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Analysis of atomic-scale phenomena and
the rhenium-effect in nickel based superalloys

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A Thesis submitted for the degree of
Doctor of Philosophy
March 2010

a tutte le donne della mia vita

Abstract

Since the 1980s, small additions of rhenium have been found to markedly improve the creep properties of nickel based superalloys. However, the underlying causes for this effect are not yet fully understood. In this work, a variety of experimental and modelling techniques have been used to evaluate possible mechanisms improving creep properties at high temperature. *Ab initio* modelling (via the Density Functional Theory) has shown that rhenium clusters are unstable in the nickel lattice. This observation was confirmed by Extended X-ray Absorption Fine Structure, which showed that rhenium atoms are dispersed in the nickel lattice. Atom Probe Tomography also found no clusters in Ni-Re alloys and in CMSX-4, a commercial single-crystal superalloy.

Atom Probe Tomography, in conjunction with Phase Field Modelling, was also used to show that the rhenium enrichment close to the γ/γ' interfaces is formed upon cooling from service temperature. Thus means that the rhenium enrichment observed with the atom probe does not play a role in the strengthening effect played by rhenium. Finally, *ab initio* modelling (via the Density Functional Theory) was used to investigate the effect of rhenium on the stacking fault energy of nickel to ascertain whether rhenium content could increase the spacing between Shockley partial dislocations.

The present work shows that rhenium clustering, the rhenium enrichment close to the γ/γ' interfaces and the rhenium effect on stacking fault energy cannot be the mechanisms underlying the rhenium-effect in nickel based superalloys. It therefore appears that single atoms of rhenium may slow down dislocation motion in the γ phase of nickel based superalloys. This is supported by the observation that rhenium is the slowest diffusing element in nickel and it is therefore expected to slow down all diffusion activated processes, such as the well-established climb-assisted glide of dislocations in the γ phase of nickel based superalloys.

Acknowledgements

First, I wish to thank my supervisors, Prof. Mike W. Finnis and Prof. Roger C. Reed. Beside being excellent examples of what a good academic and scientist should be, they also greatly helped me throughout my Ph.D. studies at Imperial College London. It was a truly fantastic opportunity to have such distinguished academics as supervisors. I would also like to thank Dr. Mike K. Miller who was as close to being a supervisor as he could ever be! I really enjoyed my two visits at ORNL and I believe he had a great input in my upbringing as a young practitioner of academic research. I look forward to working again with Mike Miller, Mike Finnis and Roger Reed in the near future.

Second, I would like to thank people who contributed to parts of my research project and who helped me start up my research. Bridget Ingham introduced me to the world of x-ray absorption spectroscopy (XAS), Nicole Benedek introduced me to CASTEP and *ab initio* simulations and Ralf Drautz and Thomas Hammerschmidt made me switch from CASTEP to VASP, beside introducing me to cluster expansions and ‘high-throughput computing’. At ORNL, Kaye Russell greatly helped me with the atom probe experiments and sample preparation: all I know about electropolishing I have learnt from her! Collaborating with Nils Warnken was a great opportunity and I enjoyed his efforts to make my life difficult by asking me questions. I would also like to acknowledge the help I received from Matt Harvey and Simon Burbidge – the administrators of high performance computing equipment. Without them, I would still be at square one! Finally, I would like to thank Alessandro de Vita for the helpful discussions on MD simulations and how these could help me learn something about the rhenium-effect.

Other VIPs also made it possible for me to get through my research project. In particular, I would like to thank Gurjit (for paying his taxes and, in turn, finance my research), Farid (for lunch time and coffee time chats), Stefano (for being a great role model of how a Ph.D. student should be like) and Ankoor (for quick escapes outside the office environment). I would also like to thank Devashish, Pavel, Lang and Richard (for the excellent times in good, old RSM101) and Giulia, Giuseppe, Leandro and Ruth (for building a strong *Italian* community in the new B321). I would also like to thank everyone who was part of the Alloys by Design consortium and, as such, of my research group.

I would also like to thank and acknowledge three people who, although they were not my supervisors, served as excellent mentors and friends: Robert Atwood, Peter Lee and David Dye. Without Robert, my computing skills would be close to nil – before meeting him I could barely install an operating system, and now I am distributing software on Sourceforge. As far as Peter and David are concerned, I think the fact that most people in the department think I am their student speaks for itself. You all had a strong input in my stay at Imperial College and I look forward to keeping in touch and working with you in the future.

The mighty team of Wardens at Wilson House also helped me greatly by giving me opportunities to vent and do fun stuff: Mike, Dominik, ~~David~~ (see above), Matina, Tim, Shweta, Dominic and Laura – THANK YOU!!! You all made my last few years at Imperial College fantastic.

This research was possible thanks to EPSRC grant EP/D04619X/1. Research at the ORNL's SHaRE User Facility was sponsored by the Scientific User Facilities Division, Office of Science, U.S. Department of Energy. I would also like to thank the Institute of Materials, Mining and Metallurgy (IoM³), Armourers & Brasiers, the Institute of Physics (IoP) and the Imperial College Trust for funding that allowed me to attend several international conferences.

Finally, I would like to thank my mum, dad and sisters – *perché sono riusciti a tirare fuori il sangue da una rapa*. Above all however, the person toward whom I will be eternally in debt is Giudi! This thesis is especially dedicated to her. There are no words to express how much she helped me to get this far. We *both* have worked really hard for this and I wish we may share the outcome together in future.

Publications

A. Mottura, N. Warnken, M.K. Miller, M.W. Finnis and R.C. Reed. *Analysis of the distribution of rhenium in nickel alloys using atom probe tomography*. Acta Materialia 58 (3), February 2010, pages 931-942.

A. Mottura, R.T. Wu, M.W. Finnis and R.C. Reed. *A critique of rhenium clustering in Ni-Re alloys using Extended X-ray Absorption Spectroscopy*. Acta Materialia 56 (11), June 2008, pages 2669-2675.

A. Mottura, R.C. Reed and M.K. Miller. *Analysis of the role of rhenium in nickel-based superalloys using Atom Probe Tomography*. Superalloys 2008, pages 891-900.

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Nomenclature

1D	One-Dimensional
1DAP	One-Dimensional Atom Probe
2D	Two-Dimensional
3D	Three-Dimensional
3DAP	Three-Dimensional Atom Probe
<i>bcc</i>	Body Centered Cubic
<i>fcc</i>	Face Centered Cubic
<i>hcp</i>	Hexagonal Close Packed
<i>tcp</i>	Topologically Close Packed
APB	Anti-Phase Boundary
APT	Atom Probe Tomography
CSF	Complex Stacking Fault
DFT	Density Functional Theory
EAM	Embedded Atom Method
EDS	Energy Dispersive Spectroscopy
EXAFS	Extended X-Ray Absorption Fine Structure
FEEM	Field Emission Electron Microscope
FIB	Field Ion Beam
FIM	Field Ion Microscope
FMM	Force Matching Method
GGA	Generalized Gradient Approximation
HEG	Homogeneous Electron Gas
LDA	Local Density Approximation

LEAP	Local Electrode Atom Probe
LOTF	Learn-on-the-fly
LSDA	Local Spin Density Approximation
MD	Molecular Dynamics
MRF	Markov Random Field
PAW	Projector Augmented Wave
PoSAP	Position Sensitive Atom Probe
SEM	Scanning Electron Microscope
SESF	Superlattice Extrinsic Stacking Fault
SFE	Stacking Fault Energy
SISF	Superlattice Intrinsic Stacking Fault
SRS	Synchrotron Radiation Source
TBC	Thermal Barrier Coating
TEM	Transmission Electron Microscope
USPP	Ultra Soft Pseudo Potentials
VASP	Vienna <i>Ab initio</i> Simulation Package
XAS	X-ray Absorption Spectroscopy

CHAPTER 1

Introduction

IN THE PRESENT WORK, a variety of experimental and simulation techniques are used to investigate the origin of the so-called rhenium-effect. Since the early 1980s, rhenium has been added to single-crystal nickel based superalloys – used in the hottest parts of gas turbines – as this element was found to improve markedly the creep properties of these materials. To date, the mechanisms underlying the rhenium-effect are still unknown.

1.1 The gas turbine

Gas turbines are amongst the most efficient heat engines known to man. Indeed, modern gas turbines can reach a *thermal* efficiency of up to 50 % [25]. Due to their high power-to-weight ratio, they are used in the aerospace industry for the propulsion of civil and military airplanes (jet engines). Thanks to their high efficiency, gas turbines are also commonly used to power electricity generators, helicopters, tanks and ships. As with every engine based on the Carnot cycle, a higher operating temperature results in greater propulsive efficiency. In gas turbines, the flame temperature in the combustion chamber reaches up to 2300 K, causing the surface of turbine blades to reach up to and beyond 1300 K [108], close to the melting temperature of the best heat resistant superalloys. At such high temperatures, advanced materials design becomes crucial to improving the service life of components.

Broadly speaking, all gas turbines have a compressor, a combustion chamber and

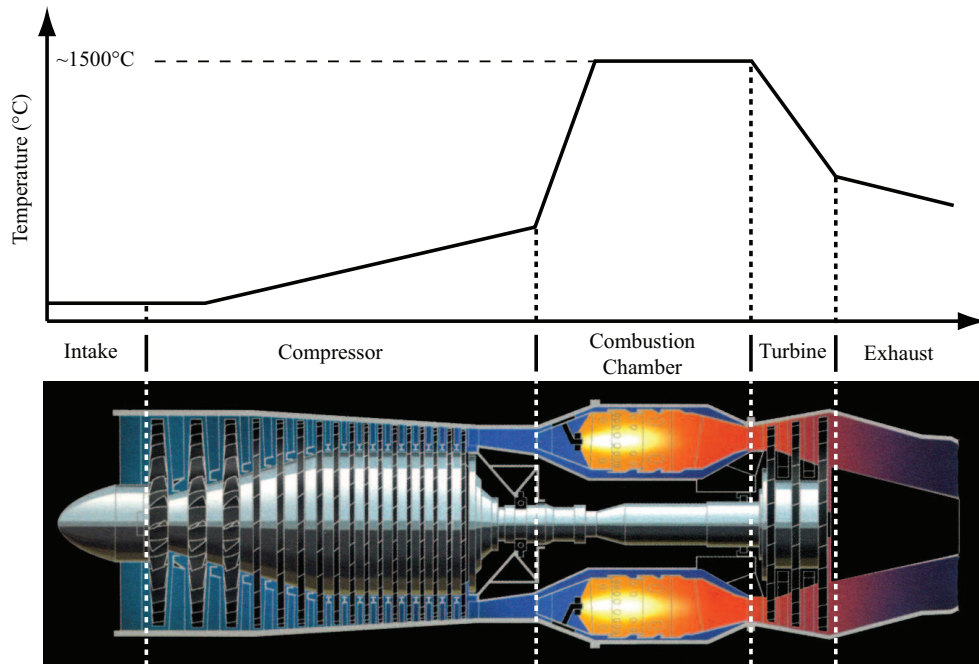


Figure 1.1: A schematic view of a military jet engine [2] and the temperature variation across the engine.

a turbine (see Figure 1.1). The compressor consists of several discs of blades used to compress air into the combustion chamber. In the combustion chamber, air is mixed with fuel and ignited. The ignition causes the hot gases to expand through the turbine, thereby generating kinetic energy. The different stages of the turbine extract some of the energy to rotate the front compressor stages by means of shafts running through the core of the engine [108]. The compressor and turbine sections of the engine are often divided into sub-stages (*e.g.* low pressure and high pressure compressor). The temperature inside the engine rises sharply in the combustion chamber, and air cools as it moves through the turbine stages (see Figure 1.1). The engine design differs slightly depending on the performance requirement of the application:

- High-bypass Turbofan engines are used for civil aerospace applications and take their name from the high bypass ratio. Most of the air sucked in by the entry fan passes beside the engine and only some of the air goes through to the combustion chamber. This design improves fuel efficiency for subsonic speeds as well as dramatically reducing noise pollution for flights over urban areas.
- Low-bypass Turbofan engines are used for military aerospace applications and

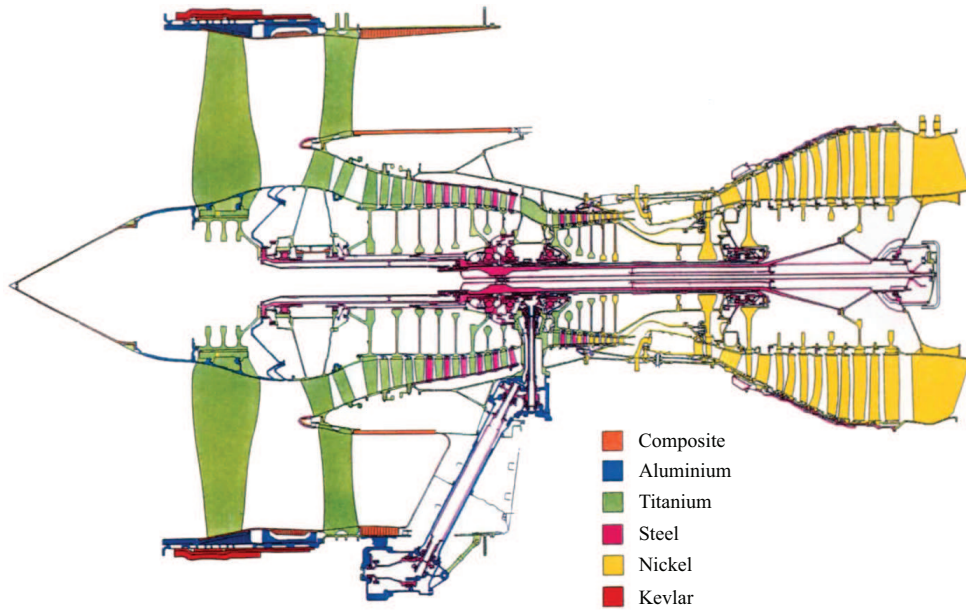


Figure 1.2: A schematic view of a civil jet engine and the materials used [104].

have a much lower bypass ratio compared with engines used in civil aerospace applications. Low-bypass engines often have afterburners positioned after the last stage of the turbine to burn-out remaining oxygen and increase thrust. This design allows more efficient supersonic speeds but also results in much higher operating noise.

- Turboshift or Turboprop engines are used for power production units, helicopters, tanks, ships as well as some planes. They have no bypass ratio and have an additional turbine stage to convert all jet thrust into kinetic energy which can be used to drive propellers, rotors and power generators. This type of engine, mounted as a Turboprop on a plane, can be extremely efficient at low air speeds (< 400 mph).

All materials used in jet engines are at the forefront of research and they are carefully designed to match the required properties of each component (see Figure 1.2). The front fan, made from high-grade titanium alloys, must resist impact with foreign objects as well as high rotational speeds. Composite materials are used to build outer protective shells such that component failures are contained within the engine. Cheaper materials, such as steel and aluminum alloys, are used for the very few non-critical parts

of the engine. Nickel superalloys are used in the hottest parts of the engine: in the combustion chamber, the last few compressor stages before the combustion chamber and, most importantly, in the turbine stages (see Figure 1.2). The only factor imposing limitations on the operating temperature, and therefore on the propulsive efficiency, is whether or not the materials in the hottest parts of the engine can withstand such temperatures. Given that the propulsive efficiency of the jet engine increases with the turbine entry temperature [25], the importance of nickel superalloys becomes apparent.

Therefore, nickel superalloys play an important role in the operation of gas turbines since they are the only materials able to withstand the high stresses and temperatures present at the core of the engine. Ultimately, the safety and environmental impact of gas turbines are directly affected by the design of new grades of nickel superalloys and better nickel superalloys are needed to make flying more environmentally and financially sustainable.

1.2 Nickel superalloys

The nickel superalloys that are used today have been developed over many years. Nowadays, such alloys contain approximately 60-70 wt.% nickel and ten or more alloying elements in varying composition, such as Cr, Co, Mo, W, Al, Ti, Ta, Nb, Re, Ru, Hf, C and B. Each additional element has a key role in improving the overall properties of the alloy. Therefore, each manufactured component, according to its specific application and location, has a particular composition and microstructure which must be optimised for best performance [104].

In general, two phases are predominant in all components: the γ phase has a simple *fcc* crystal structure whilst the γ' phase has a $L1_2$ structure based on the Ni_3Al intermetallic (see Figure 1.3 and Figure C.2). Other phases, such as γ'' , carbides, borides and *tcp* phases, are also present in minor quantities. Each phase may be favourable or un-favourable depending on the type of application the alloy has been designed for. For example, carbides and borides improve creep properties of discs when present at the grain boundaries in small quantities, but they worsen creep properties when present in single-crystal blade alloys [104].

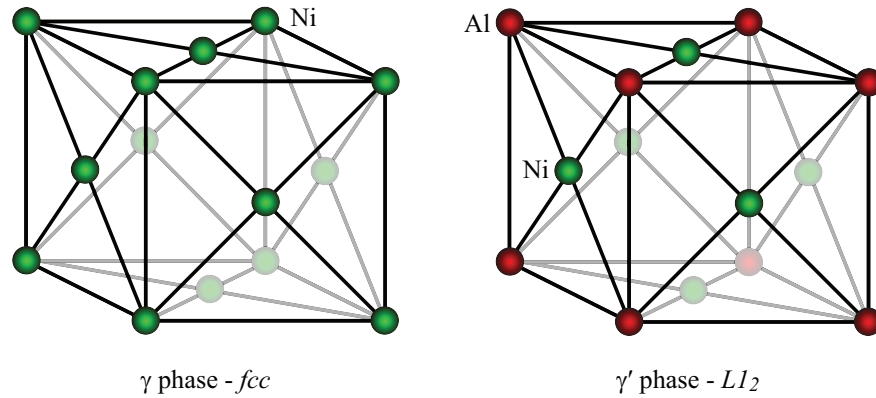


Figure 1.3: Arrangements of nickel and aluminium atoms in γ and γ' .

Nickel superalloys can be divided in two broad categories: those used for the production of discs and those used for the production of blades. These two classes have entirely different composition, microstructure, production route, failure and deformation mechanisms and, as such, they should be treated separately.

1.2.1 Disc alloys

Turbine discs are subjected to high stresses as they hold the blades and transmit the rotational force from the blades to the central shafts. As they are not directly exposed to hot gases, turbine discs only have to resist intermediate temperatures in a relatively low oxidising environment. Thus, creep deformation and component oxidation are not major concerns in the design of discs. On the other hand, the high stresses that discs have to withstand mean that fatigue is a major concern [108].

Turbine discs are typically forged or produced via a powder metallurgy route [7]. A fine grain microstructure is necessary to achieve high yield strength as well as to reduce fatigue crack growth. Elements such as carbon and boron are added to the composition to form small carbides and borides which pin grain boundaries. Rhenium is not added to the composition as it would segregate to the grain boundaries and embrittle the component [104].

Discs are considered to be critical components and disc failure usually results in serious damage to the engine itself as well as to the airframe, since the protective KevlarTM shells around the engine are not strong enough to contain a failed disc. For

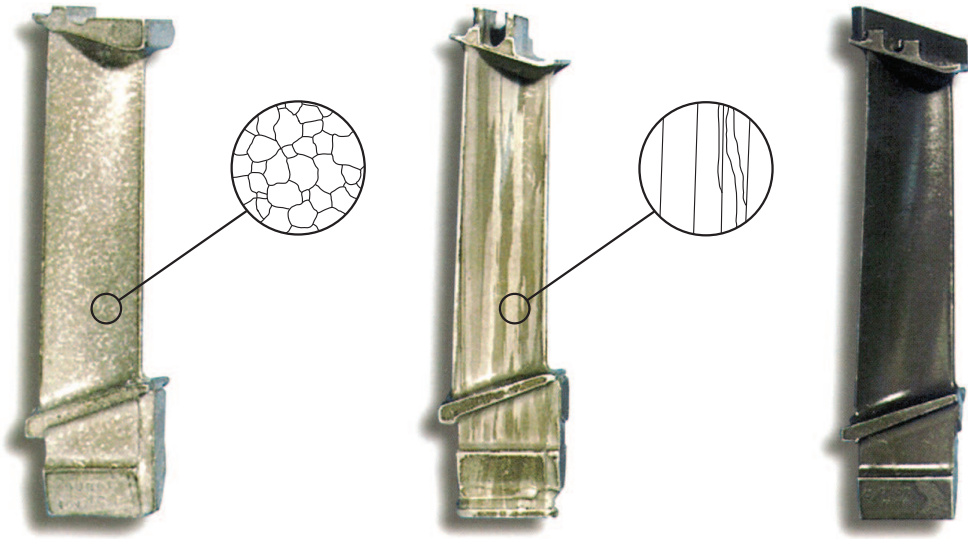


Figure 1.4: The standard cast blade, the directionally solidified blade and the single-crystal blade.

this reason, each disc is carefully selected and inspected to make sure no defects are present. Since disc alloys do not contain rhenium, these are not relevant to the present study.

1.2.2 Blade alloys

Blades are amongst the components reaching the highest temperatures; but, unlike the combustion chamber, they also have to withstand high stresses. Many years of development highlighted that grain boundaries constitute a weakness in a high temperature environment. Thus, blade alloys have developed in a different direction compared with disc alloys. During the 1970s, the detrimental effect of grain boundaries in creep conditions provided a strong drive to move away from blades with *equiaxed* grains (see Figure 1.4) [104] and directionally cast blades, which have columnar grains, became gradually more common. Since the 1980s, single-crystal superalloy blades have been widely used in the hottest parts of the engine [108].

The switch to single-crystal metallurgy allowed a major re-optimisation of alloy chemistry, such as the dismissal of carbon and boron which were used to stop grain boundary sliding. The general trends in composition across the years can be seen in Figure 1.5. Some important changes in alloy composition have occurred over the years. Aluminum content has increased steadily since it stabilises γ' , which has been recog-

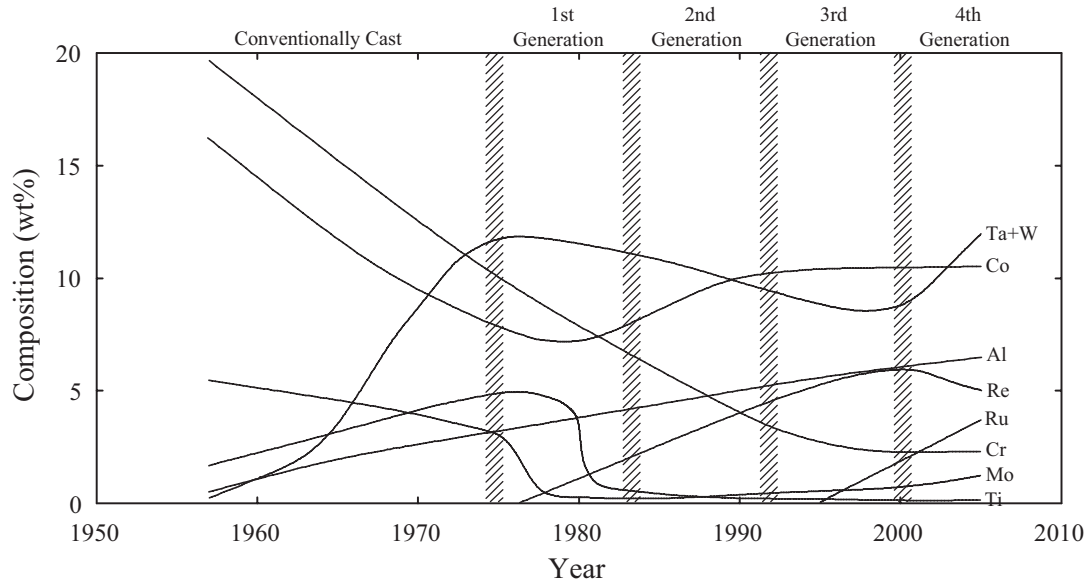


Figure 1.5: Variation in composition for the nickel superalloys across several decades [104].

nised as a strengthening phase at high temperature. Chromium content has decreased since it promotes the formation of detrimental *tcp* phases. In the past chromium played an important role in limiting oxidation, but new processing technologies, such as the application of Thermal Barrier Coatings (TBC), have made the use of chromium obsolete. At the end of the 1970s, rhenium was found to improve creep resistance considerably [133], justifying the increase in rhenium content since then.

New single-crystal blades are produced via investment casting and a single grain is allowed to grow into the blade cast using a *pig tail* grain selector [132]. Blades are grown so that the $\langle 001 \rangle$ direction is aligned along the length of the blade. This is done to exploit the creep anisotropy observed in certain single-crystal superalloys [104]. Additionally, aligning the $\langle 001 \rangle$ direction to the length of the blade also improves the fatigue life of the component because the stiffness along the $\langle 001 \rangle$ direction is lowest [104]. Typically, a miss-orientation of approximately 20° leads to an increase in stiffness of 10-30%.

Single-crystal superalloys are not single-crystal from a strictly theoretical point of view: the microstructure consists of two different phases, γ and γ' , and dislocations and defects are frequent. In blade alloys, the γ' phase grows as cuboidal precipitates inside the γ matrix phase (see Figure 1.6). Both phases have considerable amounts

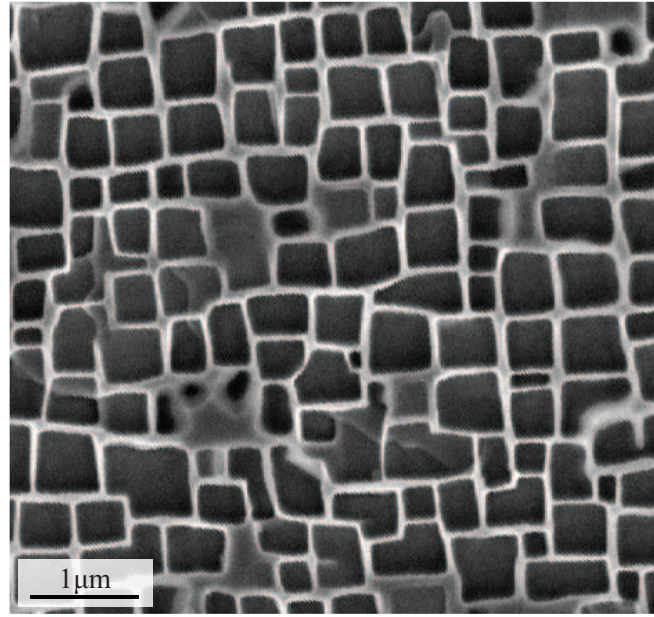


Figure 1.6: Scanning electron image of CMSX-4 showing γ' cuboidal precipitates (darker) in the γ matrix (lighter) (*courtesy of Despina Hadjiapostolidou*).

of alloying elements in solid solution: some elements tend to partition to the γ' phase (*e.g.* Ta, Ti, Co) while others tend to partition to the γ phase (*e.g.* Re, Fe, Mo) [89]. An example of how elements partition between the two different phases for a CMSX-4 alloy is provided in Table 1.1 (see §1.6). All elements are substitutional to the host lattice, both in γ and γ' , meaning that no atoms take interstitial lattice sites. In the γ' phase, elements usually have a strong preference for either nickel or aluminium lattice sites [37].

Although two phases are present, the single-crystal definition of nickel superalloys is adopted because there are no grain boundaries and the γ matrix phase is a single-crystal. Additionally, the lattice parameters of the two phases are extremely similar and the γ' precipitates are grown coherently within the matrix phase. In most commercial alloys, approximately 60-70 % of the volume consists of γ' phase precipitates, surrounded by thin γ phase channels (see Figure 1.6). The relative fraction of γ' phase as well as the size and distribution of γ' precipitates are major factors in improving the performance of the alloy because of how dislocations interact with the γ' precipitates [104].

Designing new alloys is complicated since most elements have positive as well as

negative effects on alloy performance. The main criteria to be taken into account when designing a new alloy are:

- Creep resistance – the alloy should resist relatively high stresses at temperatures close to its melting temperature.
- Castability – the alloy should be suitable for component production via investment casting.
- Stability – the alloy’s composition should be stable to avoid brittle phases forming at high temperatures.
- Coatability – the alloy should create a strong bond with the oxides used as TBCs.

In the past, the optimisation of these compositions was usually obtained experimentally, by trial-and-error based procedures [99]. However, empirical procedures are costly and time consuming and considerably delay the entry of new alloys into service in gas turbines. It is apparent that a detailed understanding of the mechanisms conferring the desired properties will lower the cost of developing new alloys and permit a more fundamental approach to their design [99].

1.3 Creep deformation

Creep is a deformation process occurring at high temperature and at stresses below the yield strength of the material. A good creep resistant alloy is able to resist stresses at temperatures close to its melting point ($> 0.5 \cdot T$). Several deformation processes are concurrent in causing creep, and dominant deformation processes depend on loading conditions, temperature, alloy composition and many other factors [104]. Broadly speaking, creep is divided into three stages, to help distinguish active deformation processes as a component deforms over time [3]:

- Primary creep – the strain rate is high and decreases with time because of work hardening processes which slow down dislocation movement
- Secondary creep – the strain rate is constant as a balance is reached between work hardening and annealing

- Tertiary creep – the strain rate increases exponentially because of necking and voiding, until the component fails

The fraction of component life spent in the three stages of creep varies from alloy to alloy and is strongly dependent on loading and temperature. Typical isothermal constant-load creep data for a single-crystal CMSX-4 specimen is shown in Figure 1.7. At low temperatures and high stresses (see Figure 1.7a), a substantial amount of primary creep can be observed. This particular stage is characterised by a large number of dislocations sweeping the microstructure, shearing the γ' precipitates and gliding within the γ phase. The shearing of the γ' precipitates requires large amounts of energy which is why this particular creep regime only happens in high loading conditions. Primary creep is usually followed by secondary creep, where the strain rate remains approximately constant: at this stage, dislocation density is high and work hardening and annealing processes are balanced [97, 102, 101, 133].

At intermediate strains and temperatures (see Figure 1.7b), tertiary creep deformation is dominant and the creep rate increases monotonically without ever reaching steady-state creep. Generally, no microstructure degradation is observed. In this stage, dislocations are confined to the γ phase and the γ' precipitates are not deformed or sheared by the dislocations. High strain results in large numbers of dislocations piling up at the γ/γ' interfaces and bending in the γ channels between the γ' precipitates. Eventually, necking and voiding are observed and the component fails [97, 96, 64, 116].

At temperatures beyond 1300 K (see Figure 1.7c), the creep rate remains stable before it increases catastrophically, with specimen rupture occurring soon after. This particular regime is characterised by rapid microstructure degradation, termed ‘rafting’, consisting of the coalescence of γ' precipitates. Eventually, the alloy will display a continuous γ' matrix phase. This is caused by dislocation networks close to the γ/γ' interfaces acting to relax the local lattice misfit between the two phases and accommodate the accumulated strain [97, 67, 105].

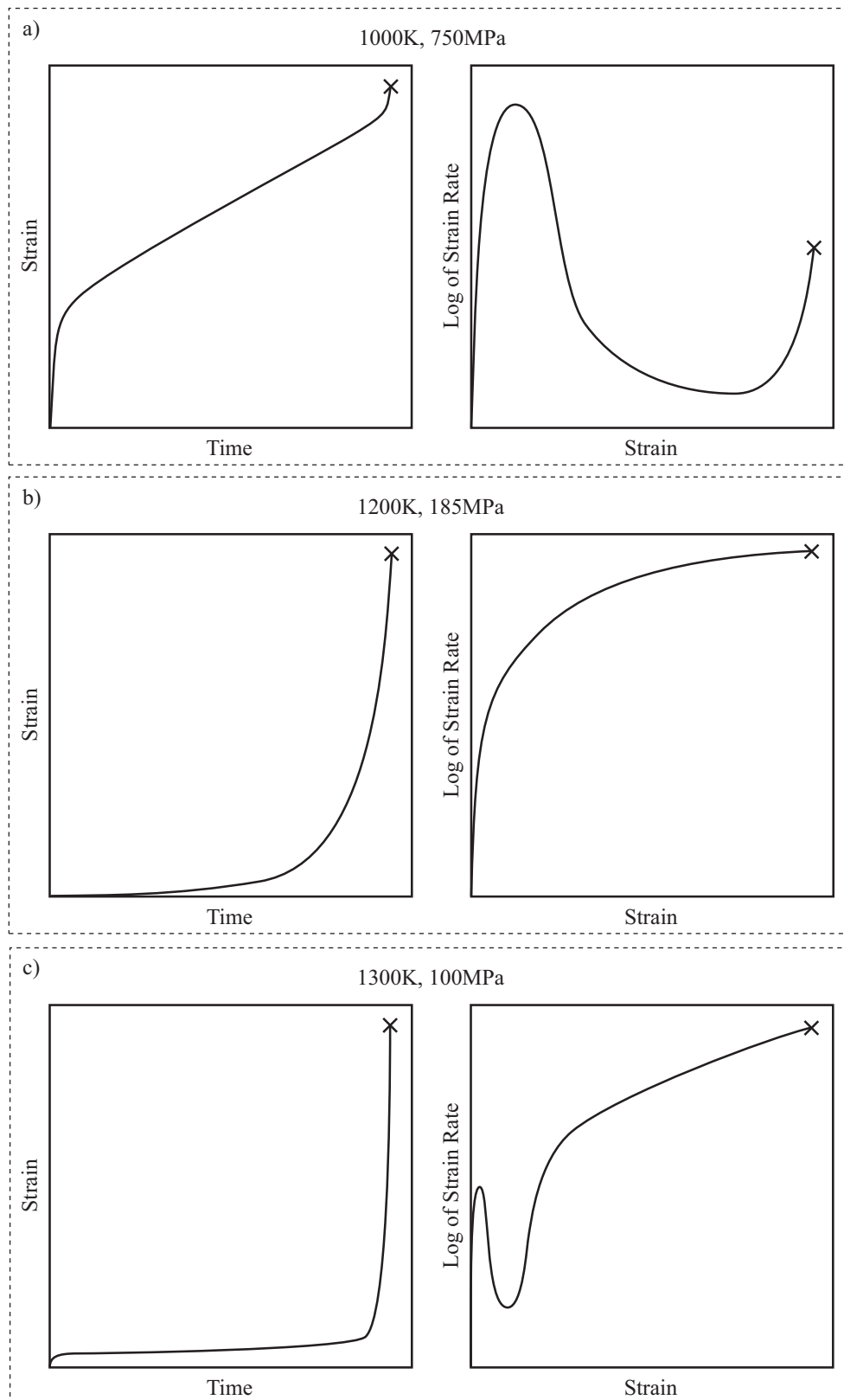


Figure 1.7: Typical isothermal constant-load creep data for an oriented CMSX-4 single crystal specimen at a) low temperature and high stress, b) intermediate temperature and intermediate stress and c) high temperature and low stress.

1.4 Dislocation theory

Dislocation processes in nickel superalloys can be very complicated. Deformation mechanisms, indeed, change with loading conditions and temperature and are affected by microstructure and its evolution through service life [97]. In this section, a description of the most common and established deformation mechanisms is provided as a key to understanding subsequent chapters and also why nickel superalloys have exceptional creep properties.

1.4.1 Dislocations in the γ phase

Deformation in the γ phase occurs, as in any other *fcc* metal, by the glide of a $a/2\langle 1\bar{1}0\rangle\{111\}$ edge dislocation. However, it is well established that the movement of an edge dislocation at high temperature occurs by the passage of two Shockley partial dislocations [104] with the reaction displayed in Equation 1.1.

$$a/2\langle 1\bar{1}0\rangle\{111\} \rightarrow a/6\langle 2\bar{1}1\rangle\{111\} + a/6\langle \bar{1}2\bar{1}\rangle\{111\} \quad (1.1)$$

The Burgers vector for the full dislocation is $a/\sqrt{2}$ while the Burgers vector for the two partial dislocations is $a/\sqrt{6}$. When the two Shockley partial dislocations become dissociated, a planar stacking fault is generated between the two dislocations on the close-packed $\{111\}$ planes. The first Shockley partial dislocation causes an intrinsic stacking fault while the second Shockley partial dislocation removes it.

The spacing between the two partial dislocations will depend upon the Stacking Fault Energy (SFE). Therefore, the SFE is very important for the strength of the alloy. This is because the two Shockley partial dislocations need to meet locally to allow the full edge dislocation to climb – the mechanism used by dislocations to move around obstacles. A high SFE will reduce the distance between the two partial dislocations thereby giving the full dislocation a higher mobility. On the other hand, a lower SFE would be desirable as it increases the spacing between the two Shockley partial dislocations thereby hindering the movement of the full dislocation through the γ phase [79].

1.4.2 Dislocations in the γ' phase

Due to the ordering of the γ' phase, the full dislocation for the $L1_2$ Ni_3Al structure is, on the $\{111\}$ planes, $a\langle\bar{1}\bar{1}0\rangle\{111\}$ which has Burgers vector equal to $a\sqrt{2}$. However, the shortest lattice vector in the $L1_2$ is $a\langle 100\rangle$, which means that, at intermediate and low stresses, the preferred slip system would be $a\langle 100\rangle\{001\}$ [104]. In practice, it is not clear whether the preferred slip system is $a\langle\bar{1}\bar{1}0\rangle\{111\}$ or $a\langle 100\rangle\{001\}$ especially because both full dislocation in γ' dissociate into two dislocations of the type $a/2\langle\bar{1}\bar{1}0\rangle$. Therefore, when a full dislocation in γ reaches the boundaries of a γ' precipitate, it will need a second full dislocation in order to enter the γ' phase [104], as seen in Equation 1.2.

$$a/2\langle\bar{1}\bar{1}0\rangle\{111\} + a/2\langle\bar{1}\bar{1}0\rangle\{111\} \rightarrow a\langle\bar{1}\bar{1}0\rangle\{111\} \quad (1.2)$$

The full dislocation in γ' is often referred to as a superdislocation, which splits into the two superpartial dislocations. The first superpartial dislocation will introduce a planar defect referred to as the Anti-Phase Boundary (APB), which is then removed by the passage of the second superpartial dislocation. As for the γ phase, the movement of a superpartial dislocation occurs by its dissociation into two Shockley partial dislocations [104]. The first partial dislocation will introduce a stacking fault, which will be removed by the second partial dislocation.

The reactions that define a dissociation of a full dislocation into several partial dislocations are more complicated in γ' than in γ . This is because the Burgers vector of a dislocation in γ' is much longer than in γ . The dissociations result in the creation of several types of planar defects, in addition to the APBs described earlier: Superlattice Intrinsic Stacking Faults (SIFS), Superlattice Extrinsic Stacking Faults (SEFS) and Complex Stacking Faults (CFS) [104]. The dislocation mechanisms in γ' become even more complicated in extreme loading conditions, as more slip systems activate to accommodate deformation [97].

The resulting behaviour is that, at intermediate and low stresses, dislocations bow in the γ channels, while getting pinned by the γ' cuboid [106]. Dislocations only sweep the γ' particles when the load is sufficient to overcome the high energy associated with

the creation of planar defects [102]. The movement of the dislocations in the γ' phase is slowed down considerably by the fact that an ensemble of dislocations is needed for glide to happen and by the fact that local reordering of the atoms at the planar fault is often necessary for planar defects to be stable [55]. The combined creep behaviour of the γ and γ' phases is what makes nickel superalloys the obvious choice for use in jet engines and gas turbines.

1.5 The rhenium-effect

Since the 1970s, small additions of rhenium have been found to markedly improve the creep resistance of nickel superalloys. In this section, the role and behaviour of rhenium in nickel superalloys is explored and theories on the mechanisms underlying the rhenium-effect are described.

1.5.1 Rhenium in nickel superalloys

Rhenium content of single-crystal superalloys has been steadily increasing since the 1980s up until the year 2000. Now, the average rhenium content of nickel superalloys has plateaued for largely two reasons: first, a higher fraction of rhenium solute atoms facilitate the formation of brittle *tcp* phases; second, the cost of rhenium (~ 500 US\$/100 g) provides a strong incentive for industry to reduce or replace rhenium in modern alloys. Indeed, rhenium often contributes up to half the cost of raw materials that are needed for a standard single-crystal superalloy. Current nickel superalloys contain 3-6 wt.% rhenium and the performance of these alloys is so dependent on rhenium that reducing its use is proving to be a difficult task [133]. These reasons have contributed to an increase in research carried out regarding the mechanisms underlying the rhenium-effect [133, 11, 52, 148], which are still largely not understood.

It is known and accepted that rhenium strongly partitions to the γ phase while the γ' phase is depleted of rhenium content. These conclusions are based on atom probe results [127, 122] (see §3.3), but also on SEM- and TEM-based Energy Dispersive Spectroscopy (EDS) [85, 125]. Indeed, it can be observed that almost no rhenium is present in the γ' phase of CMSX-4, as shown in Table 1.1. Thus, it is fair to assume that

the mechanisms leading to the rhenium-effect occur in the γ phase. This statement is strengthened by observations that alloys with a lower partitioning coefficient for rhenium also have reduced creep properties [52]. Accordingly, studies have mainly focussed on the distribution of rhenium in the γ phase and on the effect of rhenium on microstructure evolution [105]. The scientific community agrees that rhenium does not play a role in the strengthening of the γ' phase [133].

