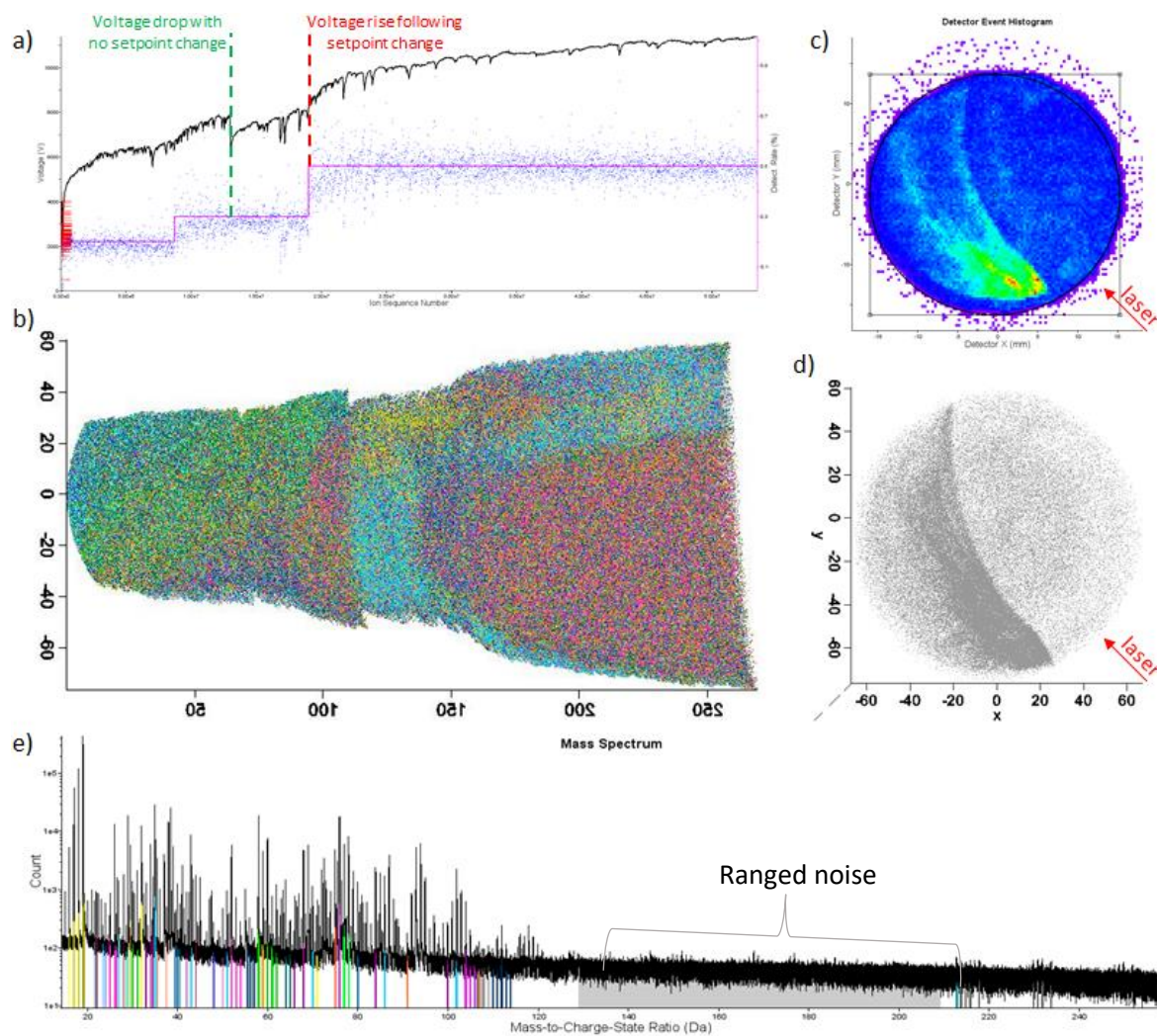


Figure 6.8 – APT Crack 3 Reconstruction. a) Voltage profile and evaporation rate setpoint during the run, with two events of interest marked in green and red. b) Reconstructed tip, using voltage to determine shape profile. c) Detector event histogram, showing excessive noise. d) Noise identified by ranging high background in rangefile shown in e).

The atom map shown in [Figure 6.8 b\)](#) was created using a voltage reconstruction, in order to prevent shape distortion caused by artificially enforcing a particular shank angle. The shape profile of the reconstruction mirrors the voltage profile, including both occasions that raising the evaporation rate setpoint lead to slight flaring, as well as the thinner waist section corresponding to the sudden voltage drop. The detector event histogram from the experiment is shown in part [c\)](#), with a visible hotspot and radiant spokes. These were confirmed to be caused by elevated background counts, as the same pattern emerges in part [d\)](#) from the ranging of background noise. The mass spectrum in part [e\)](#) is discussed further in the next section.

