

Improving The Safety And Reliability Of Reactor Pressure Vessel Steels



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To My Family.

Look for clusters, and you'll find clusters. The fine-tuning of where these clusters exist is fascinating and the question becomes 'why'?

- Adam Rutherford

Abstract

The mechanical properties of reactor pressure vessel (RPV) steels are known to degrade during operation. Hardening embrittlement, due to solute cluster/precipitate formation, and non-hardening embrittlement, as a result of solute segregation to internal interfaces, are a major concern. The ability to accurately predict changes in mechanical properties as a result of these phenomena is highly desirable within the nuclear industry, both from a safety and economic perspective. Reliable predictions of the safe operational-lifetime of the RPV are required to minimise the likelihood of failure during operation. Meanwhile, shutting down a reactor prematurely is associated with a substantial loss in potential revenue. This, combined with the high initial costs associated with nuclear power plant construction, mean that extending the operational life of current power plants and designing future reactors with longer lifetimes is economically desirable. However, this requires a detailed understanding of how the material's microstructure develops during operation and models must also be informed and validated via comparison with experimental data.

To study the effect that composition has on RPV steel response to thermal ageing, 19 alloys with systematic variations in the levels of Cu, Ni, Mn, Si, and P levels were thermally-aged at 330 °C, 365 °C, and 405 °C for over 30,000 hours. Results from Vickers hardness tests revealed that an alloy containing 0.3 at.% Cu displayed a significant increase in hardness; atom probe tomography (APT) experiments revealed Cu-rich precipitate formation in the matrix and at heterogeneous nucleation sites. Ageing temperature was observed to affect the measured precipitate number densities, sizes, and volume fractions, with higher number densities of smaller precipitates present after thermal ageing at lower temperatures. Meanwhile, a low-Cu alloy with elevated Ni, Mn, and Si levels displayed no significant hardness increase after 20,733 hours of ageing. However, a low number density of Mn-Ni-Si-rich precipitates were observed to have formed on heterogeneous nucleation sites in this alloy. Ageing temperature was observed to influence precipitate composition; precipitates analysed in the 405 °C specimens contained significantly less Si than precipitates that were detected at lower ageing temperatures.

Four alloys that had been neutron-irradiated to a fluence of 1.4×10^{20} n/cm² at 290 °C and a flux of 3.6×10^{12} n/cm²s were characterised using APT. Precipitate formation was observed on homogeneous and heterogeneous nucleation sites in all four alloys, including an alloy that contained low nominal levels of Cu (0.02 at.%), Mn (0.04 at.%), and Si (0.06 at.%). The nominal alloy composition was observed to affect precipitate composition, with lower nominal levels of Ni or Mn resulting in precipitates that contained decreased levels of Ni or Mn, respectively. Precipitate nucleation site in the matrix was not observed to affect precipitate composition. However, precipitates which were detected at carbide-matrix interfaces contained less Mn than precipitates detected in the matrix. The average compositions of the precipitates detected in the matrix were observed to be different to those predicted by thermodynamic models.

APT is well-suited to investigate solute cluster formation and grain boundary segregation in RPV steels due to its unique combination of high spatial and chemical resolution. However, the analysis and interpretation of APT data is complex, particularly when studying the early stages of cluster formation and grain boundary segregation in irradiated steels. Failure to identify and account for clusters that are intersected by the edge of the analysis volume may reduce the accuracy of size and number density measurements. A novel data analysis technique has been developed which automatically and reproducibly identifies edge clusters. After implementing this method, measurements of cluster number density, size, and composition demonstrated improved accuracy.

In selected samples, the use of transmission Kikuchi diffraction (TKD) and an original analysis method has permitted the five macroscopic degrees of freedom of a grain boundary to be determined. Meanwhile, subsequent APT analysis of the same feature enabled characterisation of

the segregation behaviour of solutes to the grain boundary. Combining information from both of these techniques has resulted in a more holistic description of the grain boundary. The segregation behaviour observed in neutron-irradiated alloys was complex and non-uniform across the interface, this highlighted the limitations of traditional methods for reporting grain boundary segregation in APT measurements. The causes of these limitations are discussed and alternative methods applied to a grain boundary from a neutron-irradiated steel that was characterised using TKD and APT.

Preface

The work presented in this doctoral thesis has been carried out at the Department of Materials, University of Oxford from **October 2015 to April 2019**, under the supervision of Prof. Michael Moody, Dr. Paul Bagot, and Prof. Jonathan M. Hyde. All of the research carried out for this thesis is original and where the work of others has been included it has been clearly referenced and acknowledged. No part of this thesis has been submitted for a degree at this, or any other university. Some of this work has been published in peer reviewed journals and presented at conferences as detailed below:

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Acronyms

APT	Atom probe tomography
DBTT	Ductile-brittle transition temperature
EBS	Electron backscatter diffraction
FIB	Focused ion beam
FIM	Field ion microscopy
ICF	Image compression factor
IVAS	Imago Visualization and Analysis Software
LBP	Late blooming phase
LEAP	Local electrode atom probe
MNSP	Mn-Ni-Si-rich precipitate
PAS	Positron annihilation spectroscopy
PWR	Pressurized water reactor
RPV	Reactor pressure vessel
SANS	Small angle neutron scattering
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TKD	Transmission Kikuchi diffraction

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Chapter I

Introduction

Nuclear power plants generated more than 20 % of the United Kingdom's electricity in 2017 [1]. Since nuclear power provides a stable base load of energy, it is well suited to be used in conjunction with renewable electricity generation sources. Therefore, as the United Kingdom plans to reduce its carbon emissions over the coming years, it is likely that the electricity generation network will become more reliant on nuclear power.

The generation of radioactive waste and the possibility of a nuclear accident are two of the primary reasons given by opponents of nuclear power. However, the United Kingdom has not had a major accident involving nuclear waste or nuclear power generation for over 60 years. Maintaining this strong safety record is of paramount importance, not only for the health and safety of employees and the public, but also because minor accidents can severely impact community support of nuclear power and may be associated with severe economic costs.

Structural components in nuclear power plants are subjected to elevated temperature and neutron irradiation during operation. Exposure to these environments can deleteriously effect the mechanical properties of the components, increasing their risk of failure. One component that is known to suffer serious deleterious changes in its mechanical properties during operation, and is prohibitively expensive to replace, is the reactor pressure vessel (RPV). The RPV is the primary containment vessel and must not fail under any circumstances. Therefore, understanding why these adverse changes in mechanical properties occur so as to predict how the mechanical properties will evolve during the component's service is critical. This will ensure the risk of RPV failure is reduced whilst also ensuring the power plant is not decommissioned unnecessarily early.

Since the RPV component is required to withstand exposure to neutron irradiation and elevated temperature during its operation, an approach to increasing safe operational lifetime is the development of new steels, primarily by varying the alloy's nominal composition. However, before these alloys can be put into service, it is necessary to study their response to long-term exposure to

conditions that simulate aspects of those experienced during operation.

The work presented in this thesis is part of an ongoing project with Rolls Royce Plc. The project aims to study the development of the mechanical properties of a series of alloys as they are exposed to long-term thermal ageing at the University of Oxford. The alloys are model steels and have systematic variations in their compositions, particularly in levels of Cu, Ni, Mn, and Si. This allows the effects of compositional changes to be methodically studied. Furthermore, a complementary set of alloys with the same composition have been neutron-irradiated in the Advanced Test Reactor 2 (ATR-2) experiment by the University of California, Santa Barbara (UCSB). Changes in the mechanical properties of the alloys are studied alongside a detailed investigation of microstructural development, with a particular focus on characterising early stage solute clustering and segregation using atom probe tomography (APT).

The thesis is divided into ten chapters, with Chapter 2 providing a critical review of the current literature associated with RPV embrittlement. This chapter discusses hardening embrittlement in low and high-Cu steels that have been exposed to thermal ageing and neutron irradiation. The causes of non-hardening embrittlement in RPV steels are also reviewed.

One of the findings of Chapter 2 was that there are very few studies which systematically vary environmental variables or composition. This makes it difficult to determine overall trends across the literature. Chapter 3 presents a quantitative statistical analysis of results that have been reported within the literature. The effect that varying environmental conditions and alloy compositions has on the development of the mechanical properties of RPV alloys is investigated.

Chapter 4 provides information on the materials and methods that were implemented during this study. Meanwhile, Chapter 5 discusses how experimental parameters were selected, and how results from APT analyses generated by different generations of Local Electrode Atom Probe's (LEAP) instruments used in this study compare. A novel APT data processing method is also presented in Chapter 5, and the limitations associated with how APT grain boundary analyses are currently reported is addressed.

The effect of thermal ageing on the mechanical properties and microstructural development of the series of model alloys is presented in Chapter 6. Precipitation was observed to have developed in both high and low-Cu steels after 20,700 hours of ageing.

Results from APT analyses of neutron-irradiated low-Cu alloys are discussed in Chapter 7. Mechanical property changes are correlated with cluster volume fractions and the effect of cluster

nucleation site on cluster composition is investigated. Several grain boundaries were analysed and the segregation behaviour of elements to these interfaces is discussed.

Chapter 8 presents results from a grain boundary whose structure was first determined using transmission Kikuchi diffraction (TKD) and novel analysis methods. APT analyses then revealed the levels of solute segregation at this interface. Combining these two techniques provides a more holistic description of the grain boundary.

A brief summary of the findings is presented in Chapter 9, whilst Chapter 10 discusses potential future research.

Chapter II

Literature Review

1 Engineering Relevance

Reactor pressure vessels (RPV) are the primary containment vessel in light-water nuclear reactors (LWNR) [2]. The RPV acts as a heat sink in the event of loss of coolant and provides secondary containment of the core [3]. The embrittlement of RPV steels is the life-limiting factor in the operational lifetime of LWNRs since RPVs are prohibitively expensive to replace [4, 5]. The majority of worldwide LWNRs are nearing the end of their originally planned operational life (25 years - 40 years), with 75 % of electricity production from nuclear power originating from reactors which have been in operation for 25 years or more (Figure 1) [6].

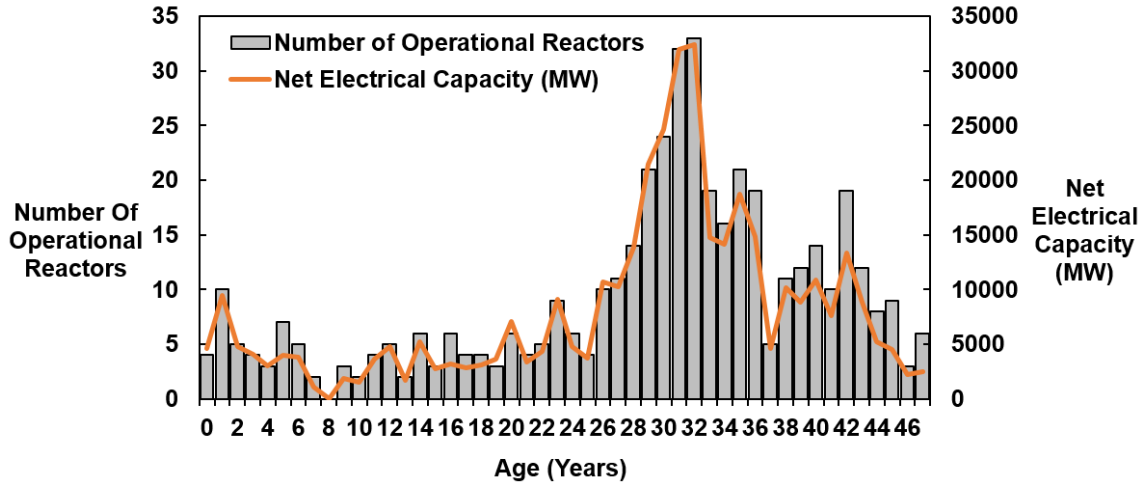


Figure 1: Graph showing the current age of operational LWNRs and their electrical capacity [6].

In order to meet current global energy requirements and reduce energy costs, it is of primary importance to extend the safe operational life-time of these ageing reactors [5, 7]. To safely extend operational lifetimes, it is important that the behaviour and embrittlement of RPV steels during operation is understood [8, 9, 10].

2 General Microstructure

RPVs are subjected to temperatures of about $290\text{ }^{\circ}\text{C} \pm 30\text{ }^{\circ}\text{C}$ and are exposed to neutron irradiation during operation [5, 11, 12]. To produce a material which is capable of operating under these extreme conditions, Fe is alloyed with several solute elements before undergoing a series of heat treatments to produce a ferritic/bainitic steel [13]; ferritic steels have a higher yield strength and undergo a lower volumetric expansion than austenitic steels during irradiation [14, 15].

There is a large variation in the compositions of different RPV steels. However, the typical composition range of RPV steels commonly used in Western pressurised water reactors (PWR) is shown in Table 1 [16].

	Cu	Si	Ni	Mn	P	Cr	Mo	C	Fe
Min	-	0.1	0.4	0.5	-	0.25	0.45	0.17	Bal.
Max	0.10	0.3	1.2	1.8	0.012	0.50	0.80	0.25	Bal.

Table 1: Standard range of compositions for RPV steels used in Western PWRs (wt.%) [16].

Cu may be added to steels to improve atmospheric corrosion resistance or aid in grain refinement [17, 18]. However, impurity levels of up to 0.3 wt.% Cu are present in some older RPV alloys [7]. This is as a result of using scrap metal to produce the RPV base metal and of using Cu-coated weld wires [7]. Elements such as Ni increase the hardenability of the alloys and decrease the initial ductile-to-brittle transition temperature of the alloy [19], whilst solutes such as Mn and Si increase strength when added as solutes.

Some of these solutes, however, can also have detrimental effects. Many studies have observed that the presence of Cu, which has a very low solubility in Fe [20], leads to the formation of Cu-rich precipitates after thermal ageing [21, 22, 23] or exposure to neutron irradiation [24, 25, 26]. These Cu-rich precipitates are responsible for the increased hardness and embrittlement of alloys during service [24, 27, 28], and are further discussed in Section 5.1. Ni has been observed to segregate to grain boundaries in steels that experienced an increase in their ductile-to-brittle transition temperature after neutron irradiation [10, 29].

As a result of these studies, the majority of manufacturers target low Cu contents ($< 0.05\text{ wt.}\%$) in their alloys, and the effects of Mn, Ni, and Si on the alloys' properties are now of primary interest. The behaviour of these elements is discussed in more detail in Section 5.2.

3 Operational Environment of RPV Steels

As stated above, RPV steels are subjected to elevated temperatures and neutron irradiation during service. Licence extensions have been awarded which permit nuclear power plants to operate for up to 60 years. To ensure safe operation on the RPV during these extensions, it is necessary to accurately predict how the mechanical properties evolve during operation.

Different parts of the RPV experience different amounts of irradiation and different temperatures during operation [30]. It is, therefore, necessary to understand the independent effect that each of these environmental variables have on the microstructure/nanostructure of the material, as well as any synergistic effects that may exist.

3.1 Thermal Ageing

The initial microstructure of many material systems evolves over time in an attempt to minimise the Gibbs free energy of the system [31]. This may result in a phase change or the formation of multiple phases with different chemical compositions. These secondary phases often inhibit dislocation motion, thereby affecting the mechanical properties of the alloy.

3.1.1 Effect of Ageing Temperature

If a new phase (a) of different chemical composition is to form, the local concentration of solute must exceed a certain value. The kinetics of this reaction are controlled by the diffusion rate of solute atoms within the host lattice [31].

The rate at which atoms overcome the energy barrier to diffusion is inversely proportional to the temperature of the system.

$$rate \propto \exp\left(\frac{-\Delta G^a}{kT}\right) \quad (1)$$

where ΔG^a is the activation free energy barrier (Figure 2), k is the Boltzmann constant, and T is the temperature in K.

Therefore, at elevated temperatures individual atoms are able to overcome the energy barrier more often and diffuse over greater distances, in a fixed time, than would be possible at lower temperatures. This means that, at elevated temperatures, the time taken to reach thermodynamic equilibrium will be less than at lower temperatures.

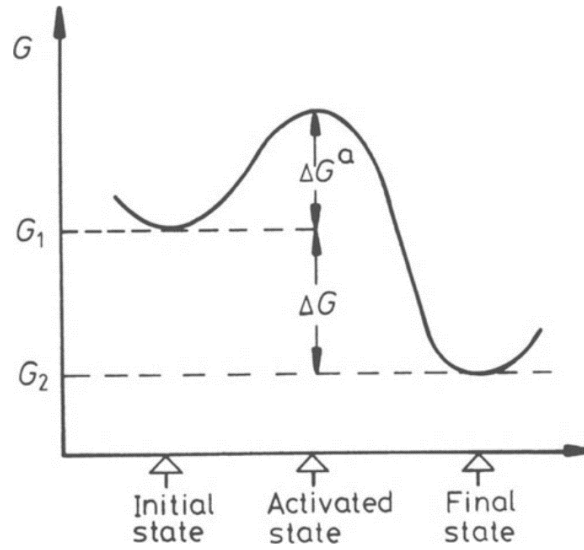


Figure 2: Schematic diagram from [31] illustrating the change in Gibbs free energy during transformation from initial to final state through an activated state of higher free energy.

Cu has a low solid-solubility in Fe at RPV operating temperatures [32]. Even at low nominal Cu concentrations there is a large thermodynamic driving force for phase separation in RPV steels. However, the solubility of Cu in Fe does increase with temperature up to approximately 850 °C; this increase in Cu solubility reduces the driving force for phase separation. However, the kinetics of the reaction are enhanced at elevated temperatures.

When deciding on the temperature selected for thermal ageing experiments it is important that the interplay between the thermodynamic driving force and kinetics of the reaction are accounted for. Too high a temperature may lead to formation of phases which are not thermodynamically favourable at temperatures experienced by the system during operation. For example, the precipitates in a very high-Cu (> 1.5 wt.%) steel specimen aged at 650 °C had a different crystal structure to precipitates observed in a specimen of the same alloy that was aged at 550 °C [33]. The precipitates observed at the different ageing temperatures also had different sizes after 30 minutes of ageing, with the precipitates in the 650 °C samples being 10 nm - 15 nm in size, whilst the size of the precipitates observed in the sample that was aged at 550 °C was 2 nm - 4 nm [33]. Regarding the kinetics of the reaction, too low an ageing temperature will mean that the time taken for the microstructure to develop towards its equilibrium state may be prohibitively long. For example, after 209,000 hours of ageing at 260 °C no significant changes in mechanical properties were noted, and only very small amounts of localised segregation were

observed in an A533B plate material [34].

RPV alloys typically contain several different alloying elements, and the driving forces for reactions at different temperatures are not known in all of these systems. In an attempt to ensure that experiments are operating in a similar thermodynamic regime to that which in-service RPVs will experience, thermal ageing experiments should be conducted at a variety of temperatures ($\sim 300\text{ }^{\circ}\text{C}$ - $400\text{ }^{\circ}\text{C}$) similar to those experienced during operation [35].

3.1.2 Effect of Ageing Time

As diffusion is a probabilistic process, the longer an alloy is held at a specific temperature, the further each atom will be able to move throughout the material. As ageing time increases in thermal ageing experiments, precipitates have been observed to form [36] and coarsen in RPV steels [37].

3.2 Neutron Irradiation

A number of phenomena occur when neutrons from the reactor core impact the RPV wall. Lattice atoms can be knocked out of position, resulting in vacancy formation and the displaced atom becoming an interstitial [38]. The interstitial atoms are highly mobile and able to diffuse over large distances [38]. Meanwhile, the vacancies created will enhance the diffusion rates within the material, allowing segregation to occur more quickly [31]. This can result in segregation of solutes to interfaces, solute cluster formation, or vacancy clusters forming. All of these defects will inhibit dislocation motion in the material, leading to an increase in strength and a decrease in toughness of the material. The vacancies created can be annihilated if they interact with an interstitial ion, reach the surface of the material, or reach a sink, such as a grain boundary [38].

The fluence experienced by a material is the number of neutrons per unit area which impact the material. The higher the fluence experienced by a steel (at fixed flux and irradiation temperature), the more matrix damage is accumulated. This leads to a greater defect density and larger changes in macroscale mechanical properties [39, 40, 41].

The flux is a measure of the rate of irradiation, and is the number of neutrons per unit time which collide with a unit area of the component. The effect of flux on mechanical property changes in Fe-based alloys is not unanimously agreed upon. As flux changes, at constant fluence and irradiation temperature, the response of the material has been found to depend on the composition

of the alloy [42, 43]. Odette et al. showed that lower fluxes have been observed to lead to larger changes in mechanical properties at high fluence, with the effect increasing with alloy solute content [44]. The authors propose that this is because there is less time for defects to recombine at high flux, but that the diffusion distance of these defects is shorter [44]. However, the same researchers previously observed that, at low fluence, increased flux led to more hardening and appeared to be independent of composition [45].

Irradiation temperature has also been shown to affect changes in mechanical properties. Overall, increased irradiation temperature is believed to increase the mobility of defects, increasing the likelihood that two defects will annihilate with one another [42]. As a result, there is likely to be more damage at lower irradiation temperatures.

4 Embrittlement of RPV Steels

Increased embrittlement raises the risk of catastrophic failure of a material [46]. Embrittlement of a polycrystalline material can be divided into two classes; hardening, or non-hardening [47]. Both types of embrittlement are associated with an increase in the ductile-to-brittle transition temperature (DBTT) and a decrease in the upper shelf energy (Figure 3) [14, 48, 49]. An increase in DBTT means that brittle fracture occurs at higher temperatures. This is unfavourable since cracks associated with brittle fracture spread more quickly and require less energy to propagate than those associated with ductile fracture.

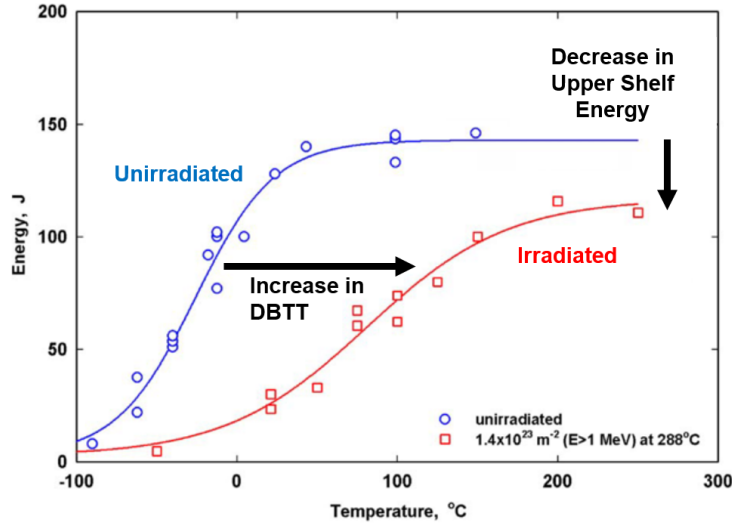


Figure 3: Graph showing the increase in the DBTT and decrease in upper shelf energy of a Palisades weld after irradiation. Adapted and reproduced with permission from [50]. Copyright © 2006 Published by Elsevier B.V.

4.1 Non-Hardening Embrittlement

Non-hardening embrittlement is associated with intergranular fracture [47]. Intergranular fracture occurs due to grain boundary embrittlement as a result of solute atom segregation [14, 51, 52], or the distribution of second-phase particles at the grain boundary [53, 54, 55, 56].

Multiple studies using both scanning Auger spectroscopy and atom probe have observed that exposure to irradiation significantly increases the level of P segregation at the grain boundaries in RPV steels [52, 53, 54, 57, 58]. It has been observed that the phosphorus monolayer coverage can increase from low levels (16 %) to much higher levels (60 %) after irradiation [53, 58]. This, in turn, leads to a higher likelihood of intergranular fracture with a study reporting up to 90 % of fracture being intergranular when phosphorus monolayer coverage is 40 % [57]. Furthermore, a linear relationship between grain boundary P concentration and shift in DBTT has also been shown [59, 60]. Toyama et al. observed the segregation of C, P and Mo to grain boundaries after low-dose irradiation whilst Si and Mn were also observed to segregate to the grain boundaries at higher doses [61]. However, this difference in segregation behaviour may be a result of the grain boundaries having different misorientation angles or physical structures. The authors observed that the monolayer coverage of P at the grain boundary was below the level required for intergranular

embrittlement in a commercial RPV [61].

Despite it being known that phosphorus accumulation increases with increasing grain boundary misorientation [10], most studies fail to report the misorientation angle between grain boundaries when measuring the level of phosphorus coverage at the boundaries.

Herbig et al. [62] have shown that the number of excess C atoms per grain boundary unit area varies with misorientation angle in a nanocrystalline pearlitic steel (Figure 4). The authors correlated grain boundary misorientation, determined using transmission electron microscopy (TEM), with the Gibbsian interfacial excess of C at the grain boundary. Atom probe tomography (APT) was used to measure the Gibbsian interfacial excess. The authors suggest that, at low angle ($\lesssim 14^\circ$) grain boundaries, there is a linear trend between C segregation and misorientation angle. However, the authors do not explain why a linear model was selected, or how the model was fitted to the data. The authors propose that the large variation in measured C excess, between grain boundaries with similar misorientation angles in the high angle ($\gtrsim 14^\circ$) grain boundaries, is due to the grain boundary plane normal and rotation axis having a more influential role in determining the segregation behaviour of C. These results emphasise the need for a more holistic approach when characterising grain boundary segregation.

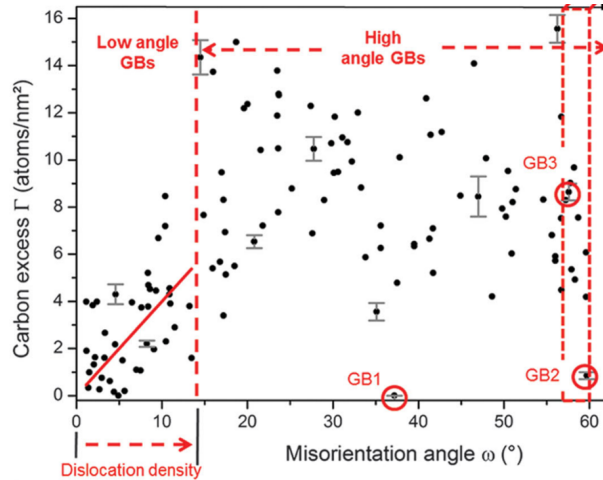


Figure 4: Graph showing the variation in excess C atoms detected at grain boundaries in a nanocrystalline pearlitic steel as a function of misorientation angle.

In an otherwise pure Fe specimen, the surface monolayer coverage of S has been observed to decrease as the monolayer coverage of Sn increased [63]. The authors proposed that this was due to site competition between Sn and S at the free surface [63]. Evidence for site competition between P

and N or C in Fe alloys has been observed in several studies [64, 65, 66, 67, 68]. The authors propose that, since grain boundary levels of P decrease as nominal C levels increase, C atoms can preferentially occupy the grain boundary sites that would be occupied by the P atoms [65, 66, 67, 68]. Lu et al. suggest that this is because C atoms are smaller than P atoms and have a higher binding energy to the grain boundary [68]. However, Guttman questioned whether P and C should be expected to occupy the same sites at the grain boundary, given that P inhabits substitutional sites and C occupies interstitial sites in α -Fe [69]. Guttman suggested that thermodynamic approaches should be considered to explain the observed experimental results [69].

Matsuyama et al. found that Mn increased the diffusion coefficient of P in Fe alloys [70]. This may be explained since the presence of Mn in Fe leads to a decrease in the diffusion activation energy of P [71]. The diffusion coefficient of P has also been determined to increase with increasing Ni concentration [72]. Park et al. observed that there was a more pronounced DBTT shift in alloys containing nominally more Ni and Mn [72], whilst Nikolaev et al. reported a 50 °C increase in DBTT when the Ni concentration was increased from 1 wt.% to 1.7 wt.% [73]. These findings suggest that there may be a synergistic effect between Ni and Mn, and the diffusion of P. However, the papers do not address whether increased grain boundary embrittlement is a result of higher nominal levels of Mn and Ni levels increasing the amount of P which segregates to the boundary, or because more Mn and Ni segregates to the boundaries.

Studies in thermally-aged alloys have also observed non-hardening embrittlement in low-Cu RPV steels [74]. It has been proposed that non-hardening embrittlement is a result of nickel phosphide formation on grain boundaries [9], as well as the diffusion of P to grain boundaries during thermal ageing [10, 75, 76]. The level of grain boundary P segregation was found to increase with increasing bulk P content and, interestingly, increasing bulk Ni content [74]. This result provides further evidence towards a possible synergistic effect between Ni and P, although the current understanding of segregation processes is limited [10].

Whilst several studies have investigated the effect of grain boundary segregation on the mechanical properties of RPV steels, there is a lack of systematic studies that holistically characterise grain boundary type as well as segregation. However, a recent paper has used a combination of transmission Kikuchi diffraction (TKD) and (APT) to determine all five grain boundary degrees of freedom, and to measure the segregation of P and C in a model Fe-C-P alloy [77].

4.2 Hardening Embrittlement

Hardening embrittlement occurs as dislocation motion becomes inhibited. In RPV steels matrix damage accumulates during operation, as a result of the collapse of point defects produced during irradiation and the precipitation of solute atoms [78]. Figure 5 demonstrates that DBTT shift increases approximately linearly with increasing Vickers hardness [79]. The authors state that the relationship is only valid if the irradiation does not result in significant non-hardening embrittlement [79].

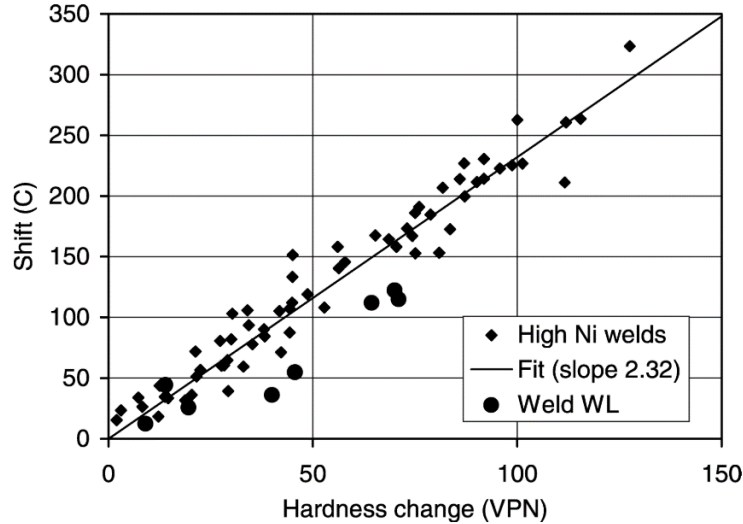


Figure 5: Relationship between DBTT and Vickers hardness for a variety of irradiated high-Ni alloys. Reproduced with permission from [79]. Copyright © 2002 Published by Elsevier B.V.

Point defects and individual solute atoms are responsible for solid-solution hardening the alloy [80]. These individual defects and solute atoms inhibit dislocation motion and increase the strength of the alloy [80]. A summary of the contribution each of these mechanisms makes to the total hardness of a thermally-aged binary Fe-Cu alloy is shown in Figure 6 [47].

In long-term thermal ageing experiments, precipitation will be the predominant cause of increased hardness of the alloys [81]. When precipitates form in an alloy, they can inhibit dislocation motion and this leads to an increase in the hardness of the alloy [24, 28, 80, 82]. During the thermal ageing of the alloy, the precipitates change in size, number, and volume fraction [37]; the effect these changes have on the alloy's mechanical properties are of great importance [13].

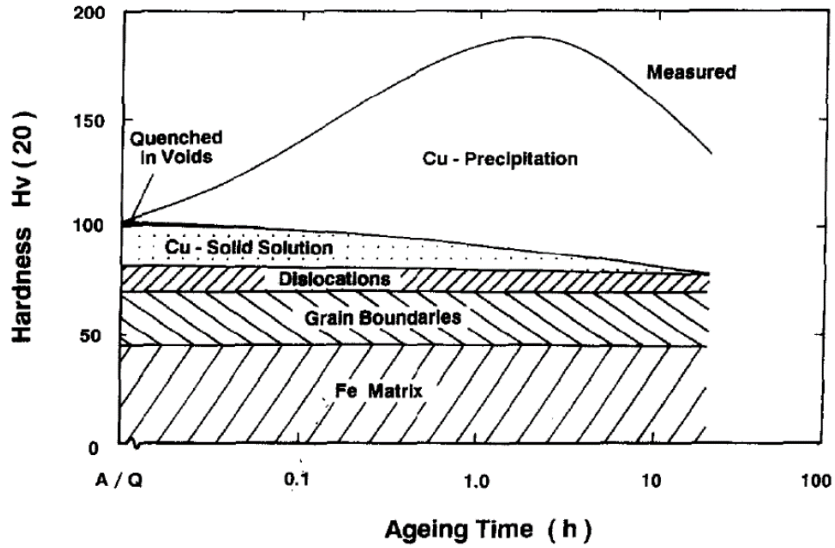


Figure 6: Schematic diagram showing the relative contributions of various microstructural components to the measured hardness of a thermally-aged (550 °C) Fe-Cu alloy. Reproduced with permission from [47]. Copyright © 1993 Published by Elsevier B.V.

4.3 Hardening Mechanism Models

Many studies on the effect of precipitates on the hardness of RPV steels have used the Russell-Brown (RB) model [21] to calculate the contribution of precipitation to the total hardness of the alloy [24, 28, 47, 83, 84, 85, 86, 87]. The model has generally been found to be in good agreement with observed hardness changes after thermal ageing [47, 84]. However, in irradiated alloys the RB model has been found to underestimate the change in yield stress and shift in DBTT; this is probably since the RB model does not account for matrix damage [24, 83, 86].