Early work with the atom probe detected small inhomogeneities in the ladder diagram for rhenium (see §3.3) [12, 13]. These inhomogeneities were thought to indicate the presence of rhenium clusters, ~ 1 nm in size, distributed in the γ phase [12, 13]. Ladder diagrams and concentration profiles were used elsewhere to corroborate these initial results and to strengthen the theory that rhenium clusters hinder dislocation motion [127, 109, 11]. More details on atom probe analysis of nickel superalloys is given in §3.3.

Rhenium also forms a large pile-up at the interfaces between the γ and γ' phases. This enrichment is found on the γ side of the interface, extending up to 10 nm into the γ channel [131]. The result is that the local concentration of rhenium very close to the γ/γ' interfaces can be up to 50 % higher than the average concentration of rhenium in the γ phase. The enrichment of rhenium close to the interface is relatively more pronounced than those of other elements. Such pronounced enrichment is due to the high partitioning coefficient of rhenium and the slow diffusivity of rhenium in nickel [131, 133]. It is not clear whether the enrichment forms during the heat treatment of the alloy – and is present at service temperature – or whether the pile-up is formed upon cooling from service temperature – and is not present at service temperature [131].

Rhenium additions result in a negative lattice γ/γ' misfit – meaning that the unit cell size of the γ' phase is smaller than the unit cell of the γ phase. This is, naturally, a consequence of the fact that rhenium is slightly larger than nickel and strongly partitions to the γ phase, increasing its lattice parameter. Therefore, rhenium is expected to slow the growth of the primary and secondary γ' particles. Additionally, it would be expected that a misfit would hinder dislocations entering the γ' precipitates as highlighted by Zhang *et al* [147].

Before proceeding any further, it is important to define what the rhenium-effect is usually considered to be within the literature. What is usually meant by rhenium-effect is the strengthening effect that rhenium generates on alloys during their primary, secondary and tertiary creep regimes when dislocations sweep the γ phase. It is recognised that rhenium also has an effect on the microstructure evolution of nickel superalloys: most importantly, rafting processes are slowed down by the presence of slow diffusing elements in the γ phase [39, 134, 105, 143, 144]. Nevertheless, it is generally agreed that rhenium has been widely adopted in second and third generation nickel superalloys because of its positive effects on creep life during the primary, secondary and tertiary regimes [62, 104, 133]. Rafting is a complicated process with most elements affecting its mechanisms. Rhenium is thought not to play an essential role. Indeed, some rhenium-containing alloys, such as CMSX-4, display a very rapid rafting process while they retain their high creep properties thanks to the addition of rhenium.

1.5.2 Possible mechanisms underlying the rhenium-effect

Over the years, several theories have been formulated to explain the rhenium-effect. These are:

1. Rhenium clusters in the γ phase, particularly close to the γ/γ' interfaces, could generate strong barriers against dislocation motion
2. Local enrichment of rhenium content near the γ/γ' interfaces could have a large impact on the topology of the interface, thereby introducing some dislocations to relax the lattice misfit and making it difficult for other dislocations to enter the γ' precipitates
3. Rhenium could decrease the stacking fault energy. A lower SFE would mean that dissociated Shockley partial dislocations would be located farther apart, thereby making dislocation climb difficult
4. Interactions between dislocations and single rhenium atoms distributed in the lattice could hinder dislocation motion, given that rhenium is the slowest diffusing element in nickel superalloys

The first theory, which is also the most widely discussed [109, 133, 52, 11], was first proposed by Blavette *et al* [12, 13]. The theory is largely based on the observation of inhomogeneities in the ladder diagram for rhenium. Wanderka *et al* [127] repeated these studies and found similar discontinuities in the ladder diagrams. The same conclusions were reached by Rüsing *et al* [109] when observing the inhomogeneities along a one-dimensional rhenium concentration profile obtained from a three-dimensional dataset. Recently, Zhu *et al* [148] adopted classical MD simulations with purpose-built EAM potentials to show that rhenium clusters 1.2 nm in size are energetically stable in the nickel lattice. It follows that such small clusters would pin dislocations and considerably extend the creep life of components. The clustering of rhenium is still a controversial topic in the superalloys' community and will be described in further detail in §3.2.

The second theory was first proposed by Warren *et al* [131]. It was suggested that the larger content of rhenium at the interfaces would increase the lattice parameter of the γ phase so that dislocations would have to overcome a higher energy barrier to enter the γ' phase [29, 148]. It has also been suggested that a more negative lattice misfit between the γ and γ' phases could slow down the rafting of the γ' precipitates while in service and therefore retard tertiary creep [39, 134]. There are two problems with this theory. First, several studies [128, 4, 54], including the present one, show that the length of Ni–Re bonds is very similar to the length of Ni–Ni bonds. It is expected that rhenium will increase lattice misfit, but not to the extent required to generate noticeable mechanical effects. Second, it is the opinion of the author that the rhenium enrichment local to the interface is due to the growth of the γ' precipitates upon cooling: rhenium would be ejected from the cuboidal precipitates into the γ channels. With this consideration in mind, it is apparent that the enrichment would not be present at service temperature and cannot play a role in the rhenium-effect. Whether or not the rhenium enrichment close to the γ/γ' interfaces has an impact on creep resistance is still a matter of debate.

The third theory was explored experimentally on several occasions. Rae *et al* [100] suggested that the simultaneous additions of Co and Re would lower the stacking fault energy enough to justify the rhenium-effect. A later study by Diologent and Caron

[29] calculated the SFE for the γ phase of several non-rhenium-containing commercial alloys and compared it with two single phase model alloys containing Re and Ru. The study showed that the SFEs were comparable across all alloys, thereby invalidating the theory. However, the results must be treated with caution due to the approximations and uncertainties in these calculations. Recently, Yu *et al* [146] studied the effect of solute elements on the SFE and looked at how the different SFEs would affect climbing velocities. The effect that rhenium has on SFE remains open to question.

The fourth theory was proposed by Fu *et al* [36], and based on the work done by Janotti *et al* [45]. This work underlined that rhenium, amongst the elements in the 5d series, is the slowest diffusing atom in the nickel lattice. It was observed that the energy barrier for the rhenium/vacancy exchange was higher than for other elements. This suggests that atomic-scale mechanisms controlling dislocation motion are slower in the presence of rhenium atoms. Rhenium could directly act on dislocations in two separate ways. First, rhenium atoms could slow down dislocation glide by pinning the line defects. Second, rhenium atoms could slow diffusion activated processes required for climb to happen. Both mechanisms could be relevant as it has been reported that deformation in the γ phase occurs by climb-assisted glide of dislocations [104].

1.6 Samples and materials

In the current work, some experimental techniques were adopted to gain a better understanding of the behaviour of rhenium compared to other solute atoms. The aims and objectives of the experimental work carried out within this project will be discussed in more details in §1.7. In this section, the information necessary to understanding subsequent chapters is provided. Further details on specimen preparation and data collection are also provided in Appendix A. Two sets of samples were analysed in this project: a set of crept and uncrept CMSX-4 specimens and a set of Ni-10 wt.% X binary alloys where X was taken to be Ta, W, Re, Ir and Pt.

Table 1.1: Solute content of CMSX-4 γ and γ' phases measured with the atom probe and nominal composition of CMSX-4 [106] in at.%.

Elements (at.%)	Cr	Co	Mo	Al	Ti	Hf	Ta	W	Re	Ni
CMSX-4	7.47	9.78	0.44	12.83	1.36	0.03	2.18	2.11	0.95	Bal.
CMSX-4 [106]	6.61	11.25	0.26	11.62	0.93	0.03	1.87	1.70	0.97	Bal.
γ	21.70	19.37	0.73	3.03	0.17	–	0.22	2.27	3.40	Bal.
γ'	2.10	9.03	0.25	18.10	1.78	–	2.84	1.81	0.39	Bal.

1.6.1 CMSX-4 superalloy

The CMSX-4 samples were taken from crept and uncrept areas of single-crystal creep specimens which had been tested at 1423 K and 100 MPa (tertiary creep regime) for several hundred hours by Reed *et al* [106]. The nominal composition of CMSX-4, along with the measured composition of the γ and γ' phase via the atom probe experiments, is shown in Table 1.1.

1.6.2 Ni-X binary alloys

The binary Ni-X alloys were prepared in the form of 400 g ingots using the vacuum induction melting process. Each binary alloy contains 10 wt.% of one of Ta, W, Re, Ir and Pt. The solute concentration was chosen to match the Re concentration in the γ phase of CMSX-4. Re was included as the solute of prime interest, but the other alloying elements, chosen from the 5d row of transition metals, were included to allow a systematic examination across the periodic table. Homogenisation was achieved by annealing the ingots at 1523 K for 7 days in flowing argon [48, 49]. No additional heat treatment was performed and the alloys were allowed to furnace cool. The composition of the binary Ni-X alloys measured with the atom probe is shown in Table 1.2.

1.6.3 Nickel superalloys vs. UHS steels

Most of the techniques used in this project to detect rhenium clusters in nickel superalloys (see §1.7) have also been used to characterise the formation of copper and nickel clusters in Ultra High Strength (UHS) steels used for pressure vessels in nuclear reactors. Although the problem of nano-sized cluster formation might carry some sim-

Table 1.2: Solute content of the binary alloys measured with the atom probe in at. %.

Elements (at.%)	Ta	W	Re	Ir	Pt	Ni
Ni-Ta	3.70	–	–	–	–	Bal.
Ni-W	–	4.40	–	–	–	Bal.
Ni-Re	–	–	3.12	–	–	Bal.
Ni-Ir	–	–	–	3.40	–	Bal.
Ni-Pt	–	–	–	–	3.35	Bal.

ilarities between the two families of alloys, there are some critical differences which should be considered in order to understand why certain data analysis methods may be more suitable when applied either to nickel superalloys or to ultra high strength steels.

Both nickel superalloys and ultra high strength steels are multi-component systems with up to 10 alloying elements. The composition is finely tuned to maximise performance at high temperature. While rhenium clusters are thought to have a positive impact on alloy properties, nickel and copper clusters in ultra high strength steels make the components brittle and lead to catastrophic failure. In ultra high strength steels, these nano-sized clusters are formed when the materials are in service: radiation damage means that large amounts of vacancies are created and these vacancies promote the formation of clusters. Furthermore, whereas the concentration of rhenium in the γ phase of nickel superalloys is ~ 3 at.%, the concentration of copper in ultra high strength steels is usually within 0-0.5 at.%.

1.7 Explaining the rhenium-effect

The objective of this project is to use a broad range of techniques to understand the atomic scale mechanisms leading to the rhenium-effect. The question of rhenium clustering has been one of the most controversial topics in the superalloys' community. Many scientists seem to agree that small rhenium clusters in the γ phase would pin dislocations and slow creep deformation thereby resulting in the rhenium-effect [133, 11]. Given the wide adoption of the rhenium clustering theory within the community, it follows that the question of rhenium clustering should be answered once and for

all within this project, using simulations and experiments. Currently, the rhenium clustering theory is based upon the observation of discontinuities in the ladder diagrams and concentration profiles for rhenium obtained with the 1D and 3D atom probe by Blavette *et al* [12, 13, 11] and Wanderka *et al* [127, 109]. No in-depth analysis was performed to look at the precise size and distribution of these clusters using more advanced clustering detection algorithms applied to datasets obtained with the latest atom probes.

Since the initial studies on the clustering of rhenium in nickel based superalloys, atom probes have undergone considerable development so that their analytical capabilities have improved markedly [69]. Most evidently, modern atom probes are able to produce three-dimensional images of the sample on a routine basis, with the field-of-view and, consequently, dataset size increased by several orders of magnitude (up to and beyond 100 million atoms). The pulse repetition rate has also increased by several orders of magnitude, enabling significantly faster data acquisition. The large size of the volume of analysis, along with commonly available high computational power, make statistical analysis of the presence of Re clusters more accurate than ever before; and will therefore help to determine whether rhenium forms clusters in nickel superalloys.

In addition to revisiting the rhenium clustering problem with the atom probe, it was deemed important to apply other techniques to establish the presence of rhenium clusters in nickel superalloys. Extended X-ray Absorption Fine Structure (EXAFS) is an experimental method that can accurately probe lattice site occupation and crystal structure within 5 Å from an atom of interest. This would allow the detection of rhenium clusters in the nickel lattice. Furthermore, *ab initio* modelling via the Density Functional Theory (DFT) can be used to investigate the stability of rhenium clusters in nickel and calculate the binding energy between two rhenium atoms in the nickel lattice. This is deemed important in order to be able to critique the work of Zhu *et al* [148].

Atom Probe Tomography (APT), in conjunction with Phase Field Modelling, can also be used to investigate the formation of the rhenium enriched areas close to the γ/γ' interfaces in single-crystal nickel superalloys. The objective would be to show whether the rhenium enrichment is formed upon cooling from service temperature or

whether the enrichment is formed upon the heat treatment of the alloy [131]. The former would mean that the enrichment would not be present at service temperature and therefore would not play a factor in the rhenium-effect.

Finally, *ab initio* modelling can also be used to investigate the effect of rhenium on the stacking fault energy of nickel [146]. If rhenium is shown to have an abnormally large effect on stacking fault energy, then it follows that dislocation climb would be slower when rhenium is added to nickel superalloys [100, 146]. Therefore, investigating the effect of rhenium on the SFE would provide useful insight into the mechanisms underlying the rhenium-effect.

CHAPTER 2

X-ray Absorption Spectroscopy

2.1 Theory of EXAFS

EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) is not widely known or appreciated in the metals research community. This is probably due to the focus that EXAFS has on atomic structure and lattice site occupation. Indeed, general x-ray absorption spectroscopy techniques are used more extensively in the ceramics and semiconductors research community. Traditionally, metallurgy has focused on microstructure and processing of materials rather than their atomic structure, which partly explains the relative scarcity of EXAFS research in metallurgy. However, nickel superalloys push the boundaries of metallurgy so far that interactions, structure and defects at the atomic scale are key factors underlying the properties of such materials. These factors make EXAFS a useful technique to deepen our understanding of this system.

EXAFS allows determination of crystal structure and lattice site occupation within 5 Å of an absorbing atom. In other words, EXAFS is able to yield the atomic structure surrounding a rhenium atom and detect the presence (or absence) of clusters embedded in the host lattice. The results are obtained by closely examining the oscillations in x-ray absorption arising when a x-ray beam is absorbed by the atoms in the examined sample [103].

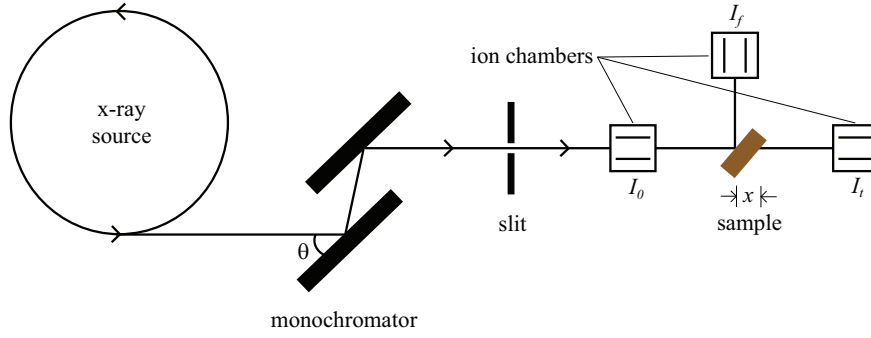


Figure 2.1: A schematic view of the experimental apparatus at the beamline.

2.1.1 Data processing

The experimental data is usually collected at a synchrotron radiation facility. Coherent monochromatic x-rays are shone through the sample while the x-ray energy (E) is increased at a steady rate using tilting single crystal silicon mirrors. The x-ray energy is chosen such that, when increased, the absorption edge for the atomic species of interest will be encountered. A schematic view of the beamline instruments is shown in Figure 2.1.

In the simplest experimental setup, the x-ray intensity is measured using ion chambers before and after the specimen. Using these measurements, the absorption coefficient of the sample, μ , will be given by Equation 2.1. I_0 and I are respectively the x-ray intensities before and after the sample, as measured by the ion chambers, and x is the thickness of the sample.

$$\mu x = -\ln \frac{I_0}{I_t} \quad (2.1)$$

Alternatively, the the absorption coefficient of the sample is proportional to the fluorescent x-ray intensity, as shown by Equation 2.2.

$$\mu \propto \frac{I_f}{I_0} \quad (2.2)$$

The energy of the x-rays is determined by the inclination of the monochromators, which is recorded simultaneously with the x-ray intensity measurements. Sometimes the data is recorded as the tilt angle of the single crystal silicon mirrors, θ . In this

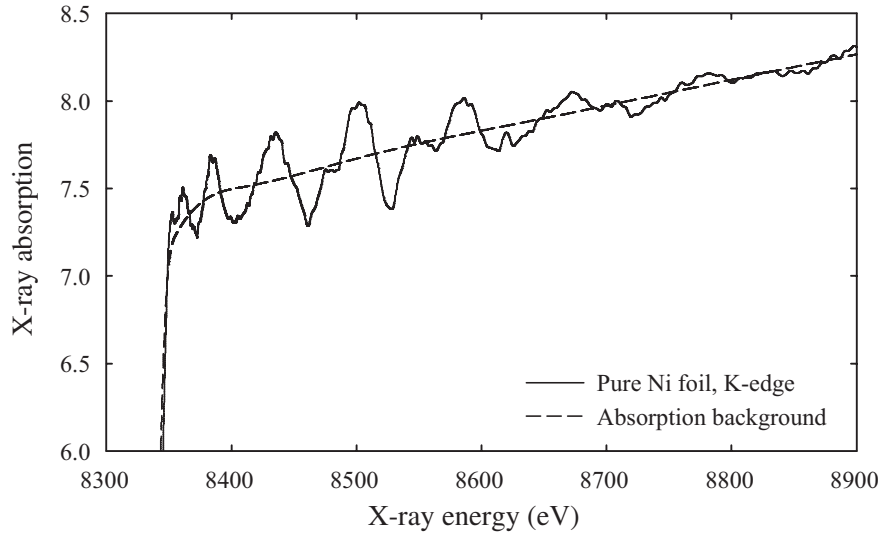


Figure 2.2: The K-edge absorption and subsequent oscillations for a pure Ni foil.

case, Bragg's law can be applied to convert the values to x-ray wavelength, λ , as shown in Equation 2.3.

$$n\lambda = 2d \sin \theta \quad (2.3)$$

The distance between the scattering atomic planes, d , of the silicon crystal is known and n is an integer determined by the order given ($n = 1$ in this situation). The relationship between Energy (E) and Wavelength (λ) is established in Planck's Law, and expressed in Equation 2.4, where h is Planck's constant and c is the speed of light.

$$E = \frac{hc}{\lambda} \quad (2.4)$$

EXAFS analysis consists of studying the oscillations in x-ray absorption, $\mu(E)$, just above the absorption edge (see Figure 2.2). The oscillations of $\mu(E)$ from 20-30 eV up to 500-1000 eV above the absorption edge of interest [107] are normalised with $\mu_0(E)$, the 'bare atom' absorption background, to obtain $\chi(E)$, the normalised, oscillatory part of the x-ray absorption (see Equation 2.5).

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)} \quad (2.5)$$

Next, the energy-independent function, $\chi(k)$, needs to be obtained from $\chi(E)$. The

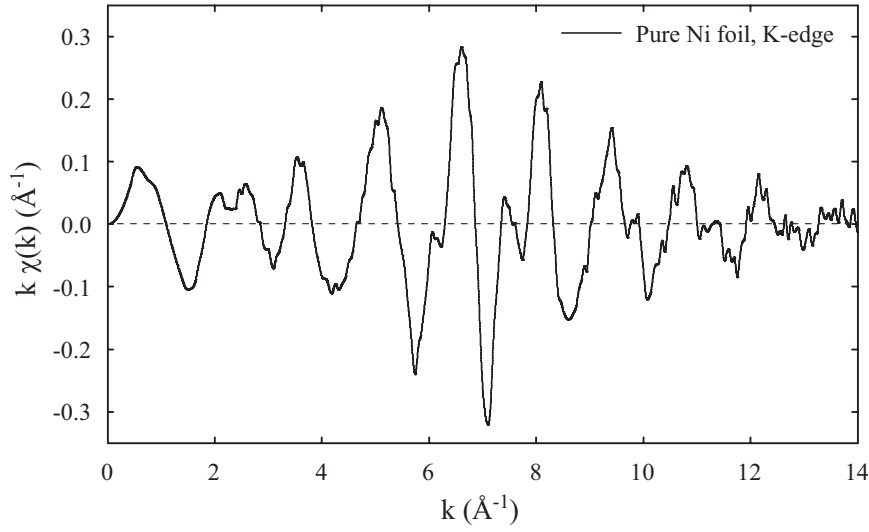


Figure 2.3: The $k\chi(k)$ function for a pure Ni foil, obtained from the data in Figure 2.2.

photoelectron energy, E , can be substituted with the photoelectron wave-vector, k , so that data from different absorption edges can be compared (see Equation 2.6).

$$k = \sqrt{\frac{2m}{\hbar^2}(E - E_0)} \quad (2.6)$$

In Equation 2.6, E_0 is the ionisation energy of the absorbing atom, $\hbar$ is Dirac's constant and m is the mass of the electron. Note that the raw $\chi(k)$ is usually weighted using a factor k^n to avoid the rapid damping of the EXAFS oscillations. Different schemes of k^n -weighting can be applied, and n can take several values in $k^n\chi(k)$. Usually, a value of $n = 1$ is used. Higher factors can be used to look at longer scattering paths in greater detail. A typical $k\chi(k)$ dataset, obtained from a pure Ni foil during the present study, is shown in Figure 2.3.

The mechanisms controlling the amplitude, frequency and damping of these oscillations are so complicated that it is practically impossible to work out the underlying lattice structure directly from experimental data. In the past, extraction of results concerning the fine structure found near the atom of interest, such as co-ordination and lattice site occupation, required the comparison of the $k\chi(k)$ experimental data with $k\chi(k)$ of known structures in order to distinguish key features in these oscillations. Nowadays a deeper knowledge of electronic theory and advances in computing power allow scientists to simulate the x-ray absorption oscillations of any crystal and

gain an understanding of complicated lattice structures.

2.1.2 The EXAFS equation

Sayers *et al* [111, 112] developed a quantitative EXAFS equation based on single point scattering theory to model the absorption oscillation. Starting from a simulated crystal structure, Equation 2.7 can be used to obtain $\chi(k)$.

$$\chi(k) = \sum_j \frac{N_j S_0^2 |f_j(k)|}{k R_j^2} \exp \left[\frac{-2R_j}{\lambda(k)} \right] \exp \left[-2\sigma_j^2 k^2 \right] \sin [2kR_j + \delta_j(k)] \quad (2.7)$$

Here, the amplitude of the oscillations as a function of k is calculated as a summation function across all possible different scattering atoms, j . The term S_0^2 is a factor to scale the overall amplitude of the EXAFS oscillations. The other parameters are path dependent: N is the number of equivalent scatterers; $f_j(k)$ is the backscattering amplitude which depends on the backscattering atom; R_j is the interatomic distance; $\lambda(k)$ is the photoelectron's mean free path; σ_j^2 is the mean-square deviation in bond length due to lattice vibration and lattice disorder; $\delta_j(k)$ is the phase shift of the photoelectron caused by the potential backscattering atom. Small modifications to Equation 2.7 allow the calculation of contributions from scattering paths involving 3 or more atoms.

Therefore, if we know $f_j(k)$, $\delta_j(k)$ and $\lambda(k)$, we can determine N , R_j and σ_j^2 . It is important to notice that $f_j(k)$ and $\delta_j(k)$ depend on the atomic number of the backscattering atom, which is why EXAFS can be used to detect chemical identities of the neighbouring atoms. Usually, atomic numbers can be detected up to an accuracy of 5. It is also worth mentioning that the relationship between R_j and $\chi(k)$ is such that EXAFS can only probe the atomic environment close to the absorbing atom.

2.1.3 Fourier transform analysis

Sayers and co-workers also pointed out that, based on Kronig short-range order theory, the Fourier transform of $\chi(k)$ with respect to k results in a spectrum with peaks that can be related to the original crystal structure of the sample [112]. In actual fact, the

Fourier transform of $\chi(k)$ yields a complex function made of a real and imaginary part. The magnitude of the Fourier transform of $\chi(k)$, also referred to as $|\chi(R)|$, results in a distribution of possible photoelectron scattering paths. An example of $|\chi(R)|$ for a pure nickel foil is shown in Figure 2.4; it should be noted that the real and imaginary part of $\chi(R)$ are not shown. Direct scattering paths, those that involve only the absorbing atom and one scattering atom, are usually dominant. The first peak seen in Figure 2.4, occurring at a path length of $2 \text{ \AA}$, is generated by the direct scattering paths from the first shell of neighbouring atoms. It may be noted that the distance between two nearest neighbours in the Ni *fcc* lattice is $\sim 2.5 \text{ \AA}$. The shift between the real interatomic distance and the first peak on the $|\chi(R)|$ graph is due to the phase shift $\delta_j(k)$. A shift of $-0.5 \text{ \AA}$ is typical.

The second, third and fourth peak (at $3.3 \text{ \AA}$, $4 \text{ \AA}$ and $4.7 \text{ \AA}$ respectively) can also be explained by looking at direct scattering paths from neighbouring shells of atoms. However, the observation that peaks in the spectra correspond to shells of neighbouring atoms becomes weaker at higher path lengths. This is due to three-legged scattering paths, those that involve 3 or more atoms, playing a greater role. Additionally, the relationship between peaks and shells of neighbouring atoms may fail depending on the atomic number of the elements present in the sample. The shape of the peaks is dependent on the electronic structure of the scattering atoms, which explains how EXAFS can be used to establish the lattice site occupation around the absorbing atom. For example, the direct scattering paths between nearest neighbours taken from the 5d row of transition metals will yield a double peak instead of the single peak observed for Ni in Figure 2.4.

The analysis of EXAFS data via the Fourier transform method has been particularly useful, since relevant photoelectron paths can be easily identified making the process of matching possible crystal structures to the experimental data much faster. Today, much of the EXAFS work builds on the model developed by Sayers and co-workers and there are several software codes that help scientists with modelling and fitting experimental data. FEFF is amongst the most established codes for modelling EXAFS interactions [86]. The success of FEFF may be due to the fact that it is a simple theoretical code which can be integrated in third party analysis packages. The

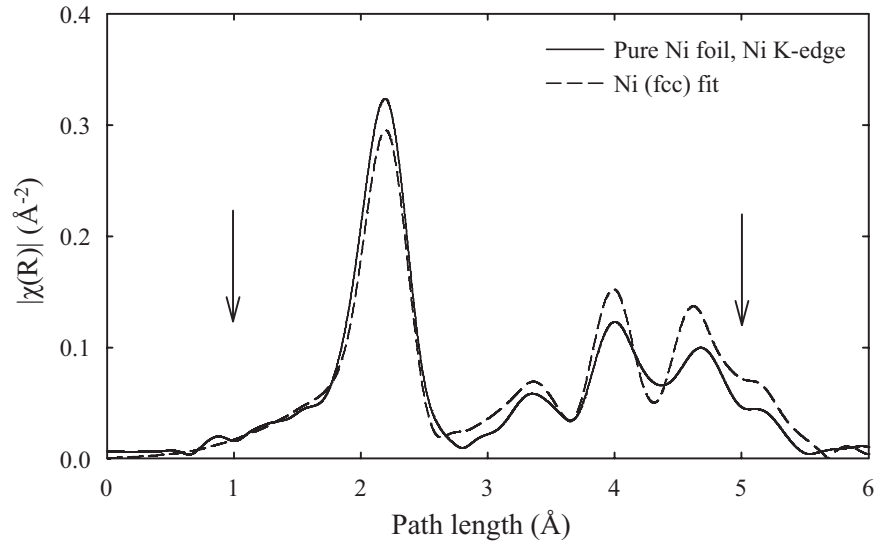


Figure 2.4: The Fourier transform of $k\chi(k)$, $|\chi(R)|$, for a pure Ni foil; with a corresponding Ni (*fcc*) fit obtained from FEFF. The arrows mark the fitting range.

code has been integrated into an analysis and fitting package called IFEFFIT [87]. Using FEFF and IFEFFIT, it is possible to simulate the EXAFS oscillations from the predicted photoelectron scattering paths, and use these to establish the crystal structure of the specimen.

2.1.4 Fitting procedure

In practice, after the absorption data is processed as described in §2.1.1, the $|\chi(R)|$ spectra is obtained by performing a Fourier transform on $k^n\chi(k)$ within the desired ranges (*i.e.* excluding the oscillations nearest to the edge and those at the highest energies). The EXAFS equation can then be used to build a simulated $|\chi(R)|$ for a given crystal by summing all the contributions from each scattering path. An accurate fit between the experimental and simulated $|\chi(R)|$ can then be achieved by modifying the values for E_0 in Equation 2.6 and S_0^2 , σ_j^2 and R_j for each scattering path j in Equation 2.7. In IFEFFIT this is done by allowing the definition of four parameters for each scattering path j :

- ΔE_0 is a correction to the ionisation energy of the absorbing atom. Although the fitting software allows for the user to set a different ΔE_0 value for each scattering path j , it can be argued that there is no real physical meaning in

defining a different ionisation energy for each scattering path. Therefore, only one ΔE_0 value should be set for all scattering paths.

- ΔR is a correction to the nearest neighbour interatomic distance. Similarly to ΔE_0 , there should be only one ΔR for all scattering paths. This last statement is only valid if all the atomic sites in the material analysed are equivalent and if the analysis does not focus on the relaxation around point defects. Although generally ΔR is mostly used as a lattice scaling factor, it may be necessary in some systems to set a different correction in nearest neighbour interatomic distance.
- S_0^2 is a scaling factor to control the importance and contribution of each path to the final spectrum. It is rather common to set different values of S_0^2 for different paths, following a predetermined scheme. One such scheme encompasses defining a different S_0^2 for different *types* of paths in order to control the importance of each type of path on the final spectrum (*e.g.* direct scattering paths versus three-legged scattering paths).
- σ^2 is the mean square deviation in bond length, as highlighted in Equation 2.7. This parameter is used to control the effect of lattice vibration and lattice disorder on the EXAFS spectrum. Also in this case, different σ^2 are set for different paths, following a predefined scheme. In some cases, σ^2 is defined as a function of path length or calculated following a Debye model.

The number of independent parameters that can be obtained from a periodic signal is given by Equation 2.8 [15, 63].

$$n \approx \frac{2\Delta k \Delta R}{\pi} \quad (2.8)$$

In Equation 2.8, Δk is the range over which the Fourier transform is performed in k-space and ΔR is the range over which the fit is performed in R-space. Given that $\Delta k \approx [2-12] \approx 10 \text{ \AA}^{-1}$ and $\Delta R \approx [1-5] \approx 4 \text{ \AA}$, then $n \approx 25$ although it may be that $n \approx 10$ if smaller ranges are used for the Fourier transform and fitting procedure. In

principle, it is best to keep the number of independent parameters as low as possible, by defining some extra parameters as algebraic expressions of independent ones [86].

2.1.5 Chemical resolution and limitations

There are two factors that should be taken into account when determining whether a system can be analysed using EXAFS. First, the absorption edge of the relevant element must be isolated from the absorption edges of other elements in the system studied. This is because the absorption oscillations following the absorption edge of interest should be free of interference from other absorption edges: collecting data from the Re L₃-edge of a system containing Re and Hf may not be possible since the Hf L₂-edge is only 200 eV above the Re L₃-edge. Second, the chemical resolution of EXAFS is relatively low and it is almost impossible to distinguish backscattering atoms of similar atomic number. The atomic number of backscattering atoms can usually be determined to an accuracy of ± 3 [107]. Therefore, it is impossible to distinguish Cu and Ni atoms when investigating Cu clusters in UHS steels [17, 18].

2.2 EXAFS and metallurgy

Although examples of the application of EXAFS analysis to metallic alloys is scarce, initial attempts to look at the crystal structure surrounding solute atoms in binary alloys was done as early as 1980, within a variety of systems, and results are described by Gurman [40].

Lengeler and Eisenberger [61] used EXAFS to make a comprehensive study on the interatomic distances and coordination numbers of Al and Cu in simple binary alloys. In this study, the authors focussed on the α (Al), θ (Al₂Cu) and θ' (Al₂Cu, metastable) phases. The samples used to study the α phase contained 0.5 at.% Cu, which remains in solid solution. Interatomic distances were established to an accuracy of 1 %, whereas the coordination numbers could only be evaluated with an accuracy of 20 %. The same authors suggest that such high errors in the evaluation of coordination numbers is due to the fact that no reliable theoretical method was available to calculate EXAFS amplitudes, limiting the methodology to the comparison of EXAFS spectra

to known references [31].

The ability to simulate EXAFS spectra from desired crystal structures, and fitting them to spectra obtained at the beamline, has considerably increased the amount of information that can be obtained from EXAFS. Balasubramanian *et al* [5, 6] used EXAFS to probe the local structure and lattice relaxation surrounding dilute Co and Fe solute atoms in γ' -Ni₃Al. The use of simulations allowed Balasubramanian *et al* to calculate how the EXAFS spectra would appear for each solute atom in both the Ni and Al sublattice. The results showed that Co is coordinated by 8 Ni atoms. No Al backscattering was observed, although this would be expected since Co is known to occupy the Ni sublattice and therefore should be coordinated by 8 Ni atoms and 4 Al atoms. The results for Fe showed only Ni backscattering, although Fe should occupy both the Ni and Al sublattice. The authors suggested that the absence of Al backscatter is due to lattice distortions in the Al sublattice surrounding the Co and Fe atoms.

Soon after the work published by the author [84], Koteski *et al* [54] published a study of lattice relaxation around refractory atoms in nickel using EXAFS. In this work, varying amounts of solute atoms from the 4d row (Mo and Ru) and 5d row (Hf, Ta, W and Re) of transition metals were added to Ni. The work of Koteski *et al* focusses on the lattice relaxation, as they argue that lattice mismatch between the γ and γ' phases is an important parameter when controlling the properties of nickel superalloys. The problem of Re clustering was neither mentioned nor discussed. The samples analysed in this work included Ni-2 at.%Ta, Ni-5 at.%W, Ni-2 at.%Re and Ni-5 at.%Re. Koteski observed that the interatomic distance to the first shell of nearest neighbours was 2.54 Å for Ni-2 at.%Ta, 2.52 Å for Ni-5 at.%W, 2.50 Å for Ni-2 at.%Re and 2.51 Å for Ni-5 at.%Re, which follows the expected trend and is predicted correctly by *ab initio* modelling via DFT. For both Ni-Re alloys, a very good fit was obtained by simulating a single rhenium atom embedded in the nickel lattice, which would suggest the absence of any Re clusters.

2.2.1 Detecting clusters with EXAFS

EXAFS has also been applied to metals in order to study clustering reactions or the initial stages of phase separation [40]. Maeda *et al* [65] used EXAFS to investigate Cu clustering in a supersaturated solid-solution of Al, containing 1.9 at.% Cu. The samples were annealed, as the study was focussed on the formation of clusters. The methodology used consisted of comparing the $|\chi(R)|$ spectra obtained from the alloys of interest to Al_2Cu references. Using this method Maeda *et al* were able to show that, after annealing, Cu atoms are coordinated by a mix of Cu and Al atoms, showing a considerable degree of clustering [65]. These results are in agreement with those discussed by Lengeler and Eisenberger [61]: evidence of considerable Cu–Cu backscattering was also observed in their annealed Al alloys with 0.5 at.% Cu content.

A similar method was adopted by Fontaine *et al* [34] to study Al alloys containing 2-2.5 at.% Cu. After quenching and annealing, most Cu concentrates in the vicinity of Guinier-Preston zones. By comparing the $|\chi(R)|$ data to known references, the authors were able to identify the structure of the Guinier-Preston zones. In contrast with the work of Maeda *et al*, Fontaine *et al* found no evidence of Cu clustering. It is argued by Gurman [40] that the discrepancy is due to the different heat treatments applied to the samples analysed in the two separate studies.

Frenkel *et al* [35] made a comprehensive study on the crystal structure and bond lengths of gold based alloys. The authors selected two systems, $\text{Au}_x\text{Cu}_{1-x}$ and $\text{Au}_x\text{Ag}_{1-x}$, in order to analyse binary alloys with high and low atomic size mismatch. The authors used Lennard-Jones potentials to simulate a range of geometries, including a completely disordered *fcc* geometry and some geometries with clustered Cu and Ag atoms. Their results showed a tendency of Cu to form clusters, with clusters of 10^5 Cu atoms best reproducing the features of the EXAFS spectrum. On the other hand, the EXAFS data for the $\text{Au}_x\text{Ag}_{1-x}$ alloys was best matched by a disordered *fcc* structure.

More recently, EXAFS was used to investigate the clustering of Cu and Ni solute atoms in UHS steels and Fe alloys. As mentioned in §1.6.3, the process of solute clustering in these alloys is a major topic of research as this is the underlying mechanism causing the embrittlement of Fe-based alloys under irradiation conditions. Earlier

studies in this field have been made with the 1DAP and 3DAP, and these will be discussed in §3.2. Kuri *et al* [59] used EXAFS to study the presence of sub-nanometer-sized Cu clusters in non-irradiated Fe-0.3 wt.% Cu and Fe-1.0 wt.% Cu. The effect of ageing was also investigated by annealing and quenching a set of specimens at 775 K for 1 hr. The EXAFS analysis was performed by comparing the first peak of the experimental EXAFS spectra (*i.e.* the one corresponding to the first shell of nearest neighbours) to several simulated EXAFS spectra of model geometries based on the Fe *bcc* lattice. All specimens showed some Cu clustering as Cu-Cu backscattering had a significant impact on the first peaks in the EXAFS spectra.

A comprehensive EXAFS study on the structure evolution of irradiated UHS steels was also performed by Cammelli *et al* [17, 18]. In this study, several non-irradiated, irradiated and irradiated and annealed steel samples were analysed using both XANES and EXAFS. Instead of using the IFEFFIT code to simulate the $|\chi(R)|$ spectra from different configurations, the analysis focussed on comparing the $|\chi(R)|$ spectra for the Ni and Cu K-edge from the different samples, taken at different stages of irradiation and annealing. This allows to analyse the evolution of the crystal structure surrounding absorbing atoms with greater details. This is a very reliable method as it does not require the use of a theoretical model and a number of fitting parameters. Instead, the crystal structure surrounding Cu and Ni atoms is probed at each stage of microstructure evolution and changes are highlighted and interpreted readily. The study shows that irradiation generates reduced backscattering from the first shell of nearest neighbours, suggesting large amounts of vacancies are created. As the specimens are exposed to high temperature, the local atomic structure surrounding Cu atoms changes and higher amount of Cu-(Cu, Ni) backscattering was observed, suggesting cluster formation. The atomic structure surrounding Ni atoms remained unchanged, suggesting a difference in behaviour between Cu and Ni. An additional irradiation and annealing treatment resulted in Ni atoms clustering as well. Due to inherent limitations of EXAFS, it was almost impossible to distinguish Cu and Ni backscatterers. The results obtained with EXAFS were compared to observations made with APT on the same samples by Miller *et al* [74].

2.2.2 Coupling EXAFS with *ab initio* simulations

It is worth mentioning the growing tendency to couple *ab initio* simulations with EXAFS analysis. When comparing the experimental EXAFS function to the simulated EXAFS function, the crystal structure used to obtain the simulated EXAFS function is very important. EXAFS is now moving away from investigating the crystal structure of relatively well defined systems. Therefore, as an added tool, *ab initio* modelling can be used to predict ionic relaxation of a desired crystal structure. The relaxed atomic positions can then be used, instead of the initial system, to obtain a more accurate EXAFS function.

2.3 Experimental procedure

2.3.1 Data collection

The EXAFS studies were conducted at Station 9.3 of the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, UK. At the SRS, the Wiggler I source enables experiments to be carried out in the range 6-30 keV, but for the present purposes the minimum and maximum values employed were 9.5 and 15.5 keV respectively. A 1 m long toroidal Pd-coated mirror situated 18 m from the source was used to collect and focus the x-ray beam. A silicon $\langle 220 \rangle$ double crystal monochromator was used throughout the experiment with a beamline angle of 9 mRad. Inchworm positions of the monochromator were set up to be 1:-233, 2:-3260 and 3:-3560. Prior to the measurements on the binary alloys, windows were calibrated against foils of pure Ni, Pt, W and Ta. During the characterisation of the binary alloys, the Ni K-edge and solute element L_3 -edges were measured for all specimens by two fluorescence scans at 620 seconds per scan. Due to the polycrystalline nature of these specimens, samples were scanned under spinning conditions. The composition of the binary alloys is shown in Table 1.2.