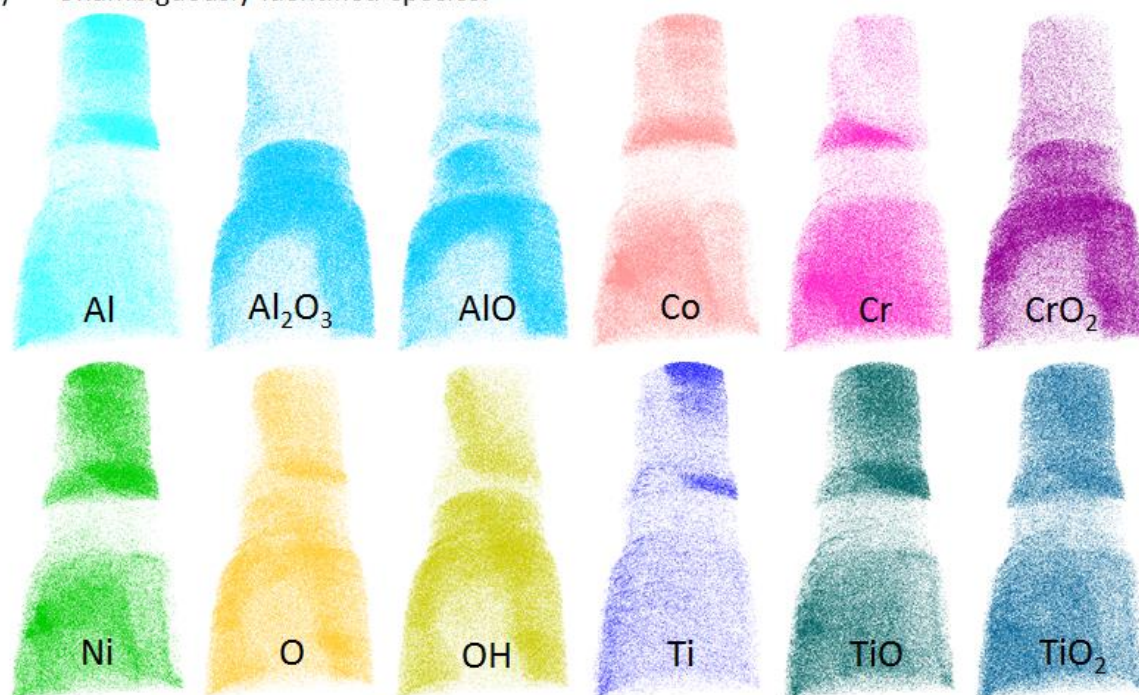
6.4.2 Crack Tip Three APT Analysis

After the reconstruction step, the mass spectra was observed to exhibit a number of potentially complicating features. The noise background appeared to be higher than the previous oxide runs, but not to an extent that would invalidate the data. A more pressing issue was the presence of extremely large peaks at 17, 18 and 19 Da, which likely correspond to OH, H₂O and H₃O respectively. When ranged, the 19 Da H₃O peak contains over 20% of the total detected ions of the entire dataset, which could also compromise data quality. In addition, a number of double peaks were identified in the mass spectra, at Da values within 0.1 Da of each other. These double peaks were also found to be present in the original time-of-flight data, so were deemed not to be a reconstruction artefact.