The RB model makes several initial key assumptions [21]:

1. The alloy contains two phases, the second of which has a lower shear modulus than the matrix and is distributed randomly as spheres
2. The particles are well-defined spatially and chemically
3. The equilibrium volume fraction has precipitated

Once these assumptions had been made, Russell and Brown fitted an equation to the observed experimental data. This fit relied upon estimations of:

1. The obstacle spacing in the slip plane (L)

2. Estimation of the effective Schmid or Taylor factor
3. Dislocation energy per unit length in an infinite media of BCC Fe (E_1^∞) and FCC Cu (E_2^∞)

When these estimates were applied, the maximum strength (τ_{max}) was calculated to be proportional to the square root of precipitate volume fraction (f):

$$\tau_{max} = \frac{0.041Gb f^{0.5}}{r_0} \quad (2)$$

where G is the shear modulus, b is the burgers vector, and r_0 is the core radius of the dislocation. Russell and Brown then found that this equation best fits the experimental data when $r_0 = 2b$. They propose that this value for r_0 “is quite reasonable” but this is based on their circular argument that “theory and experiment can be brought into exact agreement” when this value of r_0 is chosen.

In the overaged state, Russell and Brown found that the hardness was given by the sum of the matrix strength (τ_0) and the strength due to the precipitates:

$$\tau = \tau_0 + \frac{0.8Gb}{L} \left(1 - \frac{E_1^2}{E_2^2}\right)^{\frac{1}{2}} \quad (3)$$

Despite fitting experimental data reasonably well (Figure 7), the RB model is not beyond criticism; the authors note that there is uncertainty due to their estimation of the Schmid factor to be between 2.2 - 3.1, and that their “estimates of L may be subject to considerable error” [21].

Barbu et al. showed that there was an extra-hardening component in irradiated alloys, which cannot be ascribed to Cu precipitates [81]. They propose that this extra hardening-component is due to the formation of interstitial clusters [81]. Wagner et al. and Bergner et al. also questioned the validity of the RB model in irradiated alloys [88, 89]. Bergner et al. commented that their results are inconsistent with respect to the relationship between yield stress and particle radius [89]. Whilst these findings suggest that the RB model may not be applicable to irradiated alloys, this is not altogether surprising since the RB model was formulated upon observations from a thermally-aged steel [21]. Charleux et al. performed TEM analysis of a thermally-aged FeCu alloy. They found that the RB model is not directly applicable in peak-aged materials due to the presence of a kink-pair mechanism that is not accounted for [56].

The RB model was found to significantly overestimate strengthening by Osetsky et al., who performed atomic modelling experiments [90]. Osetsky et al. proposed that this occurred as the RB

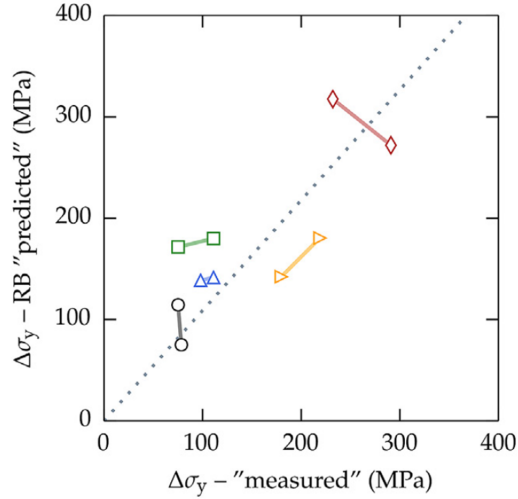


Figure 7: Comparison of measured yield stress increase to that predicted by the Russell-Brown model. The different colours correspond to individual specimens. Each specimen was irradiated to a specific fluence at two different fluxes. Reproduced with permission from [88]. Copyright © 2016 Published by Elsevier B.V.

model ignored self-interactions between the two dislocation branches which emerge from a precipitate [90].

Harry and Bacon (HB), who later developed a more accurate model to predict hardening [91], also note some issues with the RB model. Firstly, the value that Russell and Brown used for the shear modulus of Cu was based upon FCC Cu, whilst the Cu precipitates in the aged experimental alloy are likely to have been BCC in structure due to their small size. This would affect the E values chosen, since BCC Cu actually has a higher shear modulus than BCC Fe [91]. They also note that Cu precipitates in irradiated alloys are not always pure Cu [91].

The HB model used simulations to model the change in energy that a screw dislocation experiences as it passes through a precipitate [91]. It was found that the interaction energy of the dislocation scales with the size of precipitate, not precipitate spacing. Harry and Bacon hypothesised that the energy of the dislocation was reduced as it entered the copper precipitate. They proposed that a driving force for the copper to transform to a FCC structure was the reason for this decrease in dislocation energy. This was due to the instability of BCC copper rather than an elastic interaction [91].

Despite the HB model more accurately predicting hardness changes, and the several flaws in the RB model, the simplicity of the RB model has meant that it has been adopted in many studies

involving RPV steels.

5 Precipitation in RPV Steels

There are several causes for increased hardness in RPV steels that have been subjected to irradiation and/or elevated temperatures. This review will focus on Cu-rich and Mn-Ni-Si-rich precipitates (MNSPs) since these have been identified as the features which are most responsible for increasing the hardness of RPV steels during operation, and they can be characterised using APT.

5.1 Cu-rich Precipitates

Goodman et al. observed the formation of Cu-rich precipitates in thermally-aged Cu-containing steels [92]. This occurs due to the low solid solubility of Cu in Fe [18, 93, 94]. The mean particle size was observed to grow at a rate proportional to $\sqrt{t}$, where t is annealing time [92]. More recent experiments determined that the radius increased as a function of a $t^{\frac{1}{3}}$ power law [18, 95, 96]. Kolli et al. found, however, that the precipitate growth rate was not well defined by a $t^{\frac{1}{3}}$ power law [97]. They suggested that the discrepancy between their results and previous work may be due to the use of binary and ternary alloys, and the use of higher temperatures (600 °C - 750 °C) during ageing in the previous studies [97].

The Cu-rich precipitates in Fe have a BCC structure when they first nucleate [98]. During ageing, these initial precipitates transform martensitically into a twinned 9R structure [99]. The sizes at which these transformations occur are temperature dependent, with BCC to martensite transformation occurring at over 12 nm in size at 550 °C, whilst the BCC to 9R transformation was observed to occur for 4 nm precipitates at -60 °C [99]. The precipitates then transform into an FCC structure at even larger sizes (≥ 40 nm) [56, 99, 100, 101, 102, 103].

Many studies have attempted to characterise the Cu-rich precipitates with techniques such as: field ion microscopy (FIM) [23, 92, 104, 105], positron annihilation spectroscopy (PAS) [83, 86, 106, 107], small angle neutron scattering (SANS) [23, 78, 106, 107, 108, 109, 110], and atom probe tomography (APT) [83, 86, 97, 105, 106, 108, 111, 112, 113, 114, 115, 116].

Whilst a consensus has been reached on the crystal structure of Cu-rich precipitates, and that the Cu-rich precipitates can be surrounded by a Mn- and Ni-rich shell which is thought to reduce the energy of the Fe-Cu interface [12, 47, 108], the composition of the precipitates is

disputed. In particular, the incorporation of Fe into composition measurements is a controversial issue within the field.

The differences in composition arise for two main reasons. Firstly, most studies that use SANS to characterise the precipitates assume a priori that the features are non-magnetic and therefore do not contain Fe. The composition assumption is necessary so that a contrast factor can be determined for analysis [117, 118]. This assumption of likely composition biases the composition that is then ascertained during the experiment, leading to precipitates which are Fe free. This results in a high determined Cu content of the precipitates and can also lead to an underestimation of calculated number density of clusters [82]. Many other assumptions are made during SANS experiments. These assumptions, and the impact they have on experimental results, are well summarised in [117]. Secondly, in many atom probe studies the precipitates are observed to contain significant amounts of Fe. The concentration of Fe in the precipitates has been shown to change with distance from the precipitate-matrix interface [113], and as a function of precipitate size [13, 37]. From this, it can be inferred that the majority of the Fe measured in the precipitates is due to trajectory aberrations, which impact more upon smaller precipitates [113, 117]. Despite these studies, there is still no consensus as to how much, if any, of the Fe observed in the precipitates is real, or a result of aberrations.

The deviation in reported composition of the Cu precipitates is not negligible. Two studies which used atom probe tomography to measure precipitate composition independently observed a precipitate Cu content of below 15 at.% in irradiated steels [86, 119]. Meanwhile, another study found that the precipitates in a thermally-aged alloy were almost pure Cu (98 at.% Cu) when measured using atom probe analysis [120]. Fukuya et al. determined their precipitate composition of 15 at.% using a method where all ions within a $4 \text{ nm} \times 4 \text{ nm} \times 4 \text{ nm}$ box were included [86]. This is likely to lead to the inclusion of matrix atoms in the calculated precipitate composition, and may explain why their measurements contained a high Fe content. Auger et al. compared the difference in composition between irradiated and thermally-aged alloys, finding that the Cu clusters in irradiated alloys contained less Cu than the clusters in a thermally-aged alloy [121]. However, the clusters in the irradiated alloy were smaller in size than the clusters thermally-aged sample. Therefore, if the Fe in the clusters is the result of an aberration, the difference in composition of the precipitates may be explained.

As a result of the adverse affect Cu precipitation has on the mechanical properties of RPV

steels, low Cu (< 0.05 at.%) steels are now used in the hope of avoiding the precipitation of Cu-rich deleterious phases.

5.2 Mn-Ni-Si-Rich Precipitates

The use of low-Cu alloys may eliminate the formation of Cu-rich precipitates, however, another potentially serious concern has arisen instead. The formation of precipitates that are rich in Mn, Ni, and Si (MNSPs) has been observed in irradiated low-Cu RPV steels [105, 122, 123, 124, 125]. A study by Wells et al. has found that increased MNSP precipitate mole fraction leads to a corresponding increase in hardness [40]. The mechanisms of cluster formation and their influence on the mechanical properties of low-Cu RPV steels are currently poorly understood [13].

Recent scanning transmission electron microscopy with energy dispersive spectroscopy (STEM-EDS) experiments have determined that MSPs contain, on average, 6 at.% Fe [126]. However, similar to Cu-rich precipitates, the Fe content of MNSPs is debated. In order to create accurate models that predict the safe operational lifetime of RPV steels, it is essential to understand the relevant mechanisms of cluster formation and the effect they have on the mechanical properties of the alloys.

5.2.1 Modelling Studies

The thermodynamic stability of these features remains a contentious issue. Several studies have used computational models in an attempt to determine whether MNSP formation is irradiation-enhanced, or irradiation-induced but a consensus is yet to be reached.

Ngayam-Happy et al. developed a model which predicted that the Mn-Ni interaction is repulsive and that their formation at thermodynamic equilibrium is not possible [127]. Their model predicted, however, that MNSPs will form under irradiation [127].

DFT calculations by Bonny et al. predicted that Mn-Ni pairs were thermodynamically unstable [4]. However, they proposed that a synergistic effect between Ni and Mn increases the stability of Mn-Ni clusters once they reached a critical size of 4 atoms [4]. Bonny et al. proposed that the synergistic effect raises the solubility limit, which in turn pushes the solvus towards lower concentrations at a given temperature. As a result of this change in the solvus, it was predicted that Mn-Ni clusters with a B2 intermetallic structure would be thermodynamically stable in low-Cu

steels below 450K, although their formation would have a lower driving force than Cu precipitates in high-Cu RPV steels [4]. Although the clusters are predicted to be thermodynamically stable, the high vacancy-solute migration barrier of Ni and Mn means that diffusion of Ni and Mn is prohibitively slow, and the authors propose that irradiation is required to make it kinetically possible for these phases to form [4].

Messina et al. calculated that there was no synergistic effect between Mn and Ni, but their models predicted Vacancy-Mn-Ni clusters would become more stable as the number of Mn or Ni atoms in them increased [128].

Xiong et al. predicted the thermodynamic stability of MNSP phases using CALPHAD models [129]. They used two databases (UW1 & TCAL2) which predicted “generally similar overall compositions” of the MNSPs. The predicted compositions compared well with experimental observations made by Wells et al. [40].

5.2.2 Experimental Studies

Wells et al. performed atom probe analysis on a series of neutron-irradiated steels [40]. They found that MNSPs formed in both Cu-containing and Cu-free RPV alloys. The precipitates in the high-Ni, Cu-free steel were observed to have a composition very close to the Γ_2 phase ($\text{Mn}_2\text{Ni}_3\text{Si}$) predicted by Xiong et al. [40, 129]. The authors also found that there was close agreement between the predicted and observed composition in most alloys that they studied (Figure 8). Xiong et al. proposed that the differences are due to the “limited accuracy of the thermodynamic models”, with small differences in free energy leading to the selection of different phases by the CALPHAD model [129].

The formation of MNSPs has long been associated with Cu-rich precipitates in alloys containing > 0.05 wt.% Cu [8, 12]. In low-Cu and Cu-free alloys it has been proposed that MNSPs form via a heterogeneous nucleation process on point defect clusters in irradiated materials [130]. Liu et al. conducted atom probe analysis and hardness tests on a series of alloys that had undergone accelerated ageing at 425 °C [87]. They hypothesised that there may be a synergistic effect between Mn and Ni in low-Cu steels, as increasing Ni and Mn concentration was observed to increase the amount of hardening and precipitate volume fraction [87].

Atom probe analysis of grain boundaries in thermally-aged RPV steels has revealed MNSP formation after extended ageing [13]. In a high-Cu (0.5 wt.%) steel, MNSPs were associated with

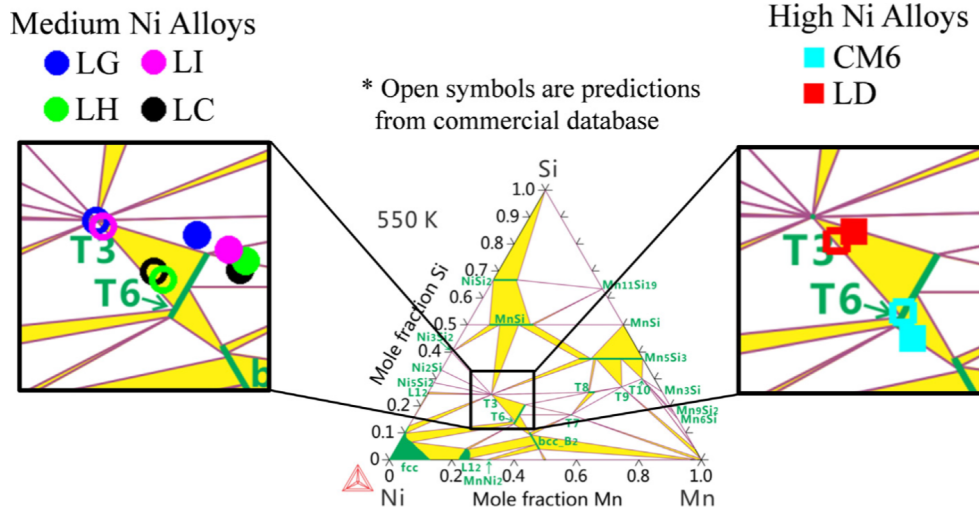


Figure 8: Comparison between MNSP compositions predicted by [129] (open symbols) and observed by [40] (filled symbols). Reproduced with permission from [40]. Copyright © 2014 Published by Elsevier B.V.

Cu precipitates, although it could not be determined which had precipitated first. The MNSPs were observed to precipitate in the absence of Cu precipitates in a low-Cu (0.03 wt.%) steel. Styman proposed that the formation of MNSPs on heterogeneous nucleation sites, such as grain boundaries, was possible due to the quicker diffusion pathway along the grain boundary [13]. However, there is very little literature about the effects of long-term thermal ageing on low-Cu RPV steels, despite recent modelling experiments suggesting that Mn-Ni-rich phases are thermodynamically stable [4, 129].

6 Outstanding Issues

Whilst the understanding of the early-stage clustering in high-Cu RPV steels, and the many developments in APT data analysis techniques, there are still outstanding issues:

- What effect does systematically varying solute concentrations have on the response of low-Cu RPV steels to long-term thermal ageing?
- Are the MNSPs that form in low-Cu RPV steels thermodynamically stable phases and do their compositions match those predicted by thermodynamic models?
- Is homogeneous precipitation of MNSPs possible?

- What is the crystal structure of the MNSPs that form?
- How long do MNSPs take to nucleate in low-Cu RPV steels during exposure to thermal ageing or irradiation, and what is the effect on hardness?
- Are MNSPs a “late-blooming phase” that rapidly increases in volume fraction after its nucleation?
- Is there any non-hardening embrittlement present in thermally-aged low-Cu RPV alloys?
- Which solutes have the most impact on the MNSPs precipitation?

Chapter III

Quantitative Analysis Of Literature

1 Introduction

Varying the composition of the steel that is used to manufacture the RPV is the principal way of optimising the response of the component to the conditions that it is exposed to. By minimising deleterious changes in mechanical properties during exposure to the extreme environments in which they operate, the safe operational lifetime of the RPV component can be maximised.

Some of the literature has focussed on the role that composition has on sensitivity to irradiation [131] and thermal ageing [13, 132], revealing the deleterious role Cu has on the mechanical properties of alloys. Many studies have also investigated the effect of varying irradiation conditions, such as temperature, fluence, and flux on the sensitivity of alloys to changes in mechanical properties during operation [133, 134, 135]; this is due to the interest in determining whether accelerated tests, which are often conducted at increased flux or irradiation temperature, accurately represent the conditions experienced by the RPV during operation.

As a result, the literature consists of a variety of studies that examine the effects of different environmental conditions on mechanical property changes of different RPV steels, as well as studies that examine compositional effects on the sensitivity to changes in mechanical properties.

Although there is a wealth of published data, it is heterogeneous; very few studies perform experiments with systematic changes in composition to investigate the role that different elements have on the sensitivity to changes in mechanical properties, and there is a large variety in the environmental conditions used across studies. This heterogeneity complicates direct cross-study comparisons since mechanical property changes are likely to be dependent on alloy composition as well as environmental factors.

Whilst reviews that summarise key findings and current understanding exist [136, 137, 138], a systematic statistical survey on the literature published by different research groups is lacking.

In order to investigate the effect of composition on changes in mechanical properties of RPV

steels, during exposure to conditions similar to those that would be experienced during operation, a systematic review of the current literature was performed. This review aimed to elucidate the relationship between Cu, Ni, Mn, Si, and P, with changes in the hardness, strength, and ductile-to-brittle transition temperature (DBTT).

2 Method

2.1 Inclusion Criteria

Inclusion criteria were pre-specified to identify relevant articles that contained information on the mechanical property changes in alloys during exposure to neutron irradiation or thermal ageing. The inclusion criteria were as follows:

1. The article had to be published in a peer-reviewed scientific journal. Although there are several databases, which contain a large quantity of data on mechanical property changes in a range of alloys during operation, these are not freely accessible
2. The article had information on changes in the hardness, strength, or DBTT of an alloy during exposure to thermal ageing or neutron irradiation
3. The investigated alloys had to be ferritic or bainitic in nature
4. Articles were published in English. Since translation into English was not viable, it was not possible to assess the suitability of articles written in other languages, so these articles were excluded from the review

2.2 Searches

Systematic searches of the platform Scopus were conducted to identify all articles published prior to January 2017 that contained the following four terms in their title or abstract: “Reactor Pressure Vessel Steel”, “RPV Steel”, “Thermal”, “Irradiation”. The first two terms were combined using the Boolean operators “OR”, as were the last two terms, whilst the terms relating to steels and conditions were combined with “AND”.

2.3 Data Extraction

The eligibility of identified articles was determined in a two-step process: title and abstract screening, and full-text retrieval and screening.

Data from all of the included articles were then manually extracted and added to a standardised excel database. If present, the following information was extracted from each study: alloy composition (wt.%), initial hardness (Hv), initial strength (MPa), and initial DBTT (K), and the change in hardness (Hv), strength (MPa), and DBTT (K). If reported in the article, information pertaining to the alloy's exposure to thermal ageing or neutron irradiation was also extracted; including: ageing temperature (K) and time (hours) for thermal ageing, and neutron flux (neutrons/cm²s), fluence (neutrons/cm²) and irradiation temperature (K) for neutron irradiation studies.

2.4 Data Synthesis and Analysis

Since units of measurement were not consistent between articles, values were converted to wt.%, Hv, MPa, K, neutrons/cm², and neutrons/cm²s where necessary. If conversion was not possible, or the units of measurement were unclear, the data were not included.

Following data extraction, data were examined via a series of simple and multiple regression analyses to investigate the effects of alloy composition and environmental conditions on initial mechanical properties and changes in mechanical properties. Predictor variables were conceptualised as different compositional levels of individual elements (e.g. Cu, Ni, Mn, Si, and P) and different environmental conditions (e.g. ageing temperature, ageing time, irradiation temperature, neutron flux, and neutron fluence). The outcome/dependent variables of interest were initial alloy hardness, initial strength, initial DBTT, change in hardness, change in strength, and change in DBTT. All predictor variables were standardised so that the relative effect of each variable could be easily compared.

Duplicate inclusions of initial properties were identified and removed from the database prior to analysis.

The Cu solubility level at service temperatures is approximately 0.05 at.% [139]. Therefore, many proposed new alloys aim to contain lower levels of Cu than this. The effect of composition on changes in mechanical properties for future generation low-Cu alloys is of interest and, given that most studies provide alloy composition in wt.%, it was decided for these analyses that low-Cu alloys

would be defined as alloys containing less than 0.05 wt.% Cu.

The following regression analyses were then carried out:

1. Effect of composition on initial hardness
2. Effect of composition on initial strength
3. Effect of composition on initial DBTT
4. Effect of composition, neutron flux, neutron fluence, and irradiation temperature on changes in hardness in neutron-irradiated alloys (including low-Cu alloys)
5. Effect of composition, neutron flux, neutron fluence, and irradiation temperature on changes in strength in neutron-irradiated alloys (including low-Cu alloys)
6. Effect of composition, neutron flux, neutron fluence, and irradiation temperature on changes in DBTT in neutron-irradiated alloys (including low-Cu alloys)
7. Effect of composition, ageing time, and ageing temperature on changes in hardness in thermally-aged alloys (including low-Cu alloys)
8. Effect of composition, ageing time, and ageing temperature on changes in strength in thermally-aged alloys (including low-Cu alloys)
9. Effect of composition, ageing time, and ageing temperature on changes in DBTT in thermally-aged alloys (including low-Cu alloys)
10. Effect of composition, neutron flux, neutron fluence, and irradiation temperature on changes in hardness in low-Cu alloys in neutron-irradiated alloys
11. Effect of composition, neutron flux, neutron fluence, and irradiation temperature on changes in strength in low-Cu alloys in neutron-irradiated alloys
12. Effect of composition, neutron flux, neutron fluence, and irradiation temperature on changes in DBTT in low-Cu alloys in neutron-irradiated alloys
13. Effect of composition, ageing time, and ageing temperature on changes in hardness in low-Cu alloys in thermally-aged alloys

14. Effect of composition, ageing time, and ageing temperature on changes in strength in low-Cu alloys in thermally-aged alloys
15. Effect of composition, ageing time, and ageing temperature on changes in DBTT in low-Cu alloys in thermally-aged alloys

Due to the added complexity associated with property changes in neutron-irradiated specimens, it was decided that separate analyses should be carried out on alloys that had been subjected to thermal ageing and neutron irradiation.

As temperature changes, different thermodynamic-driven processes become dominant. Konstantinović et al. have shown that in RPV steels, above approximately 530 °C, the most thermodynamically stable precipitate phase will change [140]. As a result, it was decided not to include thermal ageing experiments which used an ageing temperature above 530 °C.

Prior to carrying out the regression analyses, key statistical assumptions of linear regression analyses were checked. The normality assumption was examined, where the skewness and kurtosis of each outcome variable was inspected. High levels of skewness indicate that the distribution of the variable is asymmetric, with positive values indicating positive skew and negative values indicating negative skew. High positive values of kurtosis indicate that the distribution of the variable is heavy-tailed when compared to the normal distribution. The higher the absolute value of kurtosis, the greater the kurtosis.

If the skewness or kurtosis of an outcome variable was not within the range of ± 1.96 then the normality assumption was deemed to be violated as proposed in [141], and it was investigated whether a generalised linear model (GLM) should be used instead. GLMs allow non-normally distributed outcome variables to be fitted by incorporating a transformation (link) function; this function specifies how the expected value for the outcome variable relates to the linear predictor.

A GLM with a log-link function and Gaussian distribution were applied to each outcome variable that was judged to violate the multivariate normality assumptions. If the outcome variable contained negative values, such as change in hardness, then a constant value ($|\text{Minimum Value}|+0.01$) was added prior to application of the log transform to ensure that all values of the outcome variable were positive. The constant value of ($|\text{Minimum Value}|+0.01$) was selected as previous work has shown that adding large constant values prior to the log transform has a noticeable effect on the level of significance calculated in hypothesis testing [142].

The skewness and kurtosis of the log-transformed outcome variables were then inspected to

determine if they had been improved. If the skewness and kurtosis of each outcome variable had substantially improved, it was deemed that a GLM would better model the data than a simple linear model (SLM). However, if the outcome variable's skewness and kurtosis were not significantly improved, then it was decided that the GLM offered minimal benefits over the SLM, and that these benefits were probably outweighed by the error introduced from adding a constant value to the outcome variable prior to the log-transform [142].

Subjecting alloys to irradiation and thermal ageing is known to deleteriously effect mechanical properties. The effects on mechanical properties are known to be non-linearly related to some environmental conditions, for example thermodynamic stability of certain phases will change dramatically at certain temperatures. Therefore, if the effects of these environmental variables were found to non-linearly influence changes in mechanical properties, it was decided that the data should be subdivided into sections where the environmental effects were linear.

Effect sizes and corresponding 95% confidence intervals (CI) were calculated for all analyses. A significance level of $\alpha < 0.05$ was determined to indicate if an element had a significant relationship with the initial mechanical property when controlling for the other predictor variables.

3 Results

Of the 1553 papers identified, 464 could not be accessed or were published in foreign language journals. Of the remaining 1089 articles, 193 were deemed to be suitable based on the inclusion criteria above after their abstracts had been evaluated. A further 59 studies were also included after access was gained to the United States Nuclear Regulation Commission's Wide Ranging Database. This process is illustrated in Figure 9.

Of the included studies, 49 looked at the effects of thermal ageing on mechanical property changes, and 192 contained information on the effects of neutron irradiation on mechanical property changes.

Once the data had been extracted, analyses were conducted to investigate the relationship between alloy composition and mechanical properties.

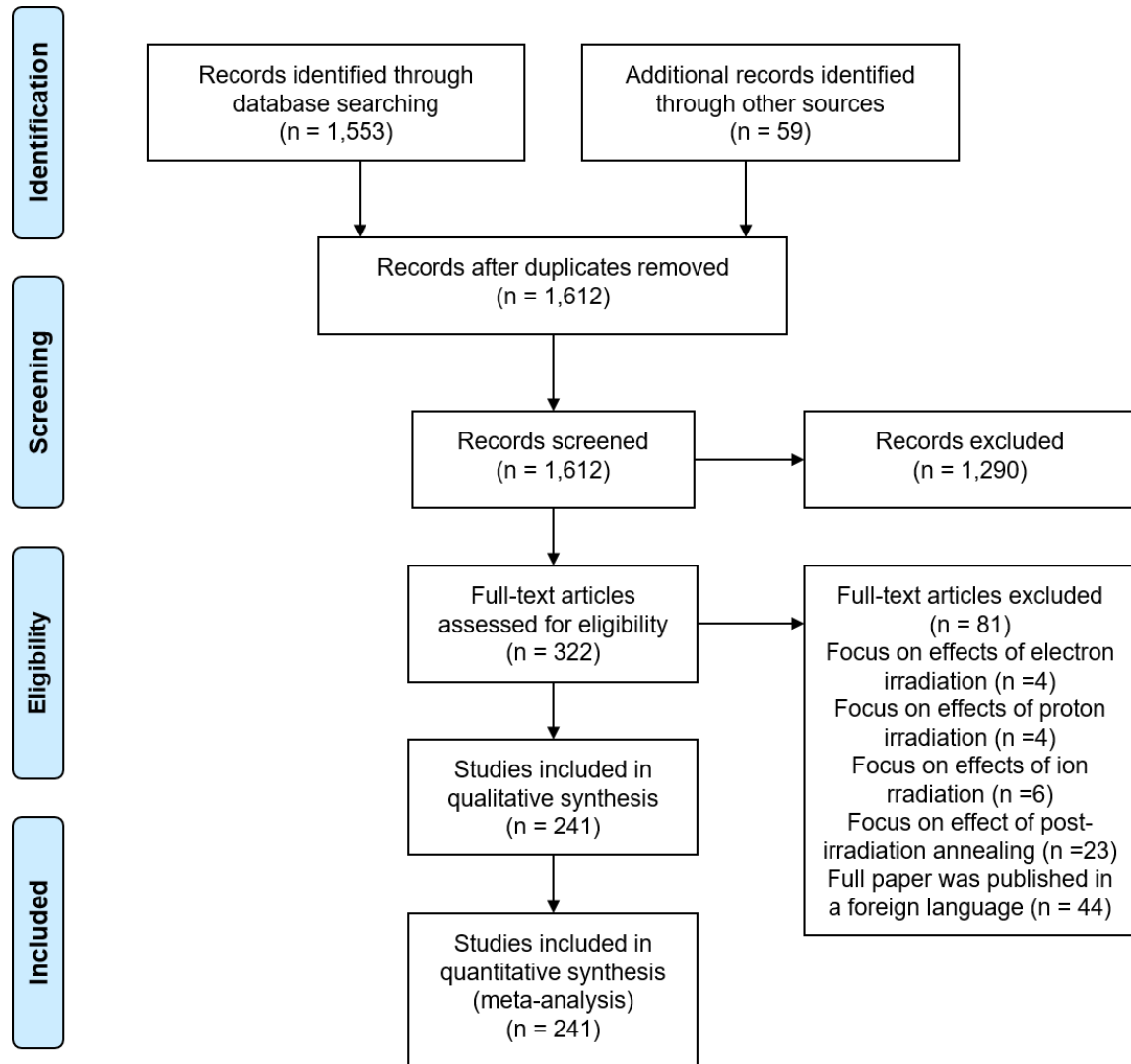


Figure 9: Flow chart demonstrating screening process of literature.

3.1 Outcome Variable Normality Checks

The distribution of the six outcome variables was checked. All six outcome variables violated the multivariate normality assumption. As a result, each outcome variable was log-transformed, and the effect of log transformations on skewness and kurtosis were examined (Table 2). The skewness and kurtosis of initial hardness improved after undergoing a log-transform and, because all values of initial hardness were positive (and did not require the addition of a constant), it was decided to use a GLM to investigate the relationship between alloy composition and initial hardness. The skewness and kurtosis of initial strength and initial DBTT was worse after performing a log transformation. Therefore, it was concluded that a linear model (LM) was best suited to modelling the data.

Hardness change, strength change, and DBTT change each contained negative values. It was thus necessary to add a constant prior to the log transform. After the log transformations, the skewness and kurtosis deteriorated for all three outcome variables. As a result, it was determined the LMs were more appropriate (Table 2).

Variable	Unadjusted Variable		Log Transformed Variable		Log Transformed Variable (after values transformed by addition of $ min + 0.01$)	Model Chosen
	Skewness	Kurtosis	Skewness	Kurtosis	Skewness Kurtosis	
Initial Hardness	1.358	6.658	-0.018	3.123	<i>N/A as was possible to perform log transform</i>	GLM
Initial Strength	-0.324	7.951	-2.309	12.685	<i>before addition of constant</i>	LM
Initial DBTT	-0.543	4.380	-1.362	7.543		LM
Hardness Change	0.831	4.446	<i>Could not be performed due to negative values</i>		-7.801 119.815	LM
Strength Change	1.546	8.991			-7.401 115.267	LM
DBTT Change	1.302	5.386			-0.797 13.954	LM

Table 2: Comparison of skewness and kurtosis of outcome variables prior to and after log transformation.

3.2 Effect Of Composition on Initial Mechanical Properties

The effects of alloy composition on the initial mechanical properties of the alloys were examined using the models specified in Table 2.

The results of multiple regression analysis ($N = 137$) indicated that increasing levels of Cu ($\beta = -0.06$, $p < 0.05$) were negatively correlated with the initial hardness, whilst Si ($\beta = 0.12$, $p < 0.01$) was significantly positively correlated with alloy initial hardness (Table 3).

Independent Variable	β with 95 % C.I.	p value
Cu	-0.06 (-0.11, -0.01)	0.029*
Ni	0.00 (-0.06, 0.06)	0.976
Mn	0.04 (-0.01, 0.08)	0.117
Si	0.12 (0.05, 0.20)	0.001**
P	-0.04 (-0.17, 0.09)	0.554

 Table 3: Dependent variable: initial hardness. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 137$.

A simultaneous entry multiple regression analysis showed Cu, Ni, Mn, Si, and P significantly accounted for 49.04 % of the variance of the initial strength ($R^2 = 0.4978$, $F(5, 336) = 66.62$, $p < 0.001$, $N = 342$). Cu ($\beta = 17.34$, $p < 0.001$) and Ni ($\beta = 36.50$, $p < 0.001$) were found to be significantly positively correlated with the initial strength, with Ni having a larger effect than Cu (Table 4).

Independent Variable	β with 95 % C.I.	p value
Cu	17.34 (11.56, 23.11)	< 0.001***
Ni	36.50 (28.67, 44.33)	< 0.001***
Mn	-1.69 (-10.05, 6.66)	0.691
Si	0.29 (-5.83, 6.40)	0.927
P	1.20 (-1.88, 4.28)	0.444

 Table 4: Dependent variable: initial strength. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 342$.