2.3.2 Analysis procedure

To aid in the accurate interpretation of the EXAFS data, a knowledge of the extent to which each solute atom relaxes within the host (nickel) lattice is required. For this

reason, all non-standard crystal structures used for the EXAFS fits were simulated with an *ab initio* total energy minimisation via DFT, using the VASP code [57, 41]. A 2x2x2 supercell (32 atoms) was used, as a single solute atom in such a supercell matches the solute concentration of the binary alloys used in the experiments. More details about these calculations can be found in §4.4.1.

In order to reduce noise and the amount of artifacts present in the data, several $\chi(k)$ datasets were averaged together to obtain a more reliable $\chi(k)$ dataset for the analysis.

In order to make the interpretation of the EXAFS spectra more transparent, we have used only four fitting parameters altogether (ΔE_0 , S_0^2 , σ^2 and ΔR), keeping each parameter fixed for all scattering paths. We believe that this method is best to investigate rhenium clustering in nickel, although the final fitting may not be as accurate as it could be obtained by adopting more parameters. By contrast, Koteski *et al* [54] defined an independent σ^2 for different scattering paths, obtaining a better agreement between the simulated and experimental EXAFS spectra.

2.4 Results

2.4.1 The Ni-Re system

To investigate the fine structure around a solute atom of rhenium and to detect any possible clustering of this element, the absorption data of the Re L₃-edge for the Ni-Re binary alloy is investigated. The Fourier transform of the oscillations of this edge will probe the local structure around the Re atoms, by providing a radial distribution of photoelectron paths from the absorbing atom, rhenium, and the surrounding scattering atoms.

The $|\chi(R)|$ spectrum for the L₃-edge of Re in the Ni-Re alloy is shown in Figure 2.5. The spectrum can be compared with simulated EXAFS spectra obtained from different crystal structure. The data is initially be compared to spectra obtained from a rhenium *hcp* crystal (the stable phase of pure Re) and from a rhenium *fcc* crystal (the native structure of Ni) – as seen in Figure 2.5a. The similarities between the hypothetical rhenium *fcc* crystal and the Re L₃-edge data at the third and fourth peak (at 4.0 Å

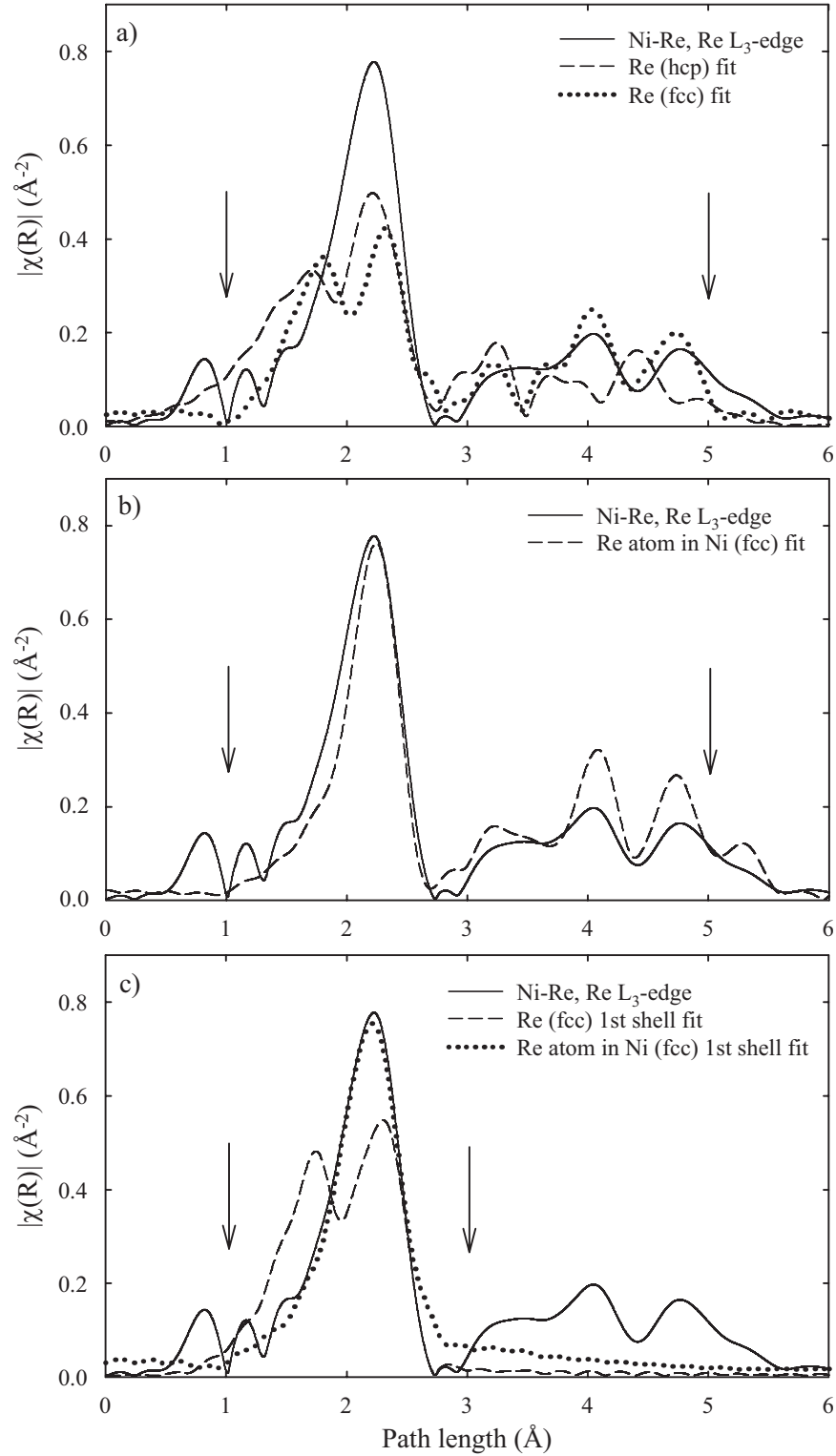


Figure 2.5: The $|\chi(R)|$ spectra obtained from the Re L_3 -edge of a Ni-Re sample. The experimental data is compared to a FEFF fits from a) a pure Re crystal in the *fcc* and *hcp* configuration, b) a single absorbing Re atom in a Ni *fcc* lattice and c) a Re atom with 12 Re neighbours and a Re atom with 12 Ni neighbours.

and 4.8 Å respectively) confirm that the underlying lattice of the sample analysed is *fcc*, consistent with the native nickel crystal structure. Discrepancies at low path lengths (1-3 Å), where the peak arising from the scattering paths from the first shell neighbours in the experimental data is matched by double peaks in both the *hcp* and *fcc* simulated structures, would suggest that the first shell of neighbouring lattice sites are not occupied by rhenium.

The $|\chi(R)|$ spectrum is then compared with a fit obtained from the simulation of a single Re absorbing atom embedded in a Ni *fcc* lattice – as shown in Figure 2.5b. The apparent similarities within the fitting range, marked by the arrows, indicate that this is the most likely atomic structure in the vicinity of an absorbing Re atom. The peaks observed at 2.1 Å, 3.2 Å, 4.0 Å and 4.8 Å of the experimental data are matched in the simulated spectra, confirming that the underlying lattice of the sample is indeed a *fcc* structure. Interestingly, the first large peak, which was not matched by the simulated pure rhenium structures in Figure 2.5a, is clearly reproduced by simulating a single rhenium atom embedded in a nickel *fcc* lattice. Given that the first peak of the $|\chi(R)|$ spectrum arises from the direct scattering paths to the first shell of neighbours, it is clear that this peak is the most relevant to the scope of this study. Careful examination of this first peak will reveal whether the absorbing Re atom is surrounded by a shell of Ni atoms, a shell of Re atoms, or a shell of both Ni and Re atoms. For this reason, the first peak of the $|\chi(R)|$ spectra is examined in greater detail.

The fits shown in Figure 2.5c are obtained by taking into consideration only the direct paths to the nearest neighbours, those that involve a photoelectron travelling from the absorbing atom to a nearest neighbour and back to the absorbing atom, for the Re *fcc* structure and a Re atom embedded in the Ni *fcc* structure. The simulated spectra therefore show the direct backscattering from 12 Ni atoms and from 12 Re atoms. This is because three-legged scattering paths and direct paths to outer shells of atoms do not contribute to the first peak arising in this $|\chi(R)|$ spectra. Only the first peak of the experimental data is being examined here and hence no fitting has been done for the spectra between 3-6 Å. The simulated spectra suggest that the double peak arises when the Re atom is coordinated by 12 Re atoms, while this is not true when the Re atom is coordinated by 12 Ni atoms. The experimental data reveals only

a single, well-defined peak thus confirming that the Re atoms are surrounded by Ni atoms only. The characteristic double peak is also observed in the spectra obtained at the beamline from pure Pt specimens, suggesting that the feature arises from the backscattering amplitude function, $f(k)$, and phase shift, $\delta(k)$, of a pair of atoms taken from the 5d series of transition metals.

2.4.2 Ni-X systems, X=Ta, W, Ir and Pt

The behaviour of Ta, W, Ir and Pt in nickel was also studied to observe trends across the periodic table. Ta and W are widely used in nickel superalloys, whereas Ir and Pt are not commonly used. The objective is to find if any clustering trend can be observed across the periodic table. In particular, W is an element of interest since it is also believed to be a creep strengthening element, although not quite as potent as Re. Investigating differences between Re, W and the other 5d elements will help to narrow down the source of the rhenium-effect.

Indications of whether these elements form clusters in nickel can be obtained by studying the first shell peak of $|\chi(R)|$, as it was done in §2.4.1 for the Ni-Re alloy. The data obtained from the L_3 -edge of the Ni-Ta, Ni-W, Ni-Ir and Ni-Pt are shown in Figure 2.6. All datasets are compared to a fit obtained from pure solute atom *fcc* lattice and to a fit obtained from a single solute atom embedded in a nickel *fcc* lattice.

The characteristic double peaks observed in the fits for the pure 5d crystals are incompatible with the single peak observed in the experimental $|\chi(R)|$ from the four binary alloys. On the other hand, the peak obtained from a single solute atom embedded in a nickel *fcc* lattice is much closer to the experimental datasets, which display a single first peak. This is confirmation that none of the elements examined form clusters when dissolved in nickel.

2.5 EXAFS and rhenium clustering

The results presented in §2.4 would indicate that rhenium is not prone to clustering when present as a solute in the nickel lattice. The detailed analysis of the spectra obtained from the Ni-Re samples shows that Re is coordinated by 12 Ni atoms and

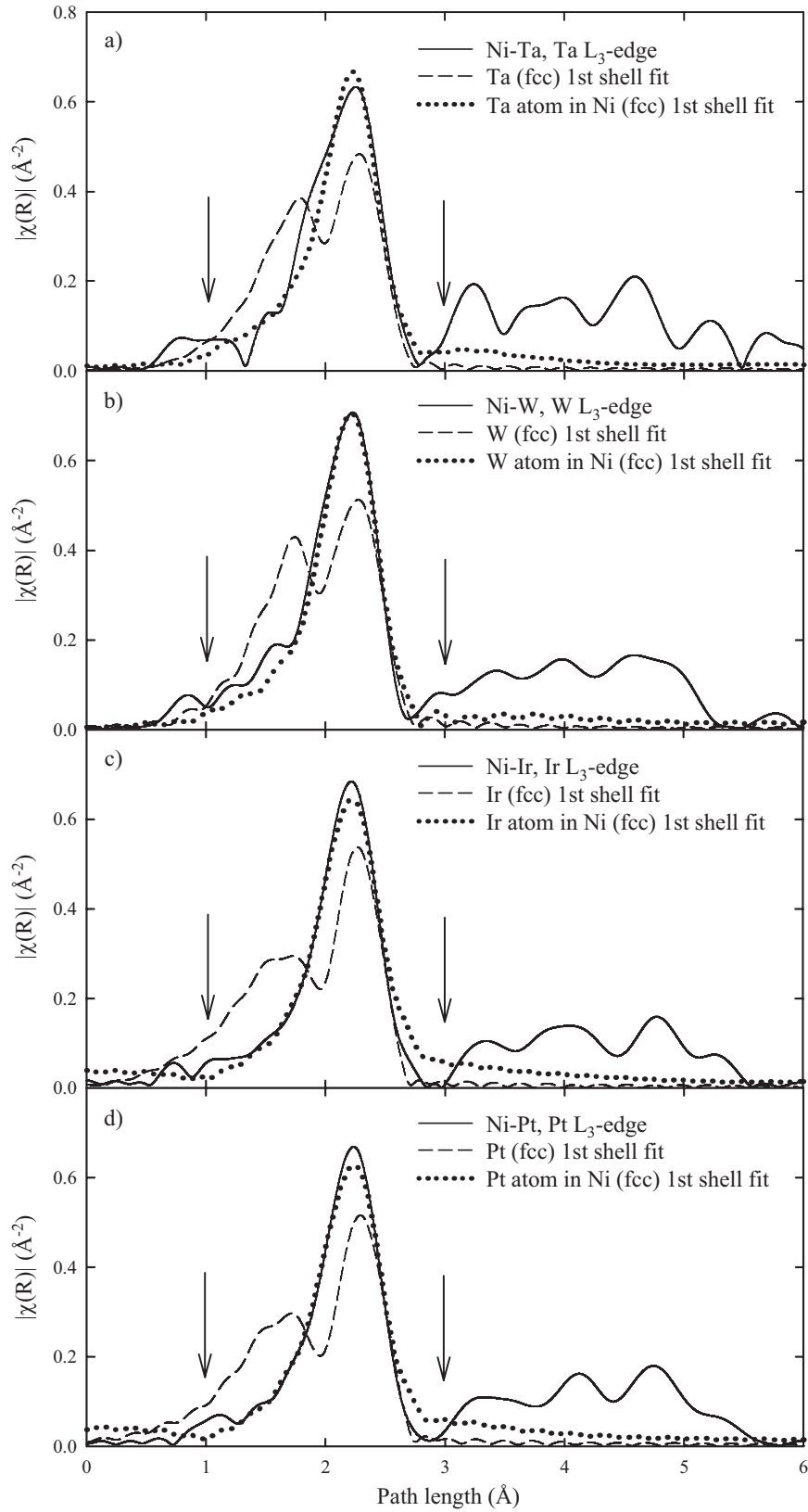


Figure 2.6: The $|\chi(R)|$ spectra obtained from the $X L_3$ -edge of the Ni- X binary alloys where X is a) Ta, b) W, c) Ir and d) Pt respectively. The first peak, arising from the direct scattering paths to the first shell neighbours, is compared to a fit obtained from a solute atom surrounded by 12 atoms of the same species. The same data is also compared to a fit obtained from a solute atom surrounded by 12 Ni atoms.

that no Re backscatter is present in the short range area of the EXAFS spectra. A similar behaviour is observed for Ni-Ta, Ni-W, Ni-Ir and Ni-Pt. It would be safe to conclude that, at these concentrations, these elements are not clustered in the nickel lattice. Given the difference in backscattering between Ni and the elements from the 5d row of transition metals, any backscattering from the latter should be clearly visible in the EXAFS spectra.

The work of Koteski *et al* [54] seems to agree with our conclusions. Although the problem of rhenium clustering is not discussed in their studies, it appears that the EXAFS spectra obtained from the Ni-2 at.%Re and Ni-5 at.%Re specimens showed no Re-Re backscattering. In fact, the simulated EXAFS spectrum for a single rhenium atom embedded in a Ni *fcc* lattice provides an excellent match to the EXAFS spectra obtained at the beamline, suggesting that no Re clustering should also be expected in Ni-5 at.%Re. The data for Ni-Ta and Ni-W also shows no Ta-Ta and W-W backscattering respectively. It is worth mentioning that the EXAFS spectra obtained by Koteski *et al* from their Ni-2 at.%Ta samples does not appear to agree with our data in the range 3-6 Å, however this could be due to that fact that our samples contain almost twice the amount of solute, which could significantly affect the data.

With these considerations in mind, and the results presented in §2.4, it seems necessary to revise the conclusions presented by Blavette *et al* in his original work [12, 13]. The binary Ni-X alloys and CMSX-4 should be studied using APT to investigate the presence or absence of rhenium clusters. Since the 1980s, atom probes have considerably improved and modern computational power also allows a better statistical treatment of the data. It is important to determine whether modern atom probe equipment and analysis techniques would corroborate the results obtained by Blavette *et al* [12, 13], or whether these would strengthen the results observed with EXAFS.

CHAPTER 3

Atom Probe Tomography

3.1 The atom probe

ATOM PROBE TOMOGRAPHY (APT) is a technique which has been continuously expanding since a 1-dimensional atom probe (1DAP) was adapted into the first 3-dimensional atom probe (3DAP) by M. K. Miller in 1986 [69]. APT causes the field evaporation of atoms from the surface of a needle-shaped specimen using a strong electric field. The chemical identities and positions of the evaporated atoms are detected, thus producing a 3D mapping of the atoms present in the specimen and achieving ‘true atomic resolution’. As such, APT has been a key technique in expanding our knowledge of materials.

3.1.1 Early developments

The first successful attempts to view atoms occurred in 1941, when E. W. Müller discovered that reversing the bias voltage on the emitter of a Field Emission Electron Microscope (FEEM) would force positively charged ions to leave the surface of the sample. In these conditions, the amount of ions emitted is limited. Therefore traces of hydrogen or helium were introduced into the system to act as an ‘imaging gas’ and enhance the image on the phosphor screen [77, 69]. These molecules are attracted to the specimen’s surface and hop on the surface until field ionisation of the gas molecules occurs by tunnelling electrons to the surface of the specimen. The positively charged ions then travel towards the phosphor screen, following a trajectory roughly perpen-

dicular to the surface of the specimen. The first Field Ion Microscope (FIM) image of a tungsten specimen with atomic resolution was achieved in 1955, after the FEEM was modified to allow the sample to be cooled with liquid nitrogen [77].

Although FIM generated the first real atomic resolution pictures, the species of the ions viewed could not be detected. This is because the imaging gas ions would strike the phosphor screen and, therefore, no chemical information on the surface atoms of the specimen could be obtained. Consequently, the FIM went through a further stage of development. The first 1DAP consisted of a FIM with a mass spectrometer attached to it so that chemical information about the evaporated ions could be obtained [78, 69]. Although a single machine could carry out both experiments, there are several differences between a FIM experiment and a 1DAP experiment which renders impossible performing both experiments at the same time. First, the AP experiment has to be carried out in a vacuum – without the use of an ‘imaging gas’ – since the gas molecules would affect the chemical analysis of the specimen. Second, the AP spectrometer can only analyse one atom at a time, resulting in only 0.1 % of the evaporated atoms being detected [69]. For this reason, a small aperture was placed in front of the specimen to limit the number of atoms reaching the spectrometer. Additionally, the use of an AC voltage pulse, rather than a simple DC voltage gradient, was introduced so that a controlled number of atoms could be removed at defined timesteps [69].

3.1.2 From 1D to 3D atom probes

In 1986, the 1DAP was developed into the first prototype of 3DAP by M. K. Miller [69]. In this first implementation, the spectrometer was removed to make space for a pair of microchannel plates. When an ion hits the inside of one of the channels on the first microchannel plate, a cascade of electrons is generated and the amount of electrons is multiplied as these travel through the plates. At the other end of the plates, a beam splitter allowed to direct the small electron beam towards two separate detectors: the first, an array of photodiodes, determined times of flight of the ions; the second, a CCD camera, detected their position. The idea was further developed to obtain the Position Sensitive Atom Probe (PoSAP) by Cerezo *et al* in 1988. In this second implementation the photodiodes and CCD camera were replaced by a wedge-

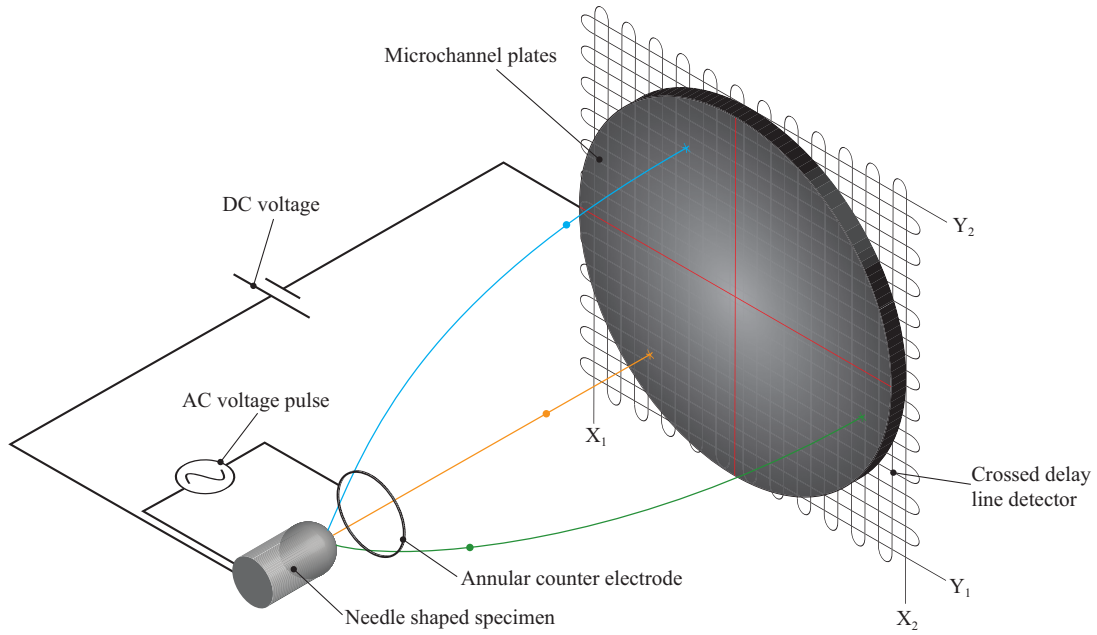


Figure 3.1: The diagram shows the setup of a Local Electrode Atom Probe (LEAP).

and-strip or backgammon anode. Since then, several designs have been proposed, all having different acronyms.

At present, all modern atom probes have a detector which employs a pair of microchannel plates: differences arise in the detector used to back the microchannel plates. Most modern atom probes use a crossed delay-line detector. In this configuration, two folded copper wires (see Figure 3.1) are oriented perpendicular to each other in order to detect the time-of-flight and x and y position of the signal. These data, together with the order of detection, are used to reconstruct the original x , y and z position of the atoms along with the mass-to-charge-state ratio. In some instruments, the superimposed voltage pulse is applied between the specimen and an annular electrode placed just in front of it, resulting in much smaller pulses and a finer control on evaporation rates (see Figure 3.1) [69].

3.1.3 Recent developments

The 3DAP is currently undergoing heavy development [51]. Since 1986, AP research and development led to major improvements in detection efficiency, speed of acquisition, dataset size and spatial and chemical resolution. Amongst all the changes that

led to these improvements, two developments have had a major impact on APT and are therefore worth mentioning.

Modern instruments are sometimes fitted with a wide-angle reflectron lens, or an energy compensation device. Most traditional 1DAP incorporated an energy compensation lens in their spectrometer but these were not part of the new 3DAP designs [69]. Modern atom probes include a reflectron lens which consists of several curved annular field electrodes with increasing potentials. Ions entering the reflectron are slowed down and then accelerated back towards the detector. The purpose of wide-angle reflectron lenses is twofold. First, the use of this lens allows to achieve a wide angle field of view (up to 43 deg). Second, and most importantly, using a reflectron lens considerably improves the mass resolution of the instrument. Unfortunately using the reflectron lens also adversely affects the detection efficiency of the instrument. The advantages and limitations provided by the reflectron lens are discussed in more detail in §3.1.5.

The option of using a laser pulse, instead of a voltage pulse, to evaporate the atoms from the specimens' surface is also becoming more common [50, 51]. In this configuration, a pico- or femto-second laser pulse is directed at the tip of the specimen in order to control the evaporation of the atoms from the surface (*i.e.* thermal evaporation instead of field evaporation). This addresses one of the main limitations of standard atom probes: poorly conductive specimens can now be analysed thanks to the use of a laser pulse (see Section 3.1.5).

3.1.4 Sample preparation

In order to obtain the necessary field strengths (20-40 V/nm) to evaporate ions from the surface of the specimens at reasonable applied voltages (5-20 kV), the sample should be a very thin needle with an end tip radius of about 10-100 nm. Ideally, the sample should approach a cylinder with a spherical cap. In reality, most samples look like a truncated cone with a spherical cap and a taper angle of $\sim 10^\circ$ or less [69]. Smaller taper angles are desirable as the initial and final specimen's radii should be as close as possible to collect larger datasets [69]. The specimen should be ~ 5 mm long, but only the initial ~ 200 nm are usually necessary for the experiment. Oftentimes, the same specimen may be used in multiple runs, after some re-polishing at the end of every

run. There are mainly two methods to prepare an atom probe specimen.

The electropolishing route is the simplest and most traditional method to obtain atom probe specimens [69]. The first step is to obtain a square cross section column which is < 1 mm thick and ~ 10 mm long. Usually, the edges of the column are rounded so that the specimen approximates a round cross section column as much as possible. The initial electropolishing is usually performed via the ‘double layer’ technique. This consists in suspending a thin layer of electrolyte on top of a dense inert liquid. The specimen is inserted through the electrolyte layer, so that the central section of the column is etched until necking and fracture occur. Then, pulse polishing may be used to finely etch the specimen. Pulse polishing consists in suspending a drop of electrolyte in a small loop, and inserting the needle-shaped specimen inside the loop. Using this method, specific areas of the specimen can be polished more precisely by moving the specimen up and down through the loop while controlling the electropolishing current with a switch and constantly monitoring the process using an optical microscope. This technique is cheap, fast and relatively simple, but limited to metallic samples [69]. Additionally, it is almost impossible to position interesting microstructural features close to the apex of the specimen, unless these are large enough to be seen with an optical microscope [69].

The Focussed Ion Beam (FIB) milling route is increasingly common, although it is considerably more expensive and complicated than electropolishing. The success of this sample preparation technique arises from the fact that specific microstructural features (*e.g.* grain boundaries, precipitates, etc.) may be placed near the apex of the needle shaped specimen, with a desired orientation [51]. Usually, three trenches are cut around the desired region and before performing a lift-out. The specimen is then attached to a substrate and an annular mask is used to mill the specimen down to the desired dimensions. The main limitation of this technique is that considerable beam damage may be observed. Limiting beam damage is possible by using a lower ion beam energy and current and minimising imaging times. However, this would considerably increase the time necessary to produce each sample.

3.1.5 Efficiency, resolution and limitations

In order to evaluate APT results, it is important to understand the main limitations of this technique. First, the detection efficiency of modern atom probes will be limited to 66 % as long as microchannel plates are used as the primary detectors. An ion is detected only when it hits the inside of one of the channels on the microchannel plate. If an ion hits the surface between the channels, or web, the instrument cannot yield any information about that ion. Given that the channels cover approximately two thirds of the microchannel plate surface, the maximum possible *theoretical* detection efficiency is 66 % [69]. To overcome this major limitation, a high transparency biased copper mesh is sometimes placed in front of the microchannel plates, in order to trap the secondary electrons produced by an ion hitting the plate's web and accelerate them back towards the detector. It has been estimated that a biased copper mesh may increase the theoretical detection efficiency to as much as 72 %. Yet, it also produces a shadow in the data and increases the noise levels [51].

The use of microchannel plates also leads to some minor losses when ions follow a trajectory which is exactly parallel to the channels of the first microchannel plate. These ions would travel through the first plate without hitting the side of the channels and therefore produce little or no signal. Standard microchannel plates have the channels angled at $\pm 8^\circ$, which is optimal for standard use (*i.e.* when most particles' trajectories are perpendicular to the plates). In an atom probe, however, some ions reach the microchannel plates at an angle of $\pm 8^\circ$ and fly through the first microchannel plate [69]. The number of ions flying through the detector is very small compared to the overall number of successful hits. However, these non-hits occur in a small area of the detector, creating a visible area of low atomic density on the atom map. Using larger plates and placing the detector further away from the specimen limits this effect [69].

Other loss mechanisms strongly depend upon the type of machine used, as well as on specific detector configuration. The presence of a wide-angle reflectron lens causes 30-40 % of the atoms to be lost before they reach the microchannel plates [51]. This is due to the copper mesh that is placed in front of the reflectron lens:

some of the atoms entering and exiting the reflectron lens will hit the mesh instead of continuing flight. Additionally, the simple two-wires crossed delay-line detector can only detect single-hit events, meaning that only 90 % of detected atoms can be successfully analysed, positioned and recorded. Some detectors adopt a third delay-line, positioned at 45° with respect to the other two wires, in order to detect dual-hit events correctly and allowing up to 98 % of detected atoms to be analysed successfully [51]. Broadly speaking, an atom probe without a wide-angle reflectron lens has an overall 55-60 % detection efficiency, while an atom probe with a wide-angle reflectron lens has an overall 40-50 % efficiency [51].

APT also has some limitations in spatial resolution. Studies have shown that the reconstructed x and y positions of the atoms can be scattered up to 5 Å from the original position in the specimen [126]. The same studies showed that the spatial resolution in the z direction is considerably more precise and reaches almost true atomic resolution. There are two causes for what are usually called trajectory aberrations.

First, the trajectory of an ion leaving the specimen's surface is highly dependent on the local crystal structure surrounding the evaporating ion [69, 51]. The trajectory will be different whether the ion evaporates from the edge or the middle of an atomic plane. The trajectory of the ions is also affected by the chemical environment surrounding the evaporating ion. The effect of crystal structure can be readily observed as datasets obtained from some specimens will display lower density areas corresponding to particular crystallographic directions. Oftentimes, the crystal structure and orientation of the specimen can be determined by observing the atomic map of raw hits during evaporation.

Second, trajectory aberrations also arise due to changes in the local radius of curvature of the specimen's tip [69, 51]. Indeed, the reconstruction of 3DAP data is based on the assumption that the tip of the specimen is perfectly spherical, which is rarely the case. This is particularly true for multiphase samples where the phases present have very different field emission coefficients, resulting in areas of the specimen evaporating faster. This ultimately leads to local magnification effects where precipitates in the reconstructed dataset appear to be larger or smaller than their 'shell' in the matrix, thereby overlapping with the matrix or resulting in a region of lower atomic density

surrounding the precipitate (*i.e.* a depleted region). Trajectory aberrations render almost impossible the determination of lattice site occupation and crystal structure via APT. They also profoundly affect the chemical characterisation of the interfaces between two phases with different field emission coefficients.

Mass resolution is also problematic, especially when analysing complicated alloys. In the present case, for example, the $^{59}\text{Co}^{2+}$ peak can almost disappear in the tail of the larger $^{58}\text{Ni}^{2+}$ peak [27]. This problem originates because atoms may evaporate from the surface at any time while the voltage pulse is strong enough to cause evaporation. Therefore, ions leave the surface with slightly different kinetic energies since the voltage pulse may provide some additional acceleration. Long peak tails can be observed on the final time-of-flight spectrum. In modern atom probes, this is usually addressed by adopting a wide-angle reflectron lens, which ‘time-focusses’ the traveling ions [70]. Ions with a higher kinetic energy travel deeper into the reflectron, whereas ions with a lower kinetic energy follow a more shallow trajectory. This creates a trade-off between higher mass resolution and detection efficiency. Ideally, it would be best to choose whether to use a reflectron lens in every experiment, depending on whether one is interested on detection efficiency or mass resolution. This is often not possible because it would be necessary to have two separate atom probes since the machines’ design is radically different. The problem of mass resolution can also be addressed by the adoption of laser-assisted evaporation. Thermal emission, rather than field emission, of the ions allows the acceleration of the particles not to be biased by a voltage pulse. Therefore the peaks on the time-of-flight spectrum remain well defined.

The final limitation of the atom probe is that only a limited number of materials can be analysed with this technique. Until recently, samples had to be highly conductive so that a voltage pulse could be applied between the sample and a counter electrode [70]. With the advent of laser-assisted evaporation some poorly conductive and non-conductive specimens can be analysed. However thermal conductivity also needs to be taken into account: the specimen needs to be cryogenically cooled at 60 K in order for the experiment to work and the heat generated by the laser beam needs to be dissipated fast [70]. Therefore, only materials with a high electric conductivity or a relatively high thermal conductivity can be analysed using a laser pulse in a modern

atom probe. Amongst metals, nickel superalloys perform rather poorly when choosing laser-assisted evaporation as the correct experiment conditions cannot be maintained.

Despite its limitations, APT is a powerful technique which can be used to study the local chemical composition and microstructure at a very fine scale. Computational techniques can help in yielding more results: atom probe simulation codes and statistical algorithms can be used to maximise the potential of 3DAPs. Finally, all inaccuracies and limitations of this technique are heavily dependent on the materials analysed and the instruments used and as such should be evaluated on a case by case basis.

3.2 Detecting clusters with atom probes

The detection and analysis of clusters is a prominent subject of debate in the atom probe community. For this reason, there are a wide variety of methods available in the literature, all having weaknesses and strengths. Describing all the methods would be impossible as most research groups adopt slightly different methodologies. In this section, only the most relevant techniques are described.

3.2.1 Visual observation

Perhaps the simplest technique for clustering detection is looking at atom maps of 2D slices to obtain visual evidence of solute clustering. Some studies to evaluate the sensitivity of this method were carried out by Miller and Reed [73]. They showed that clusters are not visible in atom maps except when bigger than approximately 1 nm in alloys with 3-4 at.% of solute atoms. The ability to observe clusters heavily depends on the relative concentration of solute atoms in the matrix: the higher the content of solute atoms, the harder it is to obtain visual evidence of small clusters. Furthermore, at higher solute concentrations, more solute atoms will appear to be in very small embryonic clusters, even when randomly distributed. Therefore, this method can only be applied to detect clustering of very dispersed species, at concentrations less than 1 at.%. Since all studies arguing for rhenium clustering in nickel superalloys found evidence of clusters ~ 1 nm in size, and given that the average rhenium content in the

γ phase is 3-6 at.%, this technique cannot be applied reliably in this case. Indeed, no rhenium clusters are visible to the naked eye when observing 2D atom maps of rhenium in a dataset obtained from CMSX-4 specimens.

3.2.2 Ladder diagrams

It is now widely accepted in the atom probe community [69, 82] that ladder diagrams (or cumulative profiles) are seldom suitable at detecting clusters of solute atoms. Yet, since ladder diagrams were a common technique used to analyse clustering 1DAP datasets, it was deemed necessary to describe it here. A ladder diagram consists in the count of atoms of a particular species plotted against all atoms collected. As such, ladder diagrams are the integral of the concentration profile along the direction of analysis. It follows that the local slope on a ladder diagram plot is equal to the local concentration of the element analysed. Ladder diagrams can also be obtained from 3DAP datasets: a suitable long and thin section of data can be cropped from the original 3D dataset to emulate results similar to those coming from 1DAPs. Ladder diagrams have shown remarkable results when looking at strong short range ordering and even lattice site occupation [127], nevertheless they may lead to the wrong conclusions when searching for solute clustering [12, 13, 127]. In order for the ladder diagrams to be reliable, they have to abide by several criteria [69]:

1. the concentration of solute atoms must not be affected by large microstructural details,
2. the spacing between the planes should be uniform,
3. similar numbers of atoms must be detected on all the atomic planes which are analysed, and
4. the overall slope of the data must match the average composition of the sample.

Therefore, ladder diagrams may be suitable to detect clustering in simple single-phase alloys, but may be misleading when examining more complicated systems, as the variation in composition due to large microstructural features may affect the results. Since the introduction of more reliable methods, ladder diagrams are not used to detect

solute clustering any longer. Nevertheless, the detection of inhomogeneities in ladder diagrams obtained by Blavette *et al* [12, 13] and Wanderka *et al* [127] is still cited as the proof of rhenium clustering in nickel superalloys [11, 133]. All these studies are described in detail in §3.3.

3.2.3 Binomial distribution method

This method is based on the principle that a random distribution of solute atoms should follow a binomial distribution, as highlighted by J. W. Christian [23]. The most common implementation of this principle is a grid-based frequency distribution analysis [80]. The technique, in 3D, involves segmenting the data into small blocks and computing the concentration of solute atoms in each block. The concentration of solute atoms in each block should follow a binomial distribution [80].

Two important things should be kept in mind when segmenting the dataset. First, the blocks should have the same volume and contain similar numbers of atoms [81]. This may prove a hard task as the atomic density across 3DAP datasets is not constant. As a result, blocks of constant volume are selected and scarcely populated blocks may be discarded. Second, the blocks should be as close to a cubic volume as possible [81]. Given a cuboidal block with 2 solute atoms occurring at the opposite, further apart ends of the block, it is apparent that the solute atoms are less likely to be correlated than those found at the opposite ends of a cubic block of equal volume [81]. A 2D implementation of this technique was used by Rüsing *et al* [109] to look at rhenium clustering in nickel superalloys, as described in §3.3

3.2.4 Maximum-separation method

The most commonly used cluster detection algorithm is the maximum-separation method [44, 124, 22]. In this method, solute atoms are part of the same cluster when they are located within $d_{\max}$ from each other. The specific details on how the algorithm works will be explained in more details in §3.4.2. The maximum-separation method is at the core of most clustering detection algorithms used in the literature [22, 72, 70, 119].

Cequerra *et al* developed a detection algorithm based on the Markov Random Field

(MRF) and the maximum-separation method [20]. MRF is an n -dimensional extension to Markov Chains. When applied to atom probe tomography, the nearest-neighbour atoms surrounding a central solute atom are considered in defining solute clusters. At present, the algorithm is still in development and Ceguerra and co-workers have agreed to allow the testing of their method on the clustering of rhenium in nickel. However, no specifics were provided into the inner workings of the algorithm.

In reality, given a 3D dataset, any code that explores the three dimensional space around a solute atom should be able to easily detect clusters in the sample. This is because uncertainties arise from the dataset obtained through APT rather than from the algorithm used to analyse the data. The question to be asked is not whether the algorithm used is able to detect clusters, but whether it is feasible to view the desired features in the given AP dataset.

3.3 Atom probe, nickel superalloys and the rhenium-effect

Nickel superalloys have been examined with atom probes since the emergence of atom probe analysis [113]. Possibly because of their complicated chemistry and fine microstructure, and their great impact on engine performance, nickel superalloys are an interesting topic for the AP community. The first AP study of the superalloys is dated 1979, and was performed at the University of Oxford by M. K. Miller *et al* [28]. Subsequently, most of the early work on superalloys was carried out by Blavette and co-workers from 1984 to 1990 [9, 10, 8, 13]. These early studies focused on describing the partitioning of alloying elements between γ and γ' , as well as composition at the interface between γ and γ' phases. The atom probe was primarily used to study two aspects of the behaviour of rhenium, in an effort to try and explain the mechanisms underlying the rhenium-effect. First, 1D and 3D atom probes were used to investigate the presence of rhenium clusters in the γ phase of nickel superalloys. Second, the 3D atom probe was used to study the distribution of rhenium at the γ/γ' interfaces in nickel superalloys.

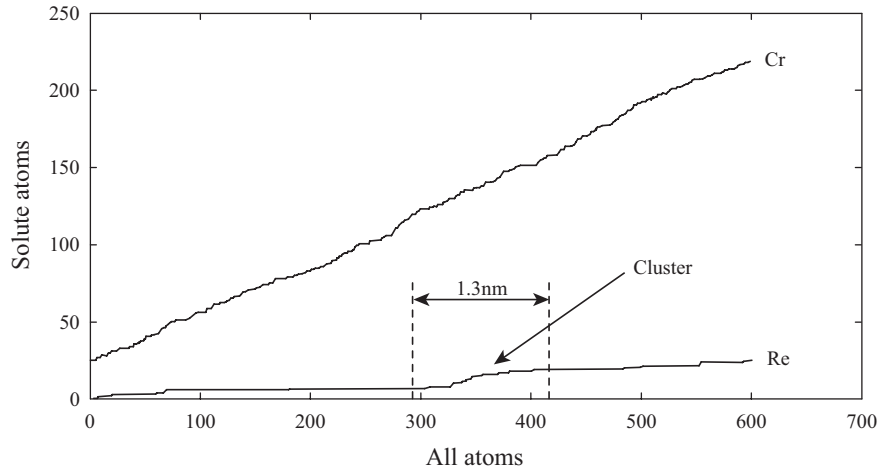


Figure 3.2: The discontinuities in the ladder diagram for a Re-doped PWA1480 superalloy in the early analysis by Blavette *et al* [12, 11].