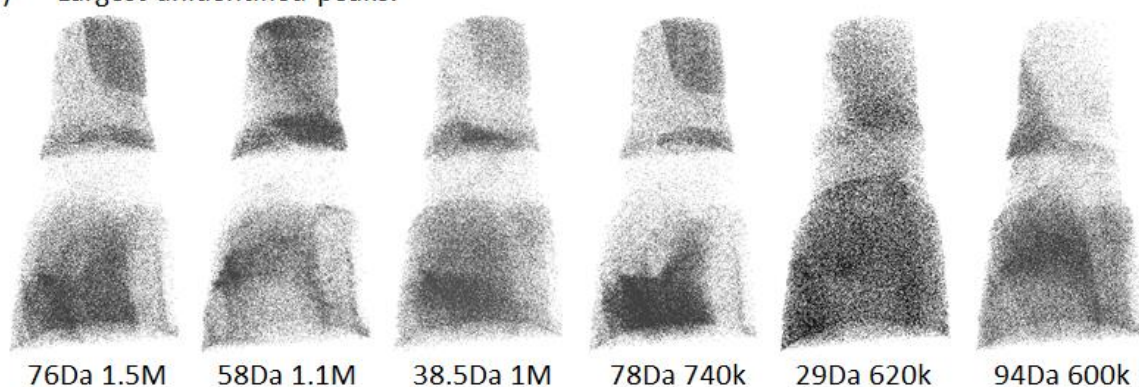
The initial ranging attempt followed an identical strategy to the previous oxide experiments, as outlined in [Chapter 5.4.1](#). Ranges were only identified as a particular ionic species if all other potential candidates could be discounted as the majority species, which was particularly difficult due to the large number of overlaps and peaks without ranging precedent. These candidate ionic species were derived using a number of methods, such as a list of previously ranged species, as well as a database of common metal oxide, carbide and nitride complex ions. A database of likely bimetal complex ions was also created, prompted by the identification of CrCo complex ions in the oxide reconstructions analysed in [Chapter 5](#). The weights.exe program in the APTtools software suite was also invaluable for finding potential candidates [\[133\]](#), however the majority of these candidates were ruled out by isotopic abundance analysis or remained inconclusive. In addition to these atom probe related sources of potential peak information, the EDX emission spectra for this tip were studied for unidentified elements, though none were found. The EDX maps also ruled out resin infiltration, which could have potentially lead to a large number of unexpected aromatic hydrocarbon species such as phenols and benzene derivatives.

The ranging process was concluded with the creation of the systematic.rrng range file, as shown in [Figure 6.8 e\)](#) and expanded upon in [Figure 6.9](#), which could unambiguously identify 22 million ions out of the 50 million detected counts. However it must be acknowledged that the 19 Da peak itself contains 10M ions, and a large number of the more ambiguous peaks remain unranged.

a) Unambiguously identified species:



b) Largest unidentified peaks:



c) Interesting peak locations:

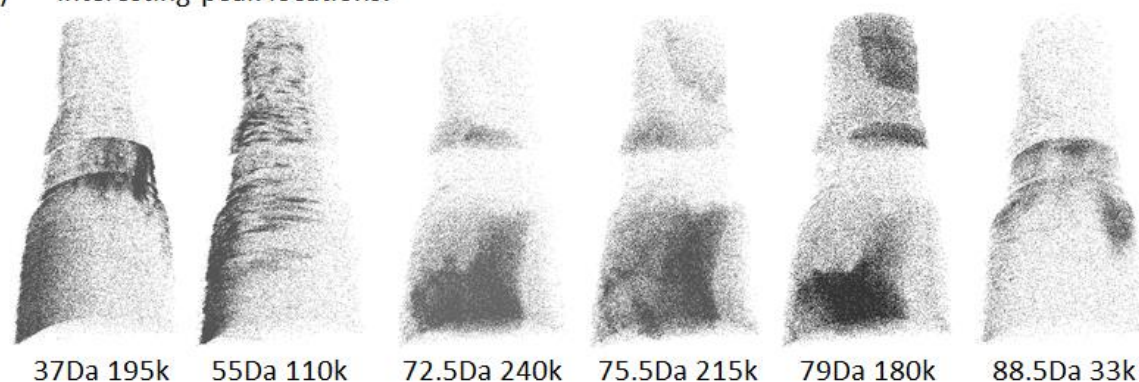


Figure 6.10 – Crack tip 3 atom maps from systematic.rng. a) Unambiguously ranged ionic species, in which other overlapping species could be ruled out as the majority. b) Location of largest unidentified peak ranges. c) Unidentified ranges with interesting locations in atom map.

Although the incomplete ranging process precluded a quantitative composition analysis, some elemental distributions could be qualitatively judged based on the more unambiguously ranged peaks shown in [Figure 6.10](#), leading to the purely qualitative ion location schematic shown below in [Figure 6.11 c](#)).

A comparison of atom maps for the γ' phase partitioning elements Ni, Al and Ti indicated the likely presence of two γ' phase precipitates at the top of the dataset. A number of other unidentified peaks are also present in these two regions, including the third and eighth largest peaks at 76Da and 78Da. A similar conclusion was reached regarding the presence of γ phase, based on the relative distributions of Cr and Co. Again, a number of unidentified peaks also similarly partition to these regions. A horizontal oxide layer traversing the reconstruction can be surmised from the location of oxygen containing species such as O, OH, CrO_2 and Al_2O_3 . Additional maps not shown that corroborate this include those of H_2O , AlO, Al_2O_2 , CrO, CrO_3 . As with the EDX overlap of Cr and O, there is a peak overlap present here between $^{27}\text{Al}^+$ and $^{54}\text{Cr}^{++}$ ions, meaning that some of the Al and AlO_x maps may include a small proportion of Cr and CrOX species, but overall the location of these oxygen-containing species leads to the conclusion that this experiment successfully captured the horizontal grain boundary observed in [Figure 6.7](#), demonstrating the effectiveness of the sample preparation approach following crack tip identification.