Multiple regression analysis of the effect of Cu, Ni, Mn, Si, and P on alloys' initial DBTT indicated that the five predictor variables significantly accounted for 23.33 % of the variance in initial DBTT ($R^2 = 0.2453$, $F(5, 314) = 20.41$, $p < 0.001$, $N = 320$). Table 5 shows that Cu ($\beta = -9.66$, $p < 0.001$) and Ni ($\beta = -4.17$, $p < 0.05$) shared a significant relationship with initial DBTT, with higher levels of Cu and Ni correlating with lower initial DBTT. Mn ($\beta = 10.12$, $p < 0.001$) and P ($\beta = 3.24$, $p < 0.001$), however, were significantly positively correlated with the initial DBTT of the alloys.

Independent Variable	β with 95 % C.I.	p value
Cu	-9.66 (-13.55, -5.78)	< 0.001***
Ni	-4.17 (-8.15, -0.18)	0.041*
Mn	10.12 (6.09, 14.16)	< 0.001***
Si	-1.53 (-5.58, 2.52)	0.461
P	3.24 (1.43, 5.05)	0.001**

 Table 5: Dependent variable: initial DBTT. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 320$.

3.3 Sensitivity of Alloys to Mechanical Property Changes During Exposure to Neutron Irradiation

The effect of alloy composition and irradiation conditions on the change in mechanical properties of the alloys was investigated using multiple linear regression models (Table 2).

A multiple regression analysis of the effect of Cu, Ni, Mn, Si, P, irradiation temperature, neutron flux, and neutron fluence on the change in hardness of alloys exposed to neutron irradiation found that the eight predictor variables accounted for 65.57 % of the variance in the data ($R^2 = 0.7087$, $F(8, 44) = 13.38$, $p < 0.001$, $N = 53$). Increasing levels of Cu ($\beta = 27.94$, $p < 0.001$) and neutron fluence ($\beta = 51.25$, $p < 0.01$) were correlated with significant increases in changes in alloy hardness, with the magnitude of the effect of neutron fluence larger than the magnitude of the effect of Cu (Table 6).

Independent Variable	β with 95 % C.I.	p value
Cu	27.94 (18.36, 37.52)	< 0.001***
Ni	-1.26 (-8.45, 5.93)	0.733
Mn	-0.07 (-10.52, 10.37)	0.989
Si	-4.58 (-11.47, 2.31)	0.199
P	3.12 (-5.42, 11.67)	0.477
Irradiation Temperature	-11.84 (-27.92, 4.23)	0.156
Neutron Flux	-5.36 (-17.61, 6.89)	0.396
Neutron Fluence	51.25 (22.65, 79.84)	0.001**

Table 6: Dependent variable: change in hardness during exposure to neutron irradiation. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 53$.

Table 7 shows the results of the multiple regression analysis of the relationship between strength changes during exposure to neutron irradiation and Cu, Ni, Mn, Si, and P levels, and irradiation temperature, neutron flux, and neutron fluence. The regression results revealed that the eight predictor variables accounted for 60.03 % of the variance ($R^2 = 0.6170$, $F(8, 184) = 37.05$, $p < 0.001$, $N = 193$). Changes in alloy strength were significantly correlated with each predictor variable, with increasing strength change correlated with increasing levels of neutron fluence ($\beta = 70.28$, $p < 0.001$), Cu ($\beta = 31.18$, $p < 0.001$), neutron flux ($\beta = 16.55$, $p < 0.001$), Si ($\beta = 12.70$, $p < 0.01$), P ($\beta = 11.52$, $p < 0.01$), and Ni ($\beta = 8.78$, $p < 0.05$). However, irradiation temperature ($\beta = -25.24$, $p < 0.01$) and Mn ($\beta = -9.34$, $p < 0.05$) were both negatively correlated with strength changes in alloys subjected to neutron irradiation.

Independent Variable	β with 95 % C.I.	p value
Cu	31.18 (15.34, 47.01)	$< 0.001^{***}$
Ni	8.78 (0.33, 17.24)	0.043*
Mn	-9.34 (-17.53, -1.15)	0.027*
Si	12.70 (3.99, 21.40)	0.005**
P	11.52 (3.36, 19.67)	0.006**
Irradiation Temperature	-25.24 (-42.95, -7.53)	0.006**
Neutron Flux	16.55 (9.23, 23.87)	$< 0.001^{***}$
Neutron Fluence	70.28 (55.20, 85.35)	$< 0.001^{***}$

Table 7: Dependent variable: change in strength during exposure to neutron irradiation. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 193$.

Multiple linear regression revealed that DBTT changes were also significantly correlated with all eight of the predictor variables (Cu, Ni, Mn, Si, and P, irradiation temperature, neutron flux, and neutron fluence). The predictor variables accounted for 51.03 % of the variance in the data ($R^2 = 0.5114$, $F(8, 3648) = 477.3$, $p < 0.001$, $N = 3657$). Increasing levels of neutron fluence ($\beta = 74.48$, $p < 0.001$), Cu ($\beta = 21.00$, $p < 0.001$), Ni ($\beta = 11.56$, $p < 0.001$), Si ($\beta = 5.39$, $p < 0.001$), Mn ($\beta = 4.50$, $p < 0.001$), neutron flux ($\beta = 4.36$, $p < 0.001$), and P ($\beta = 4.34$, $p < 0.001$) all correlated with an increase in DBTT change. Neutron fluence had the largest relative effect on DBTT change, whilst P affected DBTT with the smallest magnitude. Irradiation temperature ($\beta = -7.31$, $p < 0.001$) was negatively correlated with DBTT changes in alloys subjected to neutron irradiation (Table 8).

Independent Variable	β with 95 % C.I.	p value
Cu	21.00 (20.05, 21.95)	$< 0.001^{***}$
Ni	11.56 (10.33, 12.79)	$< 0.001^{***}$
Mn	4.50 (3.36, 5.64)	$< 0.001^{***}$
Si	5.39 (4.41, 6.38)	$< 0.001^{***}$
P	4.34 (3.07, 5.60)	$< 0.001^{***}$
Irradiation Temperature	-7.13 (-8.45, -5.81)	$< 0.001^{***}$
Neutron Flux	4.36 (3.11, 5.61)	$< 0.001^{***}$
Neutron Fluence	74.48 (70.39, 78.57)	$< 0.001^{***}$

Table 8: Dependent variable: change in DBTT during exposure to neutron irradiation. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 3657$.

3.4 Sensitivity of Alloys to Mechanical Property Changes During Exposure to Thermal Ageing

The effect of alloy composition, and thermal ageing conditions on the changes in mechanical properties of the alloys were studied using the multiple linear regression models specified in Table 2.

Multiple regression analysis (Table 9) of the effect of Cu, Ni, Mn, Si, P, ageing temperature, and ageing time on the change in hardness of alloys exposed to thermal ageing revealed that the eight predictor variables accounted for 57.45 % of the variance ($R^2 = 0.5844$, $F(7, 294) = 59.06$, $p < 0.001$). Cu ($\beta = 20.29$, $p < 0.001$, $N = 302$), Ni ($\beta = 11.85$, $p < 0.001$), and Si ($\beta = 4.96$, $p < 0.001$), were found to be positively correlated with changes in hardness during thermal ageing. Meanwhile, Mn ($\beta = -17.72$, $p < 0.001$), ageing time ($\beta = -8.54$, $p < 0.001$), ageing temperature ($\beta = -4.56$, $p < 0.001$) and P ($\beta = -2.29$, $p < 0.001$) were found to be negatively correlated with hardness changes during thermal ageing when controlling for other variables.

Independent Variable	β with 95 % C.I.	p value
Cu	20.29 (14.12, 26.45)	$< 0.001^{***}$
Ni	11.85 (8.70, 15.00)	$< 0.001^{***}$
Mn	-17.72 (-22.32, -13.11)	$< 0.001^{***}$
Si	4.96 (0.63, 9.29)	0.026*
P	-2.29 (-4.75, 0.18)	0.070
Ageing Temperature	-4.56 (-7.33, -1.79)	0.001**
Ageing Time	-8.54 (-13.31, -3.76)	0.001**

Table 9: Dependent variable: change in hardness during exposure to thermal ageing. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 302$.

Multiple linear regression analysis of the relationship between the predictor variables and changes in strength during exposure to thermal ageing revealed that the seven predictor variables accounted for 70.69 % of the variance in the data ($R^2 = 0.7801$, $F(7, 21) = 10.65$, $p < 0.001$, $N = 29$). Changes in alloy strength were only observed to be significantly positively correlated with Cu ($\beta = 84.32$, $p < 0.01$) (Table10).

Independent Variable	β with 95 % C.I.	p value
Cu	84.32 (32.91, 135.74)	0.004**
Ni	-25.20 (-65.62, 15.22)	0.235
Mn	-1.05 (-96.02, 93.91)	0.983
Si	28.40 (-59.94, 116.74)	0.535
P	-14.95 (-49.22, 19.32)	0.402
Ageing Temperature	-29.83 (-79.58, 19.92)	0.253
Ageing Time	-17.43 (-57.13, 22.27)	0.399

Table 10: Dependent variable: change in strength during exposure to thermal ageing. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 29$.

Multiple linear regression (Table 11) revealed that the predictor variables accounted for 26.59 % of the variance in the change in DBTT during thermal ageing ($R^2 = 0.3183$, $F(7, 91) = 6.071$, $p < 0.001$; $N = 99$). Ageing temperature ($\beta = 24.18$, $p < 0.001$) was significantly

positively correlated with increases in DBTT, whilst P ($\beta = -24.97$, $p < 0.001$) was negatively correlated with changes in DBTT.

Independent Variable	β with 95 % C.I.	p value
Cu	19.37 (−57.38, 96.13)	0.622
Ni	−0.84 (−8.90, 7.22)	0.839
Mn	9.47 (−5.05, 23.99)	0.204
Si	4.78 (−7.25, 16.81)	0.438
P	−24.97 (−42.33, −7.61)	0.006**
Ageing Temperature	24.18 (14.25, 34.10)	< 0.001***
Ageing Time	6.77 (0.01, 13.54)	0.053

Table 11: Dependent variable: change in DBTT during exposure to thermal ageing. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 99$.

3.5 Sensitivity of Alloys to Mechanical Property Changes During Exposure to Neutron Irradiation In Low-Cu Alloys

The effect of alloy composition, and irradiation conditions on the changes in mechanical properties of the low-Cu (< 0.05 wt.%) alloys was investigated.

Multiple regression analysis of the effect of Cu, Ni, Mn, Si, P, irradiation temperature, neutron flux, and neutron fluence on hardness changes in neutron-irradiated alloys revealed that the eight predictor variables accounted for 84.60 % of the variance in the data ($R^2 = 0.9230$, $F(8, 8) = 11.9$, $p < 0.01$, $N = 17$). In the low-Cu alloys, increasing levels of neutron fluence ($\beta = 55.53$, $p < 0.01$) and Ni ($\beta = 19.43$, $p < 0.01$) were positively correlated with hardness changes during irradiation (Table 12). Cu was significantly negatively correlated ($\beta = -12.34$, $p < 0.01$) with changes in hardness.

Independent Variable	β with 95 % C.I.	p value
Cu	−12.34 (−17.46, −7.22)	0.001**
Ni	19.43 (10.53, 28.32)	0.003**
Mn	33.54 (−88.87, 155.95)	0.606
Si	−3.20 (−12.23, 5.84)	0.508
P	3.19 (−7.27, 13.64)	0.567
Irradiation Temperature	84.62 (−97.97, 267.21)	0.390
Neutron Flux	0.12 (−6.24, 6.48)	0.971
Neutron Fluence	55.53 (29.50, 81.56)	0.003**

Table 12: Dependent variable: change in hardness of low-Cu steels during exposure to neutron irradiation. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 17$.

Multiple regression analysis on low-Cu alloys investigated the relationship between strength

changes during exposure to neutron irradiation and Cu, Ni, Mn, Si, and P levels, and irradiation temperature, neutron flux, and neutron fluence (Table 13). It was found that the eight predictor variables accounted for 72.87 % of the variance in the data ($R^2 = 0.7493$, $F(8, 97) = 36.25$, $p < 0.001$, $N = 106$). Changes in alloy strength were positively correlated with neutron fluence ($\beta = 207.83$, $p < 0.001$), neutron flux ($\beta = 34.54$, $p < 0.001$), and Si ($\beta = 21.68$, $sp < 0.01$). Irradiation temperature ($\beta = -131.19$, $p < 0.001$) was negatively correlated with changes in strength.

Independent Variable	β with 95 % C.I.	p value
Cu	2.48 (−12.38, 17.34)	0.744
Ni	5.03 (−1.23, 11.30)	0.119
Mn	2.55 (−8.36, 13.47)	0.647
Si	21.68 (5.72, 37.63)	0.009**
P	7.49 (−0.65, 15.62)	0.074
Irradiation Temperature	−131.19 (−178.44, −83.95)	< 0.001***
Neutron Flux	34.54 (23.55, 45.52)	< 0.001***
Neutron Fluence	207.83 (114.53, 301.14)	< 0.001***

Table 13: Dependent variable: change in strength of low-Cu steels during exposure to neutron irradiation. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 106$.

Multiple linear regression revealed that DBTT changes were also significantly correlated with six of the eight predictor variables: Cu, Ni, P, irradiation temperature, neutron flux, and neutron fluence (Table 14). The eight predictor variables accounted for 52.18 % of the variance in the data ($R^2 = 0.5261$, $F(8, 874) = 121.3$, $p < 0.001$; $N = 883$).

Increasing levels of neutron fluence ($\beta = 161.91$, $p < 0.001$), P ($\beta = 4.39$, $p < 0.001$), Ni ($\beta = 3.85$, $p < 0.001$), and Cu ($\beta = 2.48$, $p < 0.001$) were each correlated with increasing DBTT change. Irradiation temperature ($\beta = -7.77$, $p < 0.001$) and neutron flux ($\beta = -3.05$, $p < 0.001$), however, were negatively correlated with DBTT changes in alloys subjected to neutron irradiation.

Independent Variable	β with 95 % C.I.	p value
Cu	2.48 (1.32, 3.64)	< 0.001***
Ni	3.85 (2.77, 4.93)	< 0.001***
Mn	0.99 (−0.05, 2.03)	0.062
Si	0.50 (−0.56, 1.56)	0.355
P	4.39 (3.26, 5.52)	< 0.001***
Irradiation Temperature	−7.77 (−9.06, −6.48)	< 0.001***
Neutron Flux	−3.05 (−4.58, −1.51)	< 0.001***
Neutron Fluence	161.91 (149.07, 174.75)	< 0.001***

Table 14: Dependent variable: change in DBTT of low-Cu steels during exposure to neutron irradiation. * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; $N = 883$.

3.6 Sensitivity of Alloys to Mechanical Property Changes During Exposure to Thermal Ageing In Low-Cu Alloys

It was not possible to perform regression analyses on low-Cu alloys exposed to thermal ageing. This was because there were too few data points for the given number of degrees of freedom, meaning either regression could not be performed or the power of the regression was very low.

4 Discussion

4.1 Initial Properties

The relationship between increasing Si content with increasing initial hardness may be explained as low-Si alloys are often ferritic in nature, which is a much softer microstructure than bainite [143]. The negative correlation between Cu and initial hardness is surprising, but may be due to increasing levels of FCC Cu leading to some retained austenite, which is softer than bainite.

Nominal Ni and Cu levels were positively correlated with steel initial strength. Ni is known to increase the initial strength of steels, whilst Cu can be expected to increase the initial strength of the steels as Cu is known to precipitate out of solution during initial heat treatments [68].

P is known to embrittle grain boundaries in steels [144], so observing an increase in initial DBTT with increasing P content is unsurprising. McElroy et al. also observed segregation of Mn to prior-austenite grain boundaries led to an increase in DBTT [145] and, as an increase in nominal levels of Mn will likely lead to increased levels of Mn at the prior-austenite grain boundaries, this may explain the relationship between increased Mn levels and increased initial DBTT. The correlation between increasing levels of Cu, Ni, and Si and increasing initial DBTT is of interest, and may require further investigation.

4.2 Sensitivity of Alloys to Mechanical Property Changes During Exposure to Neutron Irradiation

Increasing experienced fluence was found to correlate with increases in hardness, strength, and DBTT of the alloys exposed to neutron irradiation. This is to be expected, since more neutrons impacting the specimen will lead to more matrix damage, increased rates of segregation and precipitation formation.

Increasing levels of Cu were associated with increasing levels of change in hardness, strength, and DBTT during neutron irradiation. The increasing change in hardness and strength may be explained by the formation of a higher volume fraction of Cu-rich precipitates as nominal Cu content increases. Whilst Lejcek et al. have shown that Cu embrittles grain boundaries in α -Fe [144].

As nominal levels of Ni, Si, and P increased, there was a correlation with increased changes of strength and DBTT during exposure to neutron irradiation. The increase in strength may be due to the increasing volume fraction of precipitates forming, whilst the increase in DBTT may be due to a higher level of these elements being present at grain boundaries. P and Si have been shown to weaken grain boundaries in α -Fe [144]. However, the same paper states that Ni strengthens grain boundaries in α -Fe, so the reason for increasing nominal levels of Ni correlating to increases in DBTT is not immediately clear.

Mn was found to significantly account for increasing changes in DBTT during neutron irradiation. Mn is known to embrittle grain boundaries in α -Fe [144], which may explain this observation. The correlation between increasing nominal levels of Mn and decreasing strength changes during irradiation is counter-intuitive, as Mn is expected to lead to the formation of MNSPs during irradiation [40] which, in turn, would lead to an increase in the strength of the alloy. However, a study using artificial neural networks to analyse the IVAR database found that Mn was not predicted to have a large effect on DBTT shift [146].

Irradiation temperature was found to be negatively correlated with changes in strength and DBTT when accounting for other variables. This is in line with the published literature [134, 147]. Performing irradiations at higher temperatures will allow for more recovery as defects annihilate with one another at a great frequency, reducing the amount of matrix damage present for a given fluence.

Increased flux rates were correlated with greater increases in strength and DBTT during neutron irradiation. This finding is in contradiction to the published literature, as several articles state that increased flux rates lead to decreased DBTT and strength changes [43, 44, 135, 148].

4.3 Sensitivity of Alloys to Mechanical Property Changes During Exposure to Thermal Ageing

The positive correlation observed between increasing nominal levels of Cu and changes in hardness and strength after thermal ageing is likely due to the formation of a higher volume fraction of precipitates as nominal levels of Cu increase. This effect has been well documented in the literature [13].

From the published data available, increasing nominal levels of Ni and Si were correlated with increased changes in hardness during thermal ageing. This correlation is likely due to the formation of a higher volume fraction of precipitates as nominal levels of these solutes increases.

Increased levels of Mn were correlated with a decrease in hardness change during thermal ageing. Since, Mn is known to be present in MNSPs in neutron-irradiated alloys [40], increasing Mn levels may be expected to lead to a higher volume fraction of precipitates and, hence, an increase in hardness. The fact that this trend was not observed when analysing the thermally-aged data from the literature suggests that this hypothesis may have to be further investigated for thermally-aged alloys.

When controlling for other variables, it was observed that increasing levels of P were correlated with a decreased shift in DBTT during exposure to thermal ageing. This result is not in line with the current consensus within the field as P is a known grain boundary embrittler [144].

Increasing ageing time and temperature was correlated with increasing changes in DBTT. This is to be expected as at higher ageing times and temperatures, the distance over which diffusion can take place is increased. It is, therefore, possible for more solute ions to diffuse to grain boundaries during the ageing process.

The negative correlation between increasing ageing time and temperature with hardness change is surprising, but the trend with ageing temperature may be due to a decreased driving force for precipitation at higher temperatures, since the solubility limit of Cu in Fe increases with increasing temperature [18]. As a result, it could be expected that a lower volume fraction of Cu precipitates will form than at lower temperatures, and so there will be a smaller change in hardness.

4.4 Sensitivity of Alloys to Mechanical Property Changes During Exposure to Neutron Irradiation in Low Cu Alloys

Regression analyses performed on low-Cu alloys subjected to neutron irradiation indicated that increasing nominal levels of Cu, Ni, P led to increased changes in DBTT. Increasing nominal levels of these solutes will likely lead to a greater degree of segregation of these solutes to grain boundaries during irradiation, and an increase in grain boundary embrittlement.

Increasing nominal levels of Ni were correlated with increased changes in alloy hardness during neutron irradiation. This is likely due to a higher volume fraction of MNSPs forming during the irradiation process. However, increasing levels of Cu were indicative of smaller hardness changes in low-Cu alloys during irradiation.

An increase in the volume fraction of precipitates forming with increased nominal Si levels may explain the trend of increased change in strength that was highlighted by the regression analyses.

Irradiation temperature was negatively correlated with changes in strength and DBTT during neutron irradiation. This is in agreement with the literature [134, 147], as previously stated.

Increased fluence was found to correlate with increases in hardness, strength, and DBTT of the alloys exposed to neutron irradiation. This is to be expected, since more neutrons impacting the specimen will lead to more matrix damage, increasing rates of diffusion and, therefore, precipitation formation [44].

Increased neutron flux positively correlated with increasing changes in strength during neutron irradiation, whilst neutron flux was negatively correlated with changes in DBTT. The positive correlation between neutron flux and strength change is in contradiction with the current literature understanding [44, 135], whilst the negative correlation of the change in DBTT with neutron flux has been observed and commented on [43, 149].

5 Conclusion

A systematic study has been conducted to investigate the relationship between compositional and environmental variables on the initial mechanical properties and the changes in mechanical properties of alloys subjected to thermal ageing or neutron irradiation. This review has shown that compositional, as well as environmental factors, influence alloy response to irradiation and thermal

ageing. Increased levels of Cu, Ni, Si, and P were observed to increase the sensitivity of alloys to mechanical property changes in high-Cu alloys during neutron irradiation, whilst Cu, Ni, and Si were observed to increase alloy sensitivity during thermal ageing.

The statistical power of the low-Cu analyses is low due to the small number of published studies using low-Cu alloys. Indeed, it was not possible to perform analyses on the thermally-aged low-Cu alloys.

Another finding of this study was that very few articles reported all variables in their studies; with some even failing to state key variables, such as neutron flux. As a result, many studies could not be included in the regression analyses since multiple regression cannot be performed when one or more of the variables are missing. This may be overcome by using more advanced data analysis techniques, but it would be beneficial if future articles reported variables using consistent units and if there was consensus in the community as to which variables should be reported. For example, there is an argument for reporting initial hardness if change in hardness is reported (since the two may be related).

Due to the large number of variables and many competing processes, the challenge of determining the individual roles of different variables is highly complex. More studies should be designed to systematically change compositional variables whilst maintaining constant environmental variables, in order to try and elucidate the effects of compositional variables. An outcome of the presented work could be to inform which compositional variables, or combination of compositional variables, should be prioritised for systematic variation.

Further work could investigate proton, ion, and electron irradiation studies. There is also the option to place the current data into an artificial neural network, similar to those in [146, 150]. This would allow the links between input and output variables to be further explored.

Chapter IV

Materials and Methods

1 Materials

1.1 Thermally-Aged Model RPV Steels

The composition (at.%) of the model RPV steels that were subjected to thermal ageing in this thesis are shown in Table 15. The model alloys were chosen so that the effect of systematically varying nominal Ni, Mn, and Si levels on the response of low-Cu steels subject to thermal ageing could be investigated. The main microstructural development of interest was the formation and growth of precipitates that would lead to an increase in the hardness of the alloys.

Alloy ID	Cu	Si	Ni	Mn	P	Cr	Mo	C	Fe
A	0.04	0.38	1.56	0.25	0.01	0.10	0.28	1.12	Bal.
B	0.04	0.39	0.23	0.25	0.05	0.11	0.29	0.91	Bal.
C	0.04	0.37	3.11	1.90	0.01	0.10	0.27	0.87	Bal.
D	0.04	0.37	3.12	1.43	0.01	0.10	0.27	1.09	Bal.
E	0.04	1.14	0.18	1.46	0.01	0.10	0.28	1.11	Bal.
F	0.25	0.37	3.12	1.43	0.01	0.10	0.27	0.87	Bal.
G	0.04	0.38	1.54	1.93	0.01	0.10	0.28	0.88	Bal.
H	0.04	0.38	0.18	1.96	0.01	0.10	0.28	0.90	Bal.
I	0.04	1.11	3.11	1.42	0.01	0.10	0.27	0.87	Bal.
J	0.04	0.09	3.14	1.44	0.01	0.10	0.27	0.88	Bal.
K	0.04	0.38	3.16	0.24	0.01	0.10	0.28	1.10	Bal.
L	0.04	0.38	1.55	0.73	0.01	0.10	0.28	1.12	Bal.
M	0.04	1.12	3.14	0.24	0.01	0.10	0.27	1.10	Bal.
N	0.17	0.39	0.23	0.25	0.01	0.11	0.28	0.91	Bal.
O	0.04	0.37	3.13	1.43	0.05	0.10	0.27	0.87	Bal.
P	0.04	0.39	0.23	0.25	0.01	0.11	0.28	1.14	Bal.
Q	0.04	0.38	0.18	1.47	0.01	0.10	0.28	1.12	Bal.
R	0.04	1.16	0.23	0.25	0.01	0.10	0.28	0.90	Bal.
S	0.04	0.38	3.15	0.72	0.01	0.10	0.27	1.10	Bal.
Alloy ID	Cu	Si	Ni	Mn	P	Cr	Mo	C	Fe

Table 15: Model RPV steel sample compositions in at.%. Nominal compositions were provided by Rolls-Royce Plc.

Prior to thermal ageing these steels were forged, rolled to 25 mm in thickness and austenitised for 1 hour at 920 °C. They were then air cooled, and tempered at 600 °C for five hours before being air cooled to room temperature. In an attempt to prevent oxidation during thermal ageing, the steels were vacuum sealed in quartz tubes prior to being placed in the furnaces.

The steels were thermally-aged at 330 °C, 365 °C, and 405 °C for the times shown in Table 16. Despite typical RPVs operating at 290 °C it is believed that, for the studied materials, the selected ageing temperatures represent similar thermodynamic regimes to those at 290 °C but offer a large increase in the kinetics [13]; reducing the amount of time required for the microstructure to develop towards its thermodynamic equilibrium state.

Sample	Cumulative Ageing Time (h)		
	First Treatment	Second Treatment	Third Treatment
A, C, F, G, H, K	11,688	20,732	30,116
B, D, E, I, J, L, M, N, O, P, Q, R, S	11,688	20,733	30,646

Table 16: Cumulative ageing times for the thermally-aged alloys after each of the ageing treatments.

Hardness tests were conducted on every sample after each ageing cycle, and atom probe tomography was used to characterise materials which exhibited changes in their properties. Hardness measurements for the as-received and thermally-aged for 11,688 hours specimens were conducted by Dr. J. Zelenty [151].

1.2 Neutron-Irradiated Model RPV Steels

Four RPV steels were irradiated in the Advanced Test Reactor 2 (ATR-2) experiment by the University of California, Santa Barbara (UCSB). The steels were neutron-irradiated to a fluence of 1.4×10^{20} n/cm² at 290 °C and a flux of 3.6×10^{12} n/cm²s.

Alloy ID	Cu	Si	Ni	Mn	P	Cr	Mo	C	Fe
C	0.04	0.37	3.11	1.90	0.01	0.10	0.27	0.87	Bal.
G	0.04	0.38	1.54	1.93	0.01	0.10	0.28	0.88	Bal.
K	0.04	0.38	3.16	0.24	0.01	0.10	0.28	1.10	Bal.
RX12	0.02	0.06	3.22	0.04	0.00	1.84	0.31	0.96	Bal.

Table 17: Model RPV steel sample compositions in at.%. Nominal compositions were provided by Rolls-Royce Plc.

The compositions of the alloys are shown in Table 17. RX12 has a higher Cr content than the other alloys as it is a cross-reference alloy, whilst the others are model alloys. However, as previous studies have not indicated any correlation between Cr levels and the formation of Mn-Ni-Si-rich precipitates, this should not impact the integrity of the study.

Three of the samples (C, G, K) were the same composition and had undergone the same initial processing route as three of the thermally-aged materials, allowing for a comparison to be made between the effects of thermal ageing and neutron irradiation. In comparison, RX12 was thicker than the model alloys. RX12 was forged before undergoing austenitisation. The alloy was then water-quenched, tempered and then subjected a stress relief treatment.

After irradiation, mechanical testing was conducted on these specimens, 0.5 mm thick 3 mm diameter discs were then extracted from each alloy. The discs were mechanically ground and polished by collaborators at UCSB.

2 Hardness Measurements

Hardness measurements were performed on the thermally-aged materials using a Vickers hardness machine with a load of 20 kgf for 10 seconds. Prior to each batch of hardness tests, a reference block, calibrated by EURO PRODUCTS, was tested to ensure that the machine was functioning correctly. The hardness of this block was reported as being $195.7 \text{ HV}_{20} \pm 1.6 \text{ HV}_{20}$ (99% CI) by the calibration laboratory. If the mean of 3 measurements performed using the hardness machine lay within this range, the machine was assumed to be operating correctly.

Prior to testing, all specimens were ground with 1200 grit SiC paper to remove any oxidised regions. Two indents were then performed on four faces of the test samples. The end faces were not flat so they were not tested, as this would have introduced unsystematic variations into the measurement. The end faces were not flat because sections for further metallographic inspection were cut from these ends of each sample.

After each of the indents had been made, the diagonals of the indent were measured using the optical microscope attached to the hardness test machine. The average diagonal length for each indent was computed and the Vickers Pyramid Number was calculated using the equation:

$$HV = \frac{1.8544 \times F}{\left(\frac{d}{1000}\right)^2} \quad (4)$$

where F is the kilogram-force used and d is the mean diagonal length of the indent (in μm). The mean HV and standard error of the mean were calculated for each sample using standard equations.

3 Atom Probe Tomography

The early stages of formation of Cu-rich and Mn-Ni-Si-rich precipitates are of primary interest. In order to study the nucleation of these features, it is necessary to implement a characterisation technique that is simultaneously capable of providing high spatial and chemical resolution. Whilst TEM has high spatial resolution, it only provides two dimensional imaging capabilities, complicating the accurate quantification of cluster number densities and volume fractions [152]. Also, TEM may not offer a high enough resolution to image very fine precipitates [153].

Atom probe tomography (APT) is a three-dimensional characterisation technique and excels at analysing 2D (interfaces) and 3D (precipitates) features. APT has a lateral spatial resolution of up to 0.2 nm [154], an in depth resolution of up to 0.06 nm [155, 156], and can detect elements, irrespective of mass, with an equivalent sensitivity (up to 100 atomic parts per million) [154]. A typical atom probe experiment collects 10^6 ions - 10^8 ions from which a 3D reconstruction of the original specimen can be generated. Depending on the number of ions detected during the experiment, the volume of the 3D reconstruction can vary from approximately $20\text{ nm} \times 20\text{ nm} \times 50\text{ nm}$ to $100\text{ nm} \times 100\text{ nm} \times 500\text{ nm}$. APT is capable of providing information on the chemical composition of different phases within a material, as well being a valuable tool to investigate the segregation of specific elements to certain features such as grain boundaries and dislocations [157].

3.1 Basic Principles

APT relies on the highly controlled field evaporation of ions from the apex of a sharp, needle-shaped specimen [158]. A high electric field is required for field evaporation to occur at the specimen surface [159]. This is achieved by superimposing a high voltage or laser pulse on top of a standing DC voltage, with the goal of evaporating no more than one atom per pulse [157]. For the required high fields to be reached at reasonable voltages (1 kV - 10 kV), the specimen must be very sharp as the generated field is inversely proportional to the tip radius [157, 160]. The electric field

(F) generated at the apex of a needle shaped specimen is:

$$F = \frac{V}{k_f R} \quad (5)$$

where V is the applied voltage, k_f is the geometric field factor accounting for the shape of the tip and R is the radius of curvature of the sample [157, 160].

Whilst the exact mechanism by which field evaporation occurs is still debated, Müller's image hump model enables full analytical treatment and is conceptually simple [157, 159]. Müller proposed that a surface atom becomes ionised and is pulled away from the surface by the applied electric field, whilst its own electrostatic image attracts the ion back to the surface. Once the ion has moved a certain field-dependent distance (the Schottky Hump) from the surface, it is fully ionised and is repelled away from the surface [157, 159].

The field evaporated ions are then accelerated by the electric field and quasi-stereographically projected onto a detector, which records both the time and position of impact for each ion. From this recorded information, the time-of-flight (TOF) is known, allowing each atom to be chemically identified using mass-to-charge-state ratios [161]. Figure 10 shows a schematic diagram of a straight flight path Local Electrode Atom Probe (LEAP).

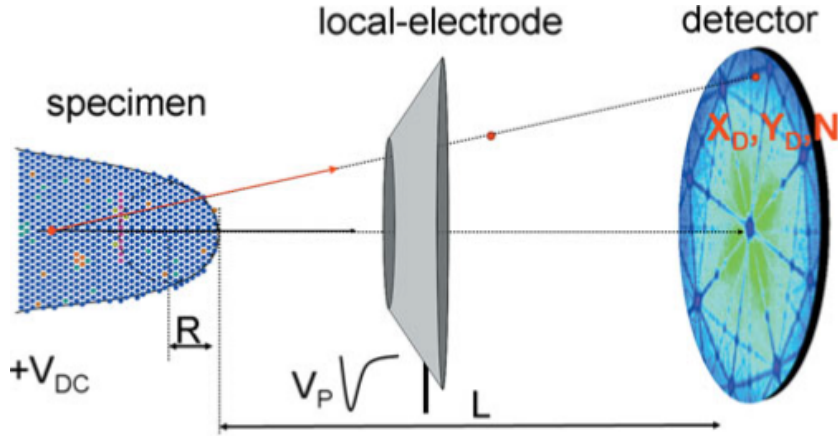


Figure 10: Schematic view of the local electrode atom probe; X_D , Y_D are the coordinates of the impact of the ion on the position sensitive detector; N refers to the position of atom within the sequence of detected atoms (N.B. not to scale). Reproduced with permission from [162]. Copyright © 2010 Published by Cambridge University Press.