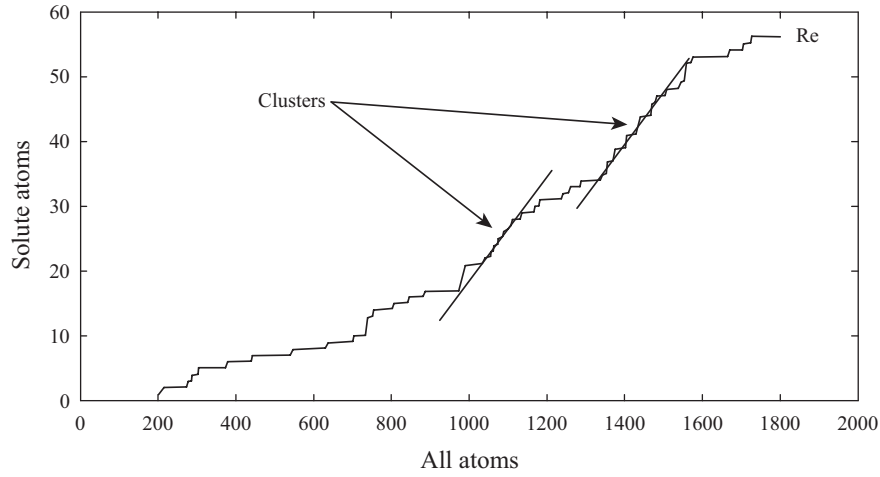


Figure 3.3: The discontinuities in the ladder diagram for Re, as detected in CMSX-4 by Wanderka *et al* [127].

3.3.1 Rhenium clustering in the γ phase

The rhenium clustering problem was first approached by Blavette in 1986 [12, 11] by looking at the ladder diagrams for rhenium in a nickel based superalloy. The same type of analysis was also used by Wanderka in 1995 [127] to examine the distribution of rhenium and other elements in nickel-based superalloys.

The results observed by Blavette *et al* [12, 11] and Wanderka *et al* [127] are shown in Figure 3.2 and Figure 3.3, and the discontinuities present in the data are highlighted. In this seminal work, the authors proposed that clusters could explain the discontinuities observed in the data. However, deviations from linearity in the ladder diagrams

– such as those marked in Figure 3.2 and Figure 3.3 – are arbitrarily selected and, as such, there is no information on the size and distribution of clusters that would have generated similar results. Additionally, ladder diagrams are unable to differentiate between real clusters (*i.e.* those forming due to a systematic clustering reaction) and random clusters (*i.e.* those forming due to the random occurrence of neighbouring solute atoms). Indeed, it can be shown that for an alloy with 3 at.% solute concentration and a completely random distribution of solute atoms, only 90 % of the solute atoms are expected to be isolated in a single atom configuration, *i.e.* with no other solute atom as nearest neighbour. The remaining 10 % of the solute atoms will have one or more solute atoms as nearest neighbours, in an embryonic cluster.

Furthermore, several factors could have influenced the results obtained by ladder diagrams from a 1D atom probe. Most significantly, microstructural features, such as the γ' precipitates, the γ matrix and the γ/γ' interfaces, generate strong compositional variations across the alloy which will result in a locally uneven solute distribution. In the early studies, this particular problem was sometimes addressed by analysing model alloys which had a composition belonging to the field of the γ matrix phase. However, nanoscale fluctuations in solute distribution could be generated by incipient secondary γ' precipitates as the γ' phase becomes more stable at lower temperatures. Moreover, the fluctuations in solute concentration detected by ladder diagrams could result from fluctuations in solute concentration within the alloys arising from incomplete homogenisation. Finally, it is also important to acknowledge that ladder diagrams obtained from a 1D atom probe examined only a few thousand atoms, whereas the 3D technology now available allows the collection of hundreds of millions of atoms, and the analysis can be carried out in all three dimensions.

Although ladder diagrams may not be the most suitable tool to examine clustering at very fine levels, it must be stated that ladder diagrams have provided great insights into superalloy metallurgy. In 1995, Wanderka *et al* [127] and Vanbarel *et al* [122] performed a comprehensive study on the atomic structure of nickel superalloys both in the γ and γ' phase. These studies were carried out on γ and γ' samples which had been oriented to align the [001] directions with the aperture. This meant that, when analysing the sample of γ' phase, planes containing 100 % nickel atoms would

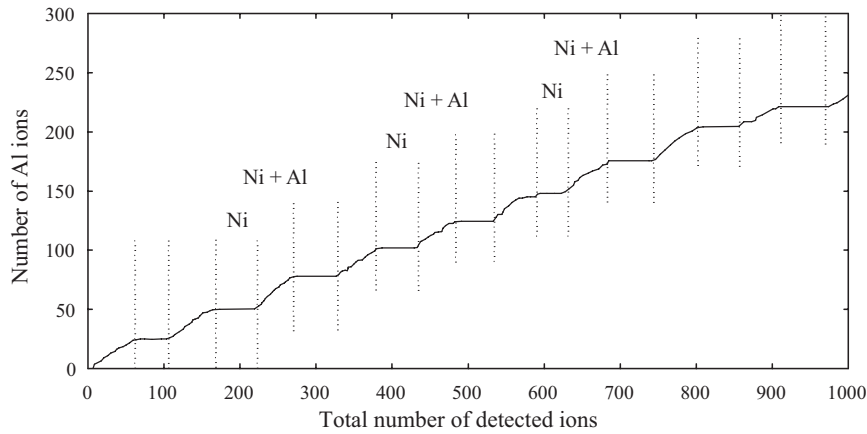


Figure 3.4: An example of the results on the lattice occupation in Ni_3Al by Wanderka *et al* [127] and Vanbakel *et al* [122].

evaporate first, followed by planes containing 50 % nickel and 50 % aluminium atoms (see Figure 3.4). Using this technique, Wanderka was able to obtain evidence that cobalt tends to occupy Ni lattice sites in the L_{12} Ni_3Al lattice structure.

The quest for the detection of Re clusters in nickel superalloys continued, using different methods of analysis. Rüsing *et al* [109] used the 3DAP to look at the distribution of Re. The analysis method involved cutting a long thin section – $1.5 \times 1.5 \times 90 \text{ nm}$ – from the 3D datasets and obtaining the concentration profile for Re along this section. As described earlier, such 1D concentration profile is the derivative of a 1D ladder diagram. The rhenium concentration was computed in 0.5 nm thick slices, and the final profile is shown in Figure 3.5. Since the concentration would sometimes fall above 2σ , Rüsing and co-workers argued that deviations from average concentrations were large enough to be an indication of the presence of rhenium clusters. A χ^2 test was also performed to check whether the rhenium concentrations in all the blocks analysed followed a binomial distribution, and the authors concluded that there was an inhomogeneous distribution of rhenium atoms in the samples analysed. In conclusion, the study suggested that rhenium clusters 1 nm in size are present in nickel superalloys.

A few factors should be taken into consideration when evaluating these results. The method does not exploit the fact that larger 3D datasets are now routinely obtained from atom probes. The statistical analysis was performed on ‘blocks’ containing only ~ 45 atoms, and was based on a sample size of less than 200 blocks. Therefore the

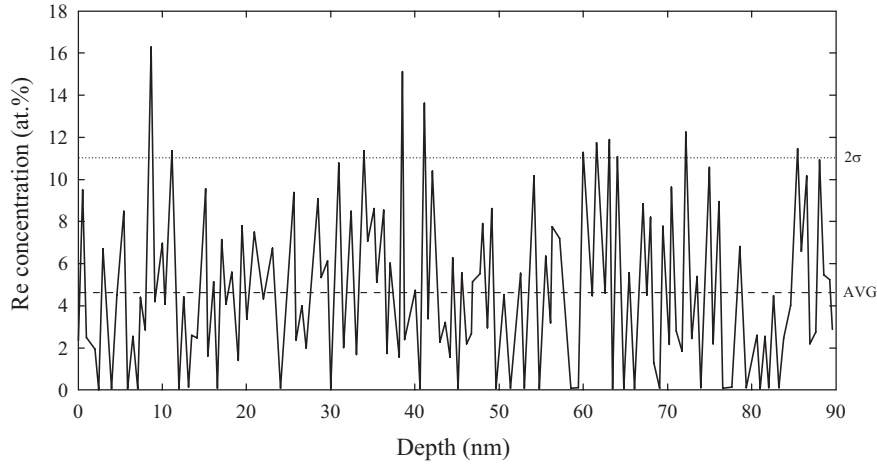


Figure 3.5: The Re concentration profile obtained by Rüsing *et al* [109] from a square cross section column, 1.5 nm wide and 90 nm long. Concentrations are computed at intervals of 0.5 nm. The dashed line shows the average rhenium concentration.

analysis was performed on only ~ 8000 atoms. Finding 5 Re atoms dispersed in a block containing 45 atoms cannot be considered an indication of rhenium clustering, as clusters 1 nm in size would contain 25 solute atoms. Also, as explained in §3.2, the blocks should be cubic for the analysis to be reliable – Rüsing *et al* adopted blocks of dimensions $1.5 \times 1.5 \times 0.5$ nm.

3.3.2 Rhenium distribution near γ/γ' interfaces

The atom probe community did not just focus on the clustering problem when investigating the rhenium-effect. Warren *et al* [131] used the 3DAP to study the distribution of rhenium in RR3000, a commercial nickel superalloy. The authors of the study observed an appreciable enrichment of rhenium close to the matrix/precipitate (γ/γ') interfaces and concluded that these enrichments could arise during the cooling phase in their experiments, while the γ' is growing and expelling Re into the γ phase. However, they also suggested that a similar but broader ‘bow wave’ of Re would also be generated during the lower temperature heat treatment of the alloy and still be present at service temperature. In their study, they speculated that such enrichment could have an effect (a) on misfit at the γ/γ' interface and (b) on the climb of dislocations during high temperature deformation processes, either of which could lead to hardening [131]. Warren *et al* did not base their theory on rhenium enriched areas observed with the

atom probe, as it is suggested that these areas form upon cooling from service temperature. Rather, they seem to infer that a larger ‘bow wave’ should form during heat treatment and should be observed at service temperature [131], however their theory cannot be confirmed with atom probe experiments.

Proximity histograms [42] were also adopted to study the distribution of rhenium close to the γ/γ' interface. Proximity histograms are a plot of local atomic concentration versus the distance to the chosen interface. Once an isoconcentration surface is defined, the method calculates local atomic concentrations of several layers of constant thickness, moving further and further away from the interface. The method can be very useful in investigating the concentration profile of solute elements around precipitates in all directions. Yoon *et al* [141, 142] adopted this method to investigate the concentrations of solute elements across γ/γ' interfaces of a René N6 alloy. Similarly to what was observed by Warren *et al* [131], Re was found to segregate near the γ/γ' interface, forming ‘bow waves’ ahead of the interface. The authors, however, make no speculations as to how the enrichment forms and whether this plays a role in the strengthening effect provided by rhenium in nickel superalloys.

Rüsing *et al* [109] also studied the distribution of rhenium across γ/γ' interfaces using both linear scans and proximity histograms. Their analysis was performed on a model nickel based superalloy (Re31) that displayed a much lower Re partitioning coefficient than Re-containing commercial superalloys such as RR3000 and CMSX-4. The authors of the study suggested that the enrichment observed by Warren *et al* [131] and Yoon *et al* [141, 142] could be caused by stress-induced diffusion arising during the rafting process [109]. However, it should be noted that, although the samples used by Warren *et al* [131] were crept, Yoon *et al* [141, 142] used samples that only received a simple heat treatment and therefore displayed no rafting of the γ' precipitates. The lower partitioning coefficient of rhenium could instead explain the absence of the rhenium enrichment, and the lower partitioning coefficient could be due to the model composition of the Re31 superalloy, a quaternary alloy containing only Ni, Al, Ta and Re.

More recent studies looked at the distribution of rhenium and its effect on the temporal evolution of the microstructure of a Ni-Cr-Al model superalloy [143, 144]. In

the first part of the study, 3DAP was used to investigate the distribution of rhenium as a function of ageing time and to investigate how this affected microstructure evolution [143]. The partitioning coefficient of rhenium between the γ and γ' phases was found to increase with ageing time, from about 1.2:1 to almost 3:1. The values obtained for the model alloy are much lower than those usually observed for Re containing commercial superalloys, which approach 20:1. Whereas some Re segregation was observed near the γ/γ' interfaces, the amount of segregation was considered too small to have any effect on the mechanics or kinetics of the system [143].

In the second part of the study, Yoon *et al* [144] compared the results obtained with APT to PrecipiCalcTM simulations [47]. By modelling the coarsening behaviour of γ' precipitates, the authors were able to show that slow diffusing elements play an important role in the structural evolution of the system. Amongst these slow diffusing elements, rhenium has the largest impact in retarding the coarsening of γ' precipitates [144]. The authors also stated that γ' nuclei precipitate at compositions that do not match the thermodynamical equilibrium of the system and that the compositions in both γ and γ' change considerably over time [144]. Yoon *et al*, however, did not speculate as to whether these mechanisms influence the strengthening effect of rhenium additions in nickel superalloys.

3.4 Data analysis

3.4.1 Experimental procedure

All alloys described in §1.6 were analysed using the local electrode atom probe (LEAP) instrument at Oak Ridge National Laboratory. The instrument has a local electrode (as described in Figure 3.1) and a detector composed of a pair of microchannel plates and three crossed delay lines (as shown in Figure 3.1). During the experiment, a voltage pulse repetition rate of 200 kHz was chosen to limit preferential evaporation. The pulse had an amplitude of 20 % of the standing voltage, and the specimen was kept at a temperature of 60 K. The LEAP at ORNL has no reflectron lens and therefore has a $\sim 60\%$ detection efficiency.

More than thirty datasets – each containing hundreds of thousands of rhenium

atoms – were collected from the CMSX-4 samples to ensure adequate characterisation of both γ and γ' phases and the γ/γ' interfaces. A similar amount of data was collected from the binary Ni-X alloys, resulting in several datasets containing hundreds of thousands of solute atoms. The compositions of the Ni-X alloys determined with the atom probe are given in Table 1.2. The nominal composition of CMSX-4, along with the compositions of the γ and γ' phases measured with the atom probe are given in Table 1.1.

3.4.2 Clustering analysis algorithm

A purpose-built computer code based on the friends-of-friends maximum-separation method [119, 72, 124] was used to investigate clustering in the atom probe datasets. As described earlier, this algorithm is usually at the core of many clustering detecting methods such as the envelope method [69, 72] and alternatives to it [119]. The algorithm defines solute atoms as part of a cluster when two or more solute atoms are found within a distance $d_{\max}$ from each other (see Figure 3.6). The algorithm sequentially explores the surroundings of every solute atom until all the nearest neighbour relationships have been established. Then, a count of clusters which are n -atoms in size is generated. Sometimes, $n_{\min}$ and $n_{\max}$ parameters are used in this algorithm to limit the number of solute atoms that are defined as nearest neighbours. When $d_{\max}$ is chosen correctly, there is no need to provide the lower and upper limit. Once the number of atoms present in each cluster is known, the relative fraction of all solute atoms in each pure-solute cluster of given size can be obtained.

Some algorithms may choose to discard certain clusters depending on their morphology, however this functionality was not included in the present code. Additionally, it should be noted that the algorithm does not attempt to evaluate whether any other atom belongs to a given cluster based on its position relative to the ‘linked’ solute atoms. This is often the purpose of more advanced algorithms based on the friends-of-friends maximum-separation method [119] and it was not deemed necessary for the present work.

The number of clusters detected depends sensitively on the value chosen for $d_{\max}$ [119, 22, 72]. A small value leads to no clusters being detected (false negative result)

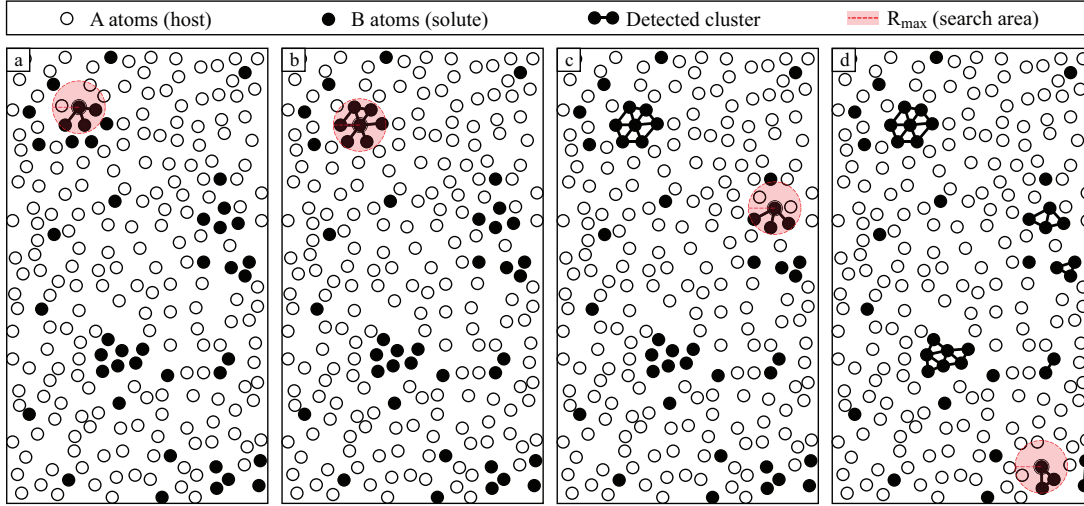


Figure 3.6: a) The algorithm checks for the presence of neighbouring solute atoms within a radius $d_{\max}$. b) If one or more solute atoms are found, the algorithm proceeds to check for more neighbouring atoms, until no more neighbouring solute atoms can be found. c) The algorithm will then look for neighbours around other solute atoms, until d) all nearest neighbour relationships are established.

whereas a very large value would lead to unrealistically large clusters being detected (false positive result). Depending on the type of system under investigation, different values of $d_{\max}$ may be adopted [119, 22, 72]. The sensitivity of the algorithm to different values of $d_{\max}$ is explained in more detail in §3.5.1.

The number of detected clusters also depends upon the local density and concentration of the solute atoms. Some variation in atomic density across a 3DAP dataset cannot be avoided, but the algorithm should be applied judiciously when investigating clustering in datasets which include separate phases of different composition. This is the case of CMSX-4, which include primary and secondary γ' precipitates in the γ matrix phase. To solve the problem and facilitate the analysis, volumes of interest were selected from the original datasets by excluding any primary or secondary γ' precipitates and avoiding any sharp change in solute concentration. Therefore, the analysis of rhenium clustering in CMSX-4 was performed in the γ phase, away from the γ/γ' interfaces where no secondary γ' are present [131].

In order to differentiate between randomly occurring clusters and true solute clusters, the results obtained from each atom probe dataset must be compared to results that would be expected for a random distribution of solute atoms. The ‘reference’ data can be obtained in two ways. The first method consists in using a simulation software

to calculate how many clusters would be detected given a random distribution of solute atoms, the typical detection efficiency of the atom probe and the scattering in atomic positions [83]. The second method consists in producing a ‘random reference’ for each dataset by randomly re-arranging the elemental identities of all atoms in that dataset, thereby giving a random mass-to-charge-state ratio to each atomic location [119]. The end result is an atom probe dataset in which the m/n spectra and the atomic positions match the original dataset, but none of the compositional variations due to microstructure, such as clusters and precipitates, are preserved. This second method is more accurate: the original dataset and its random reference share some of the artifacts which are common in 3DAP datasets, such as areas of higher or lower atomic density caused by trajectory aberrations. It follows that, if the clustering detection algorithm is applied to the original atom probe dataset and its own random reference, any solute clustering above the levels expected for a completely random distribution of solute atoms will be highlighted.

3.4.3 Atom probe simulations

As explained in §3.1.5, detection inefficiencies and trajectory aberrations severely transform 3DAP data compared with what the original lattice structure would be. As a result, much of the information that could be obtained from a ‘perfect’ dataset is lost. It is therefore necessary to assess the effects of detection efficiency and trajectory aberration on the structural features of interest, in order to determine whether such features are visible in the transformed dataset. This can be done by simulating an atom probe dataset.

The first AP simulator was coded by Miller and Hyde [71]. It aims to create a 3D dataset which has similar features to a real atom probe dataset, including the effect of detection efficiency and trajectory aberrations. Additionally, it makes it possible to influence the positioning of the atoms so that clusters and precipitates can be simulated. The simulation code creates a atom probe dataset in steps (see Figure 3.7).

1. The desired volume is filled with lattice sites following a given crystal structure and lattice parameter

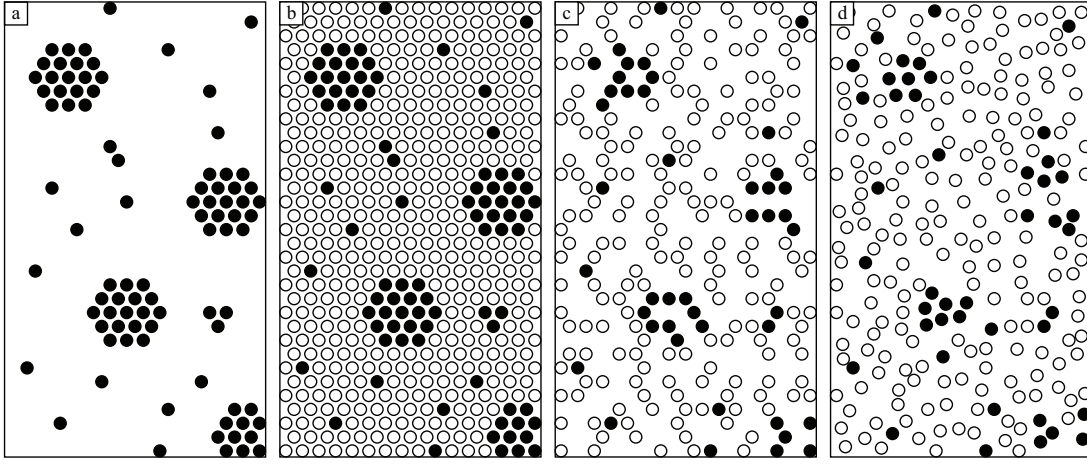


Figure 3.7: a) The lattice points are populated with a desired concentration of B atoms (solute) with the desired distribution of clusters. b) The remaining lattice points are populated with A atoms (host). c) Some atoms are randomly deleted to match a desired detection efficiency. d) The remaining atoms are displaced in the x , y and z direction following a gaussian distribution.

2. Given a solute concentration, B atoms (solute) clusters of desired size and distribution are created at random positions. The remaining B atoms are randomly placed at free lattice sites until a desired composition is achieved (see Figure 3.7a).
3. The remaining lattice sites are populated with A atoms (see Figure 3.7b).
4. To simulate detection efficiency, $\sim 40\%$ of the atoms are deleted at random (see Figure 3.7c).
5. Each remaining atom is displaced according to a Gaussian distribution of desired variance from the perfect lattice point (see Figure 3.7d).

Following this procedure, different simulated datasets with similar properties (*i.e.* efficiency, solute content, scatter) but different microstructural features (*i.e.* size and distribution of precipitates) can be created and analysed with the friends-of-friends maximum-separation algorithm. The results can be compared to test the ability of the algorithm to detect clusters of various sizes.

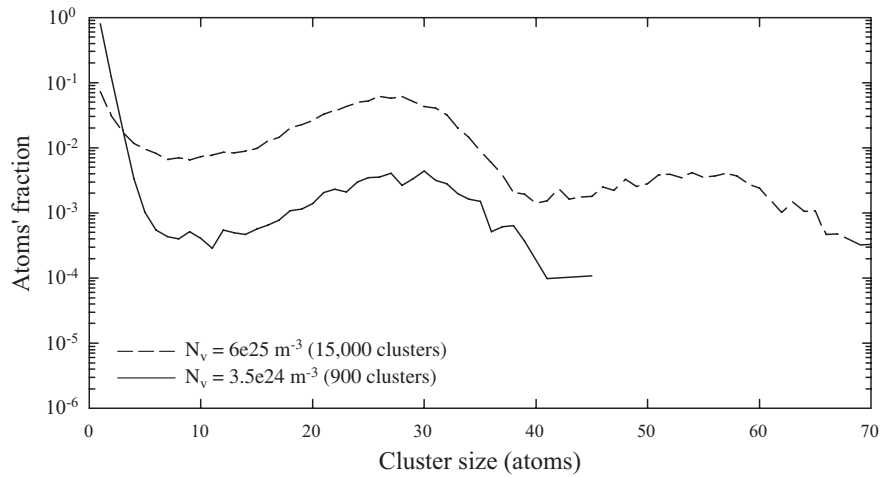


Figure 3.8: The detection of solute clusters of diameter 1 nm (~ 50 atoms), in simulated datasets with an overall solute content of 3 at.%.

3.5 Solute clustering in the γ phase

3.5.1 Algorithm validation

Before analysing the atom probe data, the ability of the computer code to detect *in principle* any small nano-sized clusters was proven. This was necessary since it is expected that the detection efficiency and position scattering of the atoms have a major impact on any ability to detect small clusters, if these are present. Therefore, the analysis technique was tested on simulated datasets with a known density of clusters of a given size. All simulated datasets consisted of hypothetical binary alloys with a 3 at.% solute concentration – similar to the rhenium concentrations in the binary alloy and in the γ phase of CMSX-4. Different datasets were created with several combinations of cluster size and density. Solute atoms not belonging to a cluster were randomly distributed within the volume, as described in §3.4.3. These datasets were analysed with the algorithm to determine whether the clusters could be detected.

Initially, several simulated datasets with clusters 1 nm in diameter – similar to those observed by Blavette *et al* [12, 13], Wanderka *et al* [127] and Rüsing *et al* [109] – were generated with different numbers of solute clusters. These were analysed with the friends-of-friends maximum-separation algorithm. The results from this first set of simulations are shown in Figure 3.8. The dashed line represents the data obtained when *all* solute atoms in the simulated alloy are part of a cluster. The graph shows

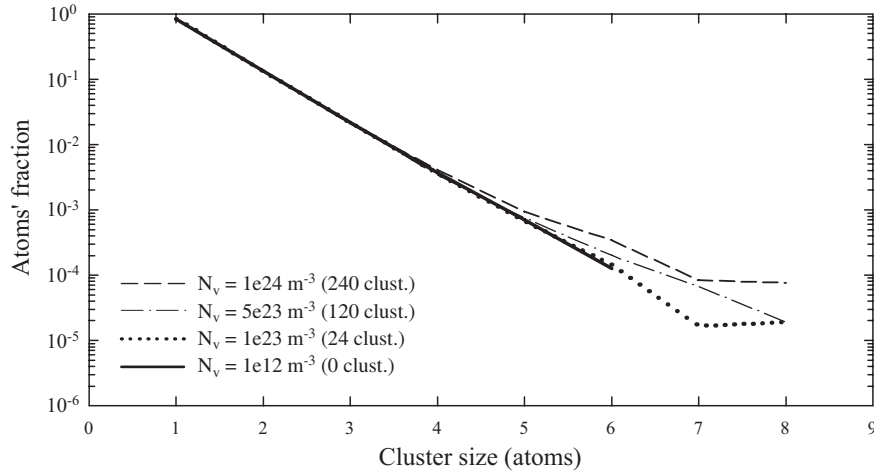


Figure 3.9: The detection of solute clusters of diameter 0.5 nm (~ 6 atoms) at different number densities and the ideal random solute distribution, in simulated datasets with an overall solute content of 3 at. %.

a cluster distribution which peaks at ~ 27 atoms, the expected cluster size (in atoms) given the $\sim 60\%$ efficiency. The second, smaller peak occurs because the high density of clusters leads to some clusters impinging on each other, forming clusters twice as large as expected. In a second test, indicated by the continuous line in Figure 3.8, a much lower number of clusters was created. In this case, fewer than 1 % of the solute atoms are part of the clusters while the remaining 99 % is randomly distributed. Nevertheless, a large peak can be observed in the distribution obtained from the friends-of-friends maximum-separation algorithm. This means that if clusters ~ 1 nm in size are indeed present in the experimental datasets, they would be detected by this analysis.

As a next step, the detection limit of the algorithm was tested. In other words, the lowest size and distribution of clusters detectable using this algorithm was determined. For this purpose, different number densities of clusters of 0.5 nm diameter were placed in datasets with the same overall solute concentration. The results were compared to a dataset in which all solute atoms are randomly distributed on the host lattice. The results of these tests are given in Figure 3.9. For a random distribution of solute atoms, the results are predicted to lie on a straight line with the slope inversely proportional to the overall solute content of the simulated alloy. It can be observed that the detection of the smaller clusters is much weaker than in Figure 3.8: no peak appears in the graph. Instead, small positive deviations from the straight line (representing a completely random distribution of solute atoms) are seen. When more clusters are present, the

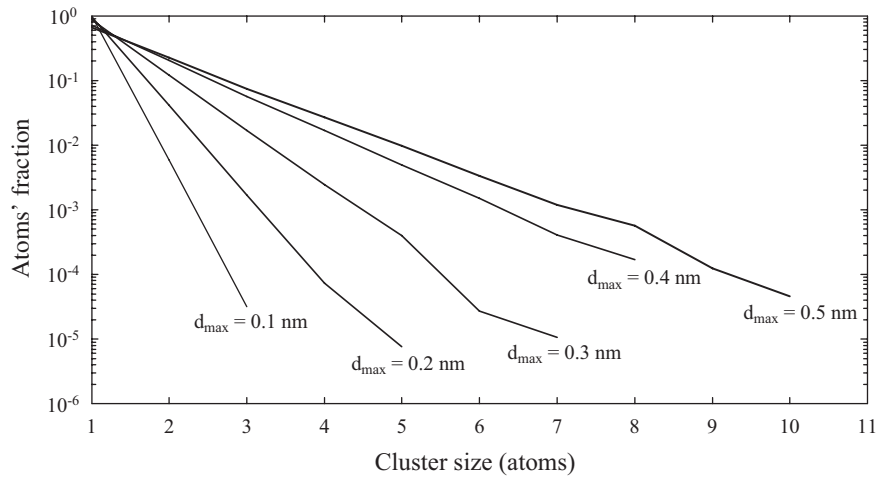


Figure 3.10: The dependence of the results of the friends-of-friends maximum-separation algorithm on different choices of $d_{\max}$.

deviation from linearity is larger. It can be concluded that this type of analysis is expected to fail only when the clusters' size approaches the typical scattering length and when the clusters' density is comparable to the density of randomly occurring clusters. Additionally, it must be noted that the detection efficiency of the atom probe heavily affects the ability to detect sub-nano-sized clusters. For this reason, atom probes with higher detection efficiencies, such as a 3DAP without a reflectron lens, are better suited for clustering analysis [60]. However, energy-compensated instruments provide a more accurate quantification of concentration variations such as those of the solute elements across the γ/γ' interfaces of the CMSX-4 datasets.

As introduced in §3.4.2, the number of clusters detected by the maximum-separation method is heavily dependent on the value chosen for $d_{\max}$ [119, 22, 72]. To test how results vary depending on chosen values of $d_{\max}$, the same Ni-Re #5120 dataset was analysed by the algorithm using values of $d_{\max}$ in the range 0.1-0.5 nm. The results are shown in Figure 3.10. When $d_{\max} = 0.1$ nm, the analysis determines that 99.4 % of the solute atoms do not have any other solute atom as nearest neighbour. By contrast, choosing $d_{\max} = 0.5$ nm means that only 66 % of the solute atoms do not have any other solute atom as nearest neighbour. The remaining 34 % of the solute atoms are part of a cluster of 2 atoms or larger. When $d_{\max} = 0.5$ nm, even clusters larger than 10 atoms are detected. Although a choice of higher $d_{\max}$ results in the detection of a much larger number of clusters, the distribution of clusters' sizes still follows a

logarithmic decay.

A survey of the literature studying copper clustering in UHS steels reveals that the $d_{\max}$ parameter is usually taken within the range 0.5-1 nm. It is important to note that the Cu content of UHS steels usually lies within the range 0-0.5 at.%. Moreover, these studies focus on the detection and characterisation of copper rich precipitates. By contrast, Re content in the γ phase of nickel superalloys is ~ 3 at.% and other studies have primarily looked at the presence of pure solute clusters. Therefore, $d_{\max}$ should not be larger than the expected lattice parameter for *fcc*-Ni. In this study, the $d_{\max}$ value was chosen to be the average between the first and second neighbour distances for a *fcc*-Ni crystal, assuming a lattice parameter of 3.52 Å, or $d_{\max} = 3$ Å.

3.5.2 Ni-Re and CMSX-4

At this point, with confidence established in the analysis technique, the algorithm was applied to the datasets obtained from the LEAP at ORNL. First, the data from the Ni-Re binary alloy was examined for the presence of clusters. The maximum-separation method was first applied to the original Ni-Re dataset and then to the random reference obtained from the same dataset.

The results of both analyses are shown in Figure 3.11. The data shown here was obtained from dataset #5120, which contains more than 1 million solute atoms. No clusters larger than 6 atoms were observed and there is no large peak corresponding to clusters ~ 1 nm in size, as seen in Figure 3.8. The absence of a peak at higher clusters sizes and the lack of the detection of clusters larger than 6 atoms in a sample containing 1 million solute atoms make a strong case that clusters ~ 1 nm in size or larger are not present in this binary alloy.

The data can then be compared to the results obtained from the random reference. Both datasets appear to have clusters smaller than 6 atoms, suggesting this is expected for a random distribution of solute atoms. Furthermore, it appears that the results from the original dataset deviate negatively from those obtained from the random reference. Indeed, all the Ni-Re binary datasets analysed consistently show lower amounts of clusters than what would be expected given a random distribution of solute atoms. Such deviations from linearity could be interpreted as weak short range ordering of Re

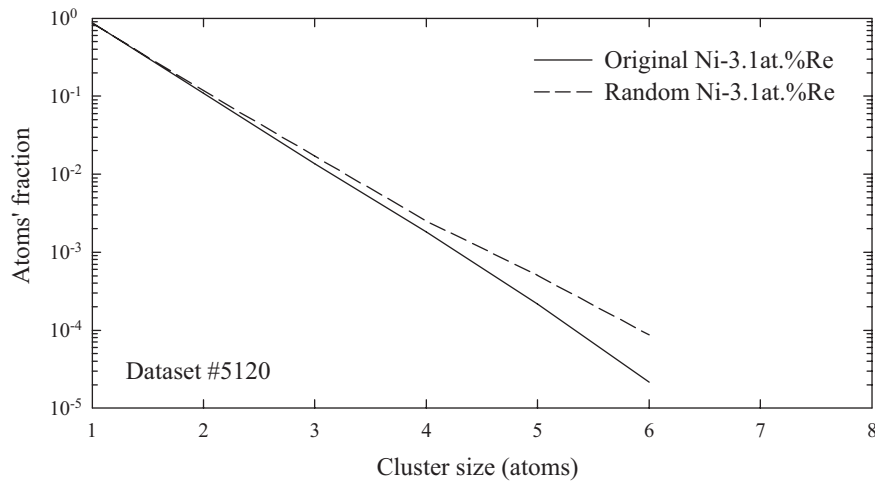


Figure 3.11: The results obtained when analysing dataset #5120 of the Ni-Re binary alloy, compared to the random reference.

in Ni at these concentrations. However, these deviations are too small to provide any clear indication of a systematic ordering reaction.

The algorithm was then applied to datasets obtained from the CMSX-4 single-crystal superalloy. In this case, sections were cut from the datasets in order to ensure that the regions of interest corresponded to the γ phase only. Additional care was taken to make sure that no secondary γ' particles were present within the chosen volumes, hence all sections were cut from the region near the γ/γ' interface, on the γ phase side, which is depleted of secondary γ' particles. The results from the analysis of the CMSX-4 #4230 dataset are compared to the random reference (see Figure 3.12). Once again, no clusters larger than 7 atoms have been detected in the volume analysed. The slightly higher number of clusters, compared to the Ni-Re binary alloy, is due to the fact that the Re content of the γ of CMSX-4 is 3.4 at.%, higher than the Re content in the Ni-Re binary alloy.

When comparing the above results to those obtained from the random reference, it can be observed that the experimental data does not deviate from the dashed line representing a random distribution of solute atoms, thus confirming that no Re clustering is present. In the case of CMSX-4, no indication of short range ordering is observed. Instead, the results from the original dataset and the random reference are a perfect match. Therefore, it can be concluded that no rhenium clusters ~ 1 nm or larger are

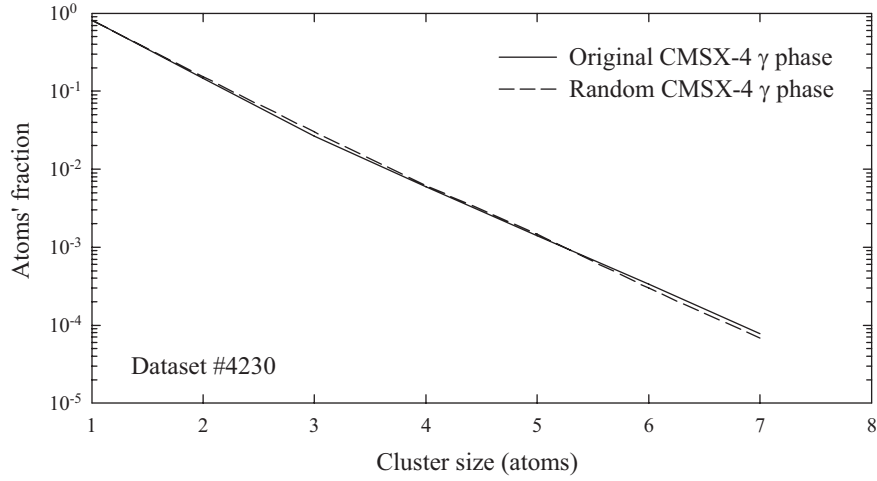


Figure 3.12: The results obtained when analysing dataset #4230 of the γ phase of CMSX-4, compared to the random reference.

present in the γ phase of CMSX-4. This contrasts with the conclusions drawn from previous work carried out with the 1DAP [12, 127] and 3DAP [109]. It is also possible to assert that no rhenium clusters have been observed above the minimum size of clusters detectable with the 3DAP and the maximum-separation algorithm.

3.5.3 Ni-X systems, X=Ta, W, Ir and Pt

The remaining Ni-X binary alloys were similarly analysed with the maximum-separation method and each dataset was compared to a random reference. The results of the analysis on datasets of Ni-Ta, Ni-W, Ni-Ir and Ni-Pt are shown in Figure 3.13. The data gathered from all the Ni-X binary alloys shows that no clusters larger than > 9 atoms were detected – equivalent to a spherical diameter of 0.6 nm. Also, results for Ni-Ta and Ni-W (see Figure 3.13a and Figure 3.13b) confirm that the datasets contain fewer clusters than expected for a completely random solute distribution. However, similarly to the case of Ni-Re, the deviations are too small to indicate the occurrence of short range ordering in Ni-Ta and Ni-W.