Below this oxidised grain boundary lies a region containing a mixture of Ni, Co and Cr, which matches the approximate composition of γ phase even though the amount of Ni appears to quantitatively be too high. Below this presumed γ phase lies a region referred to as the 'core', which is characterised by a large number of unidentified peaks, including those at 72.5, 76, 78 and 79 Da. Although these peaks appear to be primarily located in this 'core' region, the 72.5 Da peak also appears alongside the presumed γ phase, while the 76, 78 and 79 Da peaks appear alongside

presumed γ' regions. It is possible that these could all be explained by peak overlaps, but it is more likely that this core region has a composition that does not match either γ or γ' phases, instead lying between them.

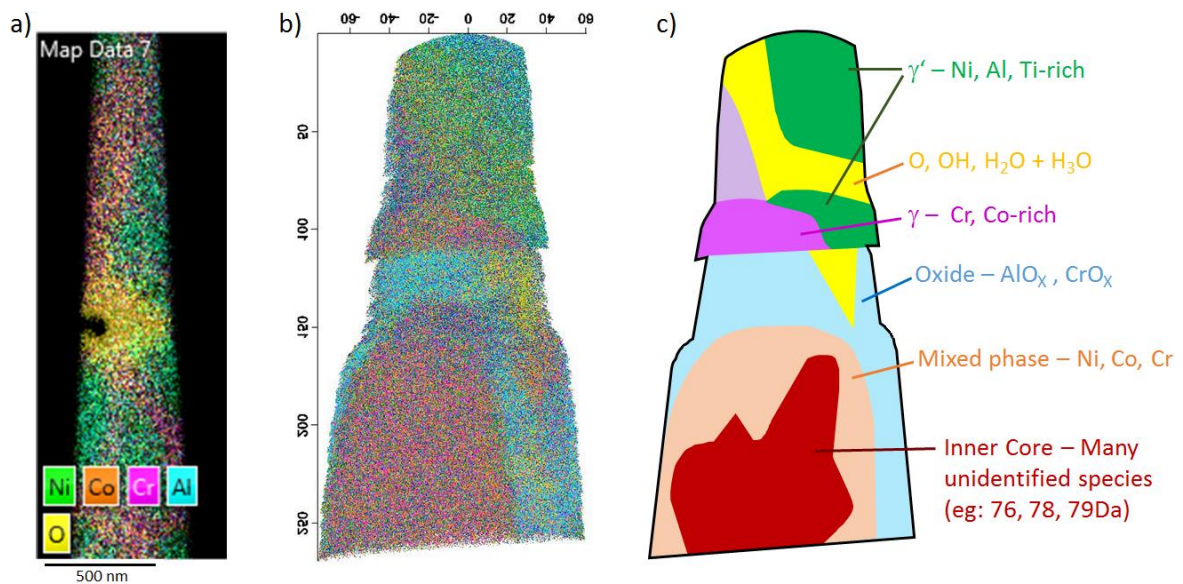


Figure 6.11 – Representations of the third crack tip sample. a) EDX maps for Ni, Co, Cr, Al and O, showing γ and γ' phases and extent of oxidation. b) APT map containing all unambiguously-ranged peaks, consisting of 22 million ranged ions out of 50 million detected. c) Schematic diagram of regions contained in the reconstruction, based on locations of elements with known phase partitioning behaviour, combined with the location of other large unidentified peaks.

6.5 Discussion

6.5.1 Optimisation of Experimental Technique

The extraction, liftout and mounting technique previously developed by Lotharukpong et al., Meisnar et al., and Kruska et al. [127–129] for analysis of grain boundaries, dislocations and stress corrosion crack tips was successfully modified for use on oxidised fatigue cracks in nickel based superalloys, enabling the creation of a number of APT samples. In addition, the novel addition of an intermediate lamella thinning step during this process enabled the use of correlative TKD and EDX analyses during the production of these APT samples. This technique has been modified repeatedly during the creation of the three final APT samples due to its high dependency on the specific crack tip morphology. After these samples had undergone APT analysis, a number of subsequent refinements have been documented to further streamline the sample preparation technique, and optimise the quality of data obtained during analysis. With regards to the initial sample preparation, a recommended change to the ETMT sample mounting strategy involves replacing or omitting the use of low-viscosity mounting resin, which was found to infiltrate cracks to the tip. This resin infiltration not only caused charging artefacts during SEM analysis, but also would be unlikely to evaporate cleanly during APT, in addition to creating many extra hydrocarbon peaks in the resulting mass spectra thus complicating peak identification.