After data collection, Integrated Visualisation & Analysis Software (IVAS) is used to apply a reverse-projection algorithm to the data and a 3D point cloud is constructed,

atom-by-atom [163, 164, 165]. The original x and y coordinates of each atom within the specimen are calculated from the detector positions. The position of the atoms in the z direction are based upon the temporal order in which the atoms are detected [166]. Corrections which account for the gradual increase in tip radius as the experiment progresses, and for a change in time-of-flights of ions as the voltage changes throughout the experiment are also applied [108, 163, 166].

The point-projection method designed by Bas et al., after the work of Blavette et al., assumes a perfectly hemispherical specimen shape and is based upon small angle approximations [163, 167]. This was shown to have limited accuracy, especially around the edges of the tomographic volume, in wide-field-of-view instruments by Gault et al. and Geiser et al. [164, 165, 168]. Gault et al. and Geiser et al. derived algorithms without any small angle approximations; it is these algorithms that are used in the reconstruction software IVAS. Larson et al. and Gault et al. have proposed that improvements could be made to the reconstruction algorithms currently used by having an image compression factor (ICF) and field factor (k_f) that vary with depth into the reconstruction, or with radial impact position on the detector [169, 170]. The ICF is required since the specimen shape and the electrostatic environment cause the field lines to be deflected towards the main axis of the specimen [157]. This may lead to a different angle between two crystallographic directions being observed on the detector than is theoretically expected [157]. The ICF adjusts for this deflection [157] and is needed to account for the non-hemispherical shape that most specimens have [169].

3.2 Sample Preparation

To generate a large enough field to induce field evaporation at the specimen surface, the sample tip must have a radius of curvature < 100 nm. It is also important that the shank angle (the half angle at the apex of the sample) is sufficiently small, such that the tip radius does not increase rapidly during the experiment [166].

Other considerations taken into account during sample preparation are: the sample must be robust enough to withstand the high stresses that the large electric field generates, and the preparation technique must not damage or alter the microstructure of the alloy.

3.2.1 Electropolishing

Electropolishing is the most conventional method for preparing samples for APT due to the simple equipment required and the speed at which samples can be prepared. Figure 11 illustrates the two stages of electropolishing.

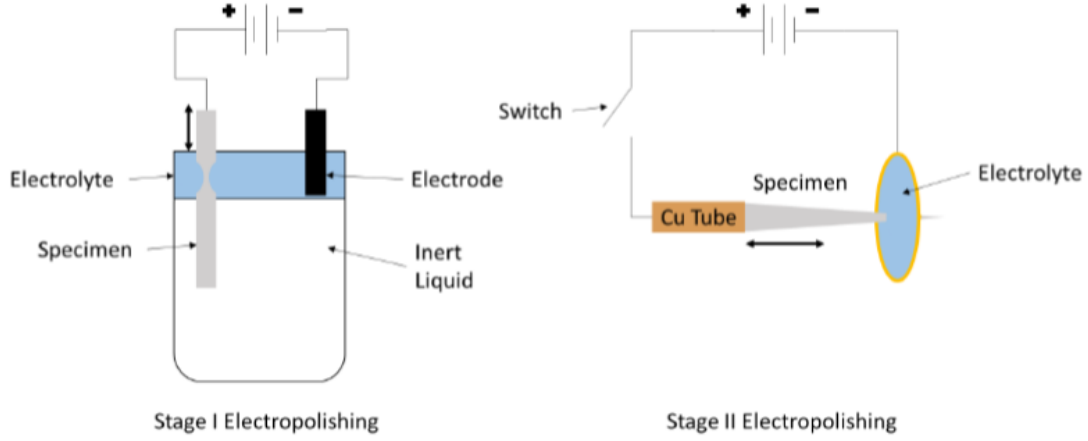


Figure 11: Schematic diagram of Stage I and Stage II Electropolishing.

Electropolishing's primary drawback is that it is not a site-specific preparation technique. This, combined with the sampling volume of a typical APT experiments, means it is unlikely that uncommon microstructural features, such as grain boundaries, will be contained in the analysed volume.

The main stages of electropolishing used to prepare samples in this thesis were:

1. Matchsticks ($0.5 \text{ mm} \times 0.5 \text{ mm} \times 25 \text{ mm}$) were cut from the bulk material.
2. Stage I Electropolishing

The matchstick was connected to a DC power source and repeatedly dipped into a layer of electrolyte floating on top of an inert liquid (GaldenTM). The matchstick acted as the anode and lost mass to the cathode (a gold wire). Since the rate of loss of material is proportional to the amount of time spent in the electrolyte, a neck was created. The circumference of the neck decreased until the sample broke into two pieces. The two needles were then removed and cleaned with ethanol and 2-isopropanol.

3. Stage II Electropolishing

This micropolishing stage was carried out by passing the needle through an electrolyte that

was suspended in a wire loop. The specimen was passed through the electrolyte until a necked region was created. When this neck broke, a specimen with a very sharp tip was created. The specimen was again cleaned with ethanol and 2-isopropanol.

The conditions used by Vaynman et al. (Stage I - 10 % perchloric acid–90 % acetic acid at 8 V – 20 V DC, Stage II - 2 % perchloric acid–98 % butoxyethanol at 12 V – 20 V DC) were used in the preparation of thermally-aged RPV steels for APT analysis [115].

3.2.2 Focused Ion Beam (FIB) Site-Specific Specimen Preparation

Unlike electropolishing, FIB sample preparation allows site-specific microstructural features, such as grain boundaries, to be analysed more routinely [171, 172]. FIB preparation typically relies on the use of high energy Ga ions to remove material from around the selected region of interest.

To create samples suitable for APT analysis, several stages are required. Reference [173] provides a comprehensive summary of FIB-based specimen preparation methods. The main steps used to prepare site-specific samples in this thesis are summarised in Figure 12 and below (typical Ga beam voltages and currents for each stage are shown in parentheses):

- (a) The desired feature was located using the SEM attached to the FIB and a protective layer (typically 1 μm - 2 μm of W/Pt) was deposited over the region of interest to protect the sample from Ga ion damage during the milling process (30 kV, 80 pA - 150 pA, W/Pt gas)
- (b) Trenches were milled, using Ga ions, around the region of interest to create a cantilever beam (30 kV, 1.5 nA - 6.0 nA)
- (c) The cantilever was welded to a micro-manipulator using W/Pt (30 kV, 80 pA - 150 pA, W/Pt gas), then the cantilever was cut free (30 kV, 300 pA - 700 pA) and removed using the micro-manipulator
- (d) Cross-sections of the beam were welded with W/Pt onto a prefabricated silicon post array (30 kV, 80 pA - 150 pA, W/Pt gas) and the lift-out bar was then cut free (30 kV, 80 pA - 300 pA)
- (e) & (f) The tips were milled using a progressively smaller annulus to create a needle with a tip radius of < 100 nm (30 kV, 80 pA - 300 pA). In order to produce a smooth surface and to reduce Ga implantation, the beam current and accelerating voltage were reduced towards the end of the milling process (2 kV - 5 kV, 80 pA)

FIB lift-out was performed on specimens that had been mechanically polished to a $1\ \mu\text{m}$ surface finish. Instruments used to prepare site-specific samples at the University of Oxford were the Zeiss N-Vision 40 and the Zeiss Crossbeam 540. At Idaho National Laboratory, a FEI Quanta 3D FEG was used to prepare neutron-irradiated samples.

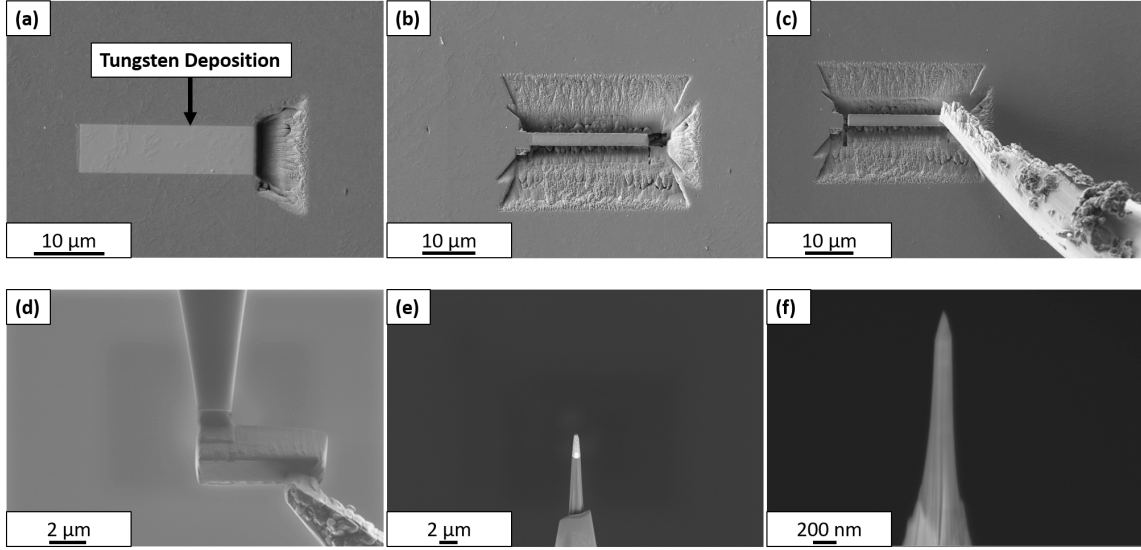


Figure 12: Stages of sample preparation using FIB lift-out.

3.2.2.1 Gallium Beam Damage Due to the accelerating voltages used, gallium ions can become implanted into the surface layer of the specimen. The large size of gallium ions may introduce high internal stresses which can lead to specimen failure during APT analysis. The microstructure can also be damaged or changed by gallium ion implantation. It is important that care is taken to minimise gallium implantation into samples [171, 173].

Dual-beam SEM-FIB instruments were used to prepare the specimens in this thesis. Dual-beam instruments allowed specimens to be imaged using electrons rather than Ga ions, minimising the number of Ga ions that hit the sample surface and could potentially cause damage.

In an attempt to reduce the number of Ga ions entering the specimens, protective layers of W or Pt were applied to samples prior to imaging with Ga ions. Also, low-energy Ga ions ($< 5\ \text{kV}$) were used to remove $\sim 200\ \text{nm}$ from the tip after the annular milling stage had created a tip suitable for APT. These procedures resulted in the analysed volume containing less than 0.5 at.% Ga. Further than 5 nm from the edge of the analysed volume, no Ga was detected above noise levels.

3.3 Limitations

Like every microscopy technique, atom probe has its limitations. Trajectory aberrations [174] and surface migration [175] of atoms must be accounted for when interpreting the data.

Trajectory aberrations alter the relative positions of the atoms and degrade the spatial resolution of atom probe data [2]. Trajectory aberrations may arise due to localised variations in electric field which lead to the undesirable lateral displacement of ions during the first instant of their time of flight [157]. They can also be caused by precipitates that require a different electric field for evaporation relative to the matrix [168]. This difference in evaporation fields between matrix and precipitates can lead to a low-field precipitate evaporating before the high-field matrix, causing a flattening of the surface as shown in Figure 13. Meanwhile, in the case of a high-field precipitate in a low-field matrix, the matrix would evaporate first resulting in the development of a localised region of high curvature. Since the reconstruction algorithm assumes that the tip is perfectly hemispherical in shape it cannot account for any localised variations in curvature. In the case of low-field precipitates, this leads to an apparent increase in local atomic density as surrounding matrix atoms are deflected inwards [157, 176].

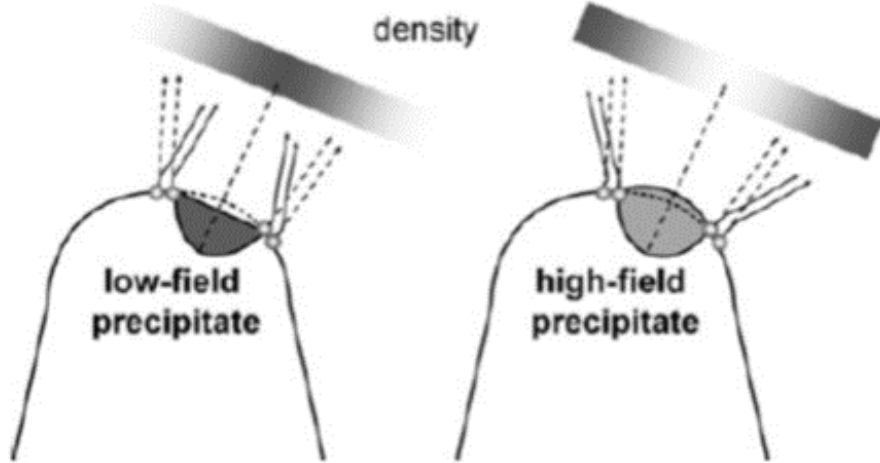


Figure 13: Trajectory aberrations and impact on the measured density of ions due to a change in the surface curvature in the case of a low- and high-field precipitate. Reproduced with permission from [157]. Copyright © 2012 Published by Springer Nature.

The apparent APT measured density of the Cu-rich precipitates is higher than the density of the matrix [13]. Since Cu has a lower evaporation field (30 Vnm^{-1}) than the Fe matrix

(35 Vnm⁻¹) [157], Cu-rich precipitates in RPV steels evaporate more readily than the surrounding matrix. This can cause a low curvature region to develop surrounding the low-field Cu-rich precipitates [157]. It has been proposed that this causes trajectory aberrations that increase the measured density of the Cu-rich precipitates [113]. Multi-technique characterisation of Cu-rich precipitates in Fe alloys supports the theory that this apparent increase in density is the result of Fe ions being projected into the precipitates [177]. The authors suggest that an upper limit for the true Fe content inside the precipitates is 6.5 at.% [177]. Similar experiments, performed on low-Cu steels, indicate that the Fe level inside Mn-Ni-Si-rich precipitates is around 6 at.% [126]. It is assumed in this thesis that most of the Fe detected inside precipitates is a result of trajectory aberrations and is, therefore, not included in cluster composition, size, or volume fraction calculations.

Surface migration of ions is also an issue during the analysis of RPV steels. It is well documented that Si and P can migrate towards major crystallographic poles during analysis, this is due to variations in electric field across the surface of the tip [178]. The roll-up of atoms, whereby atoms move on the surface of the specimen prior to evaporation, further affects the spatial resolution of APT data [179]. However, both of these effects can be minimised by optimising experimental conditions, particularly by minimising thermal energy at the surface [180].

The preferential evaporation of atoms between pulses is another issue. Preferential evaporation tends to occur to elemental-species that require a lower field to evaporate than the principal species in the materials, such as Cu in steel [180]. It arises when the field at the surface of the specimen is large enough to cause ions of certain species to evaporate between the applied voltage or laser pulses [157]. Since the time of evaporation of these ions is unknown, it is not possible to calculate their time-of-flight and, therefore, their chemical identity. This results in an underestimation of their concentration. This effect can be minimised by careful selection of experimental conditions [180].

There are several other limitations to APT, these include:

- Specimen preparation can take a significant amount of time, due to the precise sample size and shape required [181]
- Specimen failure rate is high, due to the high mechanical stresses at the apex of specimen tips [181]
- Detection efficiency of atoms within the specimen is approximately 37 % in the LEAP-3000X

HR [182], and approximately 52 % in the LEAP-5000XR [183]

- Analysis volume is limited (approximately $60 \text{ nm} \times 60 \text{ nm} \times 200 \text{ nm}$) [154]
- Some elements, such as C, are prone to evaporate as complex ions. These ions consist of multiple atoms that may dissociate after field evaporation and this can lead to an increase in the number of multiple events detected during the experiment. This results in these elements being detected in lower levels than they are truly present, causing an underestimation in compositional measurements of these species [184, 185]

3.4 Atom Probe Analysis Optimisation For RPV Steels

In order to minimise artefacts it is important that the analysis conditions used during atom probe analyses are optimised. Many atom probe studies on RPV steels have used an analysis temperature of 50 K - 55 K and a pulse fraction of 15 % - 20 %, where pulse fraction is the fraction of the standing voltage that is superimposed on the standing voltage at each pulse event [22, 86, 186]. Using a lower operating temperature, or higher pulse fraction is considered to increase the chance of sample fracture, whilst using a higher operating temperature is believed to increase the surface migration of atoms [180]. Using a lower pulse fraction is disadvantageous as preferential evaporation of species is more likely to occur between pulses due to the higher standing voltage [180].

However, the choice of these experimental conditions has only been experimentally validated by Hyde et al. [180]. The authors varied cryostat temperature, pulse fraction, and compared voltage pulsing with laser pulsing. Optimal conditions were defined as those that were determined to minimise the preferential evaporation of minor solutes (particularly Cu), level of background noise, and presence of artefacts [180]. The variation with analysis conditions of mean density of ions and mass resolution was also investigated [180].

The authors found that the preferential evaporation of Cu increased as cryostat temperature increased [180]. The migration of P and Si to major poles was also identified as increasing with laser energy. It was therefore suggested that laser mode should be avoided when analysing RPV steels, even though there was a lower level of background noise in the laser pulsing experiments [180]. There was no significant change in mass resolution noted between the different conditions.

The authors concluded that the optimal conditions to use for APT analysis of RPV steels

were to use voltage pulsing with a cryostat temperature of $\leq 55\text{K}$, and a pulse fraction of 20 % [180]. It was also recommended that data near major poles should be excluded during cluster analyses [180]. Whilst the authors varied many operational conditions, they did not vary pulse repetition rate and so it is not yet possible to say what the optimal pulse repetition rate is for analysis of RPV steels.

3.5 Interpretation of the Mass Spectra

In APT, the mass spectrum refers to the mass-to-charge-state ratio histogram generated by the experiment (Figure 14 (a)). This histogram must then be ranged, with the user assigning a chemical identity to each peak in the histogram (Figure 14 (b)). Since the lateral extents of the peaks are defined by the user, there is often a variation in ranged data from user to user [187]. This is problematic since ranging of the mass spectrum determines the number and concentration of ions present in the analysis. Hudson et al. performed an analysis of different ranging techniques, finding that variance in obtained concentration increases when data is manually ranged and as the true solute concentration decreases [187]. Determining the accuracy of different ranging techniques is difficult since the “true” composition of a real dataset is not known. Therefore, it is important to use a consistent ranging technique across all datasets to ensure that datasets can be compared to one another.

Since the detected ions can have several different charge states (normally from 1+ to 4+), two ions with different masses can have the same mass-to-charge ratio (e.g. $^{28}\text{Si}^{1+}$ and $^{56}\text{Fe}^{2+}$ both have a mass-to-charge ratio of 28 Da). This results in the mass spectrum having overlapping peaks which cannot be individually resolved. A summary of the common overlaps present in the steels analysed in this thesis are shown in Table 18. The bars above the mass spectrum in Figure 14 (b) show the mass-to-charge-state ratio of each isotope of different ions, whilst the thickness of the bars represent the natural isotopic abundance (thicker bars indicating a higher natural abundance). From these bars, overlaps can be seen; such as the $^{58}\text{Fe}^{2+}/^{58}\text{Ni}^{2+}$ overlap at 29 Da that has been ranged as “Fm”.

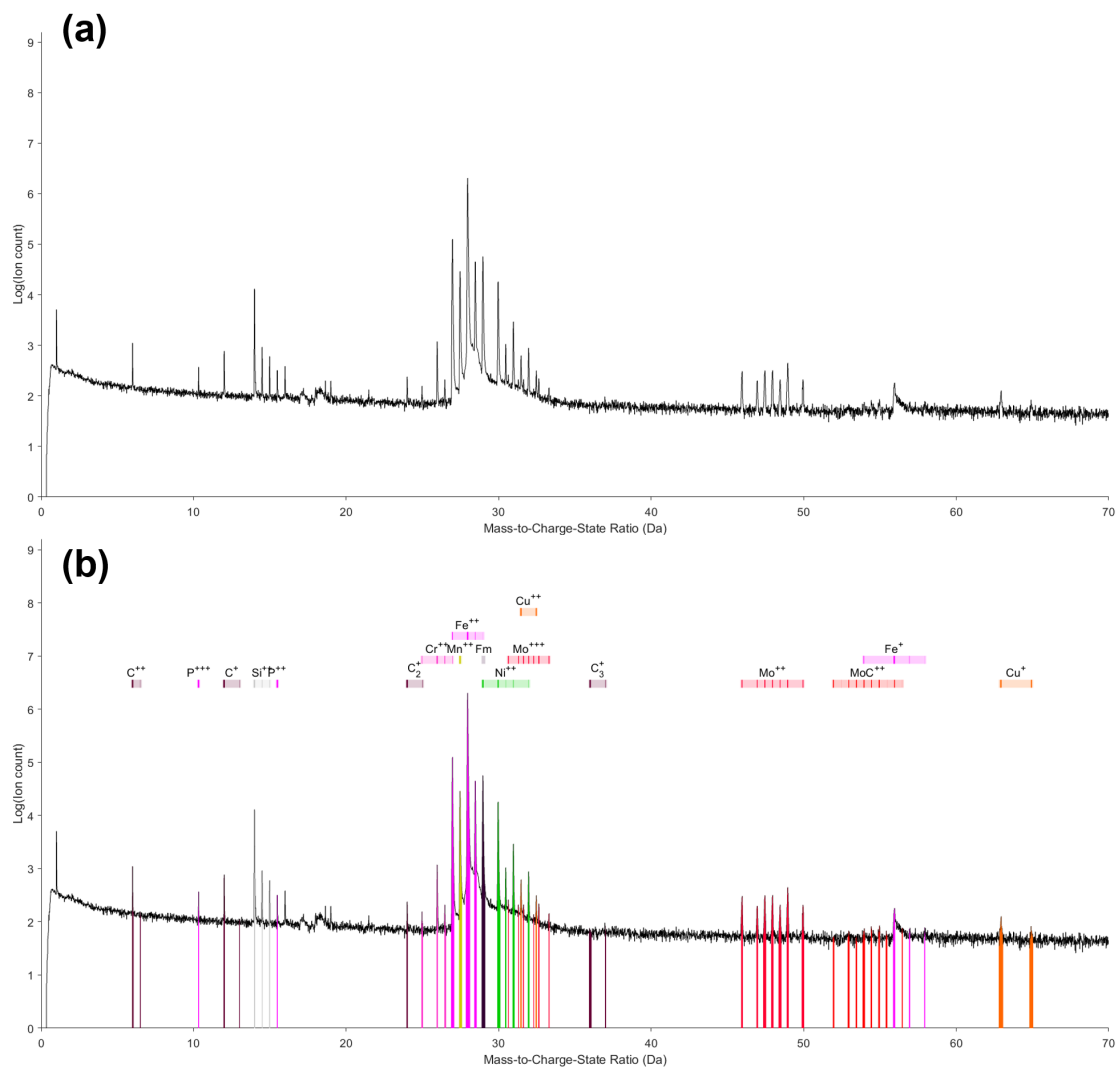


Figure 14: Typical mass spectrum generated during APT analysis of a RPV steel (a) before ranging and (b) after ranging. Plot created using AtomProbeLab v0.1.4.

Mass-to-Charge-State Ratio (Da)	Ion 1	Ion 2	Ion 3	Ranged As
14	$^{14}\text{N}^{1+}$	$^{28}\text{Si}^{2+}$	-	Si
15	$^{15}\text{N}^{1+}$	$^{30}\text{Si}^{2+}$	-	Si
25	C_2^{1+}	$^{50}\text{Cr}^{2+}$	-	Cr
27	$^{54}\text{Cr}^{2+}$	$^{54}\text{Fe}^{2+}$	-	Fe
28	$^{28}\text{Si}^{1+}$	$^{56}\text{Fe}^{2+}$	-	Fe
29	$^{29}\text{Si}^{1+}$	$^{58}\text{Fe}^{2+}$	$^{58}\text{Ni}^{2+}$	Fm
30	$^{30}\text{Si}^{1+}$	$^{60}\text{Ni}^{2+}$	-	Ni
54	MoC^{2+}	$^{54}\text{Fe}^{1+}$	-	MoC
56	MoC^{2+}	$^{56}\text{Fe}^{1+}$	-	Fe

Table 18: Potential sources of peak overlaps from APT analysis of RPV steels.

Although the identity of individual ions contributing to overlapping peaks cannot be resolved, the ‘deconvolution of peaks’ function in the IVAS reconstruction software can calculate the contribution of each overlapping ion-type to a single total peak, based on the size of adjacent non-overlapping peaks in the spectrum and known relative isotopic abundances. This would allow the number of respective $^{56}\text{Fe}^{2+}$ and $^{28}\text{Si}^{1+}$ ions in the 28 Da peak to be calculated. However, it is not possible to determine which specific ions in the reconstruction with a mass-to-charge ratio of 28 Da correspond to $^{56}\text{Fe}^{2+}$ or $^{28}\text{Si}^{1+}$, although new approaches are being developed to retrieve spatial information on ions from overlapping peaks based on interrogation of the local neighbourhood surrounding each atom [188, 189]. In order to correctly calculate the contribution of an ion to each of the other peaks it is possible to perform this deconvolution on mass spectra, as long as at least one of the isotopes does not overlap with any other isotope [157].

All compositional measurements from APT reported in this thesis are after peak overlap solving was performed with AtomProbeLab v0.1.4, using the methods proposed in [190, 191].

3.6 Cluster Searching

The detection of early stage solute clustering within atom probe data is complex, particularly in RPV steels, due to the aforementioned limitations associated with atom probe tomography data. These effects make the reliable detection of features which may initially only contain several atoms difficult.

Many different methods have been developed to identify the presence of clustering. These can be split into two larger groups; those that detect non-random distributions of elements in 3D space and those which identify and characterise individual clusters.

Non-random distributions of elements can be detected by using Frequency Distributions [192, 193, 194, 195] and Contingency Table Analysis [193]. Other techniques which identify the non-random distribution of solute elements have recently been developed and include; the Local Chemistry Method [186], Pair Correlations Function [196], and Nearest Neighbour Distance Distributions [197, 198, 199, 200].

Individual clusters can be identified and characterised using techniques such as the Maximum Separation Method [113, 116, 201], the Double Maximum Separation Method With Erosion [201], the Envelope Method [202], DBSCAN [197], Core Linkage [197], Gaussian Mixture Models [203], and Proximity Histograms and Iso-concentration Surfaces [116, 152, 204, 205]. All of these methods allow information on cluster size, number density, and composition to be obtained. Some of the above techniques are well summarised and evaluated in [2] and [16].

A variant of the maximum separation method, the core-linkage method, is widely used to identify clusters in APT datasets and was used to detect clusters in this study. As such, it will be discussed in more detail below.

3.6.1 Maximum Separation Method to Core-Linkage Method

The principal steps used to detect clusters using the maximum separation methodology can be summarised as [206, 207]:

1. The “solute” elements (i.e. the elements which are expected to be in clusters) are selected. In the case of RPV steels, these are often Cu, Mn, Ni, P, and Si.
2. A maximum separation distance (D_{max}) is selected. This is the distance around each solute atom that will be searched for neighbouring solute atoms, and is typically 0.4 nm - 0.7 nm.
3. A search is performed around each solute atom. If another solute atom lies within D_{max} the atoms are connected (Figure 15 (a)-(b)).
4. A minimum cluster size (N_{min}) is defined. This is the smallest number of atoms that constitute a cluster. If a set of connected atoms contains more than N_{min} atoms, then the connected atoms are defined as a cluster core of atoms.

The definition of a minimum cluster size is important as solute clusters are statistically likely to occur in a randomised solid solution. In order to determine how much clustering is a result of

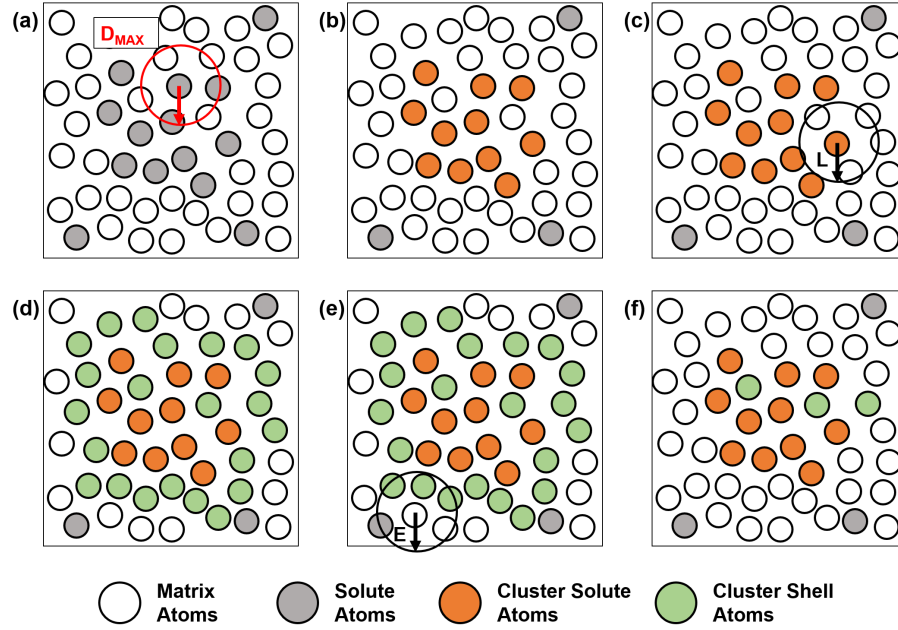


Figure 15: Schematic diagram of Maximum Separation cluster search method. (a) D_{max} parameter chosen and search is conducted around each solute atom (b) Solute atoms within D_{max} of one another are connected (c)-(d) L step includes all atoms within a distance (L) of connected solute atoms (e)-(f) Erosion step is performed.

thermal ageing or neutron irradiation, it is necessary to compare the observed distribution of elements to that in a randomised distribution [208]. Marceau et al. proposed a method for removing “random clusters” from their analysis [209]. The authors proposed a method whereby all “atomic positions were maintained as fixed and the assignment of the chemical identities of the atomic species was randomly rearranged, whilst preserving the solute concentrations measured in the experiments” [209]. The number of clusters detected in the random solid solution was then subtracted from the number of clusters detected in the real data [209].

This method was expanded upon by Styman et al. in an attempt to “identify the specific clusters in the experimental dataset which are typical of those in the randomised one” [36]. This was achieved by randomising the data and performing a cluster search using the same parameters as were used on the real data. “Background clusters” were defined as those detected in the real data that had similar composition and size to clusters detected in the randomised dataset. These were then removed from the analysis [36].

The maximum separation method was further developed by Vamousse et al. [201]. They performed a cluster search, using the method above, before introducing an envelope (L) step,

whereby all atoms within a distance (L) of the cluster core atoms are defined as belonging to the same particle (Figure 15 (c)-(d)). This results in a shell of atoms over the cluster surface; some of these atoms are removed using an erosion step. In the erosion step, all atoms within a distance (E) of matrix atoms (those not defined as being part of the cluster after the L step) are removed from the cluster (Figure 15 (e)-(f)). These steps allow a “shell” of atoms, which does not include an excess of matrix atoms, to be included around the core of the cluster. This is advantageous and allows more accurate quantification of parameters such as cluster size and shape, since clusters will often contain some atoms which were not defined as “solute elements”.

The core-linkage process follows the same steps as the maximum separation method [197]. However, order is included as another parameter. Order (O) is the number of solute atoms that must be within D_{max} of a solute atom for it to be defined as a “core” cluster atom. The maximum separation method is identical to the core-linkage method when $O = 1$. Core-linkage enables more control than the maximum separation method when performing cluster searching in APT data.

3.6.1.1 Limitations of Core-Linkage Cluster Search Algorithm

Despite the core-linkage cluster search algorithm being widely used it has limitations. The solute ions and cluster search parameters (D_{max} , L , E , O , N_{min}) are all defined by the user and the results can be strongly influenced by parameter selection [210]. This means that it is possible for two users to analyse the same dataset and detect a very different number of clusters with very different properties, making comparison of published results difficult. It is therefore important to carefully consider parameter selection [210] and to fully report the parameters that have been selected to perform the cluster search [211].

3.6.2 Peak Overlaps And Cluster Searching

One of the most important peak overlaps that needs to be addressed in mass spectra generated during APT analyses of RPV steels is the 29 Da peak. This peak may contain $^{29}\text{Si}^{1+}$, $^{58}\text{Fe}^{2+}$, or $^{58}\text{Ni}^{2+}$. As MNSPs are expected to include Ni and Si, but not Fe, including or excluding this peak during cluster analyses will effect the results of the analyses. Including the 29 Da peak will include Fe atoms in the cluster search, this will likely result in the detection of some clusters that would not be detected if the individual Fe and Ni atoms could be differentiated. However, not including this peak (^{58}Ni is the most abundant Ni isotope) in the cluster analyses will likely lead to non-identification of clusters in the material.

Some researchers do include this peak in their cluster searches, claiming that the Fe contribution to the peak is limited [212]. Other authors do not include ions contributing to the 29 Da peak in their cluster searches [213], claiming that doing this improved “the contrast between cluster and matrix” [214].

Although the natural abundance of ^{58}Fe is much lower than the abundance of ^{58}Ni (0.280 % versus 68.077 %), Fe is present in typical RPV alloys in much higher concentrations than Ni and Si. However, Figure 16 (a) shows the simulated mass spectrum peaks of Fe and Ni for a steel containing 1.5 at.% Ni. In this case, the 29 Da peak will be mainly Ni (Figure 16 (b)). This implies that not including this peak will have a larger effect on the results of the cluster search than including it.