Ni-Ir, see Figure 3.13c, is the only alloy in which the solute atoms display a very small degree of clustering at all: 3 clusters of 7 atoms in size are detected – one more than those detected in the random reference. The same argument made for Ni-Ta and Ni-W is also valid here: such small deviations from a perfect random distribution

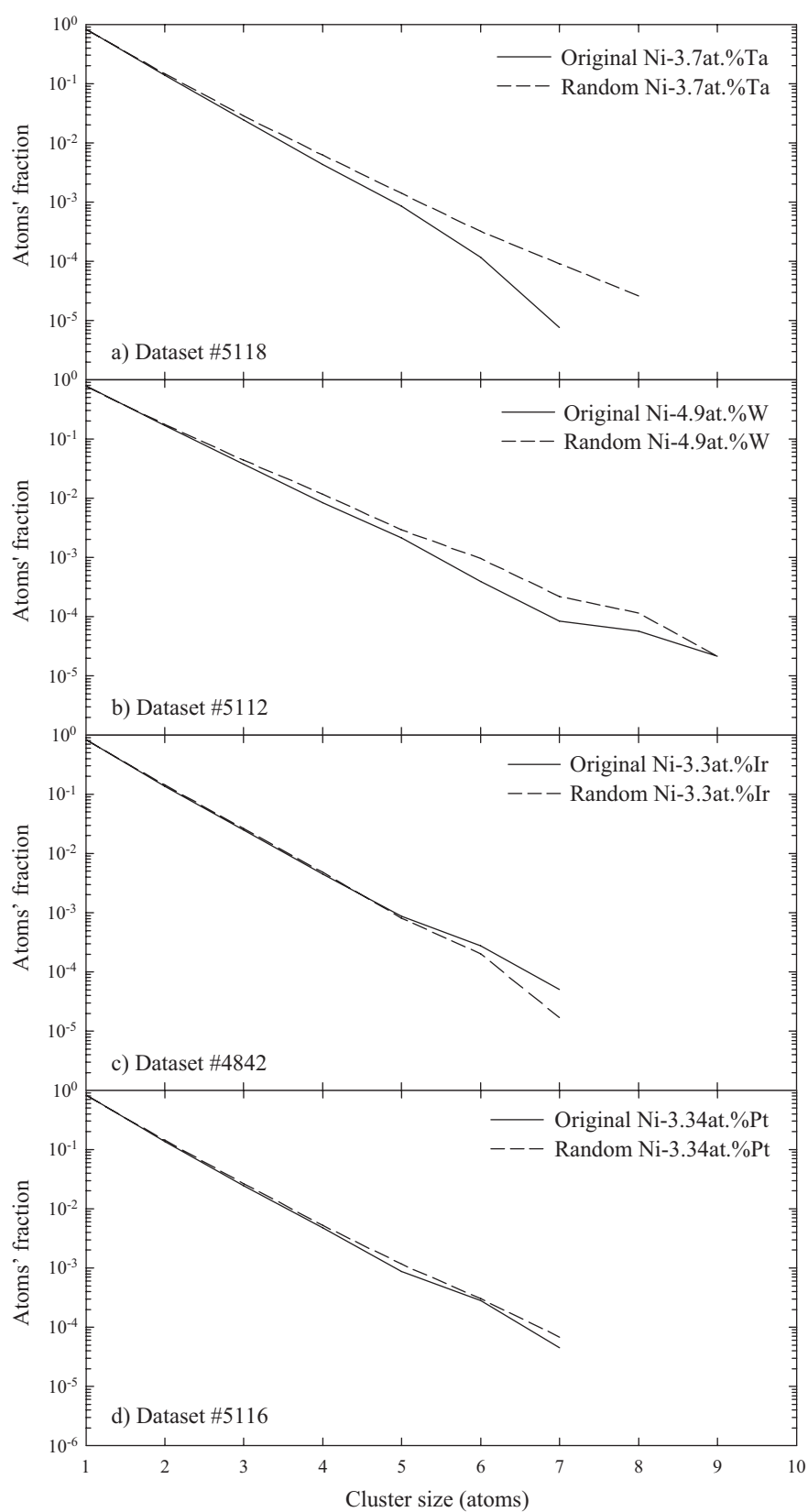


Figure 3.13: The results obtained when analysing datasets of the a) Ni-Ta, b) Ni-W, c) Ni-Ir and d) Ni-Pt alloys, comparing each analysis to the random reference.

cannot be considered proof of a systematic clustering reaction in the Ni-Ir alloy. Finally the results for Ni-Pt (see Figure 3.13d) show that Pt matches the random solute distribution of the random reference almost perfectly. Therefore, broadly speaking, the data collected from all binary alloys confirm that no significant clustering (or ordering) reactions occur when any of these 5d elements are placed in nickel. All deviations from the random distribution line obtained from the random reference can be explained by considering the size of the datasets examined, since the total number of solute atoms is many orders of magnitude larger than the solute atoms generating the deviation. Furthermore, no cluster > 9 atoms was found during our experimentation and analysis – meaning that no nano-sized precipitates were detected.

3.6 Rhenium enrichment at γ/γ' interfaces

3.6.1 Phase field simulations

In order to investigate the formation of the rhenium enrichment close to the γ/γ' interfaces, the APT data can be compared to predictions of element partitioning obtained with the phase field method. The phase field simulations were performed by N. Warnken at the University of Birmingham, using the MICRESSTM simulation software [30, 118, 117]. It can be hypothesised that the rhenium enrichment observed close to the γ/γ' interfaces forms upon cooling from service temperature to room temperature, as the γ' precipitates grow ejecting rhenium ahead of the interface. Therefore, it can be assumed that the rhenium enrichment would not be present near the γ/γ' interfaces at service temperature and consequently plays no part in the rhenium-effect.

The phase field method was used to predict the microstructure evolution during cooling from 1223 K to 923 K, assuming that diffusion would be too slow for the system to change between 923 K and room temperature. Two sets of simulations were performed. For the first set of simulations, it was deemed sufficient to model the evolution of the γ and γ' phases (and the interfaces separating them) in 1D during cooling from 1223 K at 1 K/min, 10 K/min and 100 K/min. Although 10 K/min is regarded as the realistic cooling rate which was applied to the specimens analysed with the atom probe, there is necessarily some uncertainty in it and the higher and lower rates pro-

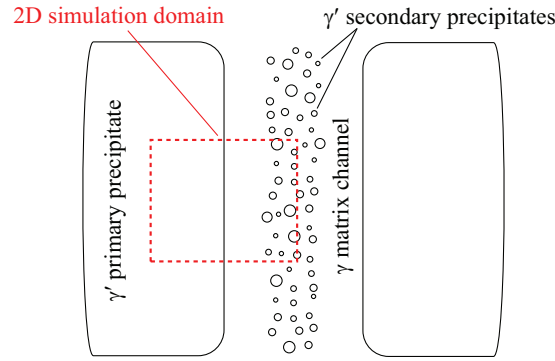


Figure 3.14: A schematic of the 2D domain for the phase field simulations.

vide a useful range for the purposes of comparison. The initial size of the primary γ' precipitates was assumed to be 500 nm. The simulation domain covered one-half the width of the γ channel (125 nm) and extended the same length into the γ' precipitate, measuring 250 nm overall.

The second set of simulations, made in 2D, took into account nucleation of secondary γ' precipitates in the γ channel (see Figure 3.14). These calculations were performed at a cooling rate of 10 K/min only, since the 2D domain results in much longer calculation times. The parameters of the nucleation model were chosen such that the distribution of the secondary γ' precipitates at the end of the simulation run would match typical values observed in the 3DAP datasets. The objective of these calculations was to observe the effect of secondary γ' nucleation on the kinetics of the γ/γ' interfaces which define the limits of the primary γ' precipitates. Both 1D and 2D systems are in equilibrium at the start of the simulation, with equilibrium solute concentration in the γ and γ' phases at 1223 K computed with the Thermo-TechTM TTNi database [110] version 6 via the TQ Thermo-CalcTM interface. Sharp interfaces between the γ and γ' phase were assumed.

All calculations were fully coupled to the Thermo-TechTM TTNi database [110] version 6 via the TQ Thermo-CalcTM interface, so that the calculated phase fractions and elemental solubilities determined will be consistent with this well-established database. Estimates for the kinetic terms needed for the diffusion calculations for the γ phase were taken from the NIST Ni superalloy mobility terms [19]. In the absence of better experimental data, diffusion in γ' was approximated by using the diagonal term of the

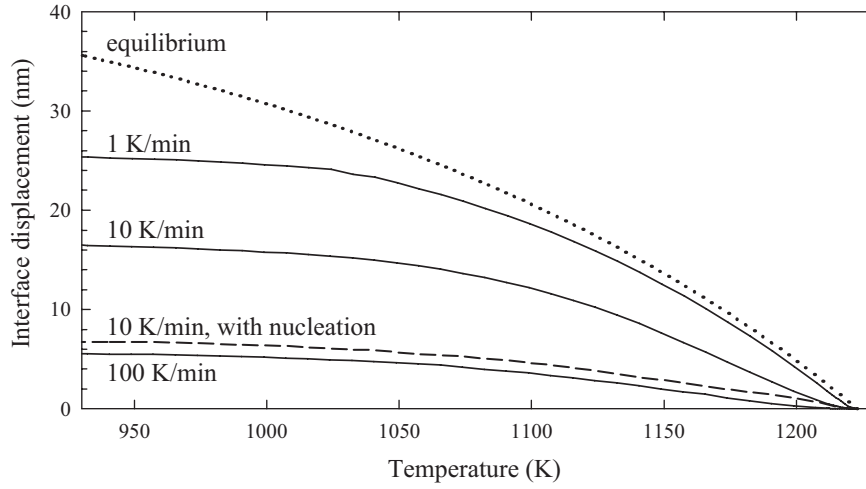


Figure 3.15: Displacement of the γ/γ' interface while cooling at different rates (solid lines) in comparison to cooling in equilibrium conditions (dotted line) and in the presence of nucleation of secondary γ' precipitates (dashed line).

γ phase diffusion matrix reduced by a factor of 10. A very similar assumption was made recently by Nijdam and Sloof [88].

Predictions obtained using the phase field method for the displacement of the primary γ/γ' interface during cooling from 1223 K to 923 K are given in Figure 3.15. The continuous lines display the data from the 1D simulations at cooling rates of 1 K/min, 10 K/min and 100 K/min whereas the dashed line represents the data from the 2D simulation, which includes the secondary γ' nucleation. The dotted line shows the interface displacement when the simulation domain is cooled under equilibrium conditions. It can be seen that interface displacement below 1000 K is negligible at all cooling rates. This is because the diffusion processes required for the solute atoms to migrate across the γ/γ' interface become much slower. It is also important to point out that the overall interface displacement changes considerably depending on cooling rate: a 1 K/min cooling rate results in the γ/γ' interface moving 25 nm, whereas a 100 K/min cooling rate results in the γ/γ' interface moving 5 nm. This is a clear indication that the growth of primary γ' precipitates is diffusion-limited, since lower temperatures and faster cooling rates result in reduced growth. Indeed, for high cooling rates the diffusion of solute elements is not fast enough to allow equilibrium growth.

The growth of the primary γ' precipitates is also affected by the nucleation of secondary γ' precipitates. The displacement of the γ/γ' interface at a cooling rate of

10 K/min is much slower in the presence of secondary γ' precipitates (see dashed line in Figure 3.15). In this case, the overall interface displacement is comparable to that observed at a cooling rate of 100 K/min for a system that does not include secondary γ' precipitates. The nucleation of secondary γ' precipitates allows the relative fraction of the γ and γ' phases to reach stability sooner, thereby stopping the growth of primary γ' precipitates. Also, the presence of secondary γ' precipitates leads to ‘soft’ impingement of solute concentration profiles generated by the growth of primary and secondary γ' precipitates, thereby shortening the diffusion length. Consequently, the displacement of the γ/γ' interface at 10 K/min is halved.

3.6.2 APT compared to phase field simulations

The calculated results confirm that the concentration trends of individual elements across the γ/γ' observed with the atom probe are fairly well reproduced by the 1D and 2D simulations at the 10 K/min cooling rate (see Figure 3.16 and Figure 3.17). All phase field simulations correctly show that Al, Ti (see Figure 3.16) and Ta (see Figure 3.17) exist in higher concentration in the γ' phase, as these are γ' stabilising elements. For these elements, a depletion zone is sometimes observed near the γ/γ' interface, on the γ' phase side. The depletion area is much larger for Ta, as this element diffuses slower in Ni than Al and Ti. The opposite trend can be observed for Cr, Co (see Figure 3.16), Mo and Re (see Figure 3.17), as these elements strongly partition to the γ phase. For these elements, an enrichment area is sometimes observed near the γ/γ' interface, on the γ phase side. The enrichment area is relatively much larger for Re, as this element is the slowest diffusing amongst all elements usually added to nickel superalloys. Tungsten, on the other hand, has no strong partitioning behaviour (see Figure 3.17). A slightly higher concentration of W is expected in the γ phase but no enrichment area is predicted by the phase field simulations. This difference in behaviour can be explained by the fact that the W equilibrium concentration in γ' increases considerably between 1273 K and 923 K. As the system cools and the γ/γ' interface moves, tungsten – similarly to Al, Ti and Ta – diffuses towards the γ' phase, against the movement of the interface.

The relative concentrations of each element in the γ and γ' phases are also repro-

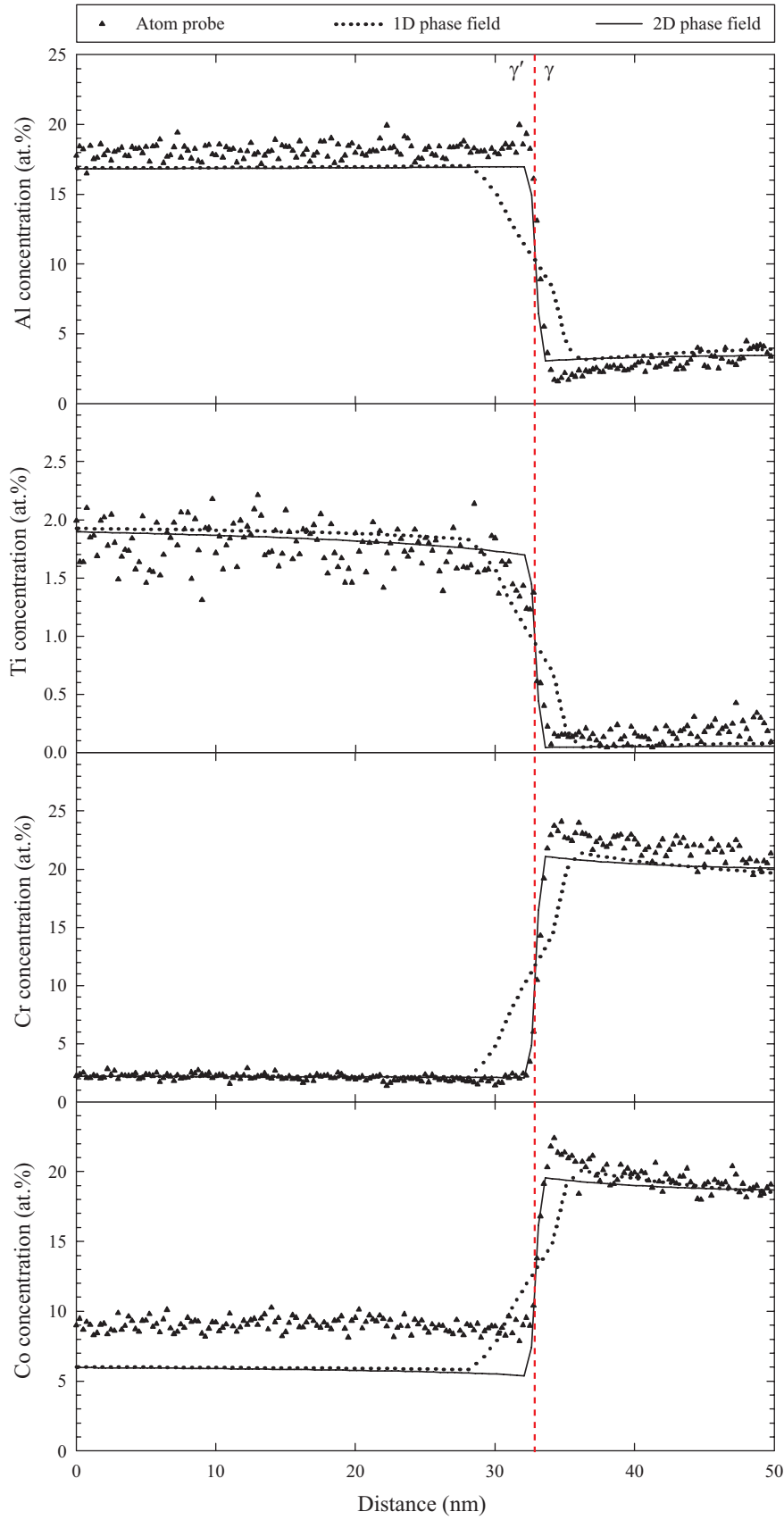


Figure 3.16: The concentration profiles of Al, Ti, Cr and Co across the γ/γ' interface in dataset #4230 measured with the atom probe and compared to predictions obtained from the 1D and 2D phase field simulations, with 10 K/min cooling rate.

duced by the phase field simulations with the exception of cobalt and molybdenum. The predicted Co concentration in the γ' phase is 30 % lower than that measured with the atom probe. A higher bulk Co concentration in the sample would not cause the discrepancies observed, since this would result in higher Co concentrations in both the γ and γ' phases. Possible mass resolution errors caused by the vicinity of Co and Ni peaks do not play a role here as these would affect the measurements of Co concentration both in the γ and γ' phases. On the other hand, the predicted Mo concentration in the γ phase is 30 % higher than that measured with the atom probe. Also in this case, a lower bulk Mo concentration or mass resolution errors cannot explain such differences. Therefore, the difference in Co and Mo content in the γ' and γ phases between phase field simulations and atom probe experiments could either be caused by the solubility of Co and Mo being affected by other solute elements or else by underlying errors in the thermodynamic database used for the simulations.

The sharpness of the γ/γ' interface is well predicted by 2D simulations, whereas 1D simulations predict a broader interface at the same cooling rate. This is because the 2D simulations include the nucleation and growth of secondary γ' precipitates, whereas the 1D simulations do not take these into account. Therefore, the nucleation and growth of secondary γ' precipitates in the middle of the γ phase channel play an important role in the evolution of the microstructure and in the concentration of solute elements at the interface between the two phases.

The Re concentration profile across the γ/γ' interface can now be looked at in more detail (see Figure 3.17). It is apparent that when secondary γ' precipitates are taken into account in the 2D simulation, the rhenium concentration profile has a sharper interface resulting in a better match to the interface observed with the atom probe. Additionally, the ‘bow wave’ predicted by the 2D simulation is on the order of ~ 10 nm leaving the Re concentration in the middle of the γ channel unaffected. In contrast, 1D simulations predict a ‘bow wave’ extending up to ~ 30 nm into the γ channel. These aspects suggest that including the nucleation of secondary γ' precipitates leads to a closer match to the experimental data: the width of the interface measured with the atom probe is ~ 2 nm and the enrichment region extends less than ~ 10 nm into the γ channel. However, equilibrium Re concentrations in γ and γ' calculated with

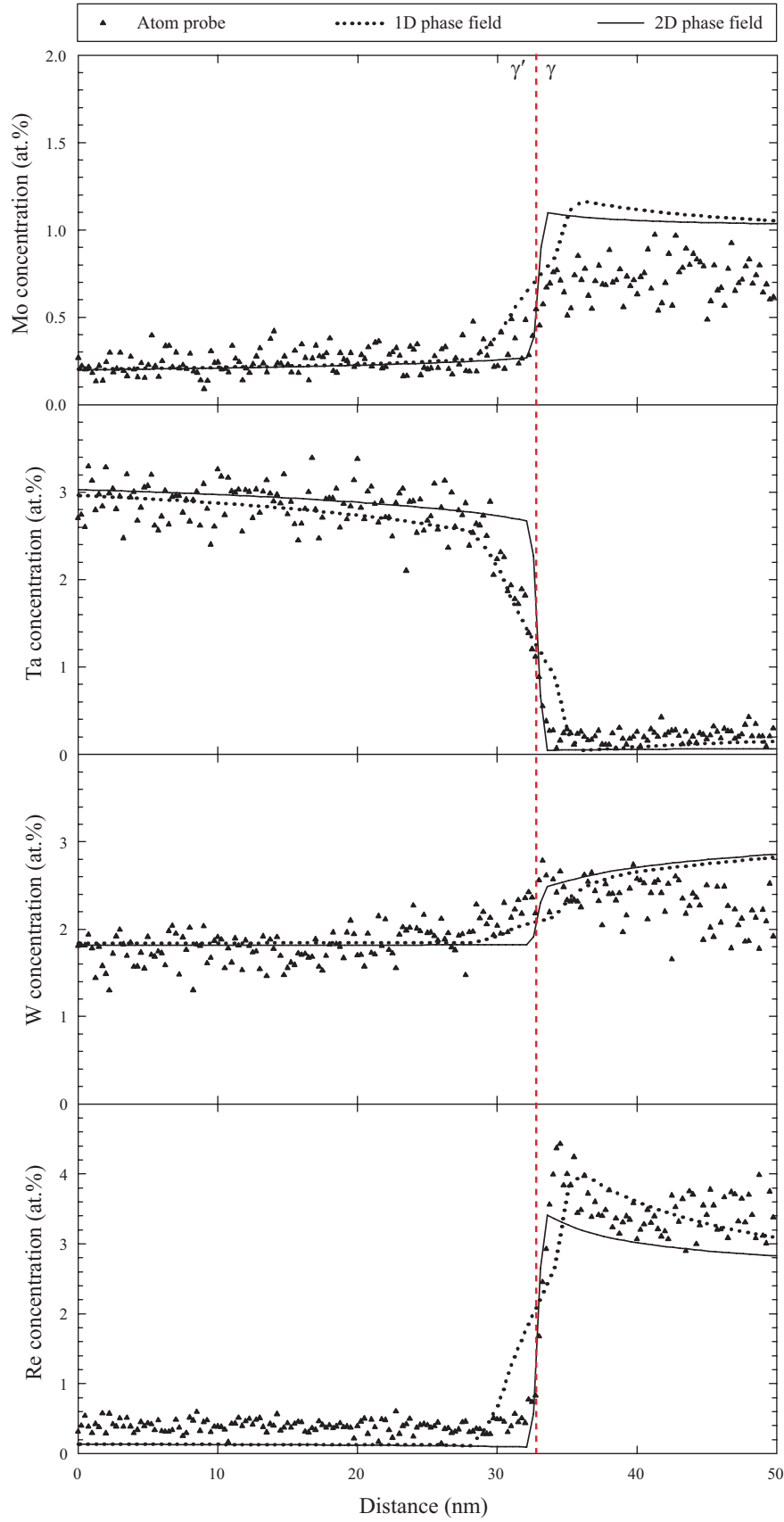


Figure 3.17: The concentration profiles of Mo, Ta, W and Re across the γ/γ' interface in dataset #4230 measured with the atom probe and compared to predictions obtained from the 1D and 2D phase field simulations 10 K/min cooling rate.

the simulation are lower than those observed with the atom probe. The predicted Re concentration in the primary γ' precipitate is 0.13 at.%, in contrast with an observed concentration of 0.39 at.%. Similarly, the Re concentration observed with the 3DAP within the γ channel is 3.39 at.%, higher than the theoretical equilibrium content obtained with the 2D simulation, 2.89 at.%. This is considered to be an indication that the CMSX-4 samples used for the 3DAP experiments have a higher overall Re content than the ideal CMSX-4 concentration used in the phase field simulation. Alternatively, this could be a consequence of the low chemical accuracy of the 3DAP used for these experiments – a 3DAP with no reflectron lens. Indeed, the vicinity of the ^{181}W peak to the ^{182}Re peak means that a fraction of W atoms could be interpreted to be Re atoms. Unfortunately, it is not possible to use the atom probe to determine the bulk concentration of CMSX-4 with accuracy, since the field of view is not large enough to provide a representative volume. Finally, the discrepancies observed could also be explained by taking preferential evaporation errors into account. However, it is thought that preferential evaporation cannot be the cause of the higher Re content in the γ phase because the types of materials examined and the fast alternating voltage pulse (200 kHz) make it unlikely that preferential evaporation has a large effect on these results [70].

3.7 APT, ladder diagrams and the rhenium-effect

The results presented in §3.5.2 exclude the possibility of nano-sized clusters of rhenium being present in nickel superalloys. The number of solute clusters of smaller size, namely 4-7 atoms, in the binary Ni-X alloys has been shown to be no more than would be expected for a random distribution of impurity atoms. A similar analysis was carried out on datasets obtained from the commercial CMSX-4 single-crystal superalloy, with the same conclusions drawn. These findings contrast with suggestions made in previous papers [12, 13, 127, 109] where the observed discontinuities in rhenium ladder diagrams and concentration profiles were explained by postulating that rhenium clusters were present. However, APT results are consistent with results obtained with the EXAFS method and via *ab initio* calculations (see Chapter 2 and Chapter 4).

Given these findings, it is of interest to determine whether ladder diagrams reconstructed from the LEAP datasets measured here – despite their not being the preferred method of analysis for clustering – would indeed display the discontinuities found in earlier work. For this purpose, ladder diagrams were constructed from a thin rectangular section cut from the γ phase of dataset #2314 obtained using the 3DAP, see Figure 3.18a. The dimensions were $2 \times 2 \times 48$ nm, so the ladder diagrams must be regarded as an integral of the concentration profile of the volume along the longest dimension. Analysis was carried out for both Re and W, to ascertain whether any discontinuities in the slopes of ladder diagrams were present for elements other than Re. Tungsten was chosen as a reference because the concentrations of Re and W in the γ phase are comparable and because there have been no suggestions in the literature so far that W forms clusters in nickel-based superalloys. Ladder diagrams for Re and W were obtained from the random reference of the same region of the dataset. The identities of the atoms in the thin rectangular sections were shuffled to simulate a random distribution of species in the datasets. The ladder diagrams obtained in this way are given in Figure 3.18b. One can see that the ladder diagrams for both Re and W are nominally straight, but if one examines them on a finer scale, discontinuities are indeed present – despite our more detailed analysis in §3.5.2 which confirms that clustering of Re (and indeed W) is not present. It can also be noted that the ladder diagrams obtained from the random references display a similar amount of discontinuities.

It follows from the above that ladder diagrams should not be used to determine whether clustering is occurring at such fine levels, since they are not able to differentiate between randomly occurring areas of higher solute content and real solute clusters. Undoubtedly, small discontinuities are observed in the ladder diagram for Re, both in the original dataset and in its random reference. However, one cannot deduce from a ladder diagram whether any discontinuities found are clusters or whether they are expected for a random distribution of solute atoms. Possible explanations for the occurrence of discontinuities in ladder diagrams in general have been discussed in §3.2 and §3.3. Here, since care has been taken to use 3DAP data from only the γ phase so that no γ' particles or nuclei are present, it seems probable that the discontinuities on the ladder diagrams [12, 13, 127] are due to random deviations in local chemistry.

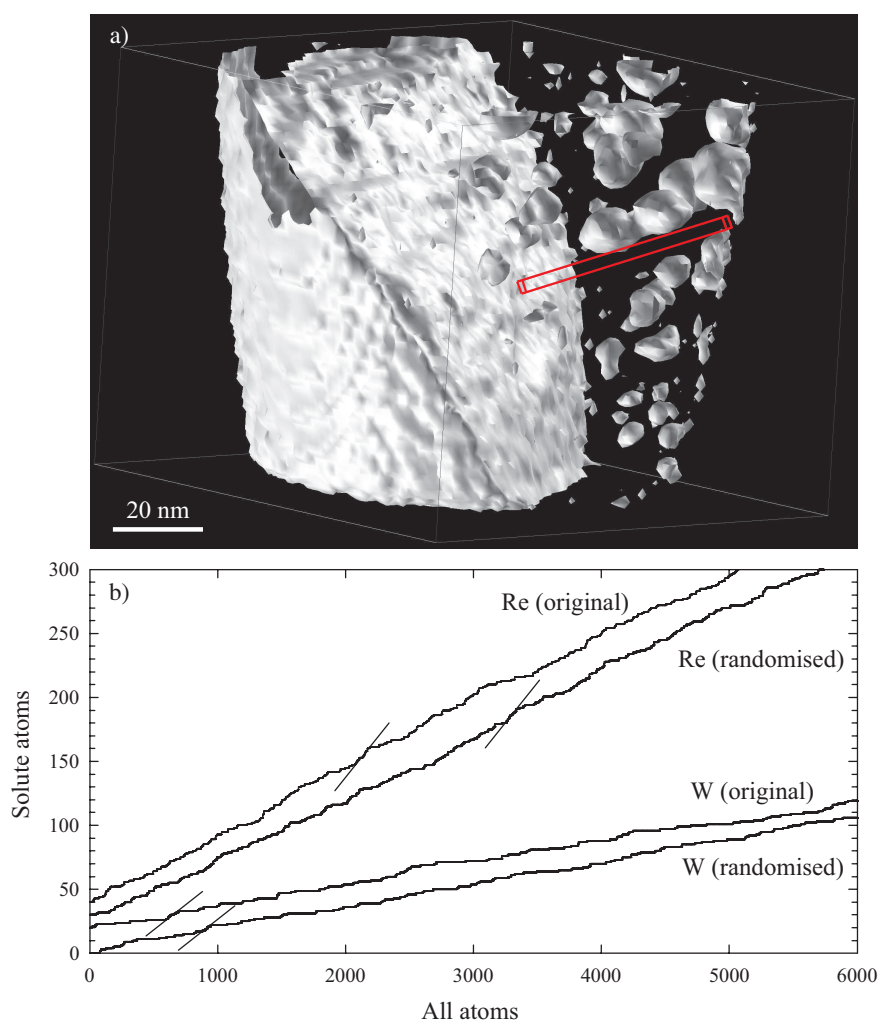


Figure 3.18: a) A ladder diagram can be obtained by cutting a thin long section from the γ phase of dataset #2314. b) The ladder diagrams obtained for W and Re, compared to ladder diagrams obtained from the random reference.

Concerning the composition profiles measured using APT close to the γ/γ' interfaces, phase field modelling has shown conclusively that the enrichment of Re can be explained by the movement of the γ/γ' interface which occurs due to the greater supersaturation arising during cooling from service temperature. It appears that the cooling rate plays a very important role in the growth of the primary γ' precipitates. Additionally, it is apparent that the nucleation of secondary γ' precipitates in the middle of the γ channel can profoundly alter the kinetics of the primary γ' growth during cooling, and thus the movement of the γ/γ' interface. In the presence of the secondary precipitates, the final interface region is much sharper and the diffusion profile ahead of the interface extends less far into the γ channel, resulting in a much better match to the atom probe data. Finally, it is important to note that the interface examined with the atom probe for this study is perpendicular to the direction of evaporation, thereby minimising local magnification effects which are assumed to be the cause of broader interfaces usually observed with the atom probe. It is therefore reasonable to assume that the sharpness of the interface observed with the atom probe is accurate.

In conclusion, the APT analysis seems to confirm the EXAFS results, and rhenium is expected not to form clusters in nickel superalloys. Therefore, clustering is not the mechanism that allows rhenium to provide its strengthening effect. It appears that rhenium atoms in the γ phase of CMSX-4 and in the binary alloys are distributed randomly. Furthermore, it has been shown that the Re enrichment near the γ/γ' interfaces forms upon cooling from service temperature, and is not present at service temperature. Therefore, the enrichment does not play a role in the strengthening effect of rhenium.

CHAPTER 4

Ab initio Modelling

4.1 Density functional theory

DENSITY FUNCTIONAL THEORY (DFT) is an electronic structure method that allows to obtain information on a given atomic system *from first principles* (*ab initio*). This means that the energy of a crystal structure and, subsequently, the interatomic distances and forces are calculated starting from first principles, without the inclusion of empirical parameters or parameters obtained from other modelling methods. The simulation work in this project has been done using the Density Functional Theory as implemented in the VASP code [41]. DFT is an *ab initio* technique although, strictly speaking, the practical implementation of DFT is not. Indeed, some parameters (*i.e.* the *exchange-correlation* energy of a free electron gas) are used to fit the *exchange-correlation* functionals.

DFT is based on the principle that the ground state energy of a system can be expressed as a functional of the ground state electron density, $n_0(\mathbf{r})$. This means that, in principle, only three variables (x , y and z) are necessary to specify the electronic energy instead of the much larger number of variables which are needed to compute wave function. This method considerably reduces the amount of computational time required to compute the energy of a given system.

Hohenberg and Kohn [43] first proved the theorems upon which DFT is based. The first theorem states that for a system of interacting particles in an external potential $V_{\text{ext}}(\mathbf{r})$, the potential is entirely dependent on the ground state electron density $n_0(\mathbf{r})$.

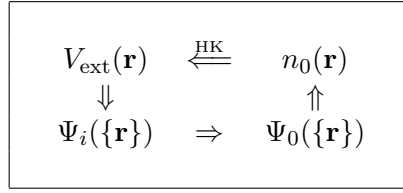


Figure 4.1: The Hohenberg-Kohn theorems complete the circle and link the external potential, $V_{\text{ext}}(\mathbf{r})$, to the ground state electron density, $n_0(\mathbf{r})$. This allows all the properties of the system to be computed once the ground state electron density, $n_0(\mathbf{r})$, is known [66].

Therefore, the Hamiltonian can be determined given only the ground state electron density $n_0(\mathbf{r})$ and, as a result, all properties can be computed once $n_0(\mathbf{r})$ is known.

The second theorem states that for a particular $V_{\text{ext}}(\mathbf{r})$, the ground state energy of the system is the global minimum of a functional $E[n]$ and the electron density, $n(\mathbf{r})$, corresponding to the minimum of the functional, is equal to the ground state electronic density, $n_0(\mathbf{r})$. Therefore, the ground state electron density, $n_0(\mathbf{r})$, can be used to compute the external potential, $V_{\text{ext}}(\mathbf{r})$, which determines the state of the system, $\Psi_i(\{\mathbf{r}\})$. In principle, the ground state of the system, and the ground state electron density, can be determined by minimising the energy functional (see Figure 4.1). Unfortunately, the exact form of the $E[n]$ functional is not known. The solution to this problem is provided by the Kohn-Sham *ansatz* [53].

4.1.1 The Kohn-Sham *ansatz*

The Kohn-Sham *ansatz* [53] provides a viable route to solving the problem of determining $E[n]$. Within this approach, the unsolvable problem of minimising the energy of a system of N interacting electrons in an external potential, $V_{\text{ext}}(\mathbf{r})$, is circumvented by substituting the original system with an auxiliary system made of N non-interacting electrons in an external potential, $V_{\text{KS}}(\mathbf{r})$, such that the ground state electronic density, $n_0(\mathbf{r})$, is the same in both systems.

At this point, the ground state electron density of the auxiliary system can be obtained by solving a single-particle equation (see Figure 4.2). The complicated many-body terms can then be included in the *exchange-correlation* energy functional of the density, $E_{\text{xc}}[n]$, which allows to obtain the energy functional of the original system, $E[n]$. Therefore, the exact *exchange-correlation* functional would allow one to calculate

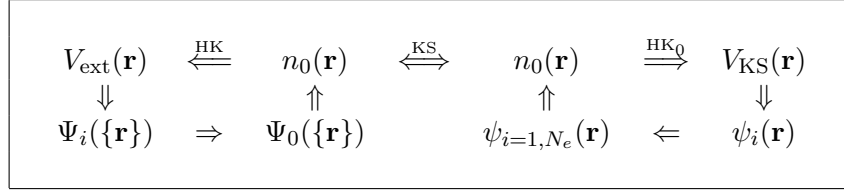


Figure 4.2: The Kohn-Sham *ansatz* helps to solve the full many-body problem by substituting the original system with a system of non-interacting particles with the same ground state electron density, $n_0(\mathbf{r})$ [66].

the ground state properties of the system with high precision. Unfortunately, the exact form of $E_{\text{xc}}[n]$, let us call it $E_{\text{xc}}^{\text{true}}[n]$, is unknown and some approximations are necessary.

4.1.2 *Exchange-correlation* functionals

The approximation adopted for the *exchange-correlation* functional, $E_{\text{xc}}^{\text{approx.}}[n]$, is one of the most important terms of DFT. DFT calculations are only accurate to the extent that the $E_{\text{xc}}^{\text{approx.}}[n]$ of choice describes $E_{\text{xc}}^{\text{true}}[n]$. The strength of DFT is that, for metallic systems, $E_{\text{xc}}^{\text{approx.}}[n]$ can be defined as a local functional of the electron density or as a local functional of the electron density *and* its gradient, and good results are obtained. Therefore, there are mainly two available approximations for the *exchange-correlation* functional: the Local Density Approximation (LDA) and the Generalized Gradient Approximation (GGA).

LDA is the simplest and oldest approximation available to $E_{\text{xc}}^{\text{true}}[n]$ [66]. Within this approximation, $E_{\text{xc}}^{\text{LDA}}[n]$ is obtained by integrating the *exchange-correlation* energy per particle of a Homogeneous Electron Gas (HEG) at the local density, times the local density, over all space [21]. The *exchange-correlation* energy per particle of the HEG can be formulated in terms of the whole electron density, or in terms of two separate spin densities, as in the Local Spin Density Approximation (LSDA). GGA is an alternative to LDA, which is often preferred as it usually leads to more accurate results [66]. In this approximation, $E_{\text{xc}}^{\text{GGA}}[n]$ is formulated in terms of the electron density *and* the magnitude of the gradient of the electron density at each point. Actually, the term GGA describes a family of functionals all based on the same principle but using different forms for the exchange and correlation functionals. The two most prominent

forms are those formulated by Perdew and Wang (PW91) [92] and by Perdew, Burke and Ernzerhof (PBE) [91].

The accuracy of DFT calculations is dependent on the approximations adopted for the *exchange-correlation* functional: this is both a strength and a weakness. On the one hand, DFT can be made more accurate by adopting new functionals and some functionals can be particularly accurate for different sets of materials. On the other hand, DFT is not, strictly speaking, *ab initio*, as the *exchange-correlation* functionals are parameterised on some reference systems. The work within this chapter has been done using the VASP implementation of the GGA-PBE functional [41]. The GGA-PBE was chosen because it is numerically reliable and provides accurate results for the transition metals [66].

4.1.3 Pseudopotentials and the Projector Augmented Waves

As explained above, DFT allows to obtain all the properties of a system from the ground state electron density. However, describing the electron density by considering each electron explicitly is computationally very intensive. It is also important to note that only valence electrons are affected by, and responsible for, the bonding to other atoms, and as such only these need to be represented explicitly. Core electrons are highly localised and do not participate in the bonding to other atoms.

Pseudopotentials are the oldest scheme to describe the electronic structure within DFT. The main idea behind pseudopotentials is that the core electrons are kept ‘frozen’ and that the nucleus and core electrons are represented by an effective potential, while only the valence electrons are explicitly described [95, 66, 33]. Because much fewer electrons are described explicitly, a considerable amount of computational time is saved. However, maintaining accuracy requires complicated functions to describe the interactions with electrons and, therefore, simulation times are still long [58]. The most successful approach to produce accurate pseudopotentials, while maintaining low computational times, is the development of ultrasoft pseudopotentials by Vanderbilt [123].

One alternative to pseudopotentials is the adoption of Projector Augmented Waves (PAW) potentials [14, 58]. In contrast to pseudopotentials, PAW potentials are an all-electron method, *i.e.* there are no ‘frozen’ core electrons and both core and valence

electrons are treated explicitly. In PAW potentials, projector functions are used to augment wave functions inside the core radius. Generally, PAW potentials are more accurate than ultrasoft pseudopotentials [58], as they require a smaller core radius and allow the full Kohn-Sham wave function to be reconstructed, instead of being represented in the core region by a pseudo wave function. The work within this chapter has been done using the PAW potentials distributed with the VASP code [14, 58, 41].

4.2 DFT applied to metallurgy

Considering the complicated chemistry of most structural metallic materials and the complicated electronic structure of transition metals, it can be appreciated that applying DFT to metallurgical problems is a daunting task. Nevertheless, due to higher computing power and more efficient codes, there is a growing interest in the application of DFT to larger and more complicated problems of metallurgy. Furthermore, the advent of PAW potentials made it possible to describe accurately transition metals, within acceptable computational timescales. The scope of DFT in metallurgy is wide-ranging. Here we describe only work that is most relevant to the study of the behaviour of solute atoms and deformation mechanisms in metallic alloys.

4.2.1 Clustering and ordering

Ab initio calculations can help to investigate the stability of various solute configurations in the host lattice. For the nickel superalloys, several studies have looked at the γ/γ' partitioning behaviour of various solute elements. Yun-Jiang Wang and Chong-Yu Wang [129] used VASP to investigate the partitioning coefficients of Cr, Co and Re and how these change with additions of Ru. As expected, all three additional elements are found to partition to the γ phase. Furthermore, it was observed that the addition of Ru reduces the high partitioning coefficient of Cr and Re by about one order of magnitude [129]. In a second study [130], the two authors investigate the lattice site preference of Re and Ru in γ' and their effects on the partitioning of Mo and W. Their results show that, whereas Ru has no effect on the partitioning coefficient of Mo and W, Re acts to increase W partitioning to the γ' phase [130].

DFT can also be used to calculate the binding energy between various solute atoms and defects, in order to investigate the early stages of clustering. In aluminum alloys, the binding energy between solute atoms is important as it reduces the diffusion of Cu and hence slows down the ageing processes that lead to Cu clustering and GP zones. Wolverton [135] used DFT to compute the binding energy between a vacancy and various solute atoms in the aluminum lattice and confirmed that Sn, Cd and In, which slow down ageing when added to aluminum alloys, had large binding energies. Wolverton also predicted that Si, Ge and Au would also slow down ageing, basing the predictions on the solute–vacancy binding energy. Shin and Wolverton [114] used the same method to investigate the solute–vacancy binding energy in magnesium alloys. Similar studies have also been carried out for Fe based alloys, where the embrittlement of certain UHS steels is controlled by vacancy diffusion and affected by solute–vacancy binding energies [90].

4.2.2 Dislocations and solute atoms

Studying the interaction between solute atoms and dislocations (or other point, linear and planar defects) is also a prominent area of research for *ab initio* techniques such as DFT. The objective is to understand and describe the atomic scale mechanisms that lead to mechanical properties. Unfortunately, investigating dislocations – particularly dislocations interacting with solute atoms – with DFT is not simple. Therefore, most studies of dislocation mechanisms in metals involve the use of empirical or semi-empirical interatomic potentials which are often tailored to reach high accuracy for a specific system. Nevertheless, a few attempts have been made to study dislocation motion within an *ab initio* framework [120].