The sample mounting procedure could also use a few modifications. The use of a blunt Cu tomography post may be a contributing factor to the excessive 17, 18 and 19 Da peaks, due to the large surface area available for adsorption of atmospheric moisture. In addition, this large flat surface caused difficulties during APT laser alignment due the presence of reflections. This is further compounded by the relatively short liftout length as seen in [Figure 6.7 b](#)), which placed the sample tip very close to the surface, with evidence of sample melting or sputtering seen in the post-mortem SEM examinations of crack tip samples one and three. It is recommended that

any future experimental attempts should adjust the sample geometry, with a liftout length of 20 μm minimum. Another potential issue caught during the post-mortem SEM analysis involved the cleaving of the second crack tip liftout at the post-sample interface, indicating that the butt weld between the tomography post and liftout may need further reinforcement. This was previously attempted by cutting and backfilling sections to create reinforcement 'keys', as suggested by Lotharukpong et al. However, this previous experiment mounted the sample onto an SEM half grid, in which the sample and mount both shared a single contiguous external surface allowing a more secure weld. Due to all of the issues mentioned previously, it is highly recommended that future attempts use appropriately-sharpened SEM half grids in place of Cu tomography posts.

The FIB-based preparation of fatigue cracks presented many unexpected problems. The intergranular crack path proved to be more tortuous than expected, especially during the FIB milling stages when the full three-dimensionality of the cracks was revealed. It was rarely obvious which direction a crack would deviate to when milling into the material, and on occasion a seemingly two-dimensional crack opened up into a large void, an example of which can be seen in [Figure 6.7](#). This greatly complicates the APT sample making procedure, as inclusion of voids will weaken sample structural integrity, while also potentially creating artefacts related to ion trajectory and secondary tips. The avoidance of voids during the creation of the third crack tip sample lead to the selection of a horizontal interface, which can also complicate APT analysis. The sudden voltage change caused by a horizontal interface can affect the specific ionic species that evaporate and their charge state ratio, leading to difficulties in mass spectra peak identification. Ultimately, it is suggested that future attempts should also make use of TEM, or potentially a more complex 3D milling procedure, in order to observe any sample integrity issues that may adversely affect sample preparation.

6.5.2 Interpretation of Available Data

Due to the problems experienced during EDX and APT analyses, restrictions should be put on any qualitative conclusions made from these data. However many useful conclusions can be made from the qualitative analyses, as long as the data are kept in appropriate context. The EDX analyses of needle tips and lamella were able to positively identify the presence and location of γ and γ' phases, combined with oxygen-enriched regions (and carbon-rich mounting resin) along certain grain boundaries and crack surfaces. These results allowed the technique to serve as an indispensable sample preparation aide, allowing a region of interest to be identified and prepared into an APT sample. Quantification of the elemental maps remains questionable however, due to the significant overlaps between O K α and Cr L α emission lines at 0.55 keV, combined with the constant deposition of C during SEM.

The APT data are subject to the same restrictions, as the extreme levels of noise and background contaminants at 17, 18 and 19Da have put limits on data quality, and the large number of unidentified peaks makes quantification of composition inadvisable. However, the careful and systematic identification of a limited number of peaks means that some speculative conclusions can be drawn. The observed copartitioning of γ' forming elements such as Ni, Al and Ti has allowed a reasonable estimate of the location of this phase, which is bolstered by the presence and location of this same phase in EDX maps. The location of oxide species such as AlO $_x$ and CrO $_x$ along a horizontal interface has shown that these sample preparation techniques are indeed viable for extraction of an oxidised grain boundary crack. The lack of unambiguously ranged data relating to TiO $_x$ species means that no conclusions can be drawn with regards to the interfacial segregation of Ti presented in [Chapter 5](#) however.

With regards to future APT analysis of crack tip reconstructions, a number of tools and procedures have been created to help with the identification of mass spectra peaks. In this instance they have been capable of ruling out the majority of potential ionic species, although with the number of potential overlaps this unfortunately was insufficient. However, with certain changes to the experimental technique to reduce noise and ionic species proliferation, they may be more successful.