All alloys on which cluster searches were performed in this thesis contained at least 1.5 at.% Ni, meaning that the majority of the 29 Da peak was likely Ni. Therefore, the 29 Da was included in the cluster search. This peak was deconvoluted when calculating cluster compositions.

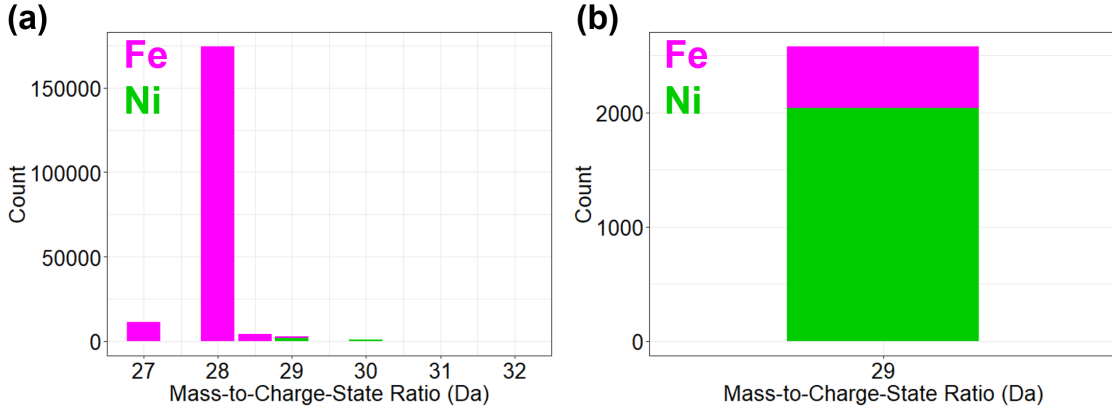


Figure 16: (a) Simulated mass spectrum peaks of Fe and Ni for a steel containing 1.5 at.% Ni. (b) Contribution of Fe and Ni to the 29 Da peak.

In the future, this issue could be approached by probabilistically labelling ions based on local composition. For example, a volume containing the nearest N neighbours could be generated around each ion with a mass-to-charge-state ratio of 29 Da. A mass spectrum could then be generated and the composition of the 29 Da peak could be deconvoluted for each volume. If the 29 Da peak in one localised mass spectrum was shown to have a composition of 19Fe-80Ni-1Si after deconvolution, then the primary ion would have a 0.19 probability of being labelled Fe, 0.80 probability of being labelled Ni, and 0.01 probability of being labelled Si. Multiple datasets could then be generated, with cluster searches being performed on all of them. This would allow some estimate as to the

systematic error introduced by including/excluding the 29 Da peak from the cluster searches.

3.6.3 Cluster Calculations

After cluster searching has been performed, the size, composition, number density, and volume fraction of clusters within the dataset can be calculated. When calculating cluster sizes and compositions it is important that only clusters wholly contained within the dataset are included. Including partial “edge” clusters will lead to an underestimation of average size whilst, in the case of appendage/core-shell clusters, including incomplete clusters may bias compositional measurements. Currently, there is no established method to identify “edge” clusters in an automated or reproducible way.

In this thesis, cluster number densities (N_d) were calculated using the equation:

$$N_d = \frac{N_{ClustersDetected} - (0.5 \times N_{EdgeClusters})}{V_{Dataset}} \quad (6)$$

where $N_{ClustersDetected}$ is the number of clusters detected in the dataset, $N_{EdgeClusters}$ is the number of detected clusters that are on the edge of the analysed volume, and $V_{Dataset}$ is the volume of the reconstructed dataset. $V_{Dataset}$ is calculated using the equation:

$$V_{Dataset} = \frac{N_{Ranged}}{\eta \times \rho_{\alpha-Fe}} \quad (7)$$

where N_{Ranged} is the number of ranged ions in the dataset, η is the detection efficiency of the instrument, and $\rho_{\alpha-Fe}$ is the number of Fe atoms expected per cubic metre in α -Fe ($85.5 \times 10^{27} \text{ m}^{-3}$). Mean number densities and standard error of the mean were calculated based on the N_d observed in each dataset for a specific alloy in a certain condition. In one instance, as a result of only one dataset being collected for a specific alloy and condition, it was not possible to calculate a standard error of the mean. The appearance of a cluster within a given volume was assumed to be a Poisson process and the error of the N_d measurement in this instance was estimated to be equal to:

$$\sigma_{N_d} = \frac{\sqrt{N_{ClustersDetected} - (0.5 \times N_{EdgeClusters})}}{V_{Dataset}} \quad (8)$$

where $N_{ClustersDetected}$ is the number of clusters detected in the dataset, $N_{EdgeClusters}$ is the number of detected clusters that are on the edge of the analysed volume, and $V_{Dataset}$ is the

volume of the reconstructed dataset.

Volume fraction percentages (V_f) were calculated using the equation:

$$V_f = 100 \times \frac{N_{Ranged}^{Cluster} - N_{Fe}^{Cluster}}{N_{Ranged}^{Dataset}} \quad (9)$$

where $N_{Ranged}^{Cluster}$ is the number of ranged atoms in all the clusters, $N_{Fe}^{Cluster}$ is the number of Fe atoms detected in all of the clusters, and $N_{Ranged}^{Dataset}$ is the total number of ranged ions in the dataset. The mean cluster V_f for an alloy in a certain state was calculated by averaging the V_f of each analysed dataset. Standard errors of the mean were also calculated.

The volume of each individual cluster ($V_{Cluster}$) was calculated by assuming that the clusters were spherical and had the same atomic density as BCC-Fe, using the equation:

$$V_{Cluster} = \frac{N_{Ranged} - N_{Fe}}{\eta \times \rho_{\alpha-Fe}} \quad (10)$$

where N_{Ranged} is the number of ranged atoms in the cluster, N_{Fe} is the number of Fe atoms detected in the cluster, η is the detection efficiency of the instrument, and $\rho_{\alpha-Fe}$ is the atomic density of BCC-Fe. N_{Fe} was subtracted since the Fe atoms in the clusters are likely the result of trajectory aberrations [177]. Cluster diameters (nm) were then calculated from this volume. Mean cluster diameters were calculated using the entire population of clusters detected for a specified condition for each alloy. The standard error of the mean was computed using established equations.

3.7 Outstanding Issues

Whilst early-stage clustering in high-Cu RPV steels has been studied using APT, the optimal analysis conditions for low-Cu RPV steels in the latest generation of atom probe instruments is unknown. Also, all cluster search techniques require user input. This complicates the interpretation of atom probe cluster analyses, unless the parameters used are reported. There is also no automated or reproducible way of identifying which clusters are on the edge of the dataset, this may impact compositional and number density calculations.

4 Electron Microscopy

Electron microscopes offer higher resolution, magnification, and better depth-of-field than conventional light microscopes [215]. As a result, electron microscopes are widely used in materials science to characterise materials [215].

Electron microscopy has been extensively used in the study of RPV steels to provide information on; the microstructure before and after irradiation [8], fracture surfaces after Charpy testing [216], and grain boundary composition changes after thermal ageing [217].

4.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) enables the surface, or near-surface structure of bulk specimens to be studied [215].

Electrons, typically 2 kV - 40 kV, are emitted from an electron gun [218]. These electrons then go through a series of condenser lenses that demagnify the electron beam until it is $\sim 2 \text{ nm} - 10 \text{ nm}$ in diameter when it hits the specimen [215]. The electrons penetrate into the specimen and, as a result of different interactions occurring, a variety of signals are generated (Figure 17); these signals can then be detected if they escape from the specimen.

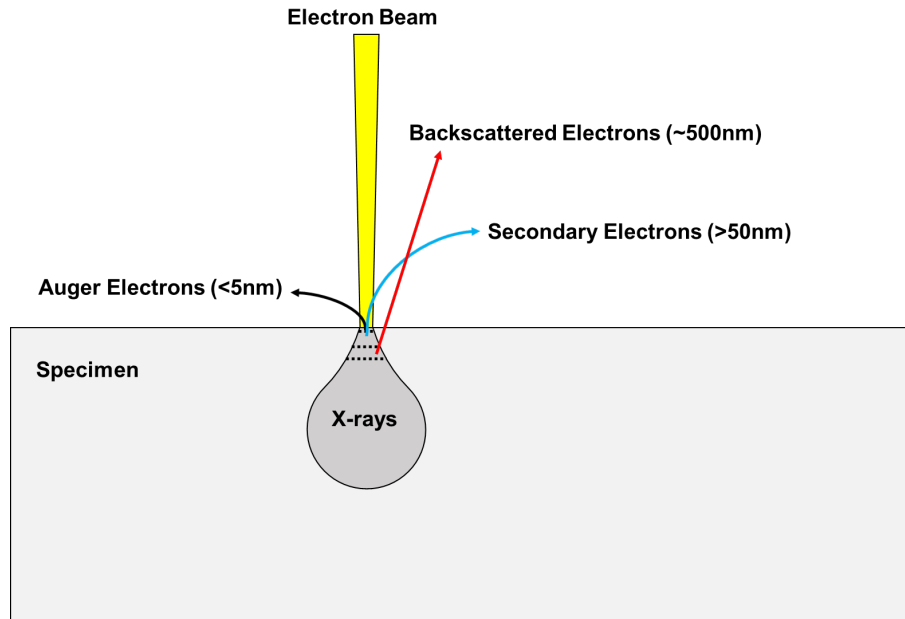


Figure 17: Schematic diagram of SEM interaction volume and the signals that may be detected, along with their approximate sampling volumes.

Auger electrons, emitted from atoms in the specimen due to interaction with an incident electron, are very low in energy and, as such, specialised equipment and an ultra high vacuum system is required to efficiently detect them [215]. Since Auger electrons have characteristic energies, their detection enables the determination of which elements are present at the specimen surface [215].

Secondary electrons have energies below ~ 50 eV and are ejected as a result of the ionisation resulting from the impact of the primary electron beam with atoms in the specimen [218]. They provide high spatial resolution, topographical information and, as they are often abundant, are commonly used as the imaging signal [215].

Backscattered electrons originate from primary electron beam electrons that pass close enough to the nucleus of an atom within the specimen to be scattered through a large angle back towards the direction of the incident beam [218]. The electron will lose energy each time it is scattered; therefore, electrons that have undergone scattering multiple times lose more energy than an electron that has undergone scattering only a few times and, consequently, will have worse spatial resolution [215]. Backscattered electrons can provide some crystallographic information as a result of electron channelling and, as atoms with higher atomic masses give brighter contrast, backscattered electrons can also provide some compositional information.

Most X-rays generated within the sampling volume will escape the specimen [215]. Measurement of the energies of these X-rays can give information on the chemical composition of the specimen, but resolution is not usually better than $1\text{ }\mu\text{m}$ [218].

Before SEM analysis, samples were mounted on SEM stubs using conductive silver epoxy, ground to 800 grit - 2500 grit using SiC paper, and then polished to a $1\text{ }\mu\text{m}$ finish using diamond solutions.

The SEM images in this thesis were taken using a working distance of 5 mm and a voltage of 5 kV, unless otherwise stated.

4.2 Electron Backscatter Diffraction (EBSD)

Electron backscatter diffraction (EBSD) uses backscattered electrons to provide crystallographic information about the specimen [219]. When the primary electron beam enters the specimen some electrons are inelastically scattered, causing electrons to travel in a wide range of directions [220, 221]. These electrons then undergo elastic and, if they are incident on atomic

planes at angles that satisfy the Bragg equation, coherent scattering into pairs of Kikuchi Cones [219, 220]. A phosphor screen, located near to the specimen, is fluoresced by the back-scattered electrons and Kikuchi bands are formed where the regions of high electron intensity intersect the screen. Since these Kikuchi patterns are characteristic of the crystal structure and orientation, crystallographic information can be ascertained by software that identifies the generated bands [219, 221]. By taking measurements across a sample, the crystal orientation can be determined at each point and a map showing grain morphology and orientations can be generated [219]. From this map, misorientation angles between different grains can be calculated.

Figure 18 (a) shows the typical hardware required for an EBSD system; the sample is normally tilted $\sim 70^\circ$ to the electron beam in order to optimise the fraction of electrons that are scattered from the sample and, therefore, the contrast in the diffraction pattern.

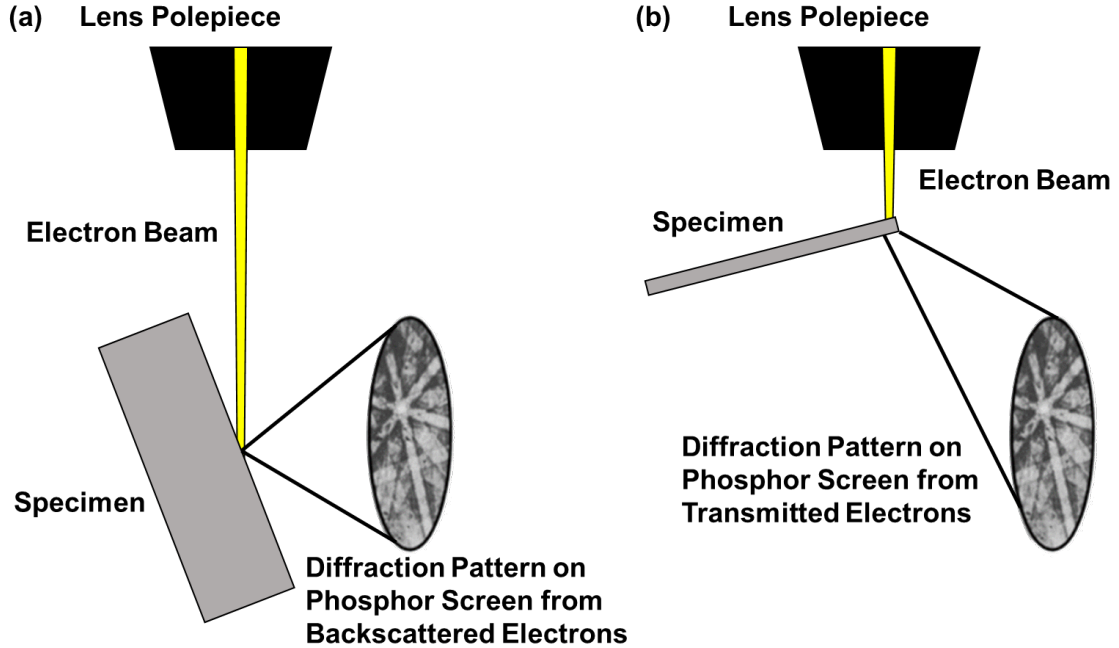


Figure 18: (a) Schematic diagram of typical EBSD installation. (b) Schematic diagram of typical TKD set-up.

Map resolution is dependent on the interaction volume of the electrons and, therefore, the atomic number of the elements in the specimen. Probe current, accelerating voltage, and frame integration also affect resolution. It is possible to resolve subgrains as small as $0.1 \mu\text{m} - 0.2 \mu\text{m}$ [222]. The smallest mis-orientation that can be determined between two grains is $\sim 0.5^\circ - 1.0^\circ$ [222].

As the diffraction pattern comes from near the surface of the specimen, it is necessary to have a flat surface that is free from damage. This was achieved by grinding specimens to 2500 grit using SiC paper, and then polishing to a 1 μm finish using diamond solutions. The specimens were then polished using colloidal silica for 20 minutes and thoroughly cleaned using water, ethanol, and 2-isopropanol.

EBSD analyses in this thesis were conducted with a specimen tilt of 70° at a working distance of 17 mm - 18 mm. 20 kV - 30 kV electrons were used with a current of 15 nA.

4.3 Transmission Kikuchi Diffraction (TKD)

Transmission Kikuchi Diffraction (TKD) relies on similar principles to EBSD, however, conventional EBSD equipment is used to detect transmitted electrons, generated by low energy-loss inelastic scattering, that have been coherently forward scattered through the specimen rather than backscattered electrons (Figure 18 (b)) [223]. As with EBSD, the generated patterns can then be used to determine crystal type and orientation.

The sample is typically tilted at angles of $\sim 10^\circ$ - 30° normal to the electron beam to maximise the fraction of electrons scattered through large angles in transmission, whilst minimising the number of electrons that backscatter onto the detector [223, 224]. Since the technique relies on the transmission of electrons through the sample, the specimen must be thin enough such that there are a sufficient number of transmitted electrons to generate a signal on the phosphor screen. Optimal sample thickness of ~ 75 nm - 200 nm have been suggested [224].

Due to the smaller interaction volume associated with TKD, Trimby estimates that the spatial resolution of TKD is between 5 nm - 10 nm [224], and the angular resolution is believed to be the same as conventional EBSD ($\sim 0.5^\circ$) [225].

Babinsky et al. have shown that the use of TKD alongside FIB sample preparation allows for a grain boundary to be more easily located in a typical APT specimen tip [226, 227]. The use of TKD alongside EBSD and APT also makes it possible for the five macroscopic degrees of freedom of the grain boundary to be determined [228]; this means that grain boundary chemistry can then be correlated with grain boundary type [229]. Use of a specialist specimen holder allows TKD to be conducted on a sample that is then orientated in the same position for APT analysis [77]. The authors determined all five degrees of freedom, and segregation levels of different elements to separate grain boundaries [77]. A possible problem associated with TKD preparation of APT

specimens include carbon contamination of the specimen during the TKD analysis [226].

4.3.1 Novel Grain Boundary Sample Preparation Method

Previously, TKD has been performed on APT specimens after they had been fabricated into needles suitable for APT analysis [77, 226, 227, 228]. This method requires the grain boundary to be contained in the APT needle volume; something that is improbable if grain size is large and a random volume is prepared for APT analysis.

Even if a grain boundary has been located along the length of a FIB lift-out bar, it is difficult to guarantee that the final APT volume will contain the grain boundary. Specimens are normally prepared from the centre of the lift-out bar, but the direction of the grain boundary underneath the specimen surface cannot normally be resolved in the SEM and may not follow the direction shown in Figure 19 (a). Figure 19 (b) demonstrates some of the possible locations of the grain boundary below the specimen surface.

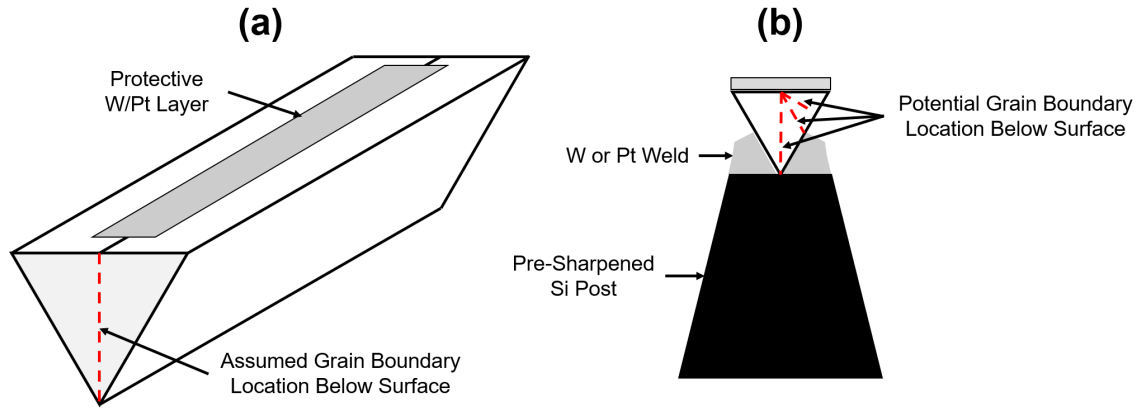


Figure 19: (a) Schematic diagram of a FIB lift-out bar and the assumed location of the grain boundary under the surface of the specimen. (b) Schematic diagram of a FIB lift-out that has been mounted on a microtip, with some of the possible locations of the grain boundary underneath the surface of the specimen shown.

In an attempt to increase the likelihood that a grain boundary (of selected misorientation) was contained within the final volume for APT analysis, a novel sample preparation method was developed alongside Dr J.O. Douglas.

Firstly, an EBSD scan was conducted on a polished sample surface (Figure 20). Once the EBSD map had been generated, the misorientation between each of the grains was determined. It was then possible to select a grain boundary with a specific misorientation. A protective layer of Pt

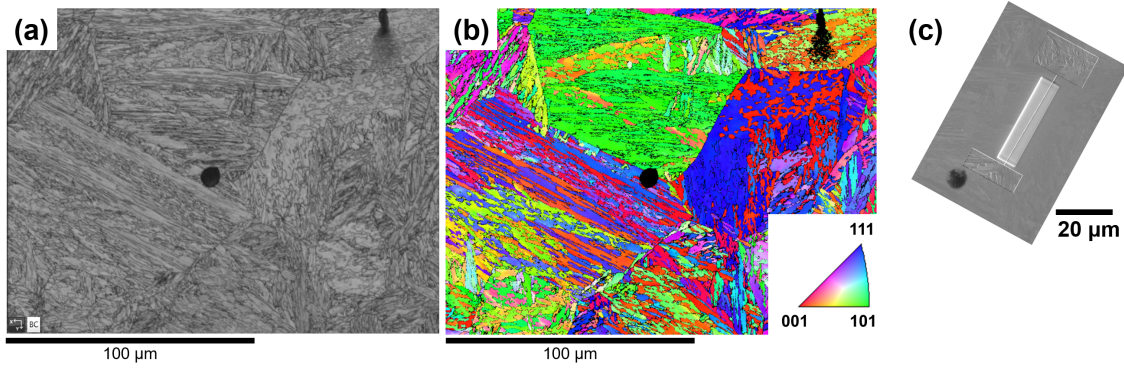


Figure 20: (a) Band contrast map for the specimen (b) EBSD map of specimen with inverse pole figure (IPF), (c) Pt deposited over selected grain boundary.

was applied to the chosen grain boundary (Figure 20 (c)), and a narrow region of Pt was deposited on top of the protective layer to indicate the estimated location of the grain boundary.

Standard FIB lift-out methods were followed to mount trapezoidal sections of this grain boundary on a standard 22 post microtip coupon (Figure 21 (a)). The lift-out bar was then thinned to ~ 200 nm - 750 nm in depth using 30 kV, 0.5 nA Ga ions (Figure 21 (b)). Thinning the specimens made it possible for enough electrons to pass through specimen to generate Kikuchi patterns that could be indexed. TKD was then performed on this specimen to reveal the location of the grain boundary under the surface (Figure 21 (d)). TKD analysis was performed using 30 kV electrons, with a current between 0.2 nA - 2 nA depending on specimen thickness.

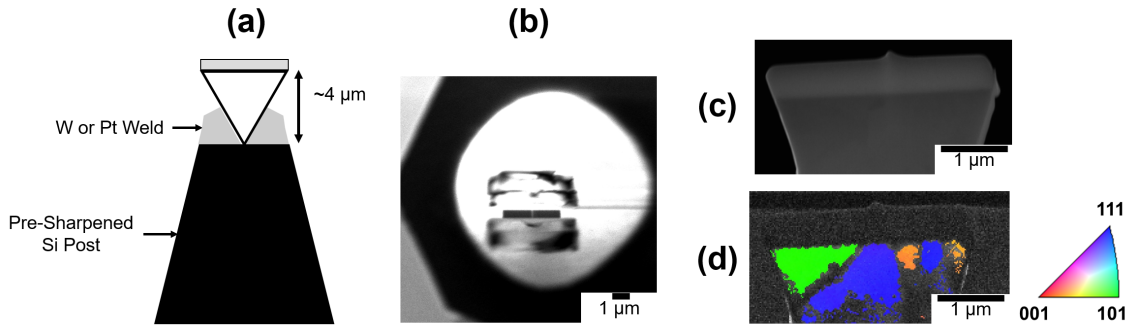


Figure 21: (a) Schematic diagram of typical FIB lift-out bar mounted on a microtip post, (b) Plan SEM view of lift-out trapeze that has been thinned to ~ 200 nm - 750 nm, (c) Side view SEM image of a lift-out bar that has been thinned, (d) TKD map generated from specimen with IPF, revealing location of grain boundary.

It was possible to perform TKD at the coincident point of the electron (SEM) and gallium

(FIB) beam, with the sample tilted such that the original specimen surface was perpendicular to the gallium beam (52° for FEI instruments, 54° for Zeiss instruments). The set-up in Figure 22 allowed imaging, milling, and TKD analysis to be performed iteratively.

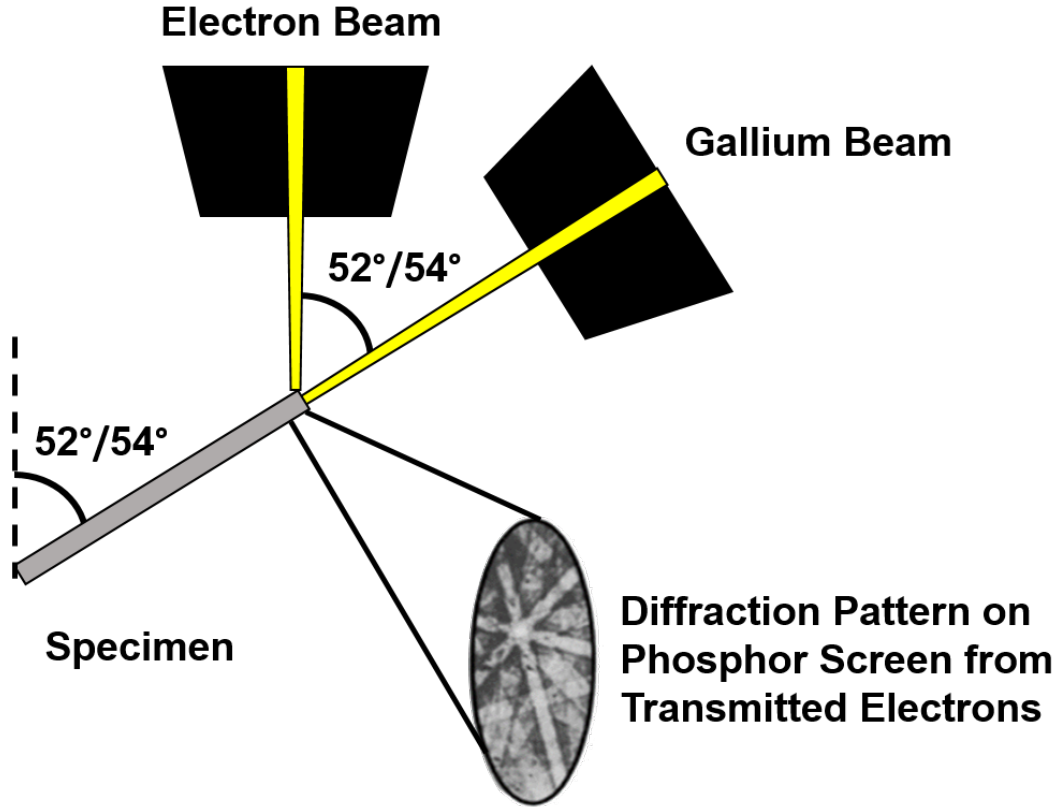


Figure 22: Schematic diagram of sample location which allowed SEM imaging, FIB milling and TKD to be iteratively applied to a specimen.

Once the location of the grain boundary was known (Figure 23 (a)), it was possible to mill the specimen with Ga ions (30 kV 80 pA - 300 pA) such the final APT needle contained the grain boundary (Figure 23 (b)). TKD was then performed on this needle (30 kV, 0.2 nA - 2 nA) to confirm that the GB was contained in the volume (Figure 23 (c)). The unindexed region around the grain boundary in Figure 23 (c) may be due to the presence of a carbide at the boundary.

This methodology allowed specific grain boundaries to be selected and contained, with greater probability, within APT specimens. The set-up demonstrated in Figure 22 reduced the time required for samples to be produced as opposed to when the working distance and tilt angle of the specimen were changed between FIB milling and TKD analysis.

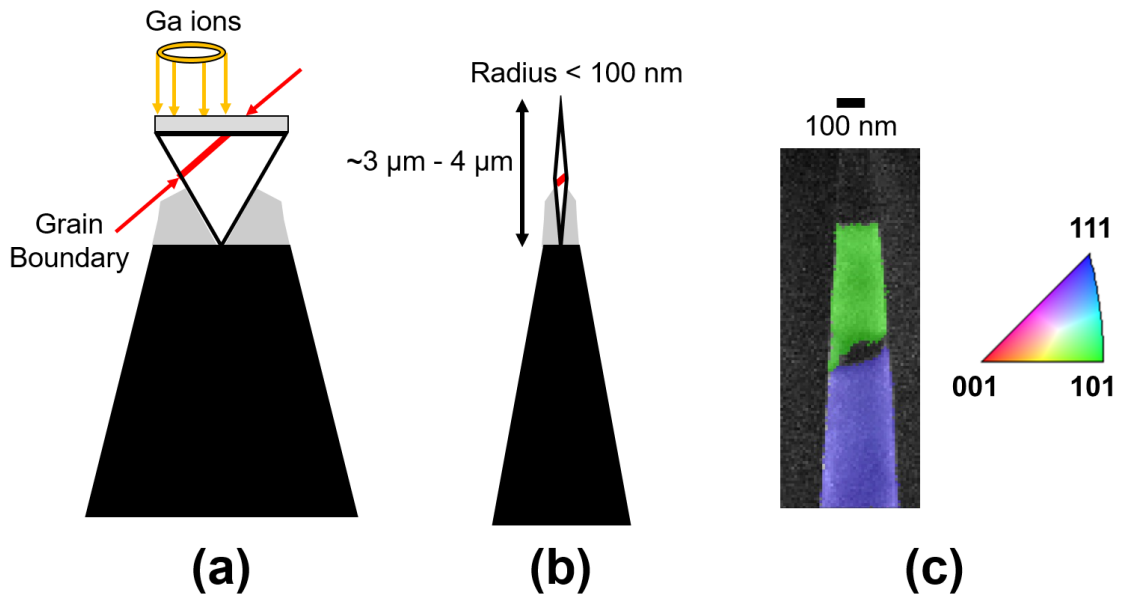


Figure 23: (a) Schematic diagram demonstrating how location of Ga ions used to mill the final sample can be selected to ensure that the grain boundary is contained in the final tip, (b) Schematic diagram showing final specimen containing grain boundary, (c) TKD map showing grain boundary from Figure 20 (b) is contained in final APT specimen.

Chapter V

Atom Probe Tomography Operating Conditions and Data Analysis Techniques

Determining the optimal operating conditions for analysing RPV steels with the LEAP-5000XR is discussed. Comparisons between quantitative cluster measurements made using the LEAP-3000X HR and LEAP-5000XR are shown. A method for automatically identifying clusters intersected by the edge of atom probe datasets is demonstrated. Finally, the methodology for determining Gibb's interfacial excess and its suitability to describe changes in grain boundary composition is discussed.

1 LEAP-5000XR Optimisation Experiments

Due to the well-known artefacts associated with atom probe tomography (APT) [157], it is important that the effect of operating conditions on data quality are assessed and optimised for a material before further APT analyses are conducted.

Previous studies have investigated the effect of temperature, pulse fraction and laser pulsing on data quality of RPV steels analysed using a LEAP-3000X HR; the study did not investigate the effect of pulse frequency [180]. The authors concluded that the optimal operating conditions (those that minimised preferential evaporation of Cu and surface migration of P and Si) were the use of voltage pulsing at an operating temperature of 50 K and a pulse fraction of 20 %.

As a significant proportion of experiments in this thesis were conducted on the LEAP-5000XR, the effects that operating temperature (K), pulse fraction (%), pulse frequency (kHz), and laser-pulse mode had on the quality of data gained on RPV steels when using the LEAP-5000XR were analysed.

A series of optimisation experiments were conducted on Alloy N (Table 19). The alloy contained similar levels of Cu, Si, Ni, and Mn, the elements of primary interest in RPV cluster formation, and was in its as-received state in an attempt to ensure that the solute distribution in

the alloy was as uniform as possible. This should minimise sample-to-sample variation, thus allowing direct comparison of the analyses. A limitation of this approach, however, is that no information will be provided on the effect of experimental conditions on trajectory aberrations.

Alloy		Cu	Si	Ni	Mn	P	Cr	Mo	C	Fe
N	wt. %	0.20	0.20	0.25	0.25	0.007	0.10	0.50	0.20	Bal.
	at. %	0.17	0.39	0.23	0.25	0.012	0.11	0.28	0.91	Bal.

Table 19: Composition of Alloy N.

The effect of experimental conditions in voltage-pulsing mode was investigated by, firstly, systematically varying operating temperature and pulse fraction at constant pulse frequency (200 kHz) to investigate the effect of operating temperature and pulse fraction (Table 20 (a)). The effect of pulse frequency was then investigated by systematically varying pulse frequency and operating temperature at constant pulse fraction (20 %) (Table 20 (b)).

Pulse Fraction (%)	Temperature (K)
15, 20, 25	50, 55, 60, 65, 70

(a) The operating pulse fractions and temperatures used in the series of experiments conducted at a constant pulse frequency of 200 kHz.

Pulse Frequency (kHz)	Temperature (K)
200, 250, 333	50, 55, 60, 65, 70

(b) The operating pulse frequencies and temperatures used in the series of experiments conducted at a constant pulse fraction of 20 %.

Table 20: Experimental conditions used to determine the optimal experimental conditions for analysing RPV steels with a LEAP-5000XR.

It has been observed that increased detection rate may lead to an increase in multiple events [161], whereby multiple ions impact the detector as a result of one pulse. Therefore, a target detection rate of 0.002 ions per pulse was used for all experiments in an attempt to minimise this effect. It is desirable to reduce the number of multiple events as certain species are more susceptible than others [157], leading to a bias in measurements if high multiple events are recorded. In particular, Si and C are more likely than other elemental species to arrive as multiple events when analysing steels [157]. Therefore, multiple events may significantly affect the compositional measurements of volumes that contain high concentrations of Si and C, such as grain boundaries,

carbides, and dislocations.