Softening and hardening mechanisms arising from solute additions have been explored by Trinkle and Woodward [121]. Particularly, the study looked at Re and Pt solute atoms and their effect on *bcc*-Mo, using DFT with flexible boundary conditions to simulate a single straight screw dislocation [136]. Using this method, the authors were able to qualitatively evaluate hardening and softening processes observed with different concentrations of solute atoms. Woodward [136] also highlights the difficulties arising from modelling dislocations with DFT using periodic boundary conditions.

Because of long-range elastic interactions it is necessary to couple the dislocation core and the long-range elastic field self-consistently. To solve the problem, Woodward [136] developed a technique, the First-Principles Green Function Boundary Condition (FP-GFBC) method, in which the dislocation core is embedded in a region that produces a bulk-like response stress field through the lattice Green Function [115].

The alternative to replicating the long-range stress fields through the Green Function is the development of hybrid methods. Within these methods, a ‘quantum’ region is embedded in a much larger system, simulated with interatomic potentials. However, in such methods dealing with the boundary conditions between the two regions is a complicated problem [24]. Csanyi *et al* addressed this problem by simulating the whole system with interatomic potentials and augmenting the potential within the core region using extra information obtained from quantum calculations [24]. Although simulating a dislocation within an *ab initio* framework is still a complicated endeavour, DFT can be used to gain information on how solute atoms affect deformation processes.

4.2.3 Lattice distortions

It is generally accepted that deformation mechanisms may be affected by lattice distortions. In nickel based superalloys, lattice mismatch between the γ and γ' phases plays an important role in microstructure evolution as well as on the dislocation’s ability to cut across the γ' particles. Additionally, it is believed that solute atoms at the γ/γ' interface exert pinning forces on misfit dislocations. Thus, many studies have investigated the effect of solute atoms on the lattice parameter of γ and γ' . Chong-Yu Wang *et al* [38, 145, 130] studied the effect of Ta, W, Re and Ru on the stability of a dislocation core at the γ/γ' interface by looking at the lattice relaxation around solute atoms in the γ' phase. The authors suggest that such effects could partly explain the rhenium-effect. However it must be noted that the γ' phase has almost no rhenium content: it is reasonable to assume that rhenium affects deformation mechanisms in the γ phase instead.

Tao Wang *et al* [128], instead, looked at the lattice relaxation surrounding various solute atoms in *fcc*-Ni. In this study, DFT was used to calculate equilibrium volumes of super-cells of $\text{Ni}_{107}\text{X}_1$, where X is one of several solute atoms present in nickel based

superalloys. This study found that Re, along with all the other solute elements, would only generate small distortions in the lattice. Ni–Re bonds would be no more than 1 % longer than Ni–Ni bonds. Similar results were obtained by Koteski *et al* [54] who used DFT to obtain the relaxation around solute atoms in much smaller supercells (27 atoms). Such small supercells were deemed sufficient as the work of Koteski *et al* focussed on comparing simulated lattice distortions to results obtained from EXAFS experiments on specimens with 2-5 at.% solute content.

It is often believed that the rhenium-effect may be explained by large lattice distortions generated by rhenium close to the γ/γ' interface [131, 133], however this hypothesis has no foundation, as shown by several *ab initio* methods and experiments [128, 54, 84].

4.2.4 Diffusion of solute atoms

Since creep deformation is diffusion controlled, it is reasonable to assume that slow diffusing solute atoms will have an effect on deformation rates at high temperatures. It was shown experimentally, by Karunaratne and Reed [49], that transition metals of similar size to nickel are the slowest diffusing elements in a nickel lattice. This is surprising since, traditionally, larger atoms are expected to be slow diffusers. Using DFT, Janotti *et al* [45, 36] were able to study the diffusion of several transition metals in the nickel lattice. The diffusion energy barrier and the vacancy formation energy adjacent to a solute atom were calculated for several solute elements in the nickel lattice. These were used to obtain the diffusion activation energy for each solute element in nickel.

Janotti *et al* were able to confirm that larger atoms diffuse much faster than smaller atoms. Rhenium, one of the smallest elements of the 5d series, was found to have a diffusion coefficient more than one order of magnitude lower than W and Ir. It was suggested that this behaviour was due to the directional d bonds: the higher the degree of bonding directionality, the harder compression becomes [45, 36]. The compressibility of the bonds for 5d elements was looked at in more detail. Solute atoms were placed in a *fcc* nickel lattice and a local pressure was applied by displacing the first shell of neighbours towards the solute atom while leaving the rest of the atoms free to relax.

The strain energy was found to differ between different solute atoms, being higher for rhenium.

Therefore, DFT was able to show and helped to explain why rhenium diffuses slowly in the nickel lattice. It was previously described, in §1.4 and §1.5, that the motion of dislocations at intermediate temperatures and loadings occurs by climb-assisted glide. It was also mentioned that dislocation climb, in creep conditions, is highly diffusion controlled [104]. Hence, rhenium could have a large effect on creep properties simply due to its lower diffusion coefficient in nickel. No other element usually added to nickel superalloys diffuses slower than rhenium in the nickel *fcc* lattice.

4.2.5 Stacking Fault Energies

Finally, deformation mechanisms are affected by SFEs. Indeed, a lower SFE would result in Shockley partial dislocations being further apart, which in turns slows down climbing mechanisms (see §1.5). Estimating the effect of solute atoms on the SFE experimentally is a hard task and results are very inaccurate [100]. In the past, empirical and semi-empirical potentials have been used to calculate the effect of solute atoms on stacking fault, but the inaccuracies involved in these simulations are also high. DFT, as an *ab initio* technique, is able to evaluate the effect of solute atoms on SFEs with much higher accuracy.

Qi and Mishra [98] evaluated the effect of solute atoms on the SFE. In their study, Qi and Mishra looked at the SFE of pure Al and how it changes with small additions of transition metals and other elements [98]. Fe was found to increase the SFE of Al considerably, whereas Ge was found to decrease it. Cu, the *fcc* metal with the lowest SFE, has no effect on the SFE of Al.

Yu and Wang [146] adopted a similar method to investigate the effect of Cr, Co, Mo, Ru, W and Re on the SFE of nickel. In this work, a single stacking fault was placed in the middle of 11 close-packed (111) planes. The effect of each solute atom was evaluated by measuring the energy difference between two relaxed structures: one with a solute atom at the stacking fault, in the middle of the supercell, and one with a solute atom far from the stacking fault, at the edge of the supercell. Their results show that the presence of Mo, W or Re at concentration of $\sim 8\%$ at the stacking fault

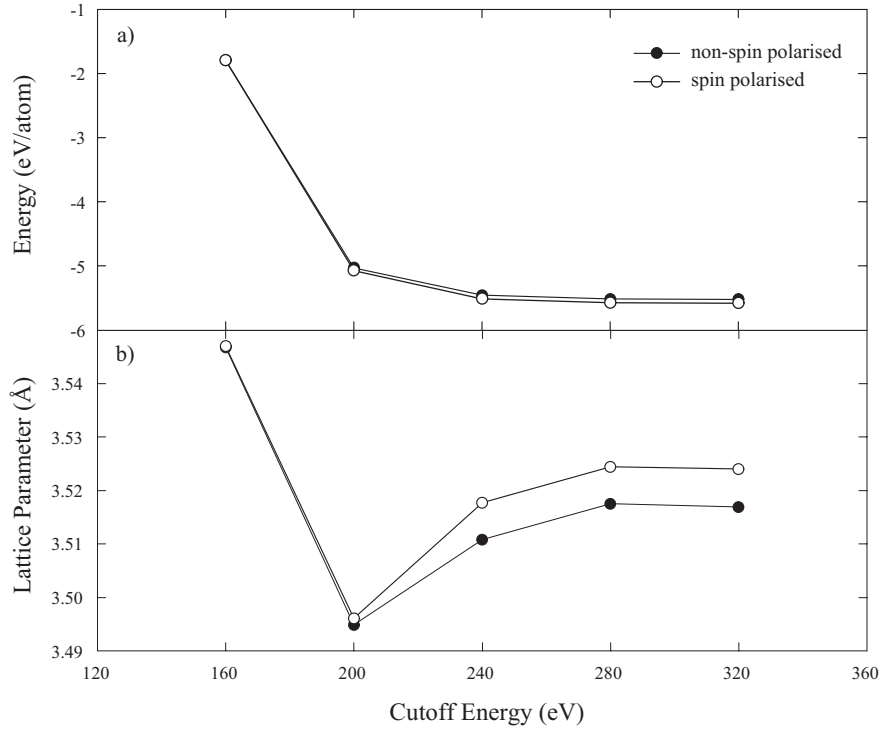


Figure 4.3: Convergence of a) total energy and b) lattice parameter at different cutoff energies for the PAW potentials.

reduces the SFE by 15-20 %. The study also tries to evaluate how the SFE and energy barrier for vacancy diffusion may affect the velocity of dislocation climbing. Results show that although Re significantly reduces dislocation climbing velocity, Ru, Mo and W seem to be more effective at reducing the speed of dislocation climbing in the nickel lattice.

4.3 Convergence tests and DFT parameters

The Vienna *Ab initio* Simulation Package (VASP) was used for the present work [41, 57]. The Generalized Gradient Approximation (GGA) for the *exchange-correlation* functional developed by Perdew, Burke and Ernzerhof [91] was used for most calculations but the Local Density Approximation (LDA) was also used as a reference in the convergence tests [21]. The Projector Augmented Wave (PAW) method was chosen over using Ultrasoft Pseudopotentials (USPP) to describe the electronic structure of the atoms [14, 58]. The PAW potentials provided within the VASP package are considered to be reliable across several systems [58]

Preliminary calculations were performed to establish the cutoff energy and k-points density required to ensure convergence. A cutoff energy of 300 eV was considered sufficient for the PAW potentials of Ni, Re and W provided in the VASP package (see Figure 4.3). The k-points generation followed a Monkhorst-Pack grid, and the dimensions of the grid were chosen so that the maximum separation between k-points would be $0.02 \text{ \AA}^{-1}$. The self-consistent loop was considered converged when the total energy difference between two consecutive steps fell below 10^{-5} eV , as suggested by the VASP manual [56]. The atomic positions were deemed to be converged when forces on all atoms fell to under $0.01 \text{ eV/\AA}$.

Calculations of $2 \times 2 \times 2$, $3 \times 3 \times 3$ and $4 \times 4 \times 4$ cubic *fcc* supercells were performed to test the convergence of point defect energies in each supercell. A $3 \times 3 \times 3$ cubic *fcc* supercell was chosen as this allowed for reasonable computational times while keeping interactions between point defects across the periodic boundary conditions to a minimum. Both spin and non-spin polarised preliminary calculations were carried out to evaluate the effect of spin on the total energy of the system and the lattice parameter. Results showed that the difference between the total energies of the systems were $\sim 0.01 \text{ eV/atom}$ and the equilibrium lattice parameter of a cubic *fcc* unit cell changed by $\sim 0.01 \text{ \AA}$, or $\sim 0.3 \%$ (see Figure 4.3). Therefore, most calculations are non-spin polarised unless otherwise stated.

The Methfessel-Paxton method [68] of order 1 was chosen to determine the filling of partially occupied bands, as this is suggested to be most accurate for evaluating forces in metals [56]. The smearing was set to be 0.2 eV , as this kept entropy contributions to the total energy negligible. For supercell calculations, projection operators were evaluated in real-space to reduce computational time.

4.4 Results

4.4.1 Lattice relaxation

The extent of lattice relaxation surrounding solute atoms is important since it is expected that alloying with elements taken from the 5d row of transition metals will profoundly affect the lattice parameter of γ and γ' . Furthermore, in order to improve

Table 4.1: Relaxation of the lattice surrounding various solute atoms in a $3 \times 3 \times 3$ nickel supercell compared to results obtained by Koteski *et al* [54] and Wang *et al* [128].

	Current Work		Ref. [54]		Ref. [128]	
	R_{nn} (Å)	ΔR_{nn} (%)	R_{nn} (Å)	ΔR_{nn} (%)	R_{nn} (Å)	ΔR_{nn} (%)
Ni	2.489	—	2.489 ^(a)	—	2.498	—
Ta	2.527	1.51	2.515	1.01	2.539 ^(b)	1.66
W	2.504	0.60	2.500	0.44	2.517 ^(b)	0.79
Re	2.496	0.27	2.494	0.20	2.513 ^(b)	0.61
Ir	2.515	1.04	—	—	—	—
Pt	2.544	2.22	—	—	—	—

^(a)Estimated from graph within [54].

^(b)Estimated ΔR_{nn} values from table within [128].

the quality of the EXAFS fits observed in §2.4, relaxed structures obtained from an accurate DFT code can be used as input to obtain more accurate simulated EXAFS spectra. In the present study, the relaxed interatomic distances were obtained for several $3 \times 3 \times 3$ *fcc* supercells containing 107 nickel atoms and 1 solute atom. These were compared to the relaxed interatomic distances obtained from a $3 \times 3 \times 3$ *fcc* supercell containing 108 nickel atoms (see Table 4.1).

When inserted into the nickel lattice, 5d row transition metals generate a systematic outward relaxation on the surrounding atoms. These range from 0.27 % for Re to 2.22 % for Pt when compared to nearest neighbour distances in the pure host. These results are compared to previous work carried out by Koteski *et al* [54] and Wang *et al* [128] in Table 4.1. When looking at the results obtained by Koteski *et al* [54] it is important to note that the authors do not provide a value for $R_{nn}^{\text{Ni-Ni}}$: the value shown in Table 4.1 is an estimate obtained from one of the graphs in their published work [54]. When looking at the results obtained by Wang *et al* [128] it is important to state that the authors only provide the absolute value for $\Delta R_{nn}^{\text{X-Ni}}$ in pm. Furthermore, it appears that Wang *et al* performed spin polarised calculations for their pure Ni system, while adopting non-spin polarised calculations for their simulations of relaxation surrounding Ta, W and Re. It is also unclear from their publication whether they calculated $\Delta R_{nn}^{\text{X-Ni}}$ by comparing spin polarised and non-spin polarised calculations. Consequently, the values shown in Table 4.1 for $R_{nn}^{\text{X-Ni}}$ are an estimate based on the value for $R_{nn}^{\text{Ni-Ni}}$ obtained

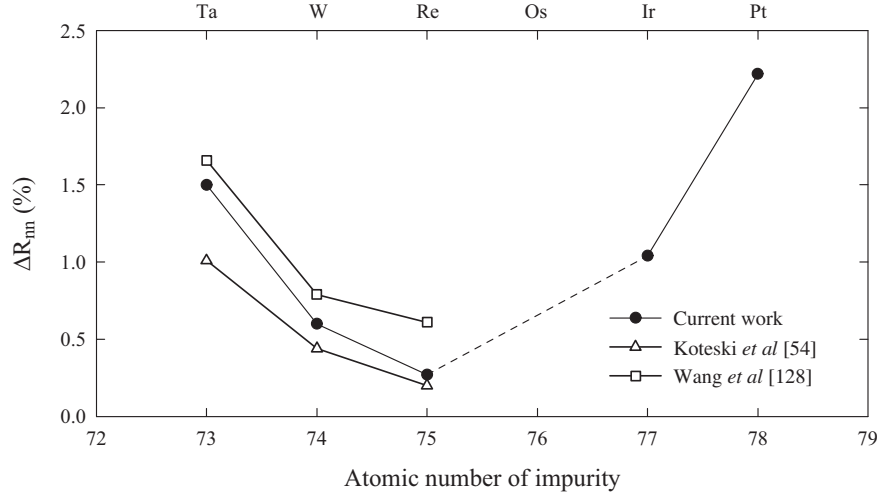


Figure 4.4: Relaxation of nearest neighbour distances across the 5d row of transition metals compared to results obtained by Koteski *et al* [54] and Wang *et al* [128].

from spin polarised calculations within their published work [128].

The results are consistent across all studies: the same trend is observed across the 5d row of transition metals and the magnitude of relaxation is consistent across all three sets of calculations (see Figure 4.4). It can be observed that Re produces the smallest outward relaxation amongst all the elements in the 5d row of transition metals. The distance between the Re substitutional solute atom and the first shell of nearest neighbours is 2.496 Å, 0.27% longer than the nearest neighbour interatomic distance in the pure *fcc*-Ni lattice calculated with the same parameters.

The results shown in Table 4.1 and Figure 4.4 are in strong disagreement with the work of Zhu *et al* [148], in which a $\Delta R_{nn}^{\text{Re-Ni}}$ of 4.09% was determined. Such a large value for the outward relaxation surrounding a Re atom in the *fcc*-Ni lattice – many times larger than that calculated with DFT in several studies [54, 128] – cannot be found anywhere else in the literature. Zhu *et al* obtained the published results from a classical MD simulation of a *fcc*-Ni $40 \times 40 \times 40$ supercell with one Re substitutional atom [148]. The work of Zhu *et al* will be discussed in further detail within §4.5.

4.4.2 Binding energies and clusters

The binding energy between two point defects, $E_{\text{bind}}^{\text{X-X}}$, in a supercell containing n atoms can be obtained using Equation 4.1, as described by Wolverson [135].

Table 4.2: Binding energy between two rhenium atoms in the nickel lattice.

Supercell size	No. of atoms	$E_{\text{bind.}}^{\text{Re-Re}}$ (eV)
$2 \times 2 \times 2$	32	-0.418
$3 \times 3 \times 3$	108	-0.421
$4 \times 4 \times 4$	256	-0.424

$$E_{\text{bind.}}^{\text{X-X}} = 2 \cdot E(\text{Ni}_{n-1}\text{X}_1) - [E(\text{Ni}_{n-2}\text{X}_2) + E(\text{Ni}_n)] \quad (4.1)$$

In Equation 4.1, $E(\text{Ni}_n)$ is the total energy of a pure nickel supercell, $E(\text{Ni}_{n-1}\text{X}_1)$ is the total energy of a supercell containing a single point defect and $E(\text{Ni}_{n-2}\text{X}_2)$ is the total energy of a supercell containing two point defects in a desired configuration. In agreement with the literature [135], a negative $E_{\text{bind.}}^{\text{X-X}}$ means that the binding of the two point defects is energetically unfavourable and that the two point defects should repel each other.

The convergence of $E_{\text{bind.}}^{\text{X-X}}$ with supercell size was checked to make sure that interaction effects between point defects across periodic boundary conditions is kept to a minimum. Therefore, $E_{\text{bind.}}^{\text{Re-Re}}$ was calculated for nearest neighbour pairs in $2 \times 2 \times 2$ (32 atoms), $3 \times 3 \times 3$ (108 atoms) and $4 \times 4 \times 4$ (256 atoms) cubic *fcc* supercells (see Table 4.2) to make sure such effects are negligible. A $3 \times 3 \times 3$ *fcc* supercell provides accurate results while converging within reasonable computational times. Therefore, all binding energy calculations were performed within $3 \times 3 \times 3$ *fcc* supercells containing 108 atoms.

The binding energy between two solute atoms in various configurations can then be calculated. The total energies of several supercells containing two rhenium solute atoms positioned at various lattice sites (see Figure 4.5) were computed using the parameters described in §4.3. The calculations were performed for Re-Re pairs and for W-W pairs, in order to provide a reference.

The binding energies between the six distinct nearest neighbour pairs of Figure 4.5, along with the X-X interatomic distances, are shown in Table 4.3. It can be observed that the binding energy between two rhenium nearest neighbours is -0.41 eV and that

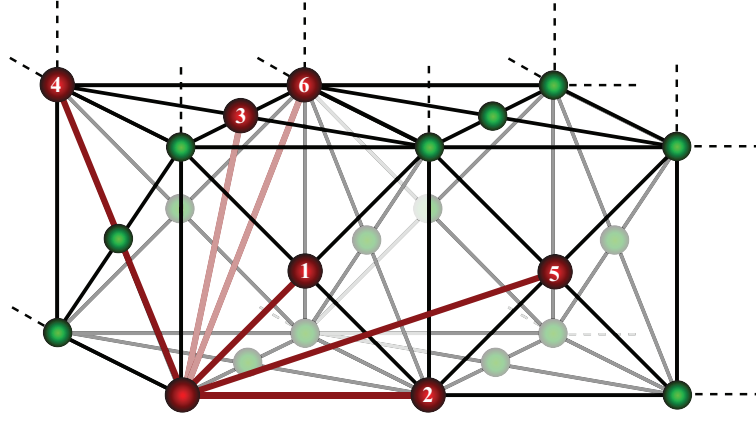
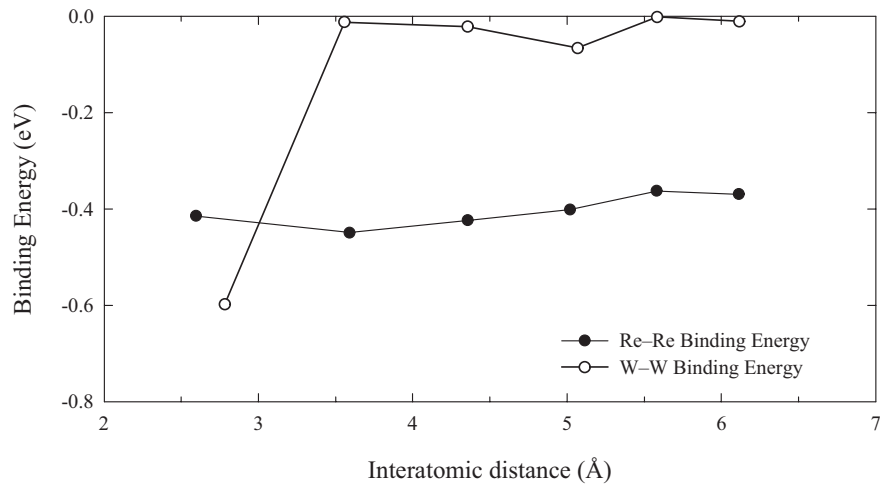


Figure 4.5: The six nearest neighbour pairs considered in the current study.

Table 4.3: The Binding energies and relaxed interatomic distances for different Re–Re and W–W pairs in a $3 \times 3 \times 3$ *fcc* Ni supercell containing 108 atoms.

	Re–Re			W–W		
	$E_{\text{bind.}}$ (eV)	R_{nn} (Å)	ΔR_{nn} (%)	$E_{\text{bind.}}$ (eV)	R_{nn} (Å)	ΔR_{nn} (%)
1 st NN	−0.415	2.596	4.32	−0.598	2.787	11.99
2 nd NN	−0.449	3.591	2.03	−0.013	3.558	1.07
3 rd NN	−0.424	4.354	1.00	−0.022	4.355	1.02
4 th NN	−0.402	5.019	0.82	−0.067	5.069	1.83
5 th NN	−0.363	5.581	0.29	−0.002	5.584	0.33
6 th NN	−0.369	6.112	0.25	−0.011	6.117	0.33

Figure 4.6: The binding energies between different Re–Re and W–W pairs in a $3 \times 3 \times 3$ *fcc* Ni supercell containing 108 atoms.

the Re–Re interatomic distance is 4.32 % longer than the standard nearest neighbour interatomic distance in the pure host lattice. It can also be observed that the binding energy between two tungsten nearest neighbours is -0.60 eV, and that the W–W interatomic distance is 11.99 % longer than the standard Ni–Ni nearest neighbour distance. A negative binding energy for both Re–Re and W–W nearest neighbour pairs means that both Re and W pairs would repel when positioned as nearest neighbours in the *fcc*-Ni lattice.

As the two solute atoms are placed further apart, Re and W display different behaviours (see Table 4.3 and Figure 4.6). The binding energy between two rhenium atoms remains relatively stable, whereas the binding energy between two tungsten atoms drops as soon as the atoms are placed as second neighbours. The behaviour of W may be explained with reference to the several stable intermetallics in the Ni–W system (see Figure C.4), which would indicate a tendency to achieve localised ordering. In contrast, there are no stable intermetallics in the Ni–Re system (see Figure C.5).

To complete the study, the binding energy of several different clusters can be calculated to check whether these clusters would be stable in *fcc*-Ni. Like in Equation 4.1, the binding energy of a cluster is calculated using Equation 4.2.

$$E_{\text{bind.}}^{\text{clust.}} = m \cdot E(\text{Ni}_{n-1}\text{X}_1) - [E(\text{Ni}_{n-m}\text{X}_m) + (m-1) \cdot E(\text{Ni}_n)] \quad (4.2)$$

In Equation 4.2, n is the total number of atoms in the supercell, $E(\text{Ni}_n)$ is the total energy of a pure nickel supercell, $E(\text{Ni}_{n-1}\text{X}_1)$ is the total energy of a supercell containing a single point defect and $E(\text{Ni}_{n-m}\text{X}_m)$ is the total energy of a supercell containing m solute atoms in a desired configuration. Therefore, $E_{\text{bind.}}^{\text{clust.}}$ is the energy difference associated with having the solute atoms dispersed in the *fcc*-Ni lattice rather than clustered in a given configuration. A negative binding energy means an energy advantage in having the solute atoms dispersed in the *fcc*-Ni lattice [135].

The results for the nearest neighbour clusters are shown in Figure 4.7. It can be observed that 3- and 4-atom nearest neighbour clusters are unstable in the *fcc*-Ni lattice, since DFT calculations yield a negative $E_{\text{bind.}}^{\text{clust.}}$. The results for the second+

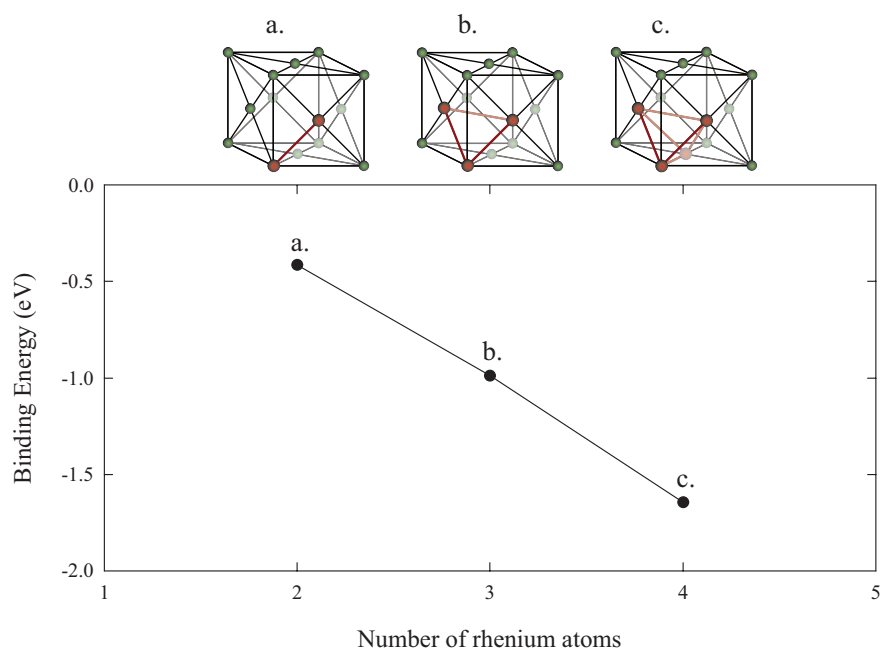


Figure 4.7: The binding energies of several nearest neighbours Re clusters in a $3 \times 3 \times 3$ fcc Ni supercell containing 108 atoms.

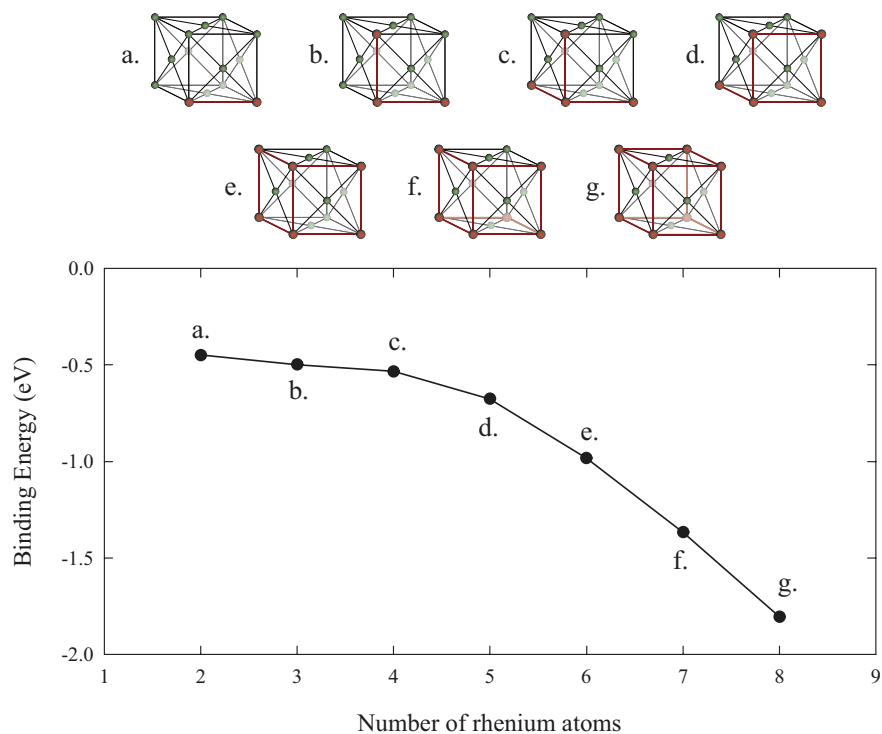


Figure 4.8: The binding energies of several second+ neighbour Re clusters in a $3 \times 3 \times 3$ fcc Ni supercell containing 108 atoms.

neighbour clusters are shown in Figure 4.8. Because of the limitation on computational resources, these calculations could not be done in $> 3 \times 3 \times 3$ supercells. As a result, the binding energies of 5-, 6- and 7-atom 2nd neighbour clusters could not be reliably obtained due to interaction across the periodic boundaries. All cluster configurations yielded a negative binding energy and are unstable in the *fcc*-Ni lattice.

It is worth mentioning that the binding energies for two Re nearest neighbours and for a 4-atom nearest neighbour cluster are in strong disagreement with results obtained by Zhu *et al* [148] using AEAM potentials. These results discussed in further detail in §4.5.

4.4.3 Database for bond order potentials

A database of the formation energies of several compounds and structures of Ni-X, where X is Ta, W, Re, Ir and Pt, was created. This was done for several reasons:

1. The energy of formation of compounds rich in nickel will suggest whether an ordering (or clustering) reaction will take place at low solute concentrations.
2. The energy of formation of all the compounds can be used to parameterise the bond-order potentials which are being developed at the University of Oxford by Pettifor *et al* within the same EPSRC research consortium.

The formation energy, ΔE_f , of the Ni_mX_n compound can be obtained using Equation 4.3.

$$\Delta E_f^{\text{Ni}_m\text{X}_n} = E_{\text{tot}}^{\text{Ni}_m\text{X}_n} - \left(\frac{m}{m+n} \cdot E_{\text{tot}}^{\text{Ni}} + \frac{n}{m+n} \cdot E_{\text{tot}}^{\text{X}} \right) \quad (4.3)$$

In Equation 4.3, m and n are the numbers of Ni and solute atoms respectively, $E_{\text{tot}}^{\text{Ni}_m\text{X}_n}$ is the total energy of the compound (in eV/atom) and $E_{\text{tot}}^{\text{Ni}}$ and $E_{\text{tot}}^{\text{X}}$ are the total energies of the reference pure structures (in eV/atom).

The results for the Ni-Ta, Ni-W, Ni-Ir and Ni-Pt systems are shown in Figure 4.9. It can be observed that the formation energies of the different compounds qualitatively follows the analytic rectangular band model formulated by Pettifor [93]. The analytic

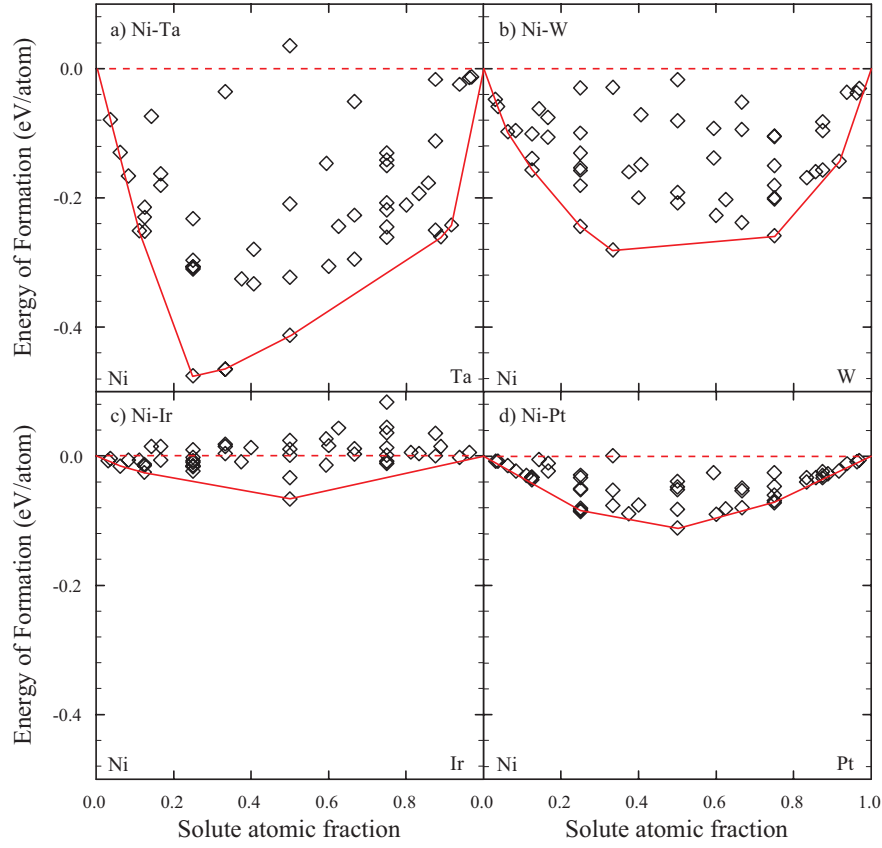


Figure 4.9: Formation energies of several crystal structures of Ni-Ta, Ni-W, Ni-Ir and Ni-Pt.

rectangular band model predicts that the heat of formation of an intermetallic is given by Equation 4.4.

$$\Delta H_f = f(\bar{N}) \cdot (\Delta N)^2 \quad (4.4)$$

In Equation 4.4, $\bar{N}$ is the average band filling of the intermetallic and ΔN is the difference in the number of electrons associated with the A and B atoms in the intermetallic [93, 94]. In other words, the energies of formation of intermetallics across the Ni-Ta system should be lower than the energies of formation of intermetallics across the Ni-Pt system. It appears from the results shown in Figure 4.9 that some of the intermetallics in the Ni-Ta and Ni-W systems have very low energies of formation, suggesting that several ordering reactions may occur in those systems. Therefore several intermetallics may be thermodynamically stable in the Ni-Ta and Ni-W systems – see Figure C.3 and Figure C.4. It follows from the above that the Ni-Ir and Ni-Pt

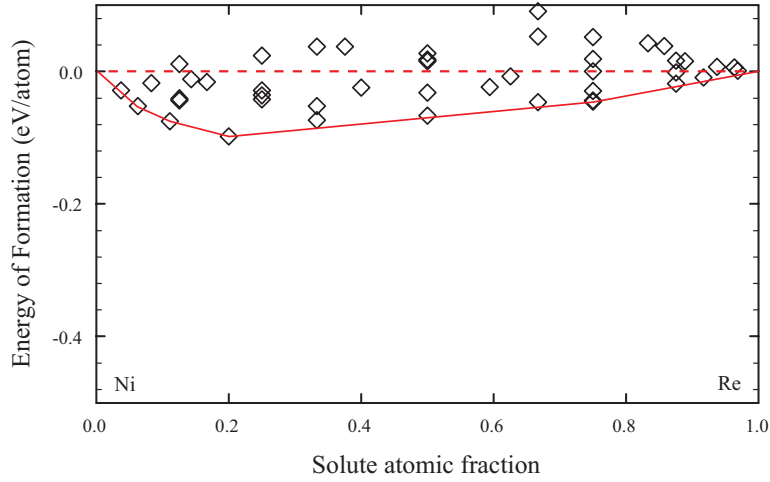


Figure 4.10: Formation energies of several crystal structures of Ni-Re.

systems are expected not to have stable intermetallics – see Figure C.6 and Figure C.7.

The formation energies of several intermetallics of the Ni-Re system are shown in Figure 4.10. Since Re has a lower band filling than Ir, the formation energies of the Ni-Re intermetallics will be in general lower than those of the Ni-Ir intermetallics. There are negative energies of formation over the whole range of composition in the Ni-Re system, suggesting that some ordering reactions may take place and that clustering of Re in nickel is unlikely.

4.4.4 Rhenium effect on SFE

Two *fcc* supercells were built by stacking several $\{111\}$ planes following the $\cdots ABC \cdots$ stacking order. While the first supercell was kept as a perfect crystal and consisted of 30 $\{111\}$ planes and 120 atoms, two intrinsic stacking faults were created in the second supercell by shifting the top 15 $\{111\}$ planes by $a/\sqrt{6}$ along the $\langle 112 \rangle$ direction.

The stacking fault energy can be calculated using Equation 4.5 [146].

$$E_{\text{sf}} = \frac{\Delta E}{A} = \frac{E_{\text{tot}}^{\text{w/sf}} - E_{\text{tot}}^{\text{w/o sf}}}{A} \quad (4.5)$$

In Equation 4.5, $E_{\text{tot}}^{\text{w/sf}}$ and $E_{\text{tot}}^{\text{w/o sf}}$ are the total energies of the supercells with and without the stacking faults respectively and A is the surface area of the fault. After relaxing the volume, the xy area of the supercell is $21.253 \text{ \AA}^2$, resulting in a total stacking fault area of $42.505 \text{ \AA}^2$ (two intrinsic stacking faults). The calculated SFE for

pure nickel is $0.0084 \text{ eV}/\text{\AA}^2$, or $135 \text{ mJ}/\text{m}^2$ – in agreement with published experimental and *ab initio* values [29, 146].

Next, the effect of rhenium on the SFE was calculated using the method described by Yu and Wang [146]. A supercell with a single stacking fault was obtained by removing a single $\{111\}$ plane from the middle of the perfect crystal supercell. Therefore, the new supercell consisted of 29 $\{111\}$ planes and 116 atoms. A single rhenium atom was either positioned on the stacking fault (configuration A) or at the edge of the supercell (configuration B). The two supercells were relaxed to obtain the ground state total energy. The effect of the rhenium solute atom on the stacking fault energy was calculated using Equation 4.6 [146].

$$\Delta E_{\text{sf}}^{\text{Re}} = \frac{E_{\text{tot}}^{\text{A}} - E_{\text{tot}}^{\text{B}}}{A} \quad (4.6)$$

In Equation 4.6, $E_{\text{tot}}^{\text{A}}$ and $E_{\text{tot}}^{\text{B}}$ are the total energies configuration A and B respectively. The reduction in total energy per unit area of stacking fault of the supercell is $-0.0019 \text{ eV}/\text{\AA}^2$, or $-31 \text{ mJ}/\text{m}^2$ which is 25 % greater than the value obtained by Yu and Wang [146]. Such a discrepancy would be expected since the concentration of rhenium on the stacking fault layer is 25 % in the current work compared to 8.3 % in the work of Yu and Wang [146]. Furthermore, the distance between the rhenium atom and the stacking fault layer in the current work is $\sim 28 \text{\AA}$ whereas it is only $\sim 12 \text{\AA}$ in the work of Yu and Wang [146]. Despite this discrepancy, both the current work and the work of Yu and Wang [146] confirm that Re lowers the SFE of nickel. However, it must be pointed out that other elements, such as Cr, Mo, Ru and W produce a similar effect on the SFE of pure nickel [146].

4.4.5 Rhenium versus tungsten

To try and explain the rhenium-effect, it appears necessary to investigate differences in behaviour between rhenium and tungsten at the atomic scale. We have seen that rhenium clusters in the γ phase, the rhenium enrichment near the γ/γ' interfaces and the rhenium effect on the SFE of the γ phase cannot be the underlying cause of the rhenium-effect. Assuming that slow diffusion may not be the only explanation for the

extraordinary strengthening effect of rhenium, then the cause of the rhenium-effect should be sought elsewhere.

As introduced in §1.4, deformation in the γ phase occurs with the glide of edge dislocations. These dislocations glide by nucleating a pair of kinks and by propagating these kinks along the dislocation line. Each atom poses an energy barrier to kink propagation. The stable configuration at the bottom of the barrier, before the jump, will consist of a near-bulk situation with the given atom in a 12-coordinated position. The unstable configuration at the top of the barrier will consist of a disordered situation with the given atom being under-coordinated. The configuration will then proceed to the stable state again. The movement of the kink will require bond breakage before the barrier and bond reformation after the barrier. It follows that a single solute atom with stronger bonds compared to those of the host lattice will result in a larger energy barrier.