6.5.3 Implications On Environmentally-Assisted Dwell Fatigue

In order to make firm assertions on the mechanism behind dwell fatigue crack propagation in the ABD alloys, the crack tip must be well defined. Due to the intergranular nature of dwell fatigue cracking, some diffusion of embrittling elements down the preceding grain boundary is to be expected. This makes defining the crack tip difficult using techniques which purely characterise elemental composition distributions.

To further study the mechanism behind dwell fatigue crack propagation, a number of conditions must be met. First, the ETMT slow-strain rate tensile experiment must be truly representative of the dwell period during which these cracks propagate, as characterised by an extended period at high load in an oxidative or corrosive environment. Experiments by Gabb et al. [\[192\]](#) have indicated that slow strain rate tensile tests are indeed a good simulation of the dwell period.

Another possible experimental factor that must be considered is that the ETMT experiments took place at 700°C rather than the 800°C that these alloys are projected to operate at, which will undoubtedly change the underlying thermodynamics and kinetics. The second condition regards the study of secondary crack tips as an analogue to primary crack tips, so it must be considered whether they are truly representative or not. As secondary crack tips may experience a longer period between oxide formation and crack propagation, differentiation between the SAGBO and DE mechanisms may be more difficult, due to the extended period after crack propagation in

dwell conditions for the oxide wedge to form unimpeded. The third condition regards the relevance of the ABD alloys to study these mechanisms. The ABD alloys are uniquely well-suited for the analysis of dwell fatigue crack propagation due to the systematic addition of Nb, which has been previously linked to increasing dwell fatigue crack propagation rates [54,83]. This has been disputed by Németh et al., who did not observe significantly higher Nb concentrations in crack tip oxides or oxygen-containing regions [120]. Unfortunately no correlative APT experiments could be performed to test this hypothesis, as no Nb-containing samples were made available for this study.

6.6 Conclusions

Samples containing fatigue cracks created using ETMT underwent surface characterisation using SEM, EDX and EBSD methods. Multiple crack tips were identified and characterised, consisting of the primary crack as well as a number of secondary cracks. EBSD maps confirm that the cracks propagate along grain boundaries, and EDX maps have shown the presence of oxygen along cracks and preceding grain boundaries.

A new liftout and mounting procedure was developed as a modification of the technique created by Lotharukpong et al., Meisnar et al., and Kruska et al. [127–129]. This procedure has undergone several refinements during the sample creation process, including the insertion of an intermediate lamella step to enable correlative EDX and TKD characterisation experiments. A number of further refinements to this sample preparation have been catalogued for further experiments. During this intermediate lamella step, EDX analysis revealed the presence of a large primary γ'_1 along the preceding grain boundary, as well as a number of Ti, Ta and W-rich carbide particles. TKD analysis revealed a number of twin boundaries.

Three APT samples were successfully created, two from secondary crack tips and one from the primary crack tip. Experimental data were obtained for the primary crack tip sample, which contained an oxidised grain boundary leading directly from the crack tip. These crack tip APT data were reconstructed and analysed. Unfortunately the signal-to-noise ratio was very small, although a small number of mass spectra peaks could be unambiguously ranged, allowing some qualitative conclusions to be made. The presence of γ' phase particles could be inferred based on the location of γ' partitioning elements including Ni, Al and Ti. A small γ phase region appears close to these γ' particles, based on the presence of Cr and Co. A 50 nm thick oxide layer consisting of AlO_x and CrO_x species also appears, demonstrating good correlation between EDX and APT data

Chapter 7. Conclusions and Future Work

7.1 Initial Characterisation of Microstructure and Phase Chemistries

This project has involved characterising a new generation of polycrystalline nickel based superalloys, with compositions derived using the Alloys-By-Design process. As novel alloys, they lack the wide background of published research that more common alloys have, so the first task was simply to characterise their chemistry and microstructure. Along with Crudden et al. [47,74], Németh et al. [120], Hisazawa et al. [157], and Collins et al. [156], this project has added to the growing body of work surrounding these alloys. More importantly, these projects are intended to test the ABD process itself, specifically the models used to predict their physical properties and establish property-composition relationships. Thus, experimental validation is required to provide important feedback, so that the underlying models can be improved and refined.

This particular subset of the ABD alloys (ABD-2, 4, 5 and 6) focussed on the viability of partially replacing Ti with Nb [74]. This was motivated by the exacerbation of oxidation rates observed with addition of Ti, as well as the calculations performed by Crudden et al. which suggest that Ti and Nb provide similar γ' strengthening effects, as determined by their effect on APB energy [32]. No adverse effects to microstructure or phase chemistry were predicted, however experimental validation of the suitability of Nb as an alloying ingredient needed to first be established.