Approximately 2,000,000 ions were collected for each unique condition, apart from the 50 K, 25 %, 200 kHz condition. This was because all samples fractured at this set of conditions before a sufficient number of ions were detected to perform reconstructions and analyse data quality.

Standard reconstruction procedures were followed and the quality of the data were assessed. The measured compositions were compared to the alloy's nominal composition and artefacts, such as surface migration to poles, were also examined. Reconstruction parameters were selected such that the interplanar spacing at crystallographic poles corresponded to the plane spacing at poles of BCC α -Fe. Typically, (110) and (200) type poles were used with expected planar spacing of 0.203 nm and 0.144 nm, respectively. This resulted in values of k_f between 4.5 - 5.1, consistent with those used in [214]. If poles were not present in the data, k_f was adjusted to the value between 4.5 - 5.1 which generated a reconstructed sample with the most similar atomic density to BCC α -Fe.

The mass spectrum generated during each experiment was ranged using IVAS 3.8.0. The compositions for each tip were then calculated using the AtomProbeLab v0.1.4 Bulk Decomposition tool. The variation of tip composition with experimental conditions was then studied.

1.1 Operating Temperature

Varying the operating temperature of the instrument, whilst keeping pulse frequency at 200 kHz, was found to significantly impact the level of Cu detected in the analysis. Figure 24 shows the level of measured Cu decreasing with increasing operating temperature. This was observed to occur at all pulse fractions in this series of experiments, however, it occurred most drastically at 15 % pulse fraction, when ~ 50 % less Cu was detected at 70 K than at 50 K.

This measured composition of P was also found to be dependent on operating temperature, with less P detected at high operating temperatures. This appeared to happen consistently at different pulse fractions (Figure 25).

Operating temperature was also observed to have a slight impact of the measured level of Ni and Mo, with more Mo being detected at higher operating temperatures and more Ni being detected at lower operating temperatures.

The reduction in the measured content of P and Cu as operating temperature increases is likely a result of preferential evaporation of ions of these elements (Chapter IV Section 3.3). This phenomena can be minimised by using lower operating temperatures when analysing RPV Steels

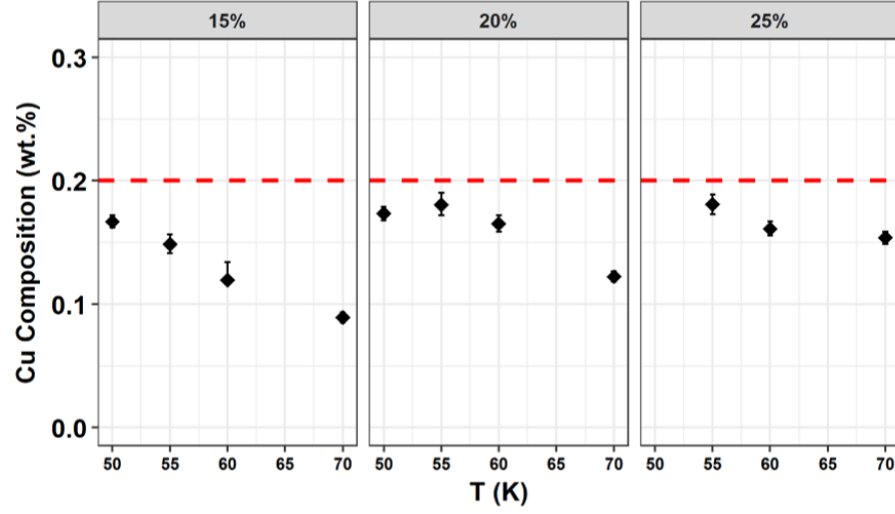


Figure 24: Graphs showing the effect of varying operating temperature at three different pulse fractions, the dashed red-line is representative of the nominal Cu content of the alloy. Error bars represent 95 % confidence intervals based on the deconvolution.

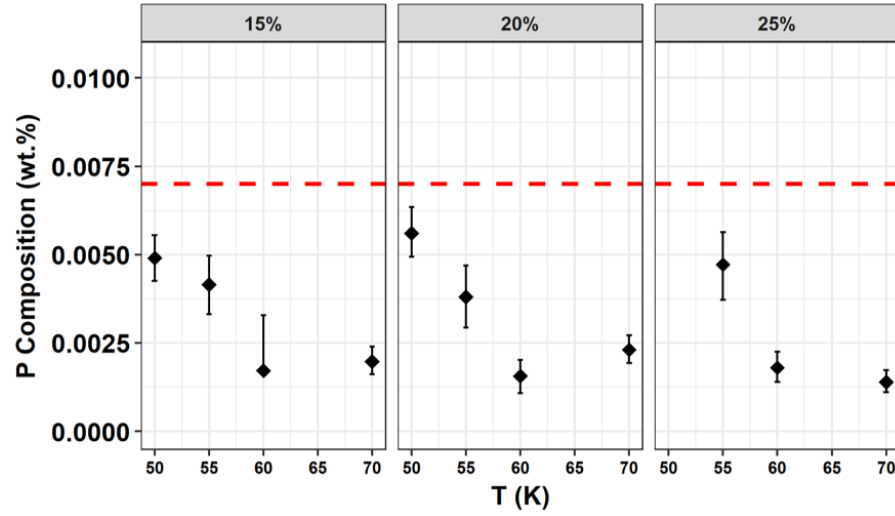


Figure 25: Graphs showing the effect of varying operating temperature at three different pulse fractions, the dashed red-line is representative of the nominal P content of the alloy. Error bars represent 95 % confidence intervals based on the deconvolution.

using a LEAP-5000XR. However, using lower temperatures increased the risk of sample fracture before 1,000,000 ions had been detected.

1.2 Pulse Fraction

The main effect of varying pulse fraction, at a constant pulse frequency of 200 kHz, was on the measured composition of Cu within the alloy. Figure 26 shows that increasing pulse fraction led to an increase in the measured Cu composition, this is likely due to fewer Cu ions undergoing preferential field evaporation. At higher pulse fractions, the required standing DC voltage for field evaporation to occur upon application of the voltage pulse is lower, reducing the probability of field evaporation occurring between pulses. Sample failure rates before 1,000,000 ions had been detected were observed to increase with increasing pulse fraction.

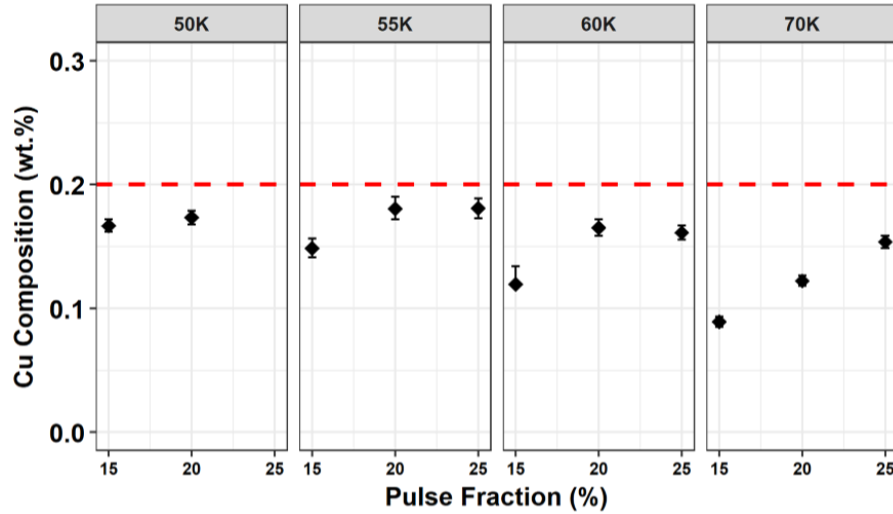


Figure 26: Graphs showing the effect of varying operating temperature at three different pulse fractions, the dashed red-line is representative of the nominal Cu content of the alloy. Error bars represent 95 % confidence intervals based on the deconvolution.

1.3 Pulse Frequency

Previous work by Miller and Russell determined that the amount of preferential evaporation decreased as pulse frequency increased from 50 Hz to 200 kHz [230]. They stated that the increased pulse frequencies led to a reduction in preferential evaporation as the sample spent less time at the standing voltage between pulses [230]. This is reasonable as the field-evaporation of ions from the

specimen is a probabilistic phenomenon, and so is more likely to occur in a longer window of time than a shorter one.

However, pulse frequency was not found to have a statistically significant effect on the measured compositions in this study. This may be because the time difference between voltage pulses at pulse frequencies of 200 kHz and 333 kHz is considerably less than the difference in time between pulse frequencies of 50 Hz and 200 kHz. Indeed, very little difference in preferential evaporation was recorded by Miller and Russell when pulse repetition rates exceeded 20 kHz [230].

1.4 Laser Pulsing

The use of laser-pulsing to analyse RPV steels has been associated with exacerbating several artefacts in the resulting APT data. Hyde et al. observed loss of about 20 % of the Cu atoms when laser pulsing (0.3 nJ - 0.6 nJ) was used, likely due to preferential evaporation [180]. Laser energy and cryostat temperature were not determined to influence the magnitude of Cu loss due to preferential evaporation [180]. The authors also observed increased Si and P surface diffusion as laser pulse energy increased, with these elements appearing to segregate to certain areas of the reconstruction [180].

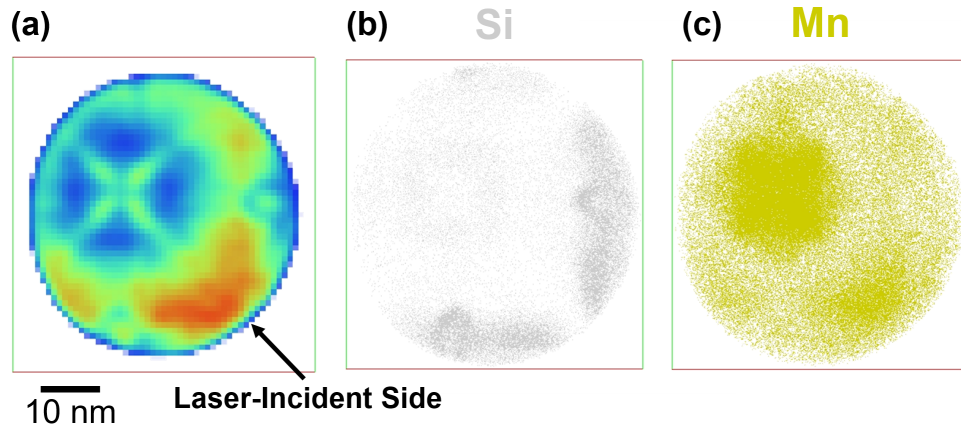


Figure 27: The effect of using 80pJ laser energy on (a) apparent density, (b) Si distribution in the alloy, and (c) Mn distribution in the alloy.

Laser pulsing was found to lead to a non-uniform density of ions within the reconstructed volume in this study (Figure 27 (a)). An apparent local increase in density was observed throughout the entire reconstruction in the area where the laser is focused on the tip. This

apparent increase in density on the incident side of the specimen has also been observed by Sha et al., and may be a result of the laser pulse energy not diffusing uniformly over the surface, leading to a higher temperature on the incident side [231]. This higher temperature will mean it is more likely for ions to evaporate from this side of the specimen than the “shadowed” side [231]. This results in the laser-incident side having a lower radius of curvature, resulting in a higher density of ions being projected onto the detector from this region [231].

Si (Figure 27 (b)) and Mn (Figure 27 (c)) were observed to be distributed non-randomly throughout the reconstruction. This may be a result of the surface diffusion of ions across the specimen surface. Hyde et al. have also reported that surface diffusion of ions was most “noticeable during laser pulsing” [180].

1.5 Discussion

As a result of the optimisation experiments, optimal operating conditions (defined as those which minimised preferential evaporation and surface segregation in the collected data) were determined and used for future APT analyses.

It was observed that data quality was optimised by using voltage pulsing rather than laser pulsing. Despite the differences in the wavelength of the lasers installed on the LEAP-3000X HR (532 nm) used in [180] and the LEAP-5000XR (355 nm) employed in this study, and also the smaller spot size of the LEAP-5000XR laser, artefacts were still discernible when laser-pulsing mode was utilised.

It was also evident that decreasing operating temperature and increasing pulse fraction improved data quality, whilst pulse frequency was not observed to have a significant effect. Preferential evaporation was reduced under these conditions as the evaporation of ions from the surface is a thermally-assisted process, so higher specimen temperatures and standing voltages increase the likelihood of evaporation occurring between pulses [162].

However, sample failure rates before a sufficient amount of data (1,000,000 ions) had been acquired were found to markedly increase as operating temperature was lowered, and pulse fraction increased. Therefore, a trade-off between data quality and obtaining enough data has to be made.

1.6 Summary

Experiments were performed to determine the optimal analysis conditions for RPV steels when using a LEAP-5000XR. It was determined that the optimal conditions were an operating temperature of 50 K, a pulse fraction of 25 %, and a pulse frequency of 200 kHz. These conditions were used, therefore, for future experiments performed on RPV materials when using the LEAP-5000XR. However, if data could not be obtained at these conditions, then data would be acquired at 50K, with a pulse fraction of 20 %, and a pulse frequency of 200 kHz.

2 LEAP-3000X HR vs LEAP-5000XR Comparison

Both the LEAP-3000X HR and LEAP-5000XR were used to characterise thermally-aged alloys in this thesis. The improved detection efficiency, the fraction of evaporated ions within the field of view of the detector that are detected, is a major difference between these two machines. The LEAP-5000XR manufacturer estimates the detection efficiency of the machine is ~ 0.52 , whilst the LEAP-3000X HR reportedly has a detection efficiency of ~ 0.37 . Understanding if/how the differences between the two instruments affects experimental results is crucial, particularly if reliable comparison of results is to be performed. Experiments were conducted to assess how the change in detection efficiency impacted measurements of cluster volume, volume fraction, composition, and number density.

An alloy (SG) that had been thermally-aged at 330 °C for 100,000 hours (Table 21) was selected. This alloy was chosen as previous APT analyses had shown that Cu-rich precipitates were present, and that these precipitates were of a variety of sizes [13, 35]. Data collected on the LEAP-5000XR were then compared to data that Dr P.D. Styman had gathered from the LEAP-3000X HR.

Alloy		Cu	Ni	Mn	Si	C	Mo	S	
SG	at.%	0.43	0.29	1.52	0.81	0.24	0.28	0.043	
	wt.%	0.49	0.31	1.50	0.41	0.052	0.48	0.025	
		P	Cr	Al	V	Sn	As	Sb	Fe
	at.%	0.043	0.047	0.010	0.0055	0.0070	0.0074	0.0023	Bal.
	wt.%	0.024	0.044	0.0048	0.0050	0.015	0.0100	0.0050	Bal.

Table 21: Nominal composition of Alloy SG (at.% & wt.%).

Data were collected using a temperature of 50K, a pulse fraction of 20 %, and a pulse frequency of 200 kHz. The target detection rate was set to 0.002 ions per pulse. Cluster searches were performed using the Core Linkage method [197]. The cluster search parameters reported in [35] were used ($D_{max} = 0.5$ and $L = E = 0.4$). N_{min} values were chosen to minimise the ratio of random:real clusters that were detected; N_{min} varied between 15 - 35.

Once cluster searches had been performed, cluster volumes, number densities and volume fractions were calculated using the equations in Chapter IV Section 3.6.3.

2.1 LEAP-3000X HR Results

Four datasets, generated by Dr. P.D. Styman, were reconstructed following standard procedures. Cu precipitates can clearly be seen in the atom maps. In Figure 28 there is strong C segregation to linear regions, this is indicative of dislocations being contained in the specimen. A large proportion of the Cu-rich precipitates appear to have formed on these heterogeneous nucleation sites, and this specimen contained a higher volume fraction of clusters than other samples analysed using the LEAP-3000X HR.

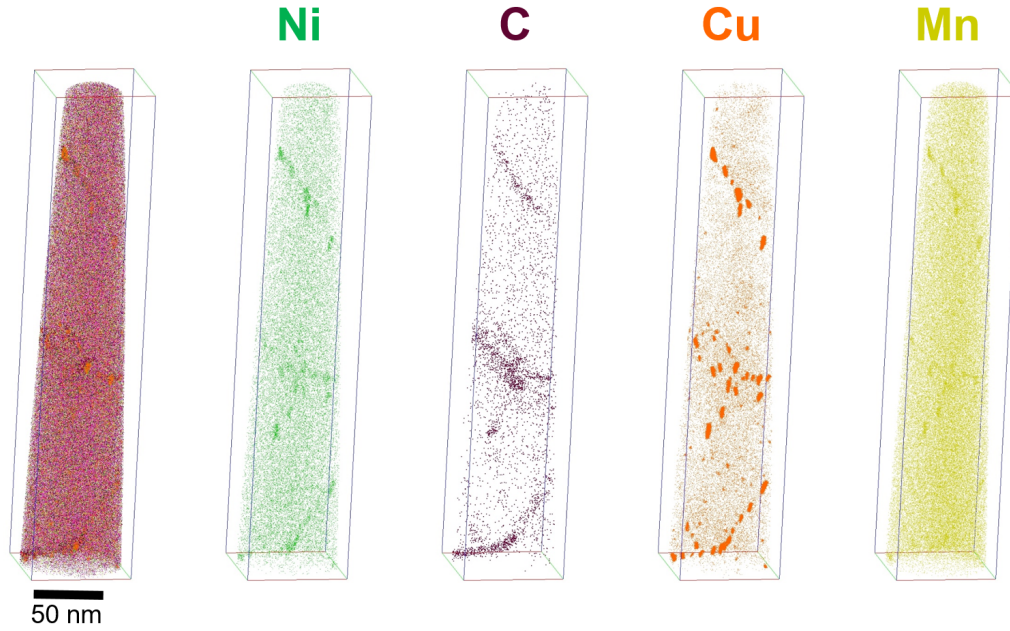


Figure 28: Atom maps of Alloy SG that has been thermally-aged for 100,000 hours at 330 °C. Analysed using LEAP-3000X HR (Run 16377).

The average number density of clusters detected in the four specimens was $8.3 \times 10^{22} \text{ m}^{-3} \pm 0.7 \times 10^{22} \text{ m}^{-3}$. The APT samples contained a volume fraction of $0.40 \% \pm 0.07 \%$ Cu-rich clusters, and the average cluster volume was $61.0 \text{ nm}^3 \pm 7.9 \text{ nm}^3$.

2.2 LEAP-5000XR Results

Five datasets obtained using the LEAP-5000XR were analysed. The average number density of clusters detected in the four specimens was $11.8 \times 10^{22} \text{ m}^{-3} \pm 1.1 \times 10^{22} \text{ m}^{-3}$. A mean volume fraction of $0.28 \% \pm 0.10 \%$ and an average cluster volume of $26.2 \text{ nm}^3 \pm 4.9 \text{ nm}^3$ was detected.

Atom maps are shown in Figure 29, and Cu-rich clusters are clearly visible.

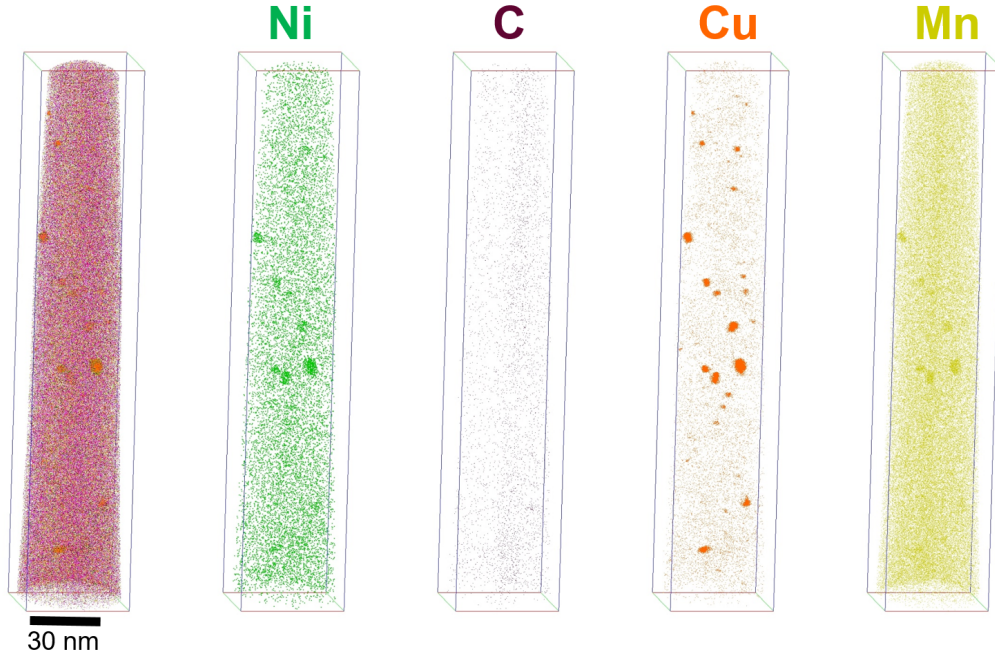


Figure 29: Atom maps of Alloy SG that has been thermally-aged for 100,000 hours at 330 °C and analysed using the LEAP-5000XR (Run 899).

2.3 Comparison of Results

A t-test ($\alpha = 0.05$) revealed that there was no significant difference between the two instruments when measuring cluster volume fractions. However, there was a significant difference in the number densities and volumes of the clusters detected between the two instruments; with a higher number density and smaller mean cluster volume being detected by the LEAP-5000XR.

The regions of high C concentration in Run 16377 (Figure 28) may indicate the presence of dislocations. Dislocations can act as heterogeneous nucleation sites for precipitates, increasing nucleation and growth rates. Indeed, this run had a higher volume fraction of clusters than any of the other datasets collected using the LEAP-3000X HR. When this run was excluded from the statistical analyses, there was no significant difference in the mean cluster volume or volume fraction detected between the two instruments ($\alpha = 0.05$). The LEAP-5000XR, however, still detected a significantly ($\alpha = 0.05$) higher number density of clusters than the LEAP-3000X HR.

It is likely that the increased detected number density in the LEAP-5000XR is due to the

detection of small clusters that do not contribute greatly to the calculated volume fractions. Indeed, the mean cluster volume is smaller for the LEAP-5000XR (26.2 nm^3) when compared to LEAP-3000X HR (40.7 nm^3). The cluster volume probability histogram for detected clusters, which are smaller than 100 nm^3 in volume, is shown for each machine in Figure 30. This plot reveals that a larger fraction of clusters that were detected using the LEAP-5000XR are small in volume ($< 10 \text{ nm}^3$), when compared to clusters detected using the LEAP-3000X HR. This indicates that the higher number density of clusters detected by the LEAP-5000XR may be due to the enhanced detection of small clusters when using the LEAP-5000XR, probably a result of the increased detection efficiency of the instrument.

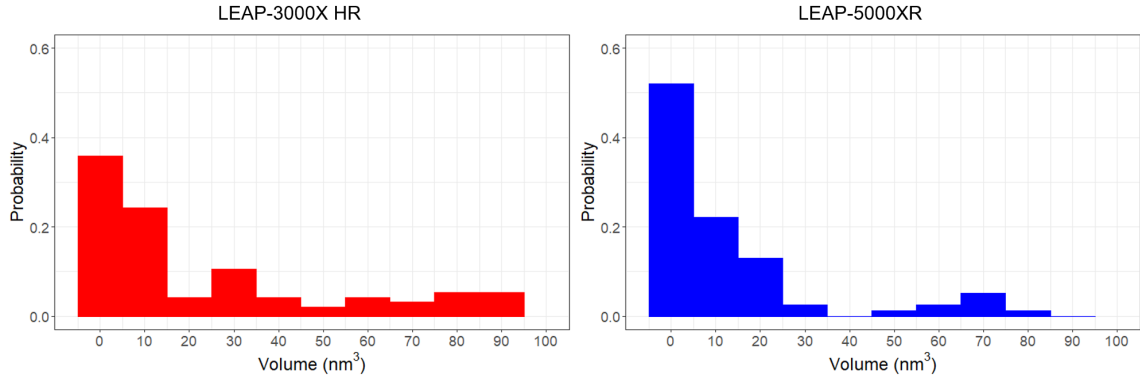


Figure 30: Probability histograms of corrected cluster volume distributions observed in the LEAP-3000X HR and the LEAP-5000XR (only clusters smaller than 100 nm^3 are shown for clarity).

Cluster compositions for each alloy are shown in Figure 31. There was no significant difference in the cluster compositions detected by each instrument.

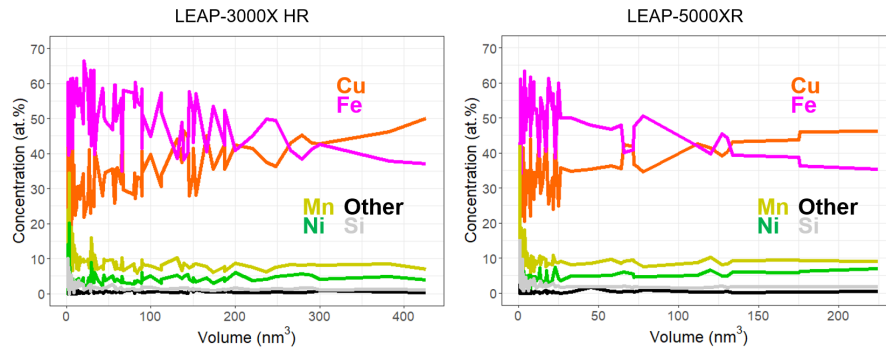


Figure 31: Cluster composition vs volume for clusters detected using the LEAP-3000X HR and the LEAP-5000XR.

2.4 Summary

Experiments were performed to determine if there was a significant difference between clusters detected by the LEAP-3000X HR compared to clusters detected by the LEAP-5000XR. Whilst significant differences were observed in the mean cluster volume, this difference was likely due to the sampling of a region that contained a high dislocation density in one of the datasets collected the LEAP-3000X HR. No significant difference was detected in cluster composition or cluster volume fraction. Slightly higher number densities of clusters, possibly due to the detection of more smaller clusters when using an instrument with a higher detection efficiency, are likely to be reported when using the LEAP-5000XR. Direct comparison of volume fraction and cluster composition results gathered from the two instruments is reasonable, as long as similar data analysis, reconstruction, and cluster search settings are used.

3 Edge Cluster Detection

Accurate cluster composition measurements are required if reliable models predicting cluster formation are to be created. Meanwhile, reported cluster size distributions and number densities must be representative of what is truly present in the system if changes in mechanical properties are to be correlated with microstructural developments.

For accurate cluster size and compositions to be reported after cluster searches have been performed, it is necessary to ensure that only clusters which are wholly contained within the dataset are included in calculations. Determining whether a cluster is bisected by the edge of a dataset may be performed manually. However, with some datasets containing more than 500 clusters (Figure 32), this can be restrictively time consuming. In addition, one user may choose to define a cluster as being on the edge of a dataset, whilst another user may decide that the same cluster is not on the edge of the dataset. This introduces subjectivity to the experimental results and effects the reproducibility of results.

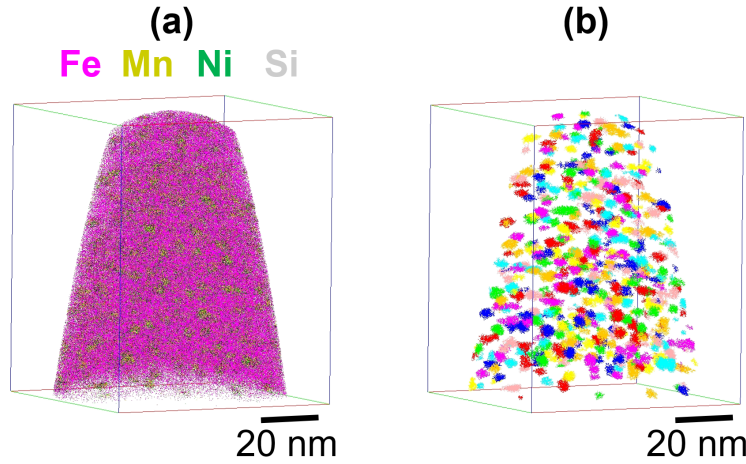


Figure 32: Figure demonstrating how (a) a typical atom probe dataset may (b) contain many hundreds of clusters.

Whilst some authors state that they do not include edge clusters in size calculations [177, 232, 233], they do not describe how they determined whether a cluster was on the edge of the dataset. There is a need for a method that can be consistently applied to atom probe tomography datasets to identify edge clusters.

3.1 α -Hull Method For Detecting Edge Clusters

An automated method for detecting edge clusters and removing them from size and composition calculations has been developed.

Firstly, cluster searches were performed on a .pos file using IVAS 3.8.0. The x , y , and z coordinates of the centre of each detected cluster were recorded (C_x , C_y , C_z). The extent in each dimension for every cluster, the maximum distance between an ion in the cluster and the cluster's centre of mass, was also determined (E_x , E_y , E_z). Each cluster was then modelled as a cuboid, as shown schematically in Figure 33, with vertices defined as shown in Table 22.

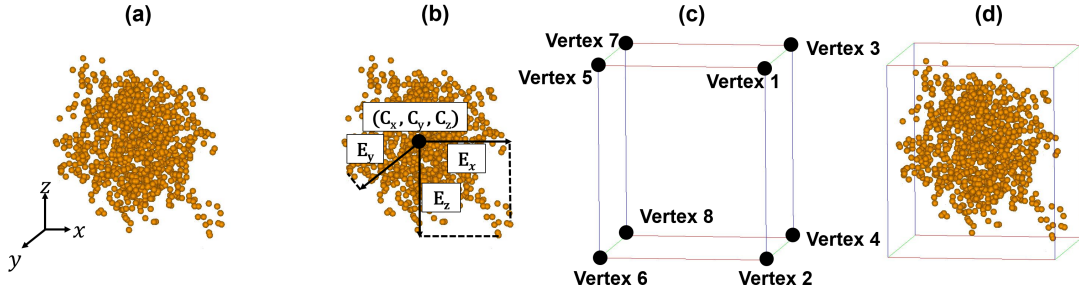


Figure 33: Schematic diagram demonstrating how for (a) each cluster (b) the centre of mass and extent is defined, (c) the position of the vertices of the cuboid based on the centre of mass and extent of the cluster and (d) the original cluster within the cuboid described by the vertices.

Vertex	x	y	z
1	$C_x + E_x$	$C_y + E_y$	$C_z + E_z$
2	$C_x + E_x$	$C_y + E_y$	$C_z - E_z$
3	$C_x + E_x$	$C_y - E_y$	$C_z + E_z$
4	$C_x + E_x$	$C_y - E_y$	$C_z - E_z$
5	$C_x - E_x$	$C_y + E_y$	$C_z + E_z$
6	$C_x - E_x$	$C_y + E_y$	$C_z - E_z$
7	$C_x - E_x$	$C_y - E_y$	$C_z + E_z$
8	$C_x - E_x$	$C_y - E_y$	$C_z - E_z$

Table 22: Table showing the co-ordinates of each vertex of the cube containing the cluster.

A single volume containing all ion locations in the original .pos file was generated using the alphashape3d package (1.3) [234] in R (3.4.2). This package implements the α -hull algorithm to create a shape or series of shapes (α -shapes), which can be concave, around a finite set of points. The key input parameter in the calculation of the α -hull is the α -value, which defines the radius of the circles (2D)/spheres (3D) used to determine the α -shape. This determines the resolution of the

generated surface(s) [234], as shown in Figure 34 .

The alphashape3d package was then used to determine if any of the vertices of each cluster’s cuboid lay outside of α -surface. If they did, the cluster was classified as an “edge” cluster, else the cluster was decided to be a “non-edge” cluster. A list of edge and non-edge clusters was returned by the code. Edge clusters were then removed from the analysis for the purpose of size and/or compositional calculations but were included in volume fraction calculations. Edge clusters were counted as 0.5 of a cluster for number density calculations.

3.2 Optimising Application To Real Data

Figure 34 shows the effect that the α -value parameter had on the shape generated around ions present in a sampled atom probe tomography dataset. In order to reduce the computational time required to generate the α -surface, the dataset was randomly sampled to contain 0.5 at.% of the original ions. Figure 34 (a) shows that selecting too small an α -value led to many volumes each containing very few points being generated (high resolution). Meanwhile, Figure 34 (c) demonstrates that setting an α -value that was too large resulted in one volume being generated containing the entire set of points, but its shape was not fully representative of the space that the points occupied (low resolution).

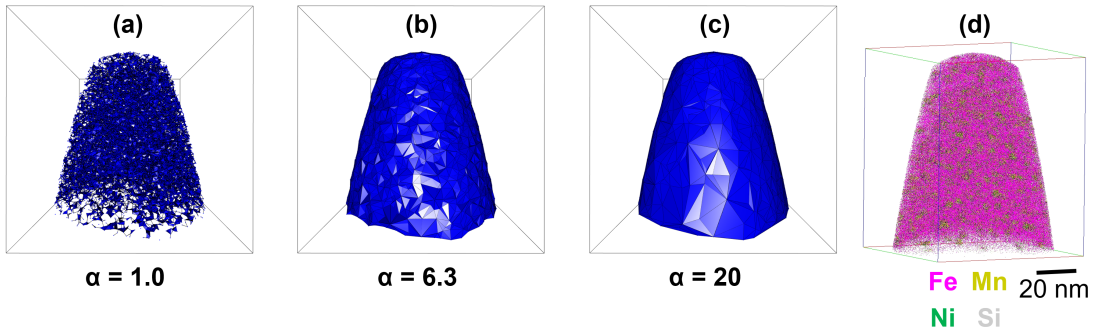


Figure 34: Effect of varying the α -value on the α -shape(s) generated around a dataset sampled to 0.5 at.% for (a) $\alpha = 1.0$, (b) $\alpha = 6.3$, and (c) $\alpha = 20$. (d) The original dataset.