If true, this theory would imply that W and Re, which are very similar in size, electronic structure and bond strength, would have a similar effect when used as solute strengtheners in the γ phase. Yet, rhenium is thought to improve creep properties substantially more than tungsten does, suggesting that other factors play a role in increasing the energy barrier. A possible hypothesis is that rhenium, due to its native *hcp* crystal structure (similar to *fcc*, 12-coordinated), may stabilise the bottom of the barrier (which is 12-coordinated). On the other hand, tungsten, due to its native *bcc* crystal structure (8-coordinated), may stabilise the under-coordinated top of the barrier thereby lowering the energy difference comparatively to rhenium.

It follows that a Re solute atom must be more stable than a W solute atom in *fcc*-Ni while a W solute atom should be more stable than a Re solute atom in a hypothetical *bcc*-Ni lattice. To investigate this, DFT calculations were done to compute the energy differences between different systems as follows. First, *fcc* and *bcc* supercells should be large enough for the interaction between single point defects across the periodic boundary conditions to be negligible. Also, these two supercells should be similar in size. Therefore, as already seen in §4.4.2, a $3 \times 3 \times 3$ *fcc* supercell (108 atoms) will be sufficient and a $4 \times 4 \times 4$ *bcc* supercell (128 atoms) is the obvious choice. The energy difference due to substituting a nickel atom with a solute atom, X, in the *fcc*-Ni lattice

Table 4.4: The calculated values for $\Delta E_X^{struct.}$, $\Delta\Delta E_X^{fcc/bcc}$ and $\Delta\Delta\Delta E_{Re/W}^{fcc/bcc}$.

Solute atom	Structure	$\Delta E_X^{struct.}$ (eV)	$\Delta\Delta E_X^{fcc/bcc}$ (eV)	$\Delta\Delta\Delta E_{Re/W}^{fcc/bcc}$ (eV)
Re	<i>fcc</i>	−7.483	−0.305	−0.095
	<i>bcc</i>	−7.178		
W	<i>fcc</i>	−8.410	−0.210	
	<i>bcc</i>	−8.200		

will be given by Equation 4.7.

$$\Delta E_X^{fcc} = -E^{fcc}(\text{Ni}_{108}) + E^{fcc}(\text{Ni}_{107}\text{X}_1) \quad (4.7)$$

Similarly, the energy difference due to substituting a nickel atom with a solute atom, X, in the *bcc*-Ni lattice will be given by Equation 4.8.

$$\Delta E_X^{bcc} = -E^{bcc}(\text{Ni}_{128}) + E^{bcc}(\text{Ni}_{127}\text{X}_1) \quad (4.8)$$

It follows that, comparatively, the energy difference between a system where the element X is in a *fcc* crystal rather than a *bcc* crystal will be described by Equation 4.9.

$$\Delta\Delta E_X^{fcc/bcc} = \Delta E_X^{fcc} - \Delta E_X^{bcc} \quad (4.9)$$

Therefore, the relative energy between having Re in a *fcc* rather than *bcc* and W in a *fcc* rather than *bcc* will be given by Equation 4.10

$$\Delta\Delta\Delta E_{Re/W}^{fcc/bcc} = \Delta\Delta E_{Re}^{fcc/bcc} - \Delta\Delta E_W^{fcc/bcc} \quad (4.10)$$

If this theory is correct, then $\Delta\Delta E_{Re}^{fcc/bcc} < 0$ while $\Delta\Delta E_W^{fcc/bcc} > 0$ which yields a very strong $\Delta\Delta\Delta E_{Re/W}^{fcc/bcc} \ll 0$. If also $\Delta\Delta E_W^{fcc/bcc} < 0$, then it is still expected that $\Delta\Delta\Delta E_{Re/W}^{fcc/bcc} < 0$. In other words, rhenium is expected to stabilise *fcc*-Ni relative to *bcc*-Ni more when compared to tungsten.

The results of this set of calculations are shown in Table 4.4. The substitution of Ni for both a Re and W atoms stabilises the *fcc*-Ni more than the *bcc*-Ni structure and $\Delta\Delta E_X^{fcc/bcc}$ is -0.305 eV and -0.210 eV for Re and W respectively. When comparing

these values, it can be observed that $\Delta\Delta E_{\text{Re/W}}^{\text{fcc/bcc}} = -0.095 \text{ eV}$, suggesting that Re, compared to W, would stabilise the *fcc*-Ni configuration more.

4.5 DFT and the rhenium-effect

The results discussed in §4.4 are further circumstantial evidence for the conclusions reached in Chapter 2 and Chapter 3. First, similarly to what was observed with EXAFS in Chapter 2 and in the work of Koteski *et al* [54], rhenium produces a small outward relaxation in the nickel lattice – the smallest amongst all the elements in the 5d row of transition metals. The distance between a rhenium atom and its shell of nearest neighbours is only $\sim 0.3\%$ longer than the standard distance between two nearest neighbour nickel atoms. Wang *et al* [128] also reached the same conclusions using DFT.

Second, DFT results suggest that rhenium does not form clusters in the *fcc*-Ni lattice: a binding energy of -0.41 eV between two neighbouring rhenium atoms means that these would repel each other to lower the total energy of the system. A negative binding energy for higher order neighbour pairs, as well as for small clusters of 3 or more rhenium atoms, help build a stronger case that rhenium does not form clusters in nickel superalloys, confirming the work presented in Chapter 2 and Chapter 3.

These results are in strong disagreement with the work of Zhu *et al* [148]. Zhu *et al* used analytic embedded atom method (AEAM) potentials [46] which have been parameterised using functions fitted to some properties obtained from DFT calculations, however:

1. Calculations made with EAM potentials are, by design, less reliable than *ab initio* calculations. For example, EAM potentials fitted to the Ni_3Re system may be very reliable for Ni_3Re and lead to the wrong results when applied to study other phases.
2. Zhu *et al* do not provide any information about which DFT calculations were used to parameterise the potentials. There are no details explaining which properties and structures were used in the parametrisation.

3. Zhu *et al* validate their potential only by showing agreement with DFT calculations of the $L1_2$ -Ni₃Re system, which may be one of the few structures – if not the only structure – used in the parametrisation of the potential.

The results of Zhu *et al* should therefore be assessed carefully. Their calculations showed that substituting a Re atom in *fcc*-Ni (γ phase) yields a decrease in total energy of 2.38 eV, while the total energy of the $L1_2$ -Ni₃Al (γ' phase) system decreases by 2.47 eV and 3.62 eV when a rhenium atom is placed on the nickel and aluminum sublattice respectively. From these values, Zhu *et al* concluded that rhenium stabilises both the γ and γ' phase and that rhenium has a preference for the Al sublattice in the γ' phase [148]. These conclusions are speculative, since it appears that no reference energy for Re was taken into account. Furthermore, according to the present work and the work of Wang *et al* [128], the substitution of a Ni atom with a Re atom in *fcc*-Ni should result in a reduction in total energy of ~ 7 eV, three times the value published by Zhu *et al* [148].

Focussing on the rhenium substitution in the γ phase, Zhu *et al* [148] obtained an outward relaxation of 4.09 % of the first shell of nearest neighbours – an unexpectedly large figure which does not agree with the current and published work [54, 128]. Zhu *et al* also studied the clustering of rhenium in the γ phase by obtaining the total energies of several $40 \times 40 \times 40$ supercells (256,000 atoms) containing from 2 to 225 rhenium atoms in both dispersed and clustered configurations [148]. The difference between the total energies of the supercells with two clustered and two dispersed rhenium atoms respectively, $\Delta E = E_{\text{clust.}} - E_{\text{disp.}}$, is simply the negative of the binding energy between two rhenium atoms, so $\Delta E = -E_{\text{bind.}}^{\text{Re-Re}}$.

The binding energy between two nearest neighbouring rhenium atoms, as calculated by Zhu *et al*, is 0.27 eV [148]. Zhu *et al* [148] also calculated that the binding energy of a 4-atom cluster is 1.17 eV. In other words, according to these results, rhenium atoms would cluster in the *fcc*-Ni lattice. This is in strong disagreement with the present work, since DFT predicts a -0.41 eV and -1.64 eV binding energy for the 2- and 4-atom cluster respectively. The study continues by defining the clustering energy, $E_c = \Delta E / N_{\text{Re}}$, and by suggesting that the clustering energy plateaus at the minimum

cluster size. Zhu *et al* conclude that the minimum size of rhenium clusters in the *fcc*-Ni lattice would be 12.2 Å in diameter, or 43 atoms [148].

The results shown in §4.4, supported by the work presented in Chapter 2 and Chapter 3, and supported by the work of Koteski *et al* [54] and Wang *et al* [128], make a strong case that:

1. rhenium produces small relaxations in the *fcc*-Ni lattice, smaller than any other element in the 5d row of transition metals, and
2. rhenium does not form clusters in the *fcc*-Ni lattice, and certainly no clusters made of 43 atoms, which would be visible in the atom probe analysis.

Finally, the results presented in §4.4.4 confirm that Re lowers the SFE of pure nickel by 18-23 % when present at a concentration of 8-25 at.% on the stacking fault plane, in agreement with the literature [146]. However, it appears that such effect on SFE is comparable to that of other solute atoms such as Cr, Mo, Ru and W. Furthermore, it should also be considered that the SFE of the γ phase of nickel based superalloys has been experimentally shown to be 20-30 mJ/m² [29, 100], much lower than the SFE of pure nickel (130 mJ/m²). Such a reduction to the SFE of pure Ni can only be explained by considering that all solute elements, and particularly Cr, Mo, Ru, W and Re, contribute to lowering the SFE of the γ phase.

Conclusions

IN THE PRESENT WORK possible mechanisms underlying the rhenium-effect have been explored using a variety of methods. Extended X-ray Absorption Fine Structure (EXAFS), Atom Probe Tomography (APT) and Density Functional Theory (DFT) have been adopted to study the distribution of rhenium in the γ phase of nickel based superalloys and the atomic scale phenomena resulting from small rhenium additions to nickel based superalloys.

5.1 Clustering in the γ phase

Since 1986, the theory of rhenium clustering in the γ phase has been dominant in explaining the extraordinary strengthening effect of rhenium in nickel based superalloys. The theory is solely based upon results obtained with the atom probe. In 1986, Blavette *et al* [12, 13] used ladder diagrams (or cumulative profiles) to examine data obtained from a 1DAP. Small discontinuities in these ladder diagrams were considered proof of rhenium clustering in nickel based superalloys. Adopting the same method, similar conclusions were reached by Wanderka *et al* [127]. In 2002, Rüsing *et al* [109] used a 1D adaptation of the binomial distribution method to show that rhenium may form clusters in a model nickel based superalloy. Part of the scientific community still considers clustering as the only valid explanation for the strengthening effect of rhenium [11, 133], citing the seminal studies by Blavette *et al* [12, 13]. Recently, Zhu *et al* [148] used classical MD to support the rhenium clustering theory, however the work

presented sheds little light on the parametrisation of the EAM potentials used for their simulations, which renders their work unreliable. All these studies claim that rhenium clusters $> 1\text{-}1.2\text{ nm}$ should be present in the γ phase of nickel based superalloys.

In the current work, it has been shown that:

1. APT and EXAFS show that rhenium does not form clusters when added to nickel at concentrations similar to the usual rhenium content in the γ phase of nickel based superalloys. The same behaviour is observed across the 5d row of transition metals: Ta, W, Ir and Pt also do not form clusters in nickel.
2. DFT modelling predicts a negative binding energy between two, three and four rhenium atoms when positioned as first and second nearest neighbours in the nickel *fcc* lattice. This is in strong disagreement with the work of Zhu *et al* [148], in which classical MD leads to different results.
3. APT shows that rhenium does not form clusters in the γ phase CMSX-4, a commercial nickel based superalloy. Several 3D datasets obtained from crept and uncrept specimens with a state-of-the-art LEAP were analysed using the maximum separation method to show that rhenium clusters are not present in the γ phase of nickel based superalloys.

Therefore, rhenium is expected to be randomly distributed in the γ phase of nickel based superalloys and no clusters $\sim 1\text{ nm}$ are expected to form according to EXAFS, APT and DFT. The clustering of rhenium cannot be the mechanism underlying the rhenium-effect.

5.2 Enrichment near γ/γ' interfaces

The second theory to explain the rhenium-effect, introduced by Warren *et al* [131], stipulates that the rhenium enrichment close to the γ/γ' interfaces plays a role in the strengthening effect of rhenium additions in nickel based superalloys. Warren *et al* suggested that a larger content of rhenium at the interfaces would result in a higher lattice misfit and hinder the entering of dislocations in the γ' phase. It has also been suggested that a higher – more negative – lattice misfit would slow down

rafting processes and retard the onset of tertiary creep [29, 134, 39]. This theory is also supported by the work of Zhu *et al* [148] in which classical MD simulations were adopted to show a high amount of lattice distortion resulting from adding rhenium to the nickel lattice.

In the current work, it has been shown that:

1. The enrichment of rhenium near the γ/γ' interfaces forms upon cooling from service temperature, as the γ' phase becomes more stable and the primary γ' precipitates grow, expelling rhenium in the γ phase. These conclusions are strongly supported by the comparison of APT data of solute concentration across the γ/γ' interfaces with phase field simulations which show that the ‘bow wave’ observed ahead of the interface is compatible with a diffusion profile.
2. The effect of rhenium on the lattice parameter of the γ phase, and therefore on the lattice misfit between the γ and γ' phases, is less than what generally assumed in some of the literature [133, 148, 131]. DFT calculations as well as the EXAFS analysis univocally show that Re–Ni interatomic distances are only $\sim 0.5\%$ longer than Ni–Ni interatomic distances, in agreement with the work of Koteski *et al* [54] and Wang *et al* [128]. Other elements, particularly W, have a much stronger effect on the lattice parameter of the γ phase.

It follows from the above that a higher concentration of rhenium near the γ/γ' interfaces cannot explain the rhenium-effect since such enrichment is not present at service temperature and only appears at room temperature, after components cool down. Furthermore, it is important to recognise that rhenium does not generate strong distortions in the lattice and that other elements, such as W, have a stronger effect on the lattice parameter of *fcc*-Ni. Undoubtedly, rhenium affects the lattice misfit between the γ and γ' phases, but the lattice parameter of the two phases also depends on all the other elements added to nickel based superalloys and the fine balance between all the solute elements yields the correct misfit which results in the best creep properties.

5.3 Stacking Fault Energy

The third theory formulated to explain the origin of the rhenium-effect was based on the concept that a lower SFE would result in the two Shockley partial dislocations being spaced further apart. This, in turn, would make it harder for the full edge dislocation to climb to another plane, since both Shockley partial dislocations would need to meet locally in order to climb. If rhenium is the main element responsible for the lowering of the SFE of the γ phase of nickel based superalloys, then this could help to explain the rhenium-effect. Some work in this area was done by Rae *et al* [100], who suggested that the simultaneous addition of Re and Co would lower the SFE enough to justify the rhenium-effect.

In the current work, it has been shown that rhenium is expected to reduce the SFE of pure Ni by 18-23 % when present at concentrations of 8-25 at.% on the stacking fault plane. These results are in agreement with the work of Yu and Wang [146]. Furthermore, the work of Yu and Wang [146] shows that the effect of rhenium on the SFE of pure nickel is comparable to other elements such as Cr, Mo, Ru and W. It has also been shown that whereas the SFE of pure nickel is 130 ± 10 mJ/m², the SFE of the γ phase of nickel based superalloys is usually 25 ± 5 mJ/m². Therefore, alloying with elements such as Cr, Mo, Ru, W and Re has a major impact on the SFE of the γ phase. However, this does not explain yet why rhenium has a particularly strong creep strengthening effect when compared to other elements.

5.4 Mechanisms underlying the rhenium-effect

Finally, some conclusions can be drawn as to what mechanisms cause the rhenium-effect. It has been conclusively shown in this work that the clustering of rhenium in the γ phase, the rhenium enrichment close to the γ/γ' interfaces and the effect of rhenium on the SFE of the γ phase cannot explain why rhenium improves creep properties of nickel based superalloys compared to other solute elements. Therefore, the reason for the rhenium-effect must be sought for elsewhere. It is important to consider the following facts:

1. Rhenium strongly partitions to the γ phase of nickel superalloys. Adding rhenium at a concentration of 1 at.% to nickel based superalloys results in a rhenium concentration of the γ phase of 3-4 at.%. Therefore, rhenium partitions to the γ phase much more strongly than any other element usually added to nickel based superalloys.
2. The majority of creep life is spent at intermediate strains and temperatures, where tertiary creep deformation is dominant. In this stage, deformation occurs by dislocations sweeping through the γ phase without entering the primary γ' precipitates. Therefore, rhenium strategically partitions to the phase with the highest dislocation activity.
3. Rhenium is the slowest diffusing element amongst all elements usually added to nickel based superalloys [36, 45]. Therefore, rhenium is expected to slow down all diffusion-controlled deformation processes.

To conclude, it can be deduced that the so-called rhenium-effect originates from the fact that small additions of rhenium to the bulk concentration of nickel based superalloys are enough to considerably increase the rhenium concentration in the γ phase, so that rhenium in the γ phase is present at concentrations similar to tungsten. Once in the tertiary creep regime, it is believed that single atoms of rhenium would provide enough pinning forces to slow down dislocations gliding in the γ phase and climbing around γ' precipitates. However, further detailed experiments and modelling will be required to put these ideas onto a firm quantitative basis.

5.5 Future work

Some further work is necessary in order to pinpoint the causes of the rhenium-effect in an irrefutable manner. It is still unclear whether rhenium has an extraordinary creep strengthening effect when compared to tungsten. In other words, rhenium and tungsten may have the same effect on creep resistance, but rhenium is much more effective simply because it strongly partitions to the γ phase, where most of the dislocation activity occurs.

Experiments should be done to test the effect of Re and W on creep resistance. Some binary Ni-Re and Ni-W single-crystal alloys could be cast with different solute concentrations in the range 0.1-4 at.%. These alloys could then be creep tested at 873 K, 1073 K and 1273 K. If single atoms of Re and W act to slow down dislocation activity, then the resulting creep life should increase linearly with solute concentration. Additionally, these tests will yield the precise contribution of Re and W to the creep resistance of the γ phase. The creep resistance of the Ni-Re alloys is expected to be slightly higher due to the lower diffusion coefficient of Re in Ni. Nevertheless, no remarkable differences in creep life are expected. Some further tests could also be done by producing single-crystal Ni-Re-W alloys with equal concentrations of Re and W and a total concentration of solute atoms in the range 1-4 at.% to investigate any coupling between Re and W.

Simulations could also help to understand how rhenium acts to slow down dislocations. First, the movement of an edge dislocation in nickel can be studied to establish how the kink moves and investigate the local coordination at the core of the dislocation. Some preliminary work was done using Molecular Dynamics (MD) with Embedded Atom Method (EAM) potentials for the Ni-Al system [76, 75]. Brommer [16] extended these potentials to the Ni-Al-Re system using the Force Matching Method (FMM) [32]. These potentials were tested to qualitatively show that rhenium exerts some pinning forces on the Shockley partial dislocations. However, no comparison with other elements was possible and no quantitative evaluation of the effect of rhenium on dislocations could be obtained.

Unfortunately, MD with EAM potentials cannot provide an accurate, quantitative evaluation of how rhenium affects dislocation movement, and how rhenium compares to tungsten as a creep strengthener. On the other hand, DFT is unable to simulate a full edge dislocation within reasonable computational times. Therefore, it is necessary to adopt a hybrid simulation technique. Amongst these, Learn-On-The-Fly (LOTF) [24] could be a suitable choice. In LOTF, a large system can be simulated using EAM potentials and DFT can be used to ‘augment’ the potentials in the ‘quantum zone’ at each step of the calculation. This methodology would be able to simulate a full edge dislocation moving in *fcc*-Ni, while retaining high accuracy near the dislocation core,

and provide the final answer to the question at the centre of the present work: why does rhenium improve creep properties in nickel superalloys?

APPENDIX A

Specimens & Samples

THIS PROJECT is based on experiments aiming to gain a better understanding of the behaviour of rhenium compared to other solute atoms. For this reason, two sets of materials were analysed with different techniques. A set of binary Ni-10 wt.%X alloys – where X was taken to be Ta, W, Re, Ir and Pt – were analysed using the LEAP at ORNL and the EXAFS beamline at Daresbury Laboratory in the UK. Additionally, crept and uncrept areas of CMSX-4 single-crystal creep specimens were analysed using the LEAP at ORNL. In this appendix, some reference information is provided to show the amount of data collected with the atom probe and at the beam line.

A.1 Ni-X binary alloy samples

The binary Ni-X alloys were prepared in the form of 400 g ingots using the vacuum induction melting process. Each binary alloy contains 10 wt.% of one of Ta, W, Re, Ir and Pt. The solute concentration was chosen to match the Re concentration in the γ phase of CMSX-4. Re was included as the solute of prime interest, but the other alloying elements, chosen from the 5d row of transition metals, were included to allow a systematic examination across the periodic table. Homogenisation was achieved by annealing the ingots at 1523 K for 7 days in flowing argon [48, 49]. No additional heat treatment was performed and the alloys were allowed to furnace cool.

A.2 CMSX-4 superalloy samples

The CMSX-4 samples were taken from crept and uncrept areas of single-crystal creep specimens used in a previous study by Reed *et al* [106]. These creep specimens were machined from rods 1 cm in diameter obtained by Rolls-Royce plc. Six creep specimens (A, B, C, D, E and F) were creep tested at 1423 K and 100 MPa (tertiary creep regime) for several hundred hours. Testing of specimens A and B was interrupted before rupture at 10 hrs. and 100 hrs. respectively. The remaining specimens – C, D, E and F – were tested until rupture which occurred after 550 hrs., 695 hrs., 1060 hrs. and 1170 hrs. respectively.

Table A.1: List of datasets obtained with the atom probe from the Ni-X binary alloys.

EXAFS – Binary alloys				
Alloy	Edge	Windowed by	Dataset #	Conditions
Ni foil	Ni K-edge	Ni foil	r40668	Non-spinned
Pt foil	Pt L ₃ -edge	Pt foil	r40644	Non-spinned
Ni-Ta	Ni K-edge	Ni foil	r40681	Spinned
		Ni foil	r40683	Spinned
	Ta L ₃ -edge	Ta foil	r40693	Spinned
		Ta foil	r40694	Spinned
Ni-W	Ni K-edge	Ni foil	r40677	Spinned
		Ni foil	r40678	Spinned
	W L ₃ -edge	W foil	r40665	Spinned
		W foil	r40666	Spinned
Ni-Re	Ni K-edge	Ni foil	r40670	Spinned
		Ni foil	r40671	Spinned
	Re L ₃ -edge	Ni-Re	r40657	Spinned
		Ni-Re	r40657	Spinned
		Ni-Re	r40658	Spinned
Ni-Ir	Ni K-edge	Ni foil	r40675	Spinned
		Ni foil	r40676	Spinned
	Ir L ₃ -edge	Ni-Ir	r40661	Spinned
		Ni-Ir	r40662	Spinned
Ni-Pt	Ni K-edge	Ni foil	r40673	Spinned
		Ni foil	r40674	Spinned
	Pt L ₃ -edge	Pt foil	r40647	Spinned
		Pt foil	r40646	Non-spinned

Table A.2: List of datasets obtained with the atom probe from the Ni-X binary alloys.

APT – Binary alloys				
Alloy	Dataset #	Specimen ID	No. of Ions	Description
Ni-Ta	4844	ms7b	42,882	Insufficient data
	4847	ms7br1	13,375,787	
	5115	ms7br2	39,755	Insufficient data
	5118	ms7br3	60,049,363	
Ni-W	4840	ms7a	5,493,555	
	5112	ms7ar1	106,311,331	Failed on voltage stop
	5113	ms7ar1	1	Insufficient data
	5114	ms7ar1	270	Insufficient data
Ni-Re	4826	ms6a	13,567,170	
	4827	ms6b	720,118	Central $\langle 111 \rangle$ pole
	4828	ms6b	3,858,394	
	5011	ms6ar1	8,255,777	Tip is blunt
	5119	ms6ar2	779,703	Insufficient data
	5120	ms6br1	26,148,284	
Ni-Pt	4834	ms6d	6,145,172	
	4835	ms6c	5,658,174	
	5116	ms6cr1	25,915,028	
	5117	ms6dr1	50,547,215	
Ni-Ir	4838	ms6e	4,740,172	
	4839	ms6f	3,641,402	
	4841	ms6er1	1,560,103	
	4842	ms6fr1	24,510,624	Tip broke

Table A.3: List of datasets obtained with the atom probe from sample C of CMSX-4, crept for 550 hours.

APT – CMSX-4 – Sample C				
Orientation	Dataset #	Specimen ID	No. of Ions	Description
Longitudinal	1502	lp5br7	9,081,655	All γ'
	2286	lp5br9	13,056,195	γ/γ' and sec. γ'
Transverse	1590	lp4br5	9,543,416	All γ'
	1641	lp4br6	3,813,857	All γ'
	1643	lp4br6	2,152,439	All γ'
	2222	lp4br7	4,672,272	
	2302	lp4br9	7,075,337	
	2320	ko3br3	5,240,612	Ruptures
	2325	ko3br4	1,020,162	
	2337	ko3br6	1,180,331	
	2291	ko3c	2,770,685	Ruptures
Uncrept	2300	ko3cr1	8,054,406	
	2314	ko3d	14,757,886	γ/γ' interface
	2317	ko3e	21,632,376	
	3839	lp7br3	106,000,000	

Table A.4: List of datasets obtained with the atom probe from sample D of CMSX-4, crept for 695 hours.

APT – CMSX-4 – Sample D				
Orientation	Dataset #	Specimen ID	No. of Ions	Description
Longitudinal	1303	lp5ar1	1,894,005	All γ'
	1493	lp6ar6	2,783,574	γ' with γ at the edge
	1498	lp6ar7	7,443,153	All γ'
	4220	lp6br2	5,748,222	γ/γ' interface – very nice
	4244	lp6br4	4,540,019	Ruptures
Transverse	1504	lp9br7	2,318,602	γ with sec. γ'
	1505	lp9br7	2,108,661	γ with sec. γ'
	4221	lp9br11	43,311,180	All γ'
Uncrept	1322	lp7ar1	1,844,525	All γ'
	1326	lp8ar1	30,159,473	$\gamma'/\gamma/\gamma'$ with sec. γ'
	2145	lp8ar3	11,566,683	γ/γ' and sec. γ'
	4578	lp8ar7	28,689,826	
	4579	lp8ar7	36,959,900	

Table A.5: List of datasets obtained with the atom probe from sample E of CMSX-4, crept for 1060 hours.

APT – CMSX-4 – Sample E				
Orientation	Dataset #	Specimen ID	No. of Ions	Description
Longitudinal	1681	lp6cr2	15,088,927	γ/γ' with sec. γ' – very nice
	4228	lp5cr7	18,333,630	All γ'
	4235	lp5cr8	4,882,172	All γ'
	4245	lp5cr10	19,830,130	
Transverse	1684	lp9cr2	9,396,032	γ with sec. γ'
	2285	ko3a	13,275,738	
	4231	lp9cr10	3,351,735	Ruptures
	4242	lp9cr13	8,049,645	
	4247	ko3ar6	19,056,959	
	4250	ko3ar7	2,296,755	
Uncrept	1660	lp7c	518,632	All γ'
	1682	lp7cr1	2,727,790	γ/γ'
	2103	lp7cr2	1,009,121	All γ' – atomic planes
	2108	lp7cr2	1,112,865	All γ'
	4227	lp7cr4	68,853,320	$\gamma'/\gamma/\gamma'$

Table A.6: List of datasets obtained with the atom probe from sample F of CMSX-4, crept for 1170 hours.

APT – CMSX-4 – Sample F				
Orientation	Dataset #	Specimen ID	No. of Ions	Description
Longitudinal	2120	lp4dr6	1, 173, 717	All γ'
	2242	lp4dr8	2, 250, 493	
	4236	lp4dr11	4, 049, 621	All γ'
	4243	lp4dr12	3, 709, 302	
	4246	lp5dr5	11, 922, 430	
	4253	lp5dr6	16, 235, 271	
Transverse	4233	ac9c	6, 913, 660	
	4238	ac9cr1	11, 238, 557	
	4248	ac9cr3	18, 615, 061	All γ
	4322	ac9cr5	1, 867, 791	
Uncrept	1615	lp7d	3, 480, 376	All γ'
	1663	lp7dr2	1, 237, 195	All γ'
	4230	lp7dr6	94, 953, 224	γ/γ' with sec. γ' – very nice

APPENDIX B

APT_o



IN THE PRESENT WORK, a large amount of data was collected with the LEAP at ORNL. Most of the data analysis was carried out by feeding the collected datasets either to a code to perform the maximum-separation friends-of-friends analysis or to a code to randomise the identities of all the ions in each dataset. It was necessary, however, to be able to view and interact with the datasets in order to check for artefacts, perform concentration analysis and select regions of interest. Usually, these tasks are performed with IVAS, a software sold by Imago Scientific Instruments – the company founded by Professor Thomas F. Kelly.

IVAS is software written in Java that allows to reconstruct atom probe datasets (*.pos files) from the raw data obtained with the atom probe (*.rhit files). Furthermore, IVAS allows to analyse the *.pos files, perform different types of concentration analysis, examine the mass-to-charge-state ratio spectra, along with many other features. The license for the IVAS software costs GBP3000-5000 – deemed too expensive for the current project. Access to the software was granted while at ORNL and for a brief time at Imperial College London, but most of the work had to be carried out without the use of IVAS.

APT_o was developed by the author of this thesis in order to avoid purchasing the IVAS license. APT_o, which stands for ‘Atom Probe Tomography, open-source’, is open-source software designed to view, explore and analyse data obtained from the 3D atom probe. It is distributed completely free, under the GPL license, and it is available on Sourceforge [137]. APT_o was developed according to the following guidelines:

1. it had to be free and open-source (IVAS is not),
2. it had to be completely cross-platform and work on Windows, Mac OS and Linux (IVAS only works on Windows),
3. it had to require low memory in order to be used on most machines,
4. it had to be graphically very efficient in order to be able to view the largest datasets on a laptop,
5. it had to support the use of multiple screens (IVAS does not),
6. it had to be well structured so that other people could modify the source code easily, and
7. it had to be easy to install and use.

For these reasons, APTo was written in C++ and great care was taken to make sure every bit of code was compatible with all operating systems. The user interface was handled by Qt [140], a cross-platform library that allows the creation of multiple *dock widgets* which can either sit within the main window or be dragged to the second monitor. The 3D graphics is handled by OpenGL [139], via the libQGLViewer libraries [138].

The most challenging task was to make the graphics fast enough so that tens of millions of atoms could successfully be viewed in 3D on a standard desktop computer. This was done by populating single 1Ds array with all the coordinates of the atoms with a particular mass-to-charge-state ratio and using `glDrawArrays()` to draw the data on the screen in an efficient manner. Furthermore, two optional functionalities can be selected by the user in order to reduce the amount of computational power required to draw the graphics. The ‘Fastdraw’ option reduces the amount of ions displayed on the screen when the user interacts with the 3D rendering window so that the user can move and rotate the object and zoom more rapidly. The ‘Level of Detail’ option progressively reduces the amount of ions displayed on the screen as the user zooms out, so that only the necessary ions are displayed.

APTo can also perform some chemical analysis. The chemical composition of the dataset can be obtained and the mass-to-charge-state ratio spectra can be displayed in a separate *dock widget*, where the user can zoom in and out to examine the fine details of each peak. Peaks on the spectra and ions in the 3D rendering window are colour coded according to the data provided in the *.rng file, a standard format also used by IVAS. In the 3D rendering window, the user can select which elements to display and whether to draw some elements as larger spheres in order to highlight them.

APTo is not intended to be a substitute for IVAS, which has got far more advance features. Instead, it is meant to be used as a tool to view any dataset on any machine, quickly and cheaply. It was also meant to stimulate exchange of open-source code in the atom probe community, which has lacked to the present day. In that it has succeeded and the International Field Emission Society (IFES) plans to launch a website where standard datasets, open-source code and best practices can be shared. Within that framework, APTo would gain a much wider user-base as outsiders will be keen in learning more about atom probe at no extra cost. Since APTo was launched in March 2009 (12 months), its source code or redistributable has been downloaded 125 times, exceeding the expectations of the author.

APPENDIX C

Reference material

IN THIS APPENDIX, some useful information is provided as a reference. A periodic table, highlighting relevant elements is shown in Figure C.1. A list of isotopes and relative abundances is shown in Table C.1. The phase diagrams for Ni-Al, Ni-Ta, Ni-W, Ni-Re, Ni-Ir and Ni-Pt are shown in Figures C.2-C.7.

Note: The subgroup numbers 1-18 were adopted in 1984 by the International Union of Pure and Applied Chemistry. The names of elements 112-118 are the Latin equivalents of those numbers.

Figure C.1: Periodic table of the elements [26].

Table C.1: List of isotopes and their abundance [27].

Isotope	Abundance	Isotope	Abundance	Isotope	Abundance	Isotope	Abundance	Isotope	Abundance
¹ H	99.985	⁵⁴ Fe	5.8	⁹⁶ Ru	5.52	¹³⁶ Ce	0.19	¹⁸⁰ W	0.13
² H	0.015	⁵⁶ Fe	91.72	⁹⁸ Ru	1.88	¹³⁸ Ce	0.25	¹⁸² W	26.3
³ He	0.000137	⁵⁷ Fe	2.2	⁹⁹ Ru	12.7	¹⁴⁰ Ce	88.48	¹⁸³ W	14.3
⁴ He	99.999863	⁵⁸ Fe	0.28	¹⁰⁰ Ru	12.6	¹⁴² Ce	11.08	¹⁸⁴ W	30.67
⁶ Li	7.5	⁵⁵ Mn	100	¹⁰¹ Ru	17.0	¹³⁸ La	0.0902	¹⁸⁶ W	28.6
⁷ Li	92.5	⁵⁸ Ni	68.077	¹⁰² Ru	31.6	¹³⁹ La	99.9098	¹⁸⁴ Os	0.02
⁹ Be	100	⁶⁰ Ni	26.223	¹⁰⁴ Ru	18.7	¹⁴¹ Pr	100	¹⁸⁶ Os	1.58
¹⁰ B	19.9	⁶¹ Ni	1.140	¹⁰² Pd	1.02	¹⁴² Nd	27.13	¹⁸⁷ Os	1.6
¹¹ B	80.1	⁶² Ni	3.634	¹⁰⁴ Pd	11.14	¹⁴³ Nd	12.18	¹⁸⁸ Os	13.3
¹² C	98.90	⁶⁴ Ni	0.926	¹⁰⁵ Pd	22.33	¹⁴⁴ Nd	23.80	¹⁸⁹ Os	16.1
¹³ C	1.10	⁵⁹ Co	100	¹⁰⁶ Pd	27.33	¹⁴⁵ Nd	8.30	¹⁹⁰ Os	26.4
¹⁴ N	99.634	⁶³ Cu	69.17	¹⁰⁸ Pd	26.46	¹⁴⁶ Nd	17.19	¹⁹² Os	41.0
¹⁵ N	0.366	⁶⁵ Cu	30.83	¹¹⁰ Pd	11.72	¹⁴⁸ Nd	5.76	¹⁸⁵ Re	37.40
¹⁶ O	99.762	⁶⁴ Zn	48.6	¹⁰³ Rh	100	¹⁵⁰ Nd	5.64	¹⁸⁷ Re	62.60
¹⁷ O	0.038	⁶⁶ Zn	27.9	¹⁰⁶ Cd	1.25	¹⁴⁴ Sm	3.1	¹⁹⁰ Pt	0.01
¹⁸ O	0.200	⁶⁷ Zn	4.1	¹⁰⁸ Cd	0.89	¹⁴⁷ Sm	15.0	¹⁹² Pt	0.79
¹⁹ F	100	⁶⁸ Zn	18.8	¹¹⁰ Cd	12.49	¹⁴⁸ Sm	11.3	¹⁹⁴ Pt	32.9
²⁰ Ne	90.48	⁷⁰ Zn	0.6	¹¹¹ Cd	12.80	¹⁴⁹ Sm	13.8	¹⁹⁵ Pt	33.8
²¹ Ne	0.27	⁶⁹ Ga	60.108	¹¹² Cd	24.13	¹⁵⁰ Sm	7.4	¹⁹⁶ Pt	25.3
²² Ne	9.25	⁷¹ Ga	39.892	¹¹³ Cd	12.22	¹⁵² Sm	26.7	¹⁹⁸ Pt	7.2
²³ Na	100	⁷² Ge	21.23	¹¹⁴ Cd	28.73	¹⁵⁴ Sm	22.7	¹⁹¹ Ir	37.3
²⁴ Mg	78.99	⁷³ Ge	7.73	¹¹⁶ Cd	7.49	¹⁵¹ Eu	47.8	¹⁹³ Ir	62.7
²⁵ Mg	10.00	⁷⁴ Ge	35.94	¹⁰⁷ Ag	51.839	¹⁵³ Eu	52.2	¹⁹⁶ Hg	0.15
²⁶ Mg	11.01	⁷⁶ Ge	7.44	¹⁰⁹ Ag	48.161	¹⁵² Gd	0.20	¹⁹⁸ Hg	9.97
²⁷ Al	100	⁷⁴ Se	0.89	¹¹² Sn	0.97	¹⁵⁴ Gd	2.18	¹⁹⁹ Hg	16.87
²⁸ Si	92.23	⁷⁶ Se	9.36	¹¹⁴ Sn	0.65	¹⁵⁵ Gd	14.80	²⁰⁰ Hg	23.10
²⁹ Si	4.67	⁷⁷ Se	7.63	¹¹⁵ Sn	0.34	¹⁵⁶ Gd	20.47	²⁰¹ Hg	13.18
³⁰ Si	3.10	⁷⁸ Se	23.78	¹¹⁶ Sn	14.53	¹⁵⁷ Gd	15.65	²⁰² Hg	29.86
³¹ P	100	⁸⁰ Se	49.61	¹¹⁷ Sn	7.68	¹⁵⁸ Gd	24.84	²⁰⁴ Hg	6.87
³² S	95.02	⁸² Se	8.73	¹¹⁸ Sn	24.23	¹⁶⁰ Gd	21.86	¹⁹⁷ Au	100
³³ S	0.75	⁷⁵ As	100	¹¹⁹ Sn	8.59	¹⁵⁶ Dy	0.06	²⁰³ Tl	29.524
³⁴ S	4.21	⁷⁸ Kr	0.35	¹²⁰ Sn	32.59	¹⁵⁸ Dy	0.10	²⁰⁵ Tl	70.476
³⁶ S	0.02	⁸⁰ Kr	2.25	¹²² Sn	4.63	¹⁶⁰ Dy	2.34	²⁰⁴ Pb	1.4
³⁵ Cl	75.77	⁸² Kr	11.6	¹²⁴ Sn	5.79	¹⁶¹ Dy	18.9	²⁰⁶ Pb	24.1
³⁷ Cl	24.23	⁸³ Kr	11.5	¹¹³ In	4.3	¹⁶² Dy	25.5	²⁰⁷ Pb	22.1
³⁶ Ar	0.337	⁸⁴ Kr	57.0	¹¹⁵ In	95.7	¹⁶³ Dy	24.9	²⁰⁸ Pb	52.4
³⁸ Ar	0.063	⁸⁶ Kr	17.3	¹²⁰ Te	0.096	¹⁶⁴ Dy	28.2	²⁰⁹ Bi	100
⁴⁰ Ar	99.600	⁷⁹ Br	50.69	¹²² Te	2.603	¹⁵⁹ Tb	100	²³² Th	100
³⁹ K	93.2581	⁸¹ Br	49.31	¹²³ Te	0.908	¹⁶² Er	0.14	²³⁴ U	0.0055
⁴⁰ K	0.0117	⁸⁴ Sr	0.56	¹²⁴ Te	4.816	¹⁶⁴ Er	1.61	²³⁵ U	0.7200
⁴¹ K	6.7302	⁸⁶ Sr	9.86	¹²⁵ Te	7.139	¹⁶⁶ Er	33.6	²³⁸ U	99.2745
⁴⁰ Ca	96.941	⁸⁷ Sr	7.00	¹²⁶ Te	18.95	¹⁶⁷ Er	22.95		
⁴² Ca	0.647	⁸⁸ Sr	82.58	¹²⁸ Te	31.69	¹⁶⁸ Er	26.8		
⁴³ Ca	0.135	⁸⁵ Rb	72.165	¹³⁰ Te	33.80	¹⁷⁰ Er	14.9		
⁴⁴ Ca	2.086	⁸⁷ Rb	27.835	¹²¹ Sb	57.36	¹⁶⁵ Ho	100		
⁴⁶ Ca	0.004	⁸⁹ Y	100	¹²³ Sb	42.64	¹⁶⁸ Yb	0.13		
⁴⁸ Ca	0.187	⁹⁰ Zr	51.45	¹²⁴ Xe	0.10	¹⁷⁰ Yb	3.05		
⁴⁵ Sc	100	⁹¹ Zr	11.22	¹²⁶ Xe	0.09	¹⁷¹ Yb	14.3		
⁴⁶ Ti	8.0	⁹² Zr	17.15	¹²⁸ Xe	1.91	¹⁷² Yb	21.9		
⁴⁷ Ti	7.3	⁹⁴ Zr	17.38	¹²⁹ Xe	26.4	¹⁷³ Yb	16.12		
⁴⁸ Ti	73.8	⁹⁶ Zr	2.80	¹³⁰ Xe	4.1	¹⁷⁴ Yb	31.8		
⁴⁹ Ti	5.5	⁹² Mo	14.84	¹³¹ Xe	21.2	¹⁷⁶ Yb	12.7		
⁵⁰ Ti	5.4	⁹⁴ Mo	9.25	¹³² Xe	26.9	¹⁶⁹ Tm	100		
⁵⁰ V	0.250	⁹⁵ Mo	15.92	¹³⁴ Xe	10.4	¹⁷⁴ Hf	0.162		
⁵¹ V	99.750	⁹⁶ Mo	16.68	¹³⁶ Xe	8.9	¹⁷⁶ Hf	5.206		
⁵⁰ Cr	4.345	⁹⁷ Mo	9.55	¹²⁷ I	100	¹⁷⁷ Hf	18.606		
⁵² Cr	83.789	⁹⁸ Mo	24.13	¹³⁰ Ba	0.106	¹⁷⁸ Hf	27.297		
⁵³ Cr	9.501	¹⁰⁰ Mo	9.63	¹³² Ba	0.101	¹⁷⁹ Hf	13.629		
⁵⁴ Cr	2.365	⁹³ Nb	100	¹³⁴ Ba	2.417	¹⁸⁰ Hf	35.100		
				¹³⁵ Ba	6.592	¹⁷⁵ Lu	97.41		
				¹³⁶ Ba	7.854	¹⁷⁶ Lu	2.59		
				¹³⁷ Ba	11.23	¹⁸⁰ Ta	0.012		
				¹³⁸ Ba	71.70	¹⁸¹ Ta	99.988		
				¹³³ Cs	100				

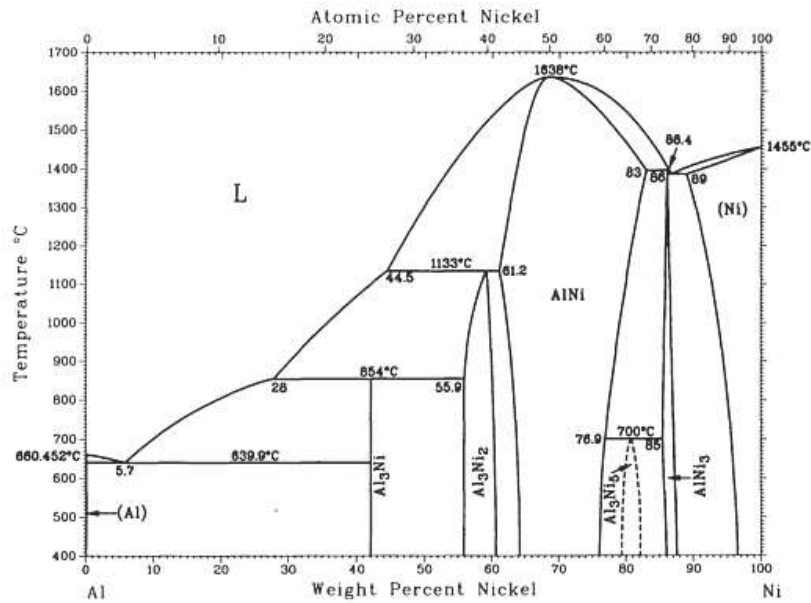


Figure C.2: The Ni-Al phase diagram [1].