This initial characterisation of the alloys in the as-received condition performed in Chapter 4 provided experimental evidence that many important alloy properties match the Thermo-Calc predictions. The microstructure was observed to consist of a bimodal distribution of secondary γ'_{II} and tertiary γ'_{III} precipitates, with a volume fraction similar to that predicted by Thermo-Calc. The composition, volume fraction, size and distributions of these γ' precipitates were not observed to

show any significant composition-dependence, although some W segregation to γ - γ' interfaces was observed during APT analyses. In addition, the experimental γ' volume fractions observed using APT and SEM tended to agree to within 3% of each other, both lying well within the limits set by Thermo-Calc using the two databases TTNi8 and TCNi8, as shown in [Table 4.2](#).

However, the experimentally-derived partitioning coefficients were observed to deviate from the thermodynamic predictions, which mirrors previous observations by Antonov et al. [\[159\]](#), and Miller et al. [\[160\]](#). In particular, thermodynamic predictions made using the TTNi8 database tended to vastly overestimate partitioning coefficients for five of the eight major alloying elements, including the γ' partitioning elements Ti, Nb and Ta which are vital for maintaining strength at high temperatures. Any strength predictions made using TTNi8 may be artificially inflated, so it is recommended that either TCNi8 is used alone, or some combination of the two databases.

An increase in grain size was also observed, matching previous observations by Hisazawa et al. [\[157\]](#) and Németh et al. [\[120\]](#). This grain size dependence on composition was not considered to require any change to the ABD process however, as grain size can be easily modified through alteration of processing route and heat treatments.

7.2 Oxidation Kinetics and Mechanism

After confirming that the phase fractions and chemistry of the ABD alloys were broadly as predicted by the models, the composition dependence of oxidation could be studied with regards to Ti:Nb ratio. Crudden had previously performed TGA experiments on these alloys using a combination of furnace exposure and microbalance weighing [\[74\]](#), which established that addition of Ti has a negative impact on oxidation resistance. These experiments were replicated during this project, albeit using much more advanced equipment which increased accuracy and a

reduced risk of oxide loss due to spallation. The TGA analysis performed in [Chapter 5.2](#) confirmed that alloys with higher Ti concentrations experienced accelerated rates of oxidation, although the mechanism behind this was still unclear.

The accepted mechanism by which Ti increases oxidation kinetics is explained in detail in [Chapter 5.5.2](#), which can be summarised as the replacement of lower valence Cr^{3+} ions with high valence Ti^{4+} ions in the chromia oxide layer, leading to vacancy creation and an increase to bulk diffusion rates. There were two factors which warranted further investigation of this mechanism; first the lab-grown pure α -chromia used by Atkinson et al. [\[172\]](#) and Blacklocks et al. [\[173\]](#) to isolate this mechanism is likely to exhibit significant differences to the complex chemistries and microstructures found in thermally-grown oxide scales. The second factor which warranted investigation of this mechanism involves Nb, which was not shown to increase oxidation kinetics, despite its tendency to form even higher-valence Nb^{5+} ions.

High resolution APT characterisation of the resultant oxide scales observed a significant amount of Ti dissolved in the chromia scales, with no correlation observed between Ti solute levels and nominal alloy Ti at.%. This indicated that the oxidation kinetics were not reliant on dopant levels, implying that the vacancy-diffusion mechanism outlined previously may not be the rate-limiting step for oxidation. Evidence for an alternate mechanism was identified through the observation of large amounts of Ti segregated to grain boundaries, in addition to elevated levels of the γ' forming elements Ta and Nb. Grain boundaries are known to act as short-circuit diffusion paths [\[21,79\]](#), and have been shown by multiple studies to have ion transport rates that are sensitive to composition, in particular Ti [\[182–185\]](#). It is plausible that Ti segregation to grain boundaries could increase ion transport along them, thus becoming the rate limiting step for oxidation. Unfortunately the composition dependence of Ti segregation across the alloys could not be

established, due to the difficulty in obtaining data for oxide grain boundaries, so this is definitely a topic for future work.

Analysis of oxide scale cross-sections verified that the oxide exists as a bilayer of external chromia above an internal alumina subscale, with multiple Ti and Nb-rich nitride particles observed to be present in the alumina layer. A composition dependence of oxide morphology was also observed, with the high-Ti alloy ABD-2 exhibiting rough, irregular chromia above deep alumina grain boundary intrusions, whereas the low-Ti alloy ABD-6 exhibited smooth external chromia and evenly-distributed internal alumina islands. This change in local oxide morphology may have an impact on properties such as scale adhesion and fatigue resistance

Ultimately, the conclusions that could be fed back into the ABD process were a confirmation of the composition-dependence of oxidation, although evidence for an alternative mechanism was found. A more thorough investigation into oxide grain boundary chemistry may be required, in order to impede or inhibit ion transport along them, and remove some of the constraints during alloy design.