It is assumed that one continuous volume is analysed during an APT experiment. Therefore, having more than one volume created by the α -hull step is not representative of the true specimen shape. Once the α -shape(s) had been generated, a test was performed to ensure that only one volume had been generated. If multiple volumes were generated, the α -value was increased until

only one volume was created.

If the original list of atomic spatial coordinates in the reconstruction is not sampled to reduce the computational time required to generate the α -shape, the time required to perform the algorithm on a personal computer is prohibitively long. Sampling the 3D point cloud will increase the average nearest neighbour distance between points. Therefore, a new α -value should be calculated. Setting $\alpha = \max(NND)$ should prevent multiple volumes from being generated, where $\max(NND)$ is the maximum of all of the nearest neighbour distances in the sampled dataset.

3.2.1 Effect of Sampling Fraction

The effect that downsampling had on the time required to perform the algorithm was investigated on a dataset that originally contained 6.7 million ions. 505 clusters were identified after cluster searches of the original .pos file.

To investigate the effect of sampling, the original dataset was randomly sampled twenty times at four different sampling fractions (0.0001, 0.001, 0.005, and 0.01). The time taken to generate an α -shape ($\alpha = \max(NND)$) for the sampled data and the number of clusters assigned as edge was recorded. These calculations were performed on a Dell Latitude E7450 laptop computer with 16 GB RAM and an Intel Core i7 CPU 2.60 GHz duo core processor.

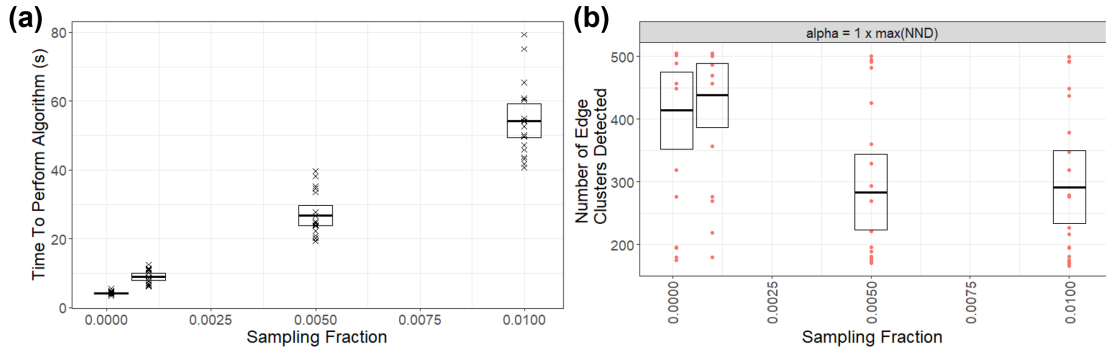


Figure 35: Figure showing the effect of sampling fraction on (a) time required to generate α -shape and determine which clusters were on the edge of the dataset and (b) the number of clusters that were classified as being on the edge of the specimen for $\alpha = \max(NND)$. Mean values and 95 % CI are displayed.

Figure 35 (a) shows that the time required to perform the algorithm decreased as the sampling fraction was reduced. However, Figure 35 (b) shows that there was a large degree of variance in the number of clusters that were assigned as edge for all sampling fractions, with all

clusters being assigned as edge in some circumstances. This occurred as the generated α -shapes were not representative of the original dataset, leading to non-edge clusters being incorrectly assigned as edge. Figure 36 (b) shows a generated α -shape that is clearly not illustrative of the original dataset. The α -shape has voids passing through it. Clusters, which were spatially located within the original data near to where these voids exist in the sampled data, will probably be assigned as edge by the algorithm.

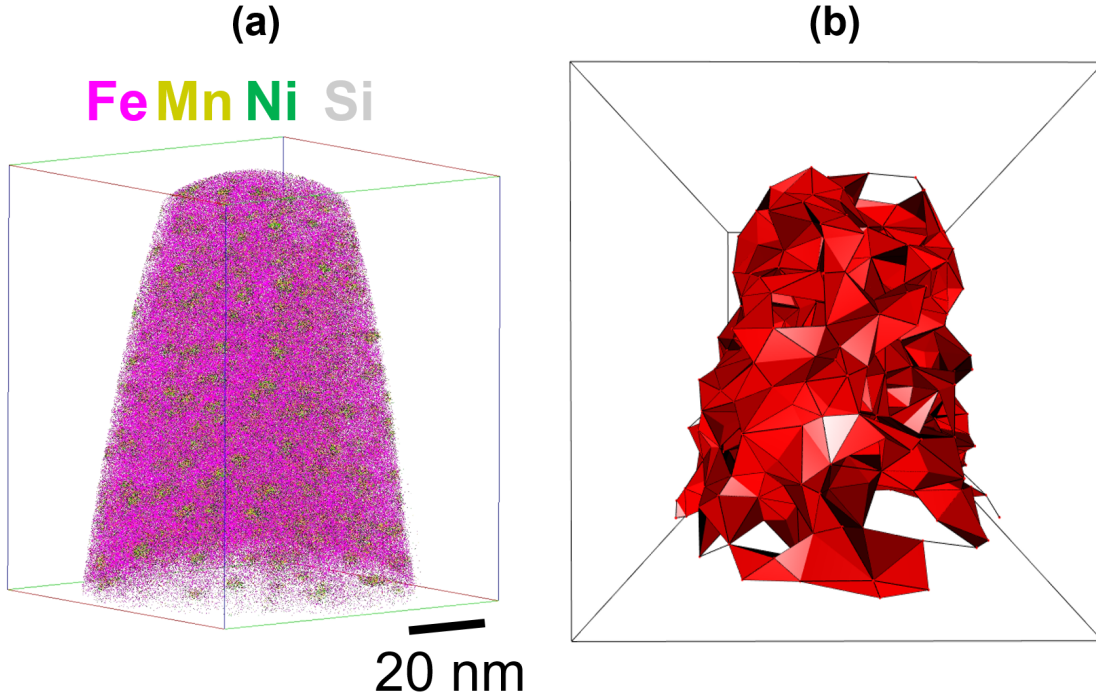


Figure 36: Figure showing (a) the shape of the unsampled data and (b) the α -shape generate around the data after sampling to 0.0001 with $\alpha = \max(NND)$.

The algorithm was incorrectly assigning many clusters as edge even at the least aggressive sampling fraction (0.01). Therefore, the effect that varying the α -value had on the number of clusters assigned as edge was studied.

3.2.2 Effect of α -Value

The original .pos file was sampled twenty times at four different sampling fractions. α -shapes were then generated around each sampled dataset using α -values of $\alpha = x \times \max(NND)$ (for $x = 1, 2, 3$, and 4), and the number of assigned edge clusters was recorded.

Figure 37 demonstrates that, when $\alpha \geq 2 \times \max(NND)$, the variance in the number of clusters assigned as edge is much reduced for all sampling fractions when compared to the case for $\alpha = \max(NND)$. α -values $\geq 2 \times \max(NND)$ were found to result in the formation of α -shapes that were characteristic of the original data and did not contain void regions.

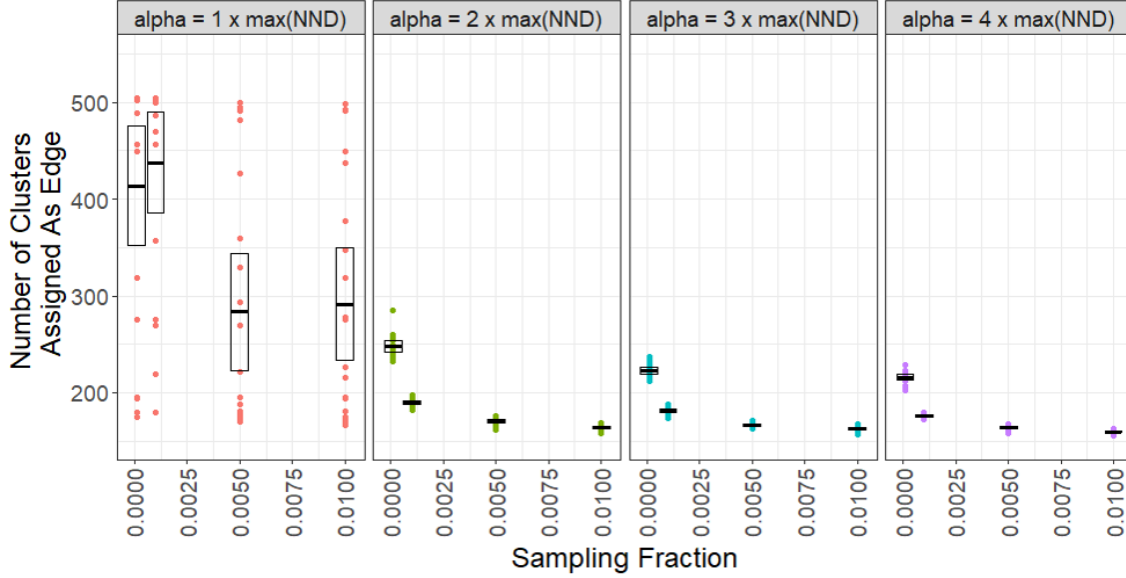


Figure 37: Figure showing the effect of varying sampling fraction and α -value on the number of clusters that were assigned as being on the edge of the specimen. Mean values and 95 % CI are displayed.

There was a significant decrease in the number of assigned edge clusters as the sampling became less intensive. This is likely a result of intensive sampling causing the volume of the data to be artificially reduced as more ions are removed during the sampling. This will result in α -shapes that are less representative of the original data and may cause clusters, which were fully contained within the original dataset, to now be defined as intersecting the edge of the field-of-view in the sampled dataset; these clusters would then be defined as edge clusters. This effect was most noticeable as the sampling fraction changed from 0.0001 to 0.001. As the sampling fraction changed from 0.005 to 0.01, the difference in the number of assigned edge clusters was small.

3.3 Application To Irregular Specimen Shapes

One of the major advantages of this method to detect edge clusters is that it can be applied to datasets of any shape. This is particularly useful as asymmetrical shapes are created when

non-matrix regions enriched in solute, such as carbides, are removed prior to performing cluster searches. Removal of these regions is necessary prior to performing cluster searches as these regions influence the calculated randomised distribution of solute in the dataset.

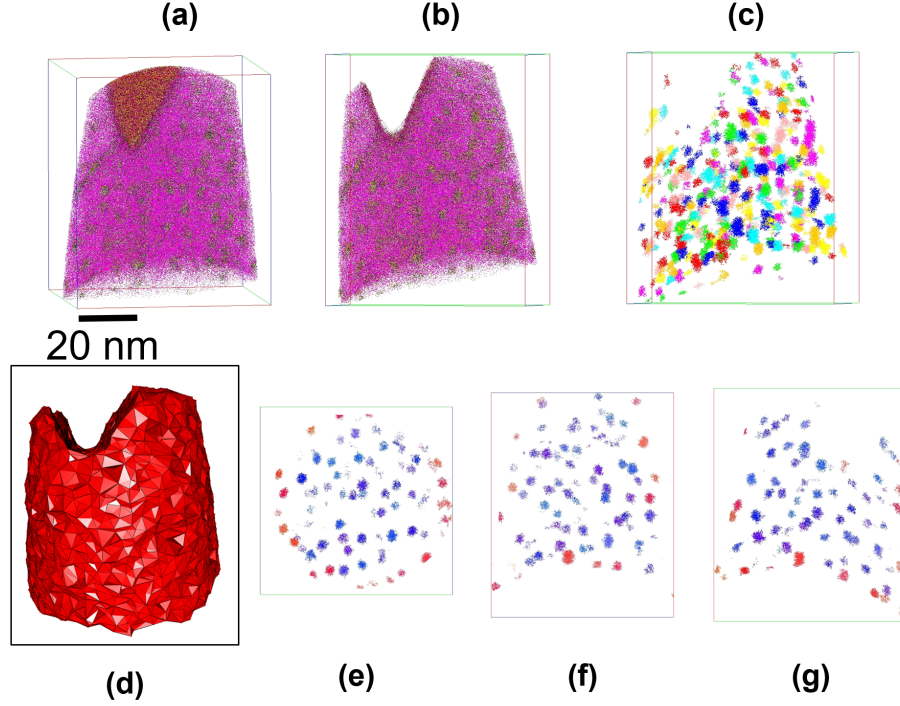


Figure 38: Figure showing (a) original data, (b) change in shape of data after removal of isosurface region containing more than 18 at.% C, (c) the clusters detected in the matrix of the dataset, (d) α -shape generated around dataset after carbide removal. (e), (f), and (g) show the clusters that were defined as edge (red) and non-edge (blue) in the y - z , x - z , and x - y perspectives respectively.

The α -hull method described above was applied to detect edge clusters in an irregularly shaped dataset. Figure 38 (a) shows the original dataset, whilst Figure 38 (b) shows the dataset after an isoconcentration surface was used to removed the carbide. The isoconcentration value used was 18 at.% C. The dataset contained 4.9 million ions after the carbide had been removed. The 356 clusters detected in the matrix of the dataset are shown in Figure 38 (c). For a sampling fraction of 0.005 and $\alpha = 2 \times \max(NND)$, the program described above took 22.7 seconds to identify 122 edge clusters. The α -shape generated around this point cloud is representative of the complex geometry of the specimen (Figure 38 (d)). Figures 38 (e), (f), and (g) are 10 nm slices through the dataset and show the clusters that were defined as edge (red) and non-edge (blue) clusters in the y - z , x - z , and x - y planes.

3.4 Application To Simulated Dataset

In order to investigate the impact that identification and removal of edge clusters had on cluster calculations, Dr. A. J. London simulated a series of cluster-containing volumes using posgen. Atoms were randomly located within a 22 nm radius sphere to create a volume with an atomic density of 20 atoms/nm³. The randomisation of location imitates the spatial error in real APT data. Meanwhile, using an atomic density of 20 atoms/nm³, which is lower than naturally present in α -Fe, is representative of the limited detection efficiency that APT instruments have. The volume had a composition of 98 at.% Fe, 1 at.% Cu, and 1 at.% Ni.

40 clusters (radius = 2 nm) were then randomly positioned, such that their centre of mass was contained within the volume of the 22 nm sphere. This was achieved by changing the chemical identity of ions within a 2 nm radius of a randomly selected location. However, a condition was imposed such that two clusters were unable to occupy the same volume. The clusters had a core-shell structure with the cores consisting of 100 at.% Cu and the shells consisting of 100 at.% Ni. The radius of the core was 1.587 nm; this value was selected so that the core and shell regions had the same volume, such that the overall composition of the clusters was 50 at.% Cu, and 50 at.% Ni.

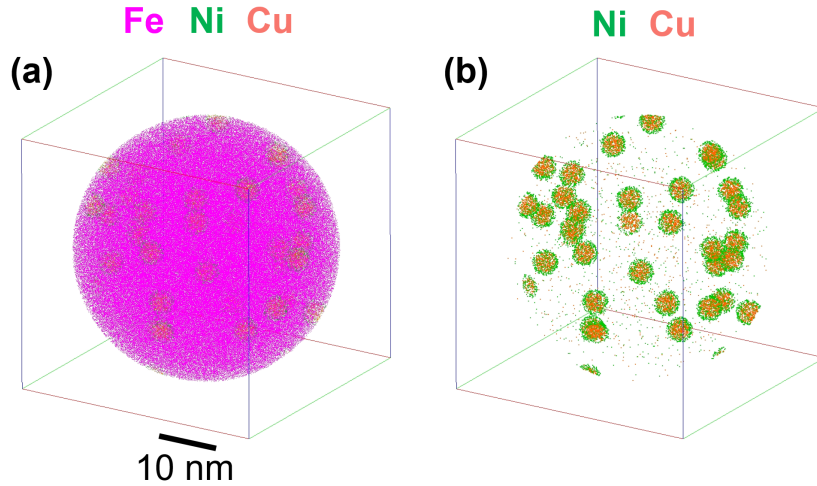


Figure 39: Atom maps displaying (a) distribution of Fe, Cu, and Ni atoms in a simulated 20 nm radius sphere and (b) distribution of Cu and Ni atoms in the same sphere.

In order to simulate the effect of an APT dataset sampling a subvolume of material, the dataset was cropped to a sphere of radius 20 nm (Figure 39). The number density of clusters in this simulated volume was $9.2 \times 10^{23} \text{ m}^{-3}$, the cluster volume fraction was 3.00 %, and the clusters had

a radius of 2 nm. Cluster searches were then conducted using the maximum separation method with $D_{max} = 0.5$, $L = E = 0.2$, and $N_{min} = 50$. Cluster calculations of size, number density, volume fraction and composition were performed using all of the clusters which were detected by the cluster search.

Edge clusters were then identified using the α -hull method outlined above. A sampling fraction of 0.01 and an α -value of 12 was used. Calculations of cluster size, number density, volume fraction and composition were conducted, whilst accounting for edge clusters, by using the equations defined in Chapter IV Section 3.6.3. These simulations were performed 2,000 times to improve statistical power.

Of the 80,000 clusters generated during the simulations, 71,552 were detected by the maximum separation cluster searches. The cluster searches did not detect some clusters, likely due to a combination of; few ions from these clusters being contained in the cropped volume when cluster centres were located ≥ 20 nm from the centre of the sphere, and the conservative N_{min} value which was used in the cluster searches.

29,142 of the detected clusters were intersected by the edge of the cropped volume i.e. the clusters centre was, prior to cropping, ≥ 20 nm from the centre of the 22 nm sphere. All 29,142 of these clusters were correctly identified as being edge clusters by the α -hull algorithm. The algorithm also incorrectly identified 8,113 of the detected clusters as being on the edge of dataset despite them being wholly contained within the 20 nm sphere's volume. This may be because modelling of the clusters as cuboids overestimates their true volume. However, another reason for this incorrect identification is that the sampling of the dataset prior generating the α -shape artificially reduces its volume. This results in some clusters, which were originally wholly contained within the sphere, being outside of the sampled volume. This issue may be overcome by selecting a less aggressive sampling fraction, however, this will increase the computational time required to perform the algorithm.

Table 23 summarises the cluster attributes for the true case, the case when all clusters that were detected after cluster searches were performed on the cropped dataset are included, and in the situation whereby edge clusters are identified and accounted for. The measured volume fraction was marginally lower than the true value for both cases when the sphere was reduced to 20 nm in radius. This is due to the conservative N_{min} value resulting in some clusters not being detected by the cluster search algorithm.

	Number Density ($\times 10^{23} \text{ m}^{-3}$)	Volume Fraction (%)	Radius (nm)
True Value in 20 nm Radius Sphere	9.2	3.00	2.00
All Detected Clusters	10.7	2.92	1.82
Measurements When Edge Clusters Identified And Accounted For	7.9	2.92	2.00

Table 23: Comparison of cluster attributes in the simulated 20 nm sphere datasets, the measured attributes in the 20 nm radius spheres after cluster searches were performed, and the measured attributes when edge clusters were accounted for in the 20 nm radius sphere datasets using the equations in Chapter IV Section 3.6.3.

Despite some clusters not being detected by the cluster search, the measured cluster number density was higher than the true number density when edge clusters were not accounted for. Meanwhile, the calculated number density underestimated the true value when edge clusters were accounted for. This underestimation may be due to the incorrect identification of some non-edge clusters as being edge, or due to the failure of the cluster search to identify all cluster contained within the 20 nm sphere. However, removing edge clusters from the analyses did improve the accuracy of cluster size calculations.

Figures 40 (a) and (b) show the true distribution of cluster compositions. As expected, the distributions are normally distributed around 50 at.% Cu and 50 at.% Ni. The spread in compositions by a few at.% arises due to counting error and from the inclusion of some Cu and Ni atoms from the matrix during the cluster search.

When cluster compositions are calculated for the detected clusters in the cropped dataset, the distribution of compositions is no longer normally distributed (Figures 40 (c) and (d)). The distributions are negatively skewed in the case of core (Cu) ions and positively skewed in the case of shell (Ni) ions. This is a result of the instances whereby only the shell of a cluster is contained within the 20 nm radius dataset. There are also instances where, as a result of a cluster being sectioned by the edge of the spherical dataset, more than half of the detected cluster consists of core ions. This results in higher measured Cu compositions at the expense of Ni. These effects would bias mean cluster compositions if all detected clusters were included in the calculations.

The composition distributions in Figures 40 (e) and (f) demonstrate how the identification and removal of edge clusters results in a measured distribution of cluster compositions which is very similar to the simulated case.

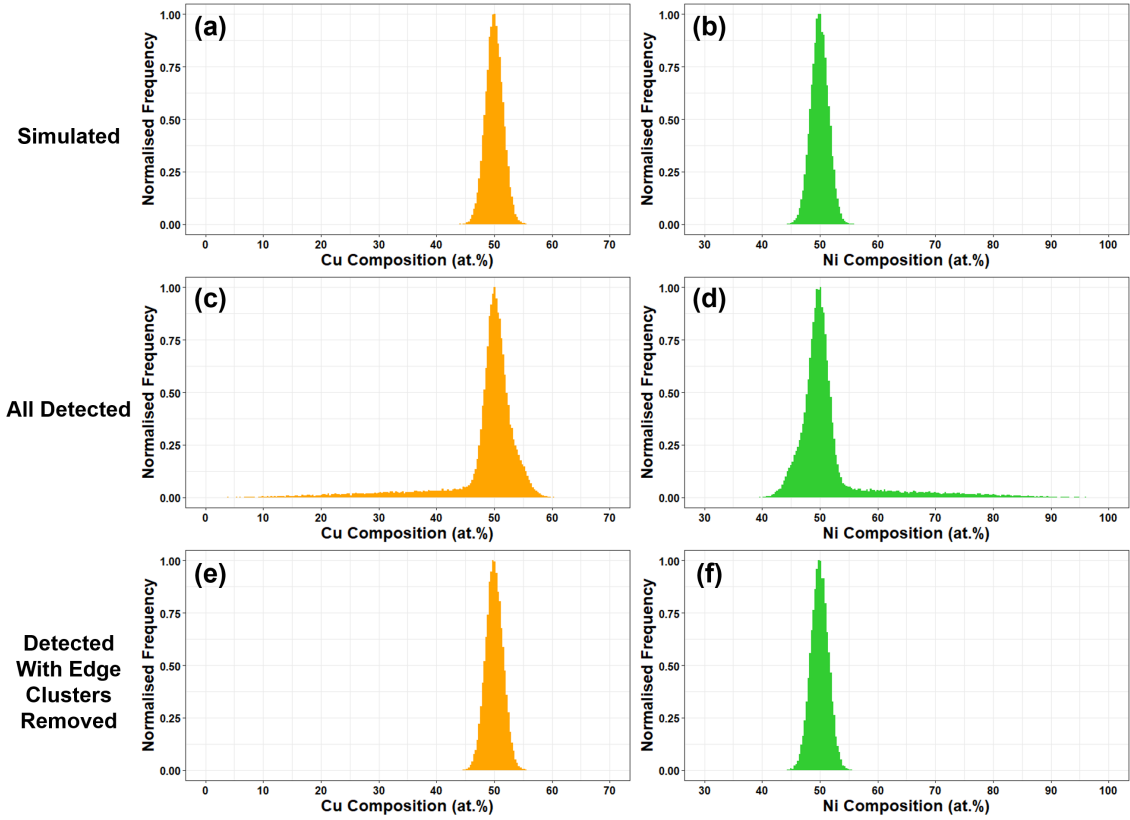


Figure 40: Normalised histograms of measured Cu and Ni compositions for (a) & (b) correct cluster compositions, (c) & (d) clusters detected after cluster searches performed on 20 nm radius datasets, (e) & (f) clusters from (c) & (d) after edge clusters identified and removed from analysis.

3.5 Discussion

The effect of varying sampling fraction and α -values on the time taken to perform the algorithm and on the number of clusters assigned as edge has been investigated. The results indicate that the parameters of sampling fraction and α must be carefully selected. Sampling the data too intensively will increase the probability of mis-assigning non-edge clusters as edge, whilst the algorithm will take a prohibitively long time if the data is not sampled intensively enough. Meanwhile, too small an α -value will lead to the generation of shapes that are not representative of the original data, particularly in the case of data that has been aggressively sampled.

Sensible values of sampling fraction and α can be determined by investigating the variation in the number of clusters assigned as being edge. For the data in this thesis sampling fractions of 0.005 were used and $\alpha = 2 \times \max(NND)$, unless otherwise specified.

The cuboidal shape likely overestimates the clusters true volume, particularly if the cluster is

non-spherical in shape and its principal axes of symmetry are not orientated along the x, y , or z axes of the experiment. As cluster volume is overestimated when using the proposed methodology, some non-edge clusters may be incorrectly classified as being edge clusters.

Simulations revealed that assigning non-edge clusters as edge will lead to an under-calculation of true cluster number densities. However, failure to account for edge clusters will lead to an over-calculation of cluster number density, an underestimation of cluster size, and perhaps also to incorrect determination of cluster compositions. Use of the aforementioned algorithm to detect edge clusters does provide the opportunity to determine lower bounds for the number density of clusters contained within a dataset. Implementation of the algorithm also improves the accuracy of size and compositional calculations.

3.6 Summary

A novel method to determine whether clusters are near the edge of the analysed volume of an APT experiment has been developed. The method uses the α -hull technique to define a surface surrounding a sampled APT dataset. The clusters detected in the original .pos file are then modelled as cuboids. Clusters are defined as being on the edge of the dataset if any of the vertices of the cuboid lie outside of the α -shape. Application of this method to simulated data indicates that the accuracy of size and compositional measurements are improved.

This methodology is, to the author's knowledge, the first proposed method for detecting edge clusters on a personal computer in a reproducible and automated manner. Its applicability to real datasets, including those of complex shape, has been demonstrated. It could be improved upon in the future by modelling the clusters as non-cuboidal shapes.

4 Quantification of Grain Boundary Segregation

The segregation of different elements to internal interfaces, such as grain boundaries, is known to have significant effects on macroscale properties [59]. Therefore, the ability to directly measure changes to grain boundary chemical composition in a material subjected to a particular treatment or environment is critical to understand, and ultimately predict, changes to physical properties.

The Gibbsian interfacial excess is an often used metric to quantify the amount of solute segregation at an interface. It is defined as the number of excess atoms of a particular element that are present, per unit area, because of the presence of an interface. The Gibbsian interfacial excess of each element can be determined from atom probe tomography data by using the methods proposed by Krakauer and Seidman [235]. Many authors have used this methodology to report grain boundary analyses performed using APT [236].

4.1 Theoretical Gibbsian Interfacial Excess Calculations for APT

Assume a material specimen subject to APT characterisation contains a grain boundary interface perpendicular to the analysis direction. The cumulative number of atoms detected of element i (N_i) will increase along the length of the analysis. The *ladder* diagram in Figure 41 (a) shows how the cumulative number of atoms of an element, which strongly segregates to a grain boundary, varies with respect to the cumulative number of all atoms (also effectively a proxy measure of distance through the analysis direction) as the analysis passes through the grain boundary. Assuming that element i is homogeneously distributed through the bulk of the first grain, Grain A, this function will initially increase linearly. As the interface is analysed, N_i increases sharply. The slope of the function will decrease again as the matrix of the grain beyond the interface, Grain B, is analysed.

Krakauer and Seidman showed that the Gibbsian interfacial excess (Γ_i) of each element, i , could then be calculated using one of two methods, both of which are mathematically identical.

4.1.1 Cumulative Count Method

The first method calculates Γ_i from the cumulative number of counts of element i using the following equation:

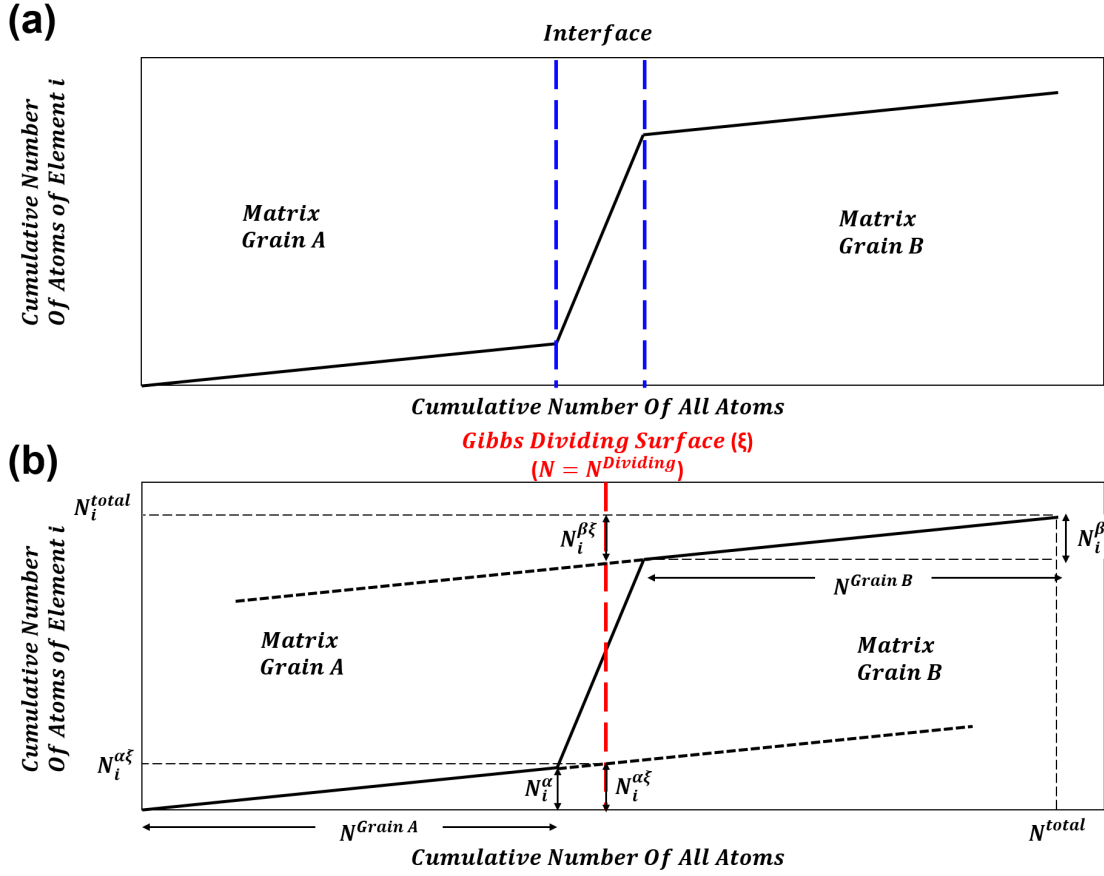


Figure 41: Schematic ladder diagrams showing (a) the expected change in cumulative count of a segregating element, i , through a region of interest containing a grain boundary, (b) how variables involved in calculating Gibbsian interfacial excess (Γ_i) are determined from cumulative atom count plots (Adapted from [235]).

$$\Gamma_i = \frac{N_i^{total} - N_i^{\alpha\xi} - N_i^{\beta\xi}}{A\eta} \quad (11)$$

where N_i^{total} is the total number of atoms of element i detected within the analysis region, $N_i^{\alpha\xi}$ is the number of i atoms that would be expected at the Gibbs dividing surface (ξ) from the profile of element i in Grain A if there was no segregation, $N_i^{\beta\xi}$ is the number of i atoms that would be expected at the Gibbs dividing surface (ξ) from the profile of element i in Grain B if there was no segregation, A is the interfacial area over which Γ_i is determined, and η is the detection efficiency of the atom probe instrument used [235].

$N_i^{\alpha\xi}$ and $N_i^{\beta\xi}$ can be calculated using the following equations:

$$N_i^{\alpha\xi} = \frac{N_i^\alpha}{N^{GrainA}} \times \xi \quad (12)$$

$$N_i^{\beta\xi} = \frac{N_i^\beta}{N^{GrainB}} \times (1 - \xi) \quad (13)$$

where N_i^α is the number of detected atoms of element i in Grain A, N^{GrainA} is the total number of atoms detected in Grain A, N_i^β is the detected number of atoms of element i in Grain B, and N^{GrainB} is the total number of detected atoms in Grain B. A schematic diagram of this is shown in Figure 41 (b). ξ defines the position of the Gibbs dividing surface within the analysed volume and is calculated by:

$$\xi = \frac{N^{Dividing}}{N^{Total}} \quad (14)$$

where $N^{Dividing}$ is cumulative number of all detected atoms up to the Gibbs dividing surface, and N^{Total} is the total number of detected atoms in the analysed volume.

4.1.2 Concentration Method

The second method calculates Γ_i from the concentration of i in the phases on either side of the interface and the concentration of i at the total volume:

$$\Gamma_i = \frac{N^{total}(C_i - C_{i(\alpha)}\xi - C_{i(\beta)}(1 - \xi))}{A\eta} \quad (15)$$

where N^{total} is the total number of atoms detected within the analysed volume, C_i is the concentration of element i in the analysed volume, $C_{i(\alpha)}$ is the concentration of element i in the matrix of Grain A, ξ is the position of the Gibbs dividing surface, $C_{i(\beta)}$ is the concentration of element i in the matrix of Grain B, A is the interfacial area over which Γ_i is determined, and η is the detection efficiency of the atom probe instrument used.