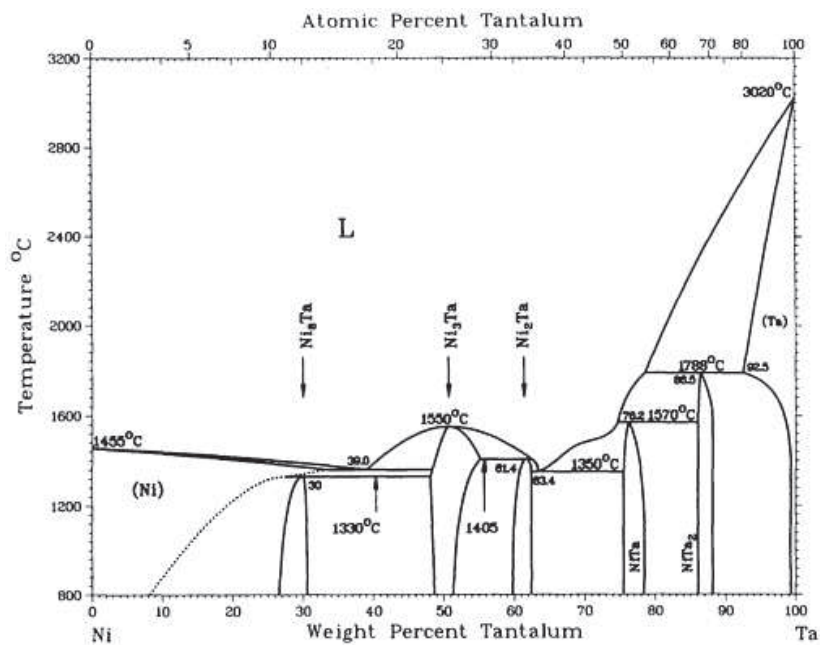


Figure C.3: The Ni-Ta phase diagram [1].

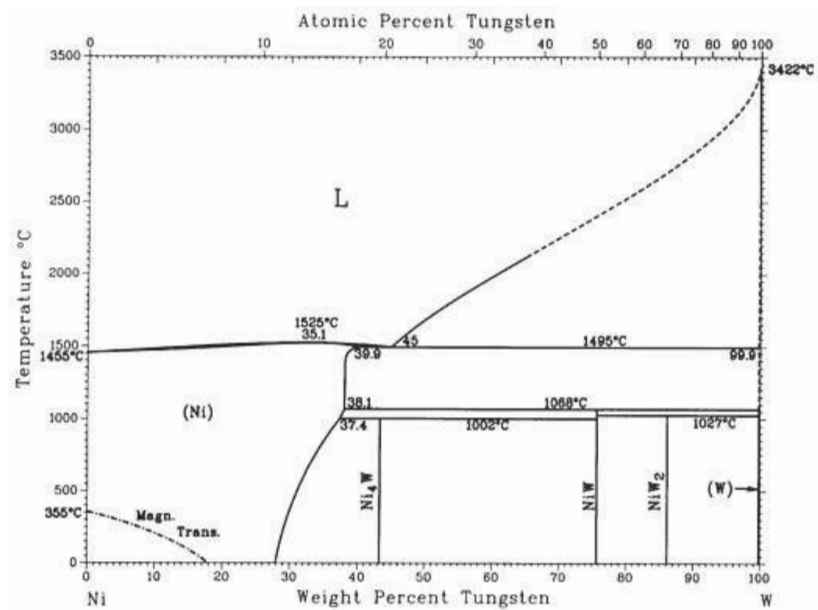


Figure C.4: The Ni-W phase diagram [1].

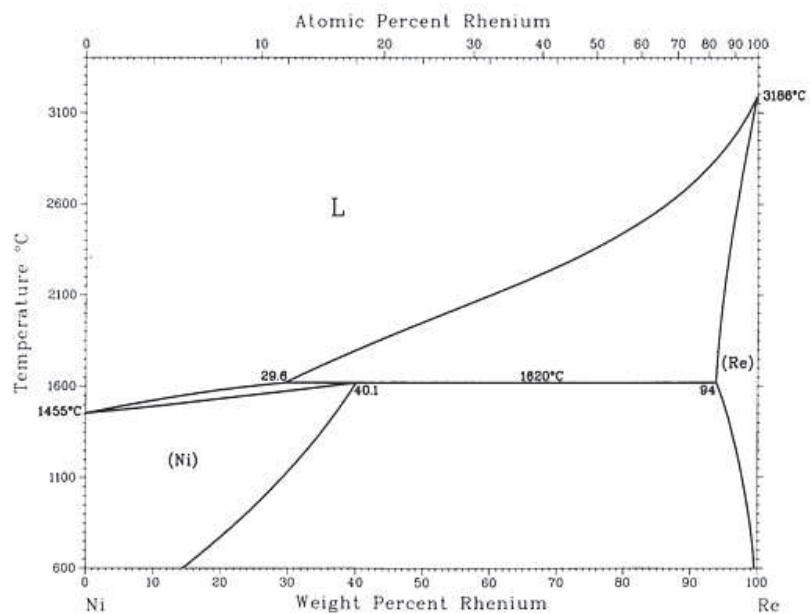


Figure C.5: The Ni-Re phase diagram [1].

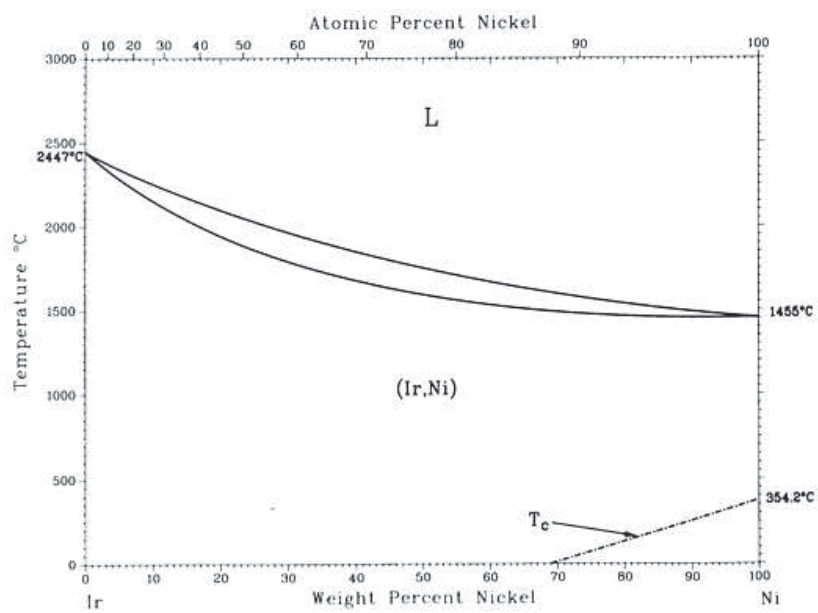


Figure C.6: The Ni-Ir phase diagram [1].

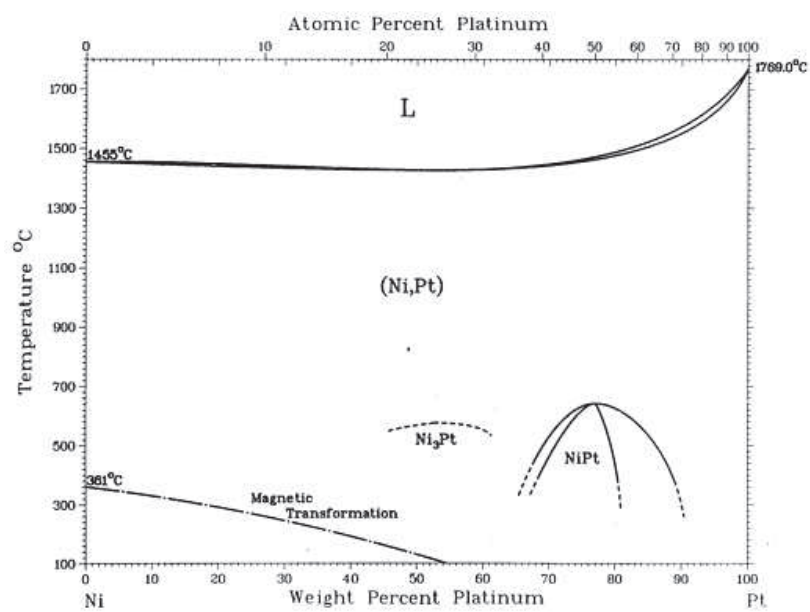


Figure C.7: The Ni-Pt phase diagram [1].

References

- [1] *Alloy phase diagrams*, volume 3 of *ASM Handbook*. 1992.
- [2] *Airplane Flying Handbook*. U.S. Government Printing Office: U.S. Federal Aviation Administration, 2004.
- [3] M. F. Ashby and D. R. H. Jones. *Engineering Materials 1: An introduction to properties, applications and design*. Butterworth-Heinemann, 2005.
- [4] M. Asta. Private Communication, 2007.
- [5] M. Balasubramanian, R. Lyver, J. I. Budnick, and D. M. Pease. Local structural order around dopant atoms in Fe- and Co-doped ternary alloys based on gamma prime Ni₃Al. *Applied Physics Letters*, 71(3):330–332, 1997.
- [6] M. Balasubramanian, R. Lyver, J. I. Budnick, and D. M. Pease. Studies on the local structure of dilute 3d transition metal ternary dopants in L1₂ ordered Ni,Al-based alloys. *Journal de Physique IV*, 7(C2):1043–1045, 1997.
- [7] M. G. Benz. Preparation of clean alloys. In C. L. Briant, editor, *Impurities in Engineering Materials: Impact, Reliability and Control*, pages 31–47. Marcel Dekker Inc., New York, 1999.
- [8] D. Blavette and A. Bostel. FIM atom-probe investigation of the interphase boundary of a nickel-base superalloy. *Surface Science*, 177(2):994–998, 1986.
- [9] D. Blavette, A. Bostel, and M. Bouet. Partitioning of alloying elements in a nickel-base superalloy containing Nb and Mo – An atom-probe study. *Journal de Physique*, 45(NC9):379–384, 1984.
- [10] D. Blavette, A. Bostel, and J. M. Sarrau. Atom-probe microanalysis of a nickel-base superalloy. *Metallurgical and Materials Transactions A*, 16(10):1703–1711, 1985.
- [11] D. Blavette, E. Cadel, C. Pareige, B. Deconihout, and P. Caron. Phase transformation and segregation to lattice defects in Ni-base superalloys. *Microscopy and Microanalysis*, 13(6):464–483, 2007.
- [12] D. Blavette, P. Caron, and T. Khan. An atom probe investigation of the role of rhenium additions in improving creep resistance of Ni-base superalloys. *Scripta Metallurgica*, 20(10):1395–1400, 1986.

- [13] D. Blavette, P. Caron, and T. Khan. An atom-probe study of some fine-scale microstructural features in Ni-based single crystal superalloys. In S. Reichman, D. N. Duhl, G. Maurer, S. Antolovich, and C. Lund, editors, *Superalloys 1988*, pages 305–314. The Minerals, Metals and Materials Society, Warrendale, PA, USA, 1988.
- [14] P. E. Blöchl. Projector augmented-wave method. *Physical Review B*, 50(24):17953–17979, 1994.
- [15] L. Brillouin. *Science and Information Theory*. Academic Press, New York, 1962.
- [16] P. Brommer. A potential for the Ni-Al-Re system based on the Mishin Ni-Al potential. *Unsubmitted*.
- [17] S. Cammelli, C. Degueldre, G. Kuri, and J. Bertsch. Study of a neutron irradiated reactor pressure vessel steel by X-ray absorption spectroscopy. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 266(21):4775–4781, 2008.
- [18] S. Cammelli, C. Degueldre, G. Kuri, J. Bertsch, D. Lützenkirchen-Hecht, and R. Frahm. Study of atomic clusters in neutron irradiated reactor pressure vessel surveillance samples by extended X-ray absorption fine spectroscopy. *Journal of Nuclear Materials*, 385(2):319–324, 2009.
- [19] C. E. Campbell, W. J. Boettinger, and U. R. Kattner. Development of a diffusion mobility database for Ni-base superalloys. *Acta Materialia*, 50(4):775–792, 2002.
- [20] A. V. Ceguerra, M. P. Moody, L. T. Stephenson, and S. P. Ringer. 3D Markov Random Field for nanocluster analysis in atom probe tomography data. *Unpublished*, 2008.
- [21] D. M. Ceperley and B. J. Alder. Ground-state of electron-gas by a stochastic method. *Physical Review Letters*, 45(7):566–569, 1980.
- [22] A. Cerezo and L. Davin. Aspects of the observation of clusters in the 3-dimensional atom probe. *Surface and Interface Analysis*, 39(2-3):184–188, 2007.
- [23] J. W. Christian. *The theory of transformations in metals and alloys*. Pergamon, 2002.
- [24] G. Csanyi, T. Albaret, M. C. Payne, and A. De Vita. “Learn on the fly”: A hybrid classical and quantum-mechanical molecular dynamics simulation. *Physical Review Letters*, 93(17):175503, 2004.
- [25] N. A. Cumpsty. *Jet propulsion: A simple guide to the aerodynamic and thermodynamic design and performance of jet engines*. Cambridge University Press, 2003.
- [26] Michael Dayah. *Periodic table of elements*. <http://www.ptable.com>, 1997.
- [27] P. De Bièvre and P. D. P. Taylor. Table of isotopic compositions of the elements. *International Journal of Mass Spectrometry and Ion Processes*, 123(2):149–166, 1993.

- [28] K. M. Delargy, A. P. Beaven, M. K. Miller, and G. D. W. Smith. Progress with FIM and atom-probe investigations of nickel-based super-alloys. *Ultramicroscopy*, 4(3):385–385, 1979.
- [29] F. Diologent and P. Caron. On the creep behaviour at 1033 K of new generation single-crystal superalloys. *Material Science and Engineering A*, 385(1-2):245–257, 2004.
- [30] J. Eiken, B. Bottger, and I. Steinbach. Multiphase-field approach for multicomponent alloys with extrapolation scheme for numerical application. *Physical Review E*, 73(6):066122, 2006.
- [31] P. Eisenberger and B. Lengeler. Extended x-ray absorption fine structure determinations of coordination numbers - limitations. *Physical Review B*, 22(8):3551–3562, 1980.
- [32] F. Ercolessi and J. B. Adams. Interatomic potentials from first-principles calculations: the Force-Matching Method. *Europhysics Letters*, 26(8):583–588, 1994.
- [33] M. W. Finnis. *Interatomic forces in condensed matter*. Oxford series on materials modelling. Oxford University Press, 2003.
- [34] A. Fontaine, P. Lagarde, A. Naudon, D. Raoux, and D. Spanjaard. EXAFS studies on Al-Cu alloys. *Philosophical Magazine B*, 40(1):17–30, 1979.
- [35] A. I. Frenkel, V. S. Machavariani, A. Rubshtein, Y. Rosenberg, A. Voronel, and E. A. Stern. Local structure of disordered Au-Cu and Au-Ag alloys. *Physical Review B*, 62(14):9364–9371, 2000.
- [36] C. L. Fu, R. C. Reed, A. Janotti, and M. Krcmar. On the diffusion of the solutes in the superalloys. In K. A. Green, T. M. Pollock, H. Harada, T. E. Howson, R. C. Reed, J. J. Schirra, and S. Walston, editors, *Superalloys 2004*, pages 189–195. The Minerals, Metals and Materials Society, Warrendale, PA, USA, 2004.
- [37] C. Y. Geng, C. Y. Wang, and T. Yu. Site preference and alloying effect of platinum group metals in γ' -Ni₃Al. *Acta Materialia*, 52(18):5427–5433, 2004.
- [38] C. Y. Geng, C. Y. Wang, and T. Yu. First-principles investigation of the alloying effect of refractory elements Ta and W in the misfit dislocation core of γ/γ' (001) interface. *Physica B: Condensed Matter*, 358(1-4):314–322, 2005.
- [39] A. F. Giamei and D. L. Anton. Rhenium additions to a Ni-base superalloy: Effects on Microstructure. *Metallurgical and Materials Transactions A*, 16(11):1997–2005, 1985.
- [40] S. J. Gurman. EXAFS study in materials science. *Journal of Materials Science*, 17(6):1541–1570, 1982.
- [41] J. Hafner. Materials simulations using VASP - a quantum perspective to materials science. *Computer Physics Communications*, 177(1-2):6–13, 2007.
- [42] O. C. Hellman, J. A. Vandenbroucke, J. Rusing, D. Isheim, and D. N. Seidman. Analysis of the three-dimensional atom-probe data by the proximity histogram. *Microscopy and Microanalysis*, 6(5):437–444, 2000.

- [43] P. Hohenberg and W. Kohn. Inhomogeneous electron gas. *Physical Review B*, 136(3B):864–871, 1964.
- [44] J. M. Hyde. *Computer modelling and analysis of microscale phase transformations*. D.phil., Oxford University, 1993.
- [45] A. Janotti, M. Krcmar, C. L. Fu, and R. C. Reed. Solute diffusion in metals: Larger atoms can move faster. *Physical Review Letters*, 92(8):085901, 2004.
- [46] R. A. Johnson. Analytic nearest-neighbor model for fcc metals. *Physical Review B*, 37(8):3924–3931, 1988.
- [47] H. J. Jou, P. Voorhees, and G. B. Olson. Computer simulations for the prediction of microstructure/property variation in aeroturbine disks. In K. A. Green, T. M. Pollock, H. Harada, T. E. Howson, R. C. Reed, J. J. Schirra, and S. Walston, editors, *Superalloys 2004*, pages 877–886, Seven Springs, PA, USA, 2004. The Minerals, Metals and Materials Society, Warrendale, PA, USA.
- [48] M. S. A. Karunaratne, P. Carter, and R. C. Reed. Interdiffusion in the face-centred cubic phase of the Ni-Re, Ni-Ta and Ni-W systems between 900 and 1300 degrees C. *Material Science and Engineering A*, 281(1-2):229–233, 2000.
- [49] M. S. A. Karunaratne and R. C. Reed. Interdiffusion of the platinum-group metals in nickel at elevated temperatures. *Acta Materialia*, 51(10):2905–2919, 2003.
- [50] G. L. Kellogg and T. T. Tsong. Pulsed laser-induced atom-probe mass-spectroscopy. *Ultramicroscopy*, 5(2):259–260, 1980.
- [51] T. F. Kelly and M. K. Miller. Atom probe tomography. *Review of Scientific Instruments*, 78(2):031101, 2007.
- [52] V. Kindrachuk, N. Wanderka, J. Banhard, D. Mukherji, D. Del Genovese, and J. Roösler. Effect of rhenium addition on the microstructure of the superalloy Inconel 706. *Acta Materialia*, 56(7):1609–1618, 2008.
- [53] W. Kohn and L. J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140(4A):A1133–A1138, 1965.
- [54] V. Koteski, H.-E. Mahnke, J. Belosevic-Cavor, B. Cekic, and G. Schumacher. Experimental and theoretical study of lattice relaxation around refractory atoms in nickel. *Acta Materialia*, 56(17):4601–4607, 2008.
- [55] L. Kovarik, R. R. Unocic, J. Li, P. Sarosi, C. Shen, Y. Wang, and M. J. Mills. Microtwinning and other shearing mechanisms at intermediate temperatures in Ni-based superalloys. *Progress in Materials Science*, 54(6):839–873, 2009.
- [56] G. Kresse and J. Furthmuller. *VASP the guide*.
- [57] G. Kresse and J. Furthmuller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Physical Review B*, 54(16):11169–11186, 1996.
- [58] G. Kresse and D. Joubert. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B*, 59(3):1758–1775, 1999.

- [59] G. Kuri, C. Degueldre, J. Bertsch, and J. Rothe. Local atomic structure in iron copper binary alloys: An extended x-ray absorption fine structure study. *Journal of Nuclear Materials*, 362(2-3):274–282, 2007.
- [60] D. J. Larson and M. K. Miller. Cluster detection and quantification. *Microscopy and Microanalysis*, 15(2):252, 2009.
- [61] B. Lengeler and P. Eisenberger. Extended x-ray absorption fine structure analysis of inter-atomic distances, coordination numbers, and bmean relative displacements in disordered alloys. *Physical Review B*, 21(10):4507–4520, 1980.
- [62] J. Li, D. Tang, R. Lao, S. Liu, and Z. Wu. Effects of Rhenium on Creep Rupture Life of a Single Crystal Superalloys. *Journal of Materials Science and Technology*, 15(1):53–57, 1999.
- [63] F. W. Lytle, D. E. Sayers, and E. A. Stern. Report on the international workshop on standards and criteria in x-ray absorption spectroscopy - March 7-9, 1988 - Brookhaven National Laboratory. *Physica B: Condensed Matter*, 158(1-3):701–722, 1989.
- [64] A. Ma, D. Dye, and R. C. Reed. A model for the creep deformation behaviour of single-crystal superalloy CMSX-4. *Acta Materialia*, 56(8):1657–1670, 2008.
- [65] H. Maeda, T. Tanimoto, H. Terauchi, and M. Hida. EXAFS studies on the fluctuations of solute in Al-1.9at%superasaturated solid-solution. *Physica Status Solidi A - Applied Research*, 58(2):629–633, 1980.
- [66] R. M. Martin. *Electronic structure: basic theory and practical methods*. Cambridge University Press, 2004.
- [67] N. Matan, D. C. Cox, C. M. F. Rae, and R. C. Reed. On the kinetics of rafting in CMSX-4 superalloy single crystals. *Acta Materialia*, 47(7):2031–2045, 1999.
- [68] M. Methfessel and A. T. Paxton. High-precision sampling for Brillouin-zone integration in metals. *Physical Review B*, 40(6):3616–3621, 1989.
- [69] M. K. Miller. *Atom probe tomography*. Kluwer Academic and Plenum Press, New York, 2000.
- [70] M. K. Miller and Forbes. Atom probe tomography. *Materials Characterization*, 60(2009):461–469, 2009.
- [71] M. K. Miller and J. M. Hyde. An atom probe simulator. In *11th European Congress on Electron Microscopy*, Dublin, Ireland, 1996.
- [72] M. K. Miller and E. A. Kenik. Atom probe tomography: A technique for nanoscale characterization. *Microscopy and Microanalysis*, 10(3):336–441, 2004.
- [73] M. K. Miller and R. C. Reed. Analysis of rhenium clustering in CMSX-4 nickel-based superalloys. In J.M. Howe, D.E. Laughlin, J.K. Lee, U. Dahmen, and W.A. Soffa, editors, *Proceedings of Solid-Solid Phase Transformation in Inorganic Materials*, volume 2, pages 537–542, Point Hilton Resort, Squaw Peak, Phoenix AR, 2005. The Minerals, Metals and Materials Society, Warrendale, PA, USA.

-
- [74] M. K. Miller, M. A. Sokolov, and K. F. Nanstad, R. K. Russell. APT characterization of high nickel RPV steels. *Journal of Nuclear Materials*, 351(1-3):187–196, 2006.
- [75] Y. Mishin. Atomistic modeling of the γ and γ' phases of the Ni-Al system. *Acta Materialia*, 52(6):1451–1467, 2004.
- [76] Y. Mishin, D. Farkas, M. J. Mehl, and D. A. Papaconstantopoulos. Interatomic potentials for monoatomic metals from experimental data and ab initio calculations. *Physical Review B*, 59(5):3393–3407, 1999.
- [77] E. W. Müller. Field Ion Microscopy. *Science*, 149:591–601, 1965.
- [78] E. W. Müller. The atom-probe field ion microscope. *Naturwissenschaften*, 57(5):222–230, 1970.
- [79] F. A. Mohamed and T. G. Langdon. Transition from dislocation climb to viscous glide in creep of solid solution alloys. *Acta Metallurgica*, 30(6):779–788, 1974.
- [80] M. P. Moody, L. T. Stephenson, A. V. Ceguerra, and S. P. Ringer. Quantitative binomial distribution analyses of nanoscale like-solute atom clustering and segregation in atom probe tomography data. *Microscopy Research and Technique*, 71(7):542–550, 2008.
- [81] M. P. Moody, L. T. Stephenson, P. V. Liddicoat, and S. P. Ringer. Contingency table techniques for three dimensional atom probe tomography. *Microscopy Research and Technique*, 70(3):258–268, 2007.
- [82] A. Mottura, A. Ceguerra, M. P. Moody, S. P. Ringer, M. W. Finnis, R. C. Reed, and M. K. Miller. Examination of clustering in binary alloys. In *Atom Probe Workshop*, Gothenburg, Sweden, 2007.
- [83] A. Mottura, M. K. Miller, and R. C. Reed. Atom probe tomography analysis of possible rhenium clustering in nickel-based superalloys. In R. C. Reed, P. Caron, T. Gabb, E. Huron, and S. Woodard, editors, *Superalloys 2008*, pages 891–900, Seven Springs, PA, USA, 2008. The Minerals, Metals and Materials Society, Warrendale, PA, USA.
- [84] A. Mottura, R. T. Wu, M. W. Finnis, and R. C. Reed. A critique of rhenium clustering in Ni-Re alloys using extended X-ray absorption spectroscopy. *Acta Materialia*, 56(11):2669–2675, 2008.
- [85] H. Murakami, H. Harada, and Y. Saito. Design and analysis of Ni-base superalloys on an atomistic basis. *Journal of the Japan Institute of Metals*, 63(6):723–732, 1999.
- [86] M. Newville. EXAFS analysis using FEFF and FEFFIT. *Journal of Synchrotron Radiation*, 8(2):96–100, 2001.
- [87] M. Newville. IFEFFIT: interactive XAFS analysis and FEFF fitting. *Journal of Synchrotron Radiation*, 8(2):322–324, 2001.
- [88] T. J. Nijdam and W. G. Sloof. Modelling of composition and phase changes in multiphase alloys due to growth of an oxide layer. *Acta Materialia*, 56(18):4972–4983, 2008.

- [89] S. Ochiai, Y. Oya, and T. Suzuki. Alloying behaviour of Ni_3Al , Ni_3Ga , Ni_3Si and Ni_3Ge . *Acta Metallurgica*, 32(2):289–298, 1984.
- [90] T. Ohnuma, N. Soneda, and M. Iwasawa. First-principles calculations of vacancy-solute element interactions in body-centered cubic iron. *Acta Materialia*, 57(20):5947–5955, 2009.
- [91] J. P. Perdew, K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters*, 77(18):3865–3868, 1996.
- [92] J. P. Perdew and Y. Wang. Accurate and simple analytic representation of the electron-gas correlation energy. *Physical Review B*, 45(23):13244–13249, 1992.
- [93] D. G. Pettifor. *A quantum-mechanical critique of the miedema rules for alloy formation*, volume 40 of *Solid State Physics - Advances in Research and Applications*, pages 43–92. Academic Press, New York, 1987.
- [94] D. G. Pettifor. Electron theory in materials modeling. *Acta Materialia*, 51(19):5649 – 5673, 2003.
- [95] W. E. Pickett. Pseudopotential methods in condensed matter applications. *Computer Physics Reports*, 9(3):115–197, 1989.
- [96] T. M. Pollock and A. S. Argon. Creep resistance of CMSX-4 nickel base superalloy single crystals. *Acta Metallurgica et Materialia*, 40(1):1–30, 1992.
- [97] T. M. Pollock and R. D. Field. *Dislocations and high temperature plastic deformation of superalloy single crystals*, volume 11 of *Dislocations in Solids*. Elsevier, Amsterdam, 2002.
- [98] Y. Qi and R. K. Mishra. Ab initio study of the effect of solute atoms on the stacking fault energy of aluminum. *Physical Review B*, 75(22):224105, 2007.
- [99] C. M. F. Rae. Alloys by Design: modelling next generation superalloys. *Materials Science and Technology*, 25(4):479–489, 2009.
- [100] C. M. F. Rae, K. Kakechi, and R. C. Reed. In J. Lecomte-Beckers, M. Carton, F. Schubert, and P.J. Ennis, editors, *Materials for Advanced Power Engineering*, volume 1, Julich, 2002.
- [101] C. M. F. Rae and R. C. Reed. Primary creep in single crystal superalloys: Origins, mechanisms and effects. *Acta Materialia*, 55(3):1067–1081, 2007.
- [102] C. M. F. Rae and L. Zhang. Primary creep in single crystal superalloys: some comments on effects of composition and microstructure. *Materials Science and Technology*, 25(2):228–235, 2009.
- [103] B. Ravel. A practical introduction to multiple scattering theory. *Journal of Alloys and Compounds*, 401(1-2):118–126, 2005.
- [104] R. C. Reed. *The superalloys: fundamentals and applications*. Cambridge University Press, 2006.
- [105] R. C. Reed, D. C. Cox, and C. M. F. Rae. Kinetics of rafting in a single crystal superalloy: effects of residual microsegregation. *Materials Science and Technology*, 23(8):893–902, 2007.

- [106] R. C. Reed, N. Matan, D. C. Cox, M. A. Rist, and C. M. F. Rae. Creep of CMSX-4 superalloy single crystals: effects of rafting at high temperature. *Acta Materialia*, 47(12):3367–3381, 1999.
- [107] J. J. Rehr and R. C. Albers. Theoretical approaches to x-ray absorption fine structure. *Reviews of Modern Physics*, 73(3):621–654, 2000.
- [108] Rolls-Royce. *The jet engine*. Rolls-Royce plc, Derby, 2008.
- [109] J. Rüsing, N. Wanderka, U. Czubyko, V. Naundorf, D. Mukherji, and J. Rosler. Rhenium distribution in the matrix and near the particle-matrix interface in a model Ni-Al-Ta-Re superalloy. *Scripta Materialia*, 46(3):234–240, 2002.
- [110] N. Saunders. Phase Diagram Calculations for Ni-based Superalloys. In R. D. Kissinger, D. J. Deye, D. L. Anton, M. V. Nathal, T. M. Pollock, and D. A. Woodford, editors, *Superalloys 1996*, page 101. TMS, Warrendale, 1996.
- [111] D. E. Sayers, F. W. Lytle, and E. A. Stern. *Point scattering theory of x-ray absorption fine structure*, volume 13 of *Advances in X-Ray Analysis*. Plenum Press, New York, 1970.
- [112] D. E. Sayers, E. A. Stern, and F. W. Lytle. New technique for investigation of noncrystalline structures - fourier analysis of extended x-ray absorption fine structure. *Physical Review Letters*, 27(18):1204–1208, 1971.
- [113] D. N. Seidman, C. K. Sudbrack, and K. E. Yoon. The use of 3-D atom-probe tomography to study nickel-based superalloys. *JOM*, 58(12):34–39, 2006.
- [114] D. Shin and C. Wolverton. First-principles study of solute-vacancy binding in magnesium. *Acta Materialia*, 58(2):531–540, 2010.
- [115] J. E. Sinclair, P. C. Gehlen, R. G. Hoagland, and J. P. Hirth. Flexible boundary-conditions and non-linear geometric effects in atomic dislocation modelling. *Journal of Applied Physics*, 49(7):3890–3897, 1978.
- [116] N. K. Sinha. Constant-load tertiary creep in nickel-base single crystal superalloys. *Material Science and Engineering A*, 432(1-2):129–141, 2006.
- [117] I. Steinbach, B. Bottger, J. Eiken, N. Warnken, and S. G. Fries. CALPHAD and phase field modeling: A successful liaison. *Journal of Phase Equilibria and Diffusion*, 28(1):101–106, 2007.
- [118] I. Steinbach, F. Pezzolla, B. Nestler, M. Seesselberg, R. Prieler, G. J. Schmitz, and J. L. L. Rezende. A phase field concept of multiphase systems. *Physica D: Nonlinear Phenomena*, 94(3):135–147, 1996.
- [119] L. T. Stephenson, M. P. Moody, P. V. Liddicoat, and S. P. Ringer. New techniques for the analysis of fine-scaled clustering phenomena within atom probe tomography (APT) data. *Microscopy and Microanalysis*, 13(6):448–463, 2007.
- [120] D. R. Trinkle. Lattice Green function for extended defect calculation: Computation and error estimation with long-range forces. *Physical Review B*, 78(1):014110, 2008.

- [121] D. R. Trinkle and C. Woodward. The chemistry of deformation: How solutes soften pure metals. *Science*, 310(5754):1665–1667, 2005.
- [122] G. P. E. M. Van Bakel, K. Hariharan, and D. N. Seidman. On the structure and chemistry of Ni_3Al on an atomic-scale via atom-probe field-ion microscopy. *Applied Surface Science*, 90(1):95–105, 1995.
- [123] D. Vanderbilt. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. *Physical Review B*, 41(11):7892–7895, 1990.
- [124] D. Vaumousse, A. Cerezo, and P. J. Warren. A procedure for quantification of precipitate microstructures from three-dimensional atom probe data. *Ultramicroscopy*, 95(1-4):215–221, 2003.
- [125] A. Volek, R. F. Pyczak, R. F. Singer, and H. Mughrabi. Partitioning of Re between γ and γ' phase in nickel-base superalloys. *Scripta Materialia*, 52(2):141–145, 2005.
- [126] F. Vurpillot, G. Da Costa, A. Menand, and D. Blavette. Structural analyses in three dimensional atom probe. A Fourier transform approach. *Journal of Microscopy*, 203:295–302, 2001.
- [127] N. Wanderka and U. Glatzel. Chemical composition measurements of a nickel-base superalloy by atom probe field ion microscopy. *Material Science and Engineering A*, 203(1-2):69–74, 1995.
- [128] T. Wang, L. Q. Chen, and Z. K. Liu. Lattice parameters and local lattice distortions in fcc-Ni solutions. *Metallurgical and Materials Transactions A*, 38A(3):562–569, 2007.
- [129] Y. J. Wang and C. Y. Wang. A first-principle survey of the partitioning behaviors of alloying elements on γ/γ' interface. *Journal of Applied Physics*, 104(1):013109, 2008.
- [130] Y. J. Wang and C. Y. Wang. The alloying mechanisms of Re, Ru in the quaternary Ni-based superalloys γ/γ' interface: A first principles calculation. *Material Science and Engineering A*, 490(1-2):242–249, 2008.
- [131] P. J. Warren, A. Cerezo, and G. D. W. Smith. An atom probe study of the distribution of rhenium in a nickel-based superalloy. *Material Science and Engineering A*, 250(1):88–92, 1998.
- [132] G. A. Whittaker. Precision casting of aero gas turbine components. *Materials Science and Technology*, 2(5):436–441, 1986.
- [133] B. Wilson and G. Fuchs. Primary creep: secondary gamma prime and the rhenium effect. *JOM*, 60(7):43–48, 2008.
- [134] S. Wöllmer, T. Mack, and U. Glatzel. Influence of tungsten and rhenium concentration on creep properties of a second generation superalloy. *Material Science and Engineering A*, 319-321:792–795, 2001.
- [135] C. Wolverton. Solute-vacancy binding in aluminum. *Acta Materialia*, 55(17):5876–5872, 2007.

- [136] C. Woodward and S. I. Rao. Flexible ab initio boundary conditions: simulating isolated dislocations in bcc Mo and Ta. *Physical Review Letters*, 88(21):216402, 2002.
- [137] WWW. *Website for APTo*. <http://apto.sourceforge.net/>.
- [138] WWW. *Website for libQGLViewer*. <http://www.libqglviewer.com/>.
- [139] WWW. *Website for OpenGL*. <http://www.opengl.org/>.
- [140] WWW. *Website for Qt*. <http://qt.nokia.com/>.
- [141] K. E. Yoon, D. Isheim, R. D. Noebe, and D. N. Seidman. Nanoscale studies of the chemistry of a Rene N6 superalloy. *Interface Science*, 9(3-4):249–255, 2001.
- [142] K. E. Yoon, R. D. Noebe, O. C. Hellman, and D. N. Seidman. Dependence of interfacial excess on the threshold value of the isoconcentration surface. *Surface and Interface Analysis*, 36(5-6):594–597, 2004.
- [143] K. E. Yoon, R. D. Noebe, and D. N. Seidman. Effects of rhenium addition on the temporal evolution of the nanostructure and chemistry of a model Ni-Cr-Al superalloy. I: Experimental observations. *Acta Materialia*, 55(4):1145–1157, 2007.
- [144] K. E. Yoon, R. D. Noebe, and D. N. Seidman. Effects of rhenium addition on the temporal evolution of the nanostructure and chemistry of a model Ni-Cr-Al superalloy. II: Analysis of the coarsening behavior. *Acta Materialia*, 55(4):1159–1169, 2007.
- [145] S. Yu, C. Y. Wang, and T. Yu. The first-principles study on the doping effect of Re in Ni3Al. *Progress in Natural Science*, 18(7):861–866, 2008.
- [146] X. X. Yu and C. Y. Wang. The effect of alloying elements on the dislocation climbing velocity in Ni: A first-principles study. *Acta Materialia*, 57(19):5914–5920, 2009.
- [147] J. X. Zhang, J. C. Wang, H. Harada, and Y. Koizumi. The effect of lattice misfit on the dislocation motion in superalloys during high-temperature low-stress creep. *Acta Materialia*, 53(17):4623–4633, 2005.
- [148] T. Zhu, C. Y. Wang, and Y. Gan. Effect of Re in γ phase, γ' phase and γ/γ' interface of Ni-based single-crystal superalloys. *Acta Materialia*, in press, 2010.