7.3 Fatigue Crack Tip Characterisation

One of the potential issues caused by addition of Nb relates to its fatigue performance. Several studies on high-Nb alloys such as IN718 have shown that addition of Nb decreases dwell fatigue resistance [83,84,110]. However there is debate as to whether this is caused by segregation of elemental Nb, or by preferential oxidation of Nb to form brittle Nb₂O₅. This is closely related to the DE/SAGBO debate regarding the mechanism underlying dwell fatigue.

This project was intended to conclude with high-resolution characterisation of fatigue crack tips, in order to study the underlying mechanism of dwell fatigue cracking, and look for evidence of Nb

segregation or Nb oxides at these crack tips. Unfortunately no fatigue crack tip samples from any of the three Nb-containing ABD alloys were available, so the this section of the project was shifted to focus on developing the underlying sample preparation and analysis methods.

The existing FIB liftout and mounting procedure developed by Lotharukpong et al., Meisnar et al., and Kruska et al. [127–129] was successfully modified for use on Ni superalloy fatigue crack tips, including the intermediate lamella thinning step that enabled correlative EDX and TKD characterisation experiments. These methods confirmed that the cracks propagate along grain boundaries, and EDX maps have confirmed the presence of oxygen along cracks and preceding grain boundaries. These maps were also invaluable for assisting the creation of three APT samples, two from secondary crack tips and one from the primary crack tip. Experimental data were obtained for the primary crack tip sample which contained an oxidised grain boundary leading directly from the crack tip.

Difficulties were encountered when analysing the crack tip APT data, which have been traced back to sample geometry and running conditions. A number of ranging techniques were developed to analyse the noisy data, which allowed a number of mass spectra peaks to be unambiguously identified, allowing some qualitative conclusions to be made. The presence of γ' phase particles could be inferred based on the location of γ' partitioning elements, and a small γ phase region was identified based on the presence of Cr and Co. A 50 nm thick oxide layer consisting of AlO_x and CrO_x species also appears, which correlates with EDX and SEM images, as well as a sudden voltage drop seen during the APT experiment.

7.4 Future Work

The research presented in this thesis has covered the following topics:

1. Peak identification and ranging procedures have been developed for the systematic ranging of APT data from complex systems, including highly-alloyed systems exposed to high temperature environmental damage.
2. Characterisation data have been obtained, allowing comparison with thermodynamic predictions, in order to optimise models used during the Alloys-By-Design process
3. Evidence has been presented for oxide grain boundary diffusion being the rate-limiting step for oxidation kinetics in the studied nickel superalloys, rather than the bulk diffusion mechanism previously assumed.
4. A technique for extraction of fatigue crack tips has been developed and refined, allowing nanoscale APT characterisation of crack tip regions to be obtained, in addition to correlative EDX and TKD.

In regards to the first point, many of the ion identification peak ranging strategies developed during this project follow an algorithm specifically designed to prevent misidentification of peaks. These algorithms were performed manually during this project, but it should be feasible to automate many of the steps. Two of the software suites used during this project to cross-reference various values (AtomProbeLab and APTtools) were both developed in this group to automate other tasks. The expertise to implement some of these algorithms is here, and they could be a great time-saving measure for future researchers using spectrum based techniques.

The second point refers to the application of findings back to the ABD process. The oxidation-strength tradeoff that was focussed on during this project is one of many such tradeoffs, all of which have their own recommendations for changes. Ultimately, a concerted group effort will be required in order to process these data into a form which can be directly applied to the models

used. One immediate recommendation involves double checking partitioning results that have used thermodynamic predictions from a single database.

Point three is potentially the most important, as these results are another piece of evidence arguing for the greater role of grain boundaries in determining oxidation kinetics, especially in the complex thermally-grown oxides. Experiments have already been performed using ^{18}O tracer gasses to monitor anion transport, but these neglect to capture cationic transport up from the metal into the oxide. Further experimentation with model oxides could be a useful approach, using grain morphologies more similar to those found in thermally-grown oxide scales, to investigate if the ion transport mechanism changes with Ti at.%.

Further characterisation efforts on dwell fatigue crack tips are likely already underway, which will hopefully provide more experimental evidence to explain the underlying dwell fatigue crack growth mechanism. This will require refinements to sample preparation techniques, such as the method developed here for correlative EDX, TKD and APT on the same needle, to determine the chemistry and microstructure of fatigue crack tips.

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