C_i , $C_{i(\alpha)}$, and $C_{i(\beta)}$ are calculated from the cumulative count plot in Figure 41 (b) using the following equations:

$$C_i = \frac{N_i^{total}}{N^{total}} \quad (16)$$

$$C_{i(\alpha)} = \frac{N_i^\alpha}{N_{GrainA}} \quad (17)$$

$$C_{i(\beta)} = \frac{N_i^\beta}{N_{GrainB}} \quad (18)$$

where N_i^{total} is the total number of detected atoms of element i in the analysed volume and N^{total} is the total number of detected atoms in the analysed volume, N_i^α is the total number of detected atoms of element i in the matrix of Grain A, N_{GrainA} is the total number of detected atoms in Grain A, N_i^β is the total number of detected atoms of element i in the matrix of Grain B, and N_{GrainB} is the total number of detected atoms in Grain B.

4.2 Issues Adapting to Experimental APT Data

Either of the methods outlined above can be used to calculate Γ_i from APT data. However, there are several factors that make the calculation of Gibbsian interfacial excess values more complex when using real data as opposed to in the theoretical case above.

4.2.1 Atomic Density Variations

An artefact that has potential to impact the calculation of Gibbsian interfacial excess is the apparent change in atomic density throughout reconstructed atom probe tomography datasets.

Crystallographic poles are known to impact the observed local atomic density in APT data [179]. However, as these features run vertically down the reconstruction [158, 237], they can easily be identified and accounted for.

A more troubling artefact is the apparent change in density of interfaces in reconstructed data. Figure 42 (a) shows an atom map of Mn and Ni ions; an area enriched in these elements, a grain boundary, can be observed. Also in this figure a region of interest (ROI) and analysis direction are highlighted, across which a 1D atomic density profile measurement has been applied (Figure 42 (c)). A density plot of this same reconstruction (Figure 42 (b)) shows a varying density (ions/nm³) throughout the tip, with the grain boundary region having a higher apparent atomic density than the bulk of the reconstructed material. Indeed, the 1D atomic density profile along the ROI from Figure 42 (a) shows that there is a slight decrease in the number of atoms detected per

bin as the matrix-boundary interface is approached. A higher atomic density is then detected at the interface than on either side of it (Figure 42 (c)).

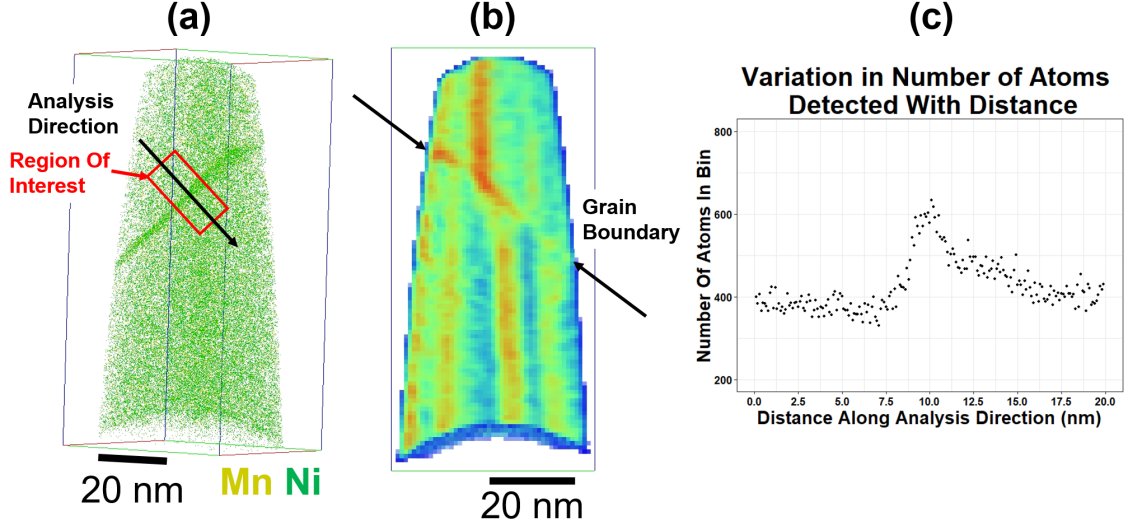


Figure 42: (a) Atom map showing the segregation of Mn and Ni to a grain boundary and a 10 nm × 10 nm region of interest through the boundary, (b) Density plot showing the variation in number of ions detected per nm³ in the reconstructed volume, and (c) Graph showing the variation in number of atoms detected per 0.1 nm bin along the region of interest in (a).

As α -Fe has a BCC crystallographic structure and a lattice parameter of 0.286 nm it has an expected density of approximately 85 atoms/nm³. Since the detection efficiency of the LEAP-5000XR is $\eta \approx 0.52$, the expected density of atoms in the reconstructed volume would be 44 atoms/nm³. Therefore, for a 10 nm × 10 nm ROI and fixed bin width of 0.1 nm, approximately 440 atoms would be expected per inspected bin. Either side of the grain boundary, the number of atoms per bin is around 440, as expected. However, at the interface the density is around 36 % higher, with over 600 atoms being detected in some bins.

As the grain boundary is likely to have a different composition to the surrounding matrix, the unphysically high measured atomic density at the grain boundary may be the result of the local magnification effect [157]. The magnitude of the local magnification effect at interfaces has been shown to be minimised when the interface is perpendicular to the analysis direction during field evaporation [238].

Furthermore, the variation in atomic density between a grain boundary and the surrounding matrix has previously been shown to arise in grain boundaries which undergo simulated field

evaporation [239]. The authors observed that the change in atomic density at the grain boundary occurred even in simulated materials with homogeneous evaporation fields, indicating that the measured atomic density within APT reconstruction is affected by the structural defect of a grain boundary as well as by the varying evaporation fields of the elements present at the boundary [239].

Since both of these effects can lead to more atoms of each species being detected at the boundary, there is an apparent excess of all atoms at the boundary. Therefore, if one were to simply measure the number of atoms of element i within a sampling bin (of fixed width) versus distance, it may appear that there are an excess of i atoms when, in reality, i shows no segregation to the interface. Therefore, it is important to use either bins containing a fixed number of ions, or to use concentration to calculate Γ_i .

4.2.2 Required User Parameter Input

Another factor that greatly affects the reproducibility of Gibbsian interfacial excess calculations is the large number of parameters that must be selected by the user performing the analysis. These parameters, such as defining the extents of Grain A and Grain B, or the position of the Gibbs dividing surface, can have a large effect on the calculated excess values.

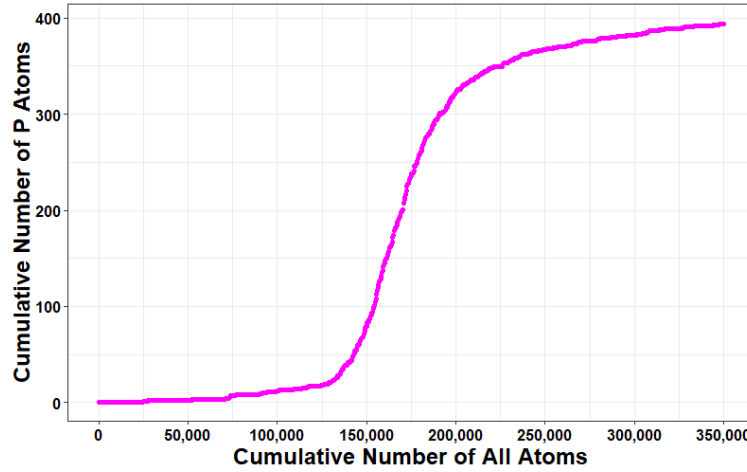


Figure 43: Cumulative plot of number of P atoms vs cumulative number of all atoms across a region of interest encountering a grain boundary perpendicular to the direction of analysis.

Cumulative plots derived from real experimental data, such as that presented in Figure 43, rarely contain three regions that are as clearly distinct as in the model shown in Figure 41 (a). Maruyama et al. considered several possibilities as to why the difference between the theoretical

case and real data arose [238]. They concluded that the difference was most likely due to a combination of the grain boundary not being perfectly perpendicular with the region of interest, and due to a degradation in spatial resolution as a result of the local magnification effect [238].

As a result of the apparent defocusing due to the local magnification effect, the positions where Grain A ends and the interface begins, and where the interface ends and Grain B begins, respectively, are no longer clearly defined. The user performing the analysis must make a subjective decision as to where to define the positions of these boundaries.

Selection of the positions defining the extents of the grain boundary can significantly impact the calculation of Γ_i . Figure 44 demonstrates the way in which two independent users may define the position of the grain boundary encountered in Figure 43. The effect this has on the calculated Γ_i is not trivial, as demonstrated by the resulting measurements presented in Table 24. Reducing the sensitivity of the calculated Γ_i with respect to user input is therefore critical to make such measurements meaningful and robust.

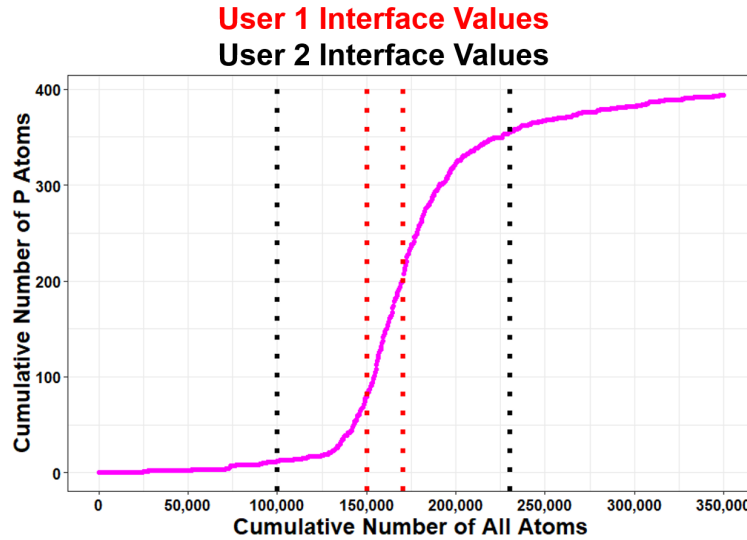


Figure 44: Cumulative plot of number of P atoms vs cumulative number of all atoms, showing where two users could define the interface region as beginning and ending.

User	Interface Start (Cumulative Number Of All Atoms)	Interface End (Cumulative Number Of All Atoms)	Γ_P (Excess Atoms nm ⁻²)
1	150,000	170,000	1.00
2	100,000	230,000	1.69

Table 24: The effect of selected interface start and end values on the calculated Gibbsian interfacial excess values of P (calculated using the methods proposed by Krakauer and Seidman) [235].

Varying the location of the Gibbs dividing surface (ξ) within the interface region can also have a large affect on the values calculated for Γ_i . This is because the concentrations of element i may be different in Grain A and Grain B. As a result, the predicted values of $N_i^{\alpha\xi}$ and $N_i^{\beta\xi}$ will change depending on where ξ is defined as being within the interface (Figure 45). Whilst this will affect the calculation, it is possible to report upper and lower values of Γ_i .

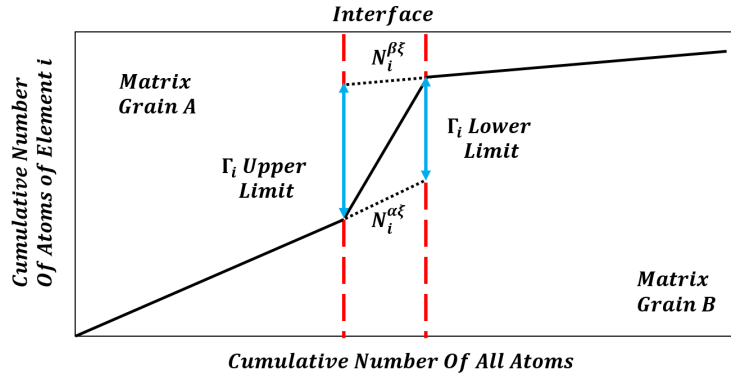


Figure 45: Schematic digram demonstrating how the values of $N_i^{\alpha\xi}$ and $N_i^{\beta\xi}$ (dashed lines) predicted at the Gibbs dividing surface depend on the where the Gibbs dividing surface is placed within the interface region.

4.2.3 Loosely Defined Variables

Another issue, when applying the method described by Krakauer and Seidman [235] to real data, is that the definitions for some of the variables involved in the calculations of Γ_i are not strict.

For example, the authors define $C_{i(\alpha)}$ and $C_{i(\beta)}$ as “the atomic concentrations of element i in the homogeneous regions of phases α and β , i.e., the bulk regions of the two phases.” However, the segregation of solutes to interfaces can lead to a denuded zone around the interface [240], meaning that phases α and β are not homogeneous. Furthermore, precipitate or cluster formation occurs in many material systems and means that individual grains/phases are often not homogeneous.

If this occurs, then what is precisely meant by the definition of the “homogeneous regions of phases α and β ” is no longer rigid. Figure 46 demonstrates four different regions in the same material which may be considered “homogeneous” by a user who is calculating Gibssian interfacial excess values. This will affect the calculated Γ_i values and, therefore, the reproducibility of results.

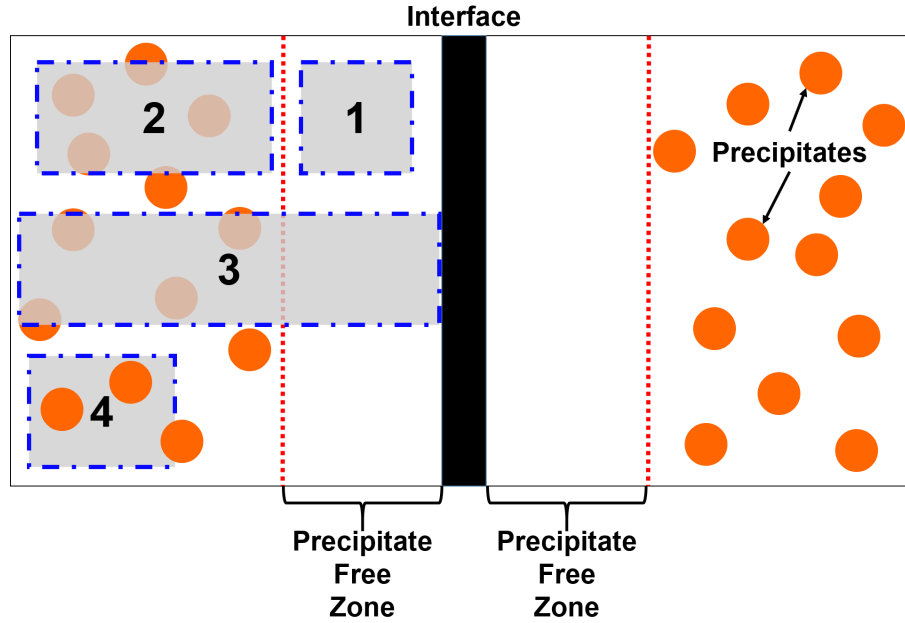


Figure 46: Schematic diagram demonstrating presence of a precipitate free zone adjacent to an interface, and the four different regions that independent users could decide best reflect the “homogeneous” regions of phase α .

In Figure 46, Region 1 may be considered “homogeneous” as this is the area adjacent to interface and contains no other phases. However, the choice of Region 2 may also be justified since this region is representative of phase α before the precipitate free zone formed. Region 3 could be selected as it samples both the region adjacent to the interface and phase α away from the interface, offering a compromise between Region 1 and Region 2. Region 4 selects the matrix of phase α away from the interface, but does not incorporate the precipitates in the matrix. This choice could be justified, since the precipitates may be a different phase to the α matrix. There is no widely accepted protocol on how to proceed in this circumstance, and a user could reasonably select any of the regions to describe the homogeneous region of phase α .

4.2.4 Interface Homogeneity

Another issue that arises when analysing real data is that segregation is often not homogeneous across the interface. Figure 47 (a) is an atom map showing the distribution of Ni and Mn within a region of a neutron-irradiated steel. There is an enrichment of these elements to a planar feature, likely a grain boundary, that is highlighted in Figure 47 (b). If this planar region is isolated, it is clear upon visual inspection that the segregation of Ni and Mn (Figure 47 (c)), and Si (Figure 47 (d)) is non-uniform across the grain boundary.

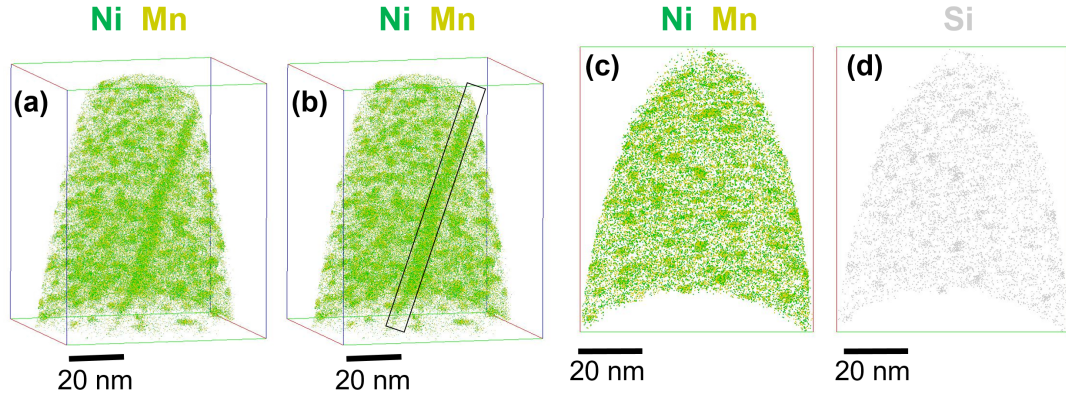


Figure 47: Atom maps for a neutron-irradiated steel showing (a) the distribution of Ni and Mn atoms in the reconstruction, (b) the grain boundary region extracted for further analysis, and the non-uniform distribution of (c) Ni and Mn, and (d) Si across the grain boundary.

In this case, the reporting of a single value to quantify the Gibbsian interfacial excess does not seem appropriate. Figure 48 demonstrates how the calculated Gibbsian interfacial excess value of Ni can vary by more than one order of magnitude if different small areas of the grain boundary are independently sampled. A measurement which samples an area not enriched in solute (black) results in an excess value of $\Gamma_{Ni} = 1.1 \text{ atoms/nm}^2$, whilst a value of $\Gamma_{Ni} = 18.6 \text{ atoms/nm}^2$ is determined if a region locally enriched in solute is analysed (blue). Sampling a larger area (red) will average out these affects. However, the reporting of a single value provides no information as to how homogeneously each element is distributed across the boundary. Some studies have applied a mesh to the interface to be analysed and reported a map that shows the variation of Γ_i across the boundary [236]. This is an improvement, but Γ_i will still vary for each region depending on the size of the mesh, something that remains user defined. It is also a qualitative, not quantitative description.

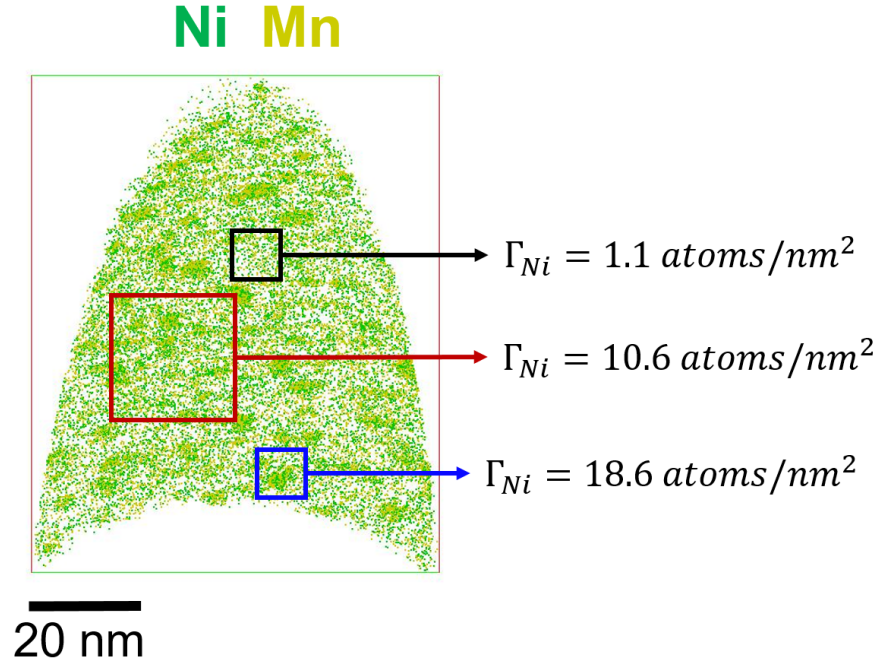


Figure 48: Atom maps for a grain boundary from a neutron-irradiated steel, showing the variation of Gibbsian interfacial excess values calculated for different areas.

4.3 Suitability Of Applying Γ_i To Meaningfully Describe Real Material Systems

As well as the issues arising when trying to calculate the Gibbsian interfacial excess from APT data, the validity of using the Gibbsian interfacial excess to correlate changes in properties with the evolution of grain boundary nature in real material systems is debatable.

The quantity Γ_i is not a true measure of the nature of the interface. It is a measure of the composition of the interface with respect to the composition of two phases either side of it.

Consider a scenario where two batches of material are produced. One batch may have a higher overall impurity (C_i) level than the other (Table 25), but the segregation behaviour of this impurity element to grain boundaries may be different in each system. If grain boundaries from each of these materials were then analysed, the composition profiles shown in Figure 49 may be collected.

Batch	C_i (at.%)	C_i^α (at.%)	$C_i^{Boundary}$ (at.%)	Γ_i (atoms/nm ²)
Good	0.08	0.00	0.80	8.0
Bad	0.93	0.90	1.20	3.0

Table 25: Table showing the variation in composition of different regions in two batches of a material, as well as calculated Γ_i values (assuming $\eta = 1$, $A = 1000 \text{ nm}^2$, $N = 100,000$ atoms, and $\xi = 0.5$).

It is clear that there is a higher concentration of the impurity element, i , at the interface in the “bad batch” material. However, Table 25 shows that the calculated value of Γ_i is actually higher for the “good batch”.

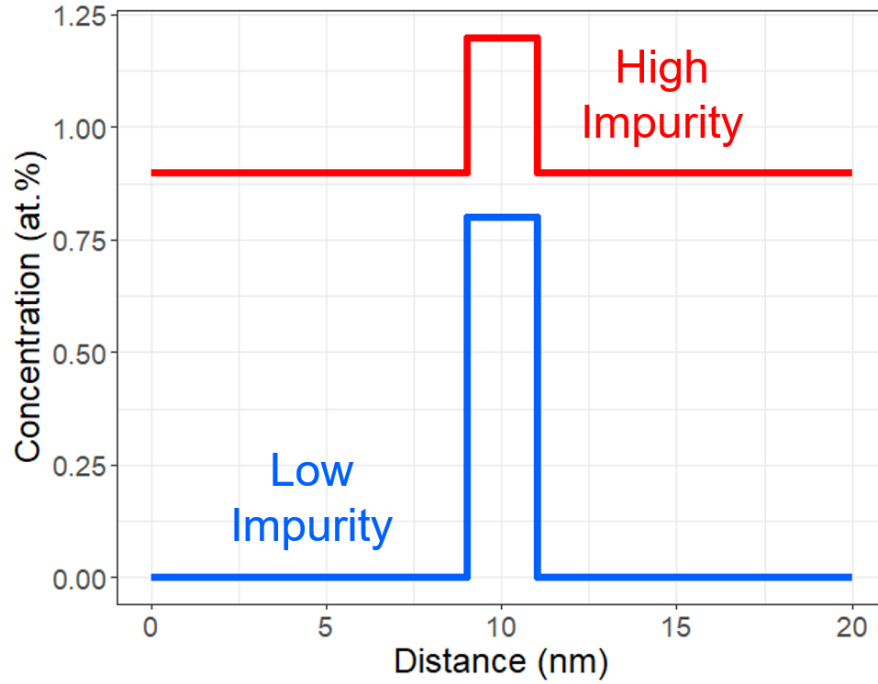


Figure 49: Modelled concentration profiles across the same type of interface in two respective batches of the same material with different impurity levels.

This raises the question as to what is more important in determining macroscale material properties, the composition of the interface, or the composition of the interface with respect to the matrix. If it is the composition of the interface that is of most importance, then the validity of applying Γ_i to relate the character of microstructural interfaces to material properties is questionable. Reporting the Gibbsian interfacial excess of each element, together with the composition of phases α and β would provide a more holistic description of the interface.

A key assumption made by Gibbs in his model was that the interface is a 2D plane [241]. This is likely not true for many interfaces in reality. Guggenheim treated the interface as an interphase with a finite thickness [242]. Since it is known that most grain boundaries do not take the form of idealised 2D features, assuming all segregation is confined to a single plane is likely naive. If this assumption is made, interfacial excess values higher than those permitted by the atomic density of the material are possible. This may be evidence for more than one monolayer of coverage at the interface, however, there is no way to confirm the lattice site location of the excess atoms in the enriched region.

The use of the Gibbsian interfacial excess values to calculate thermodynamic quantities relies on the assumption that the system is at thermodynamic equilibrium. However, many materials subject to APT are not at thermodynamic equilibrium at the time of analysis. Therefore, Γ_i should not be used to calculate thermodynamic quantities. In the case of non-equilibrium segregation, the segregation will be to a zone of “considerably greater width around the appropriate interface than occurred with the equilibrium mechanism...” [243]. The authors state that this zone may vary in thickness from the nanometre to micrometre scale [243]. Therefore, assuming all of the segregation is confined to a single plane does not accurately reflect what is physically present in the system and thereby will lead to an overestimation of the Gibbsian interfacial excess.

4.4 Desirable Developments For Reporting Grain Boundary Analyses

If the Gibbsian interfacial excess is to remain the superior choice for characterising APT analyses of grain boundaries, several developments are desired.

Firstly, the subjective user input in determining where the interfacial region begins and ends should be eliminated. As shown above, this can have a large effect on reported values. The selected location of the Gibbs dividing surface can also affect the calculated values of Γ_i . The description of the “homogeneous regions of phases α and β ” needs further clarification, else a new definition of $C_{i(\alpha)}$ and $C_{i(\beta)}$ is needed. Additionally, a way of describing the homogeneity of segregation to the interface is required. This has been done qualitatively [236, 244], but needs to be done quantitatively if numerical models are to be implemented to relate changes in grain boundary properties with changes in their character.

However, if a new way of reporting APT grain boundary characterisations is to be developed, it is important that the results convey information that is meaningful and useful in answering the

questions posed. Information that will likely affect grain boundary properties includes, but is not limited to, the following: width of segregation zone, composition of zone, homogeneity of elemental distributions, the misorientation angle of the boundary, and the plane of the boundary in each grain. These parameters can be critical in influencing material properties and should be reported. The new method should also be reproducible, with limited user input.

4.5 Systematic Method For Calculating Gibbsian Interfacial Excess For Real Data

A method to minimise user input has been developed for calculating Gibbsian interfacial excess values for grain boundaries analysed via APT. To demonstrate this method, a region of interest containing a grain boundary was extracted from an APT dataset. A $20\text{ nm} \times 20\text{ nm} \times 30\text{ nm}$ region of interest, containing an enriched region of Mn, Ni, and P is shown in Figure 50. The steel is in its as-received state and the enriched region is likely to be a grain boundary.

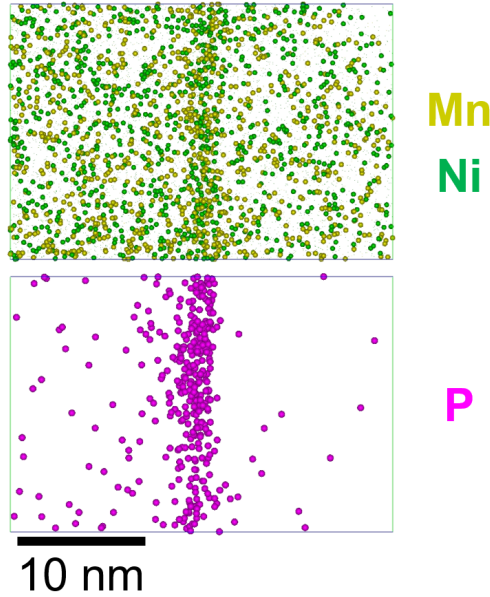


Figure 50: Region of interest ($20\text{ nm} \times 20\text{ nm} \times 30\text{ nm}$) from an APT reconstruction of a steel containing a grain boundary. The entire reconstruction for this as-received steel is presented in Figure 42.

4.5.1 Determining Interface Start and Finish

Two independent users are unlikely to choose the same positions to define the extents of the interface, affecting the values of N_i^α and N_i^β . In this study, to make Γ_i calculations more objective, values for the start and end of the interface were systematically determined via two different methods; the *Outlier Method* and the *Poisson Method*. These two methods were then critically assessed to determine their suitability when applied to real data.

Consider a series of bins, each containing a fixed number of ions, sampling a region across a grain boundary. If element i strongly segregates to the interface, it is expected that the bins at the interface will contain a higher concentration of i than the bins sampled in the surrounding matrix. It should, therefore, be possible to define the location of the start and end of the enriched region using statistical methods. The enriched region may be defined as the region where the number of atoms of element i observed in a bin (N_i^{Bin}) is significantly higher to what could be reasonably expected based on the distribution of element i in the matrix ($N_{Threshold}$).

Therefore, a one-dimensional concentration profile was taken perpendicularly to the grain boundary. To minimise the influence of density changes through the boundary, the concentration profile was measured such that each bin contained a fixed number of atoms. The number of atoms of each element in each bin was then plotted against position. Figure 51 (a) shows the observed distribution of P atoms in the ROI from Figure 50. Both methods for systematically determining where the interface starts and ends determine a value for $N_{Threshold}$. The interface region was then defined as beginning at the first bin where $N_i^{Bin} \geq N_{Threshold}$, and the end of the interface was defined as the final bin where $N_i^{Bin} \geq N_{Threshold}$ (Figure 51 (b) & (c)).

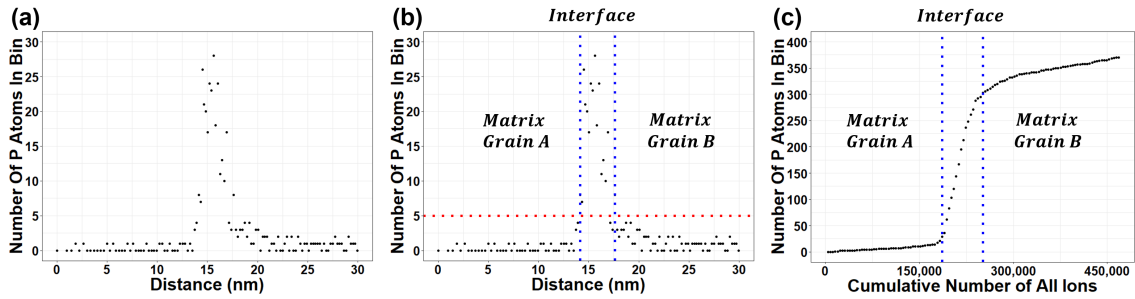


Figure 51: (a) Plot of number of P atoms per bin (N_P^{Bin}) vs distance along a region of interest containing a grain boundary, (b) Plot of N_P^{Bin} vs distance with interface cutoff values (blue) based on $N_{Threshold}$ value (red). (c) Cumulative number of P atoms vs cumulative number of all atoms along region of interest with cutoff values (blue).

4.5.1.1 Outlier Method

The first proposed method for determining $N_{Threshold}$ is to use the median, and interquartile ranges (IQRs) of the distribution of N_i^{Bin} from the matrix in the region of interest (Figure 51 (a)). From the median and IQRs of N_i^{Bin} in the matrix, a value that is unlikely to be observed if the values of N_i^{Bin} are normally distributed (an outlier) may be defined as a value that is more than $1.5 \times \text{IQR}$ above the third quartile. Therefore, $N_{Threshold}$ can be defined as:

$$N_{Threshold} = \text{Third Quartile} + (1.5 \times \text{IQR}) \quad (19)$$

where the Third Quartile is the number which is greater than 75 % of the values of N_i^{Bin} in the matrix, and the IQR is the range between the First and Third Quartile.

Once $N_{Threshold}$ has been calculated, N_i^α , N_i^β and the location of Grains A and B can be determined (Figure 52 (a) and (c)).

4.5.1.2 Poisson Method

The second method for calculating $N_{Threshold}$ is to assume that N_i^{Bin} in the matrix of the material followed a Poisson distribution. If the distribution of N_i^{Bin} in the matrix follows a Poisson distribution, the probability ($P(x)$) of observing x atoms of element i in a bin can be calculated using:

$$P(x) = \frac{e^{-\lambda} \lambda^x}{x!} \quad (20)$$

where λ is the mean of N_i^{Bin} .

From this, $N_{Threshold}$ is then defined as the value of x for which $P(x) < \alpha$ for $\alpha = 0.05$, since values of x that lead $P(x) < 0.05$ represent statistically unlikely occurrences. However, since multiple bins in the region of interest are tested, multiple comparisons will be made between the calculated $N_{Threshold}$ value and the observed distribution. Therefore, it is necessary to use the Šidák Correction to adjust the significance level. If a correction is not made, the likelihood of making a Type II error is increased.

$$\alpha_{(Adjust)} = 1 - (1 - \alpha)^{(1/m)} \quad (21)$$

where $\alpha_{(Adjust)}$ is the adjusted significance value, α is the original significance level, and m is the

number of tests conducted (in this case, the number of bins in the region of interest).

Figures 52 (b) and (d) show the position of the interface calculated when using the *Poisson Method* to determine $N_{Threshold}$ and, subsequently, N_i^α , N_i^β .

4.5.1.3 Comparison Between Outlier and Poisson Methods

For elements that strongly segregate to grain boundaries, the *Outlier Method* (OM) and *Poisson Method* (PM) are both effective at determining where the interface begins and ends, as demonstrated in Figure 52. Therefore, selecting the most strongly segregating element as element i is proposed. However, the most strongly segregating element may sometimes display only low levels of segregation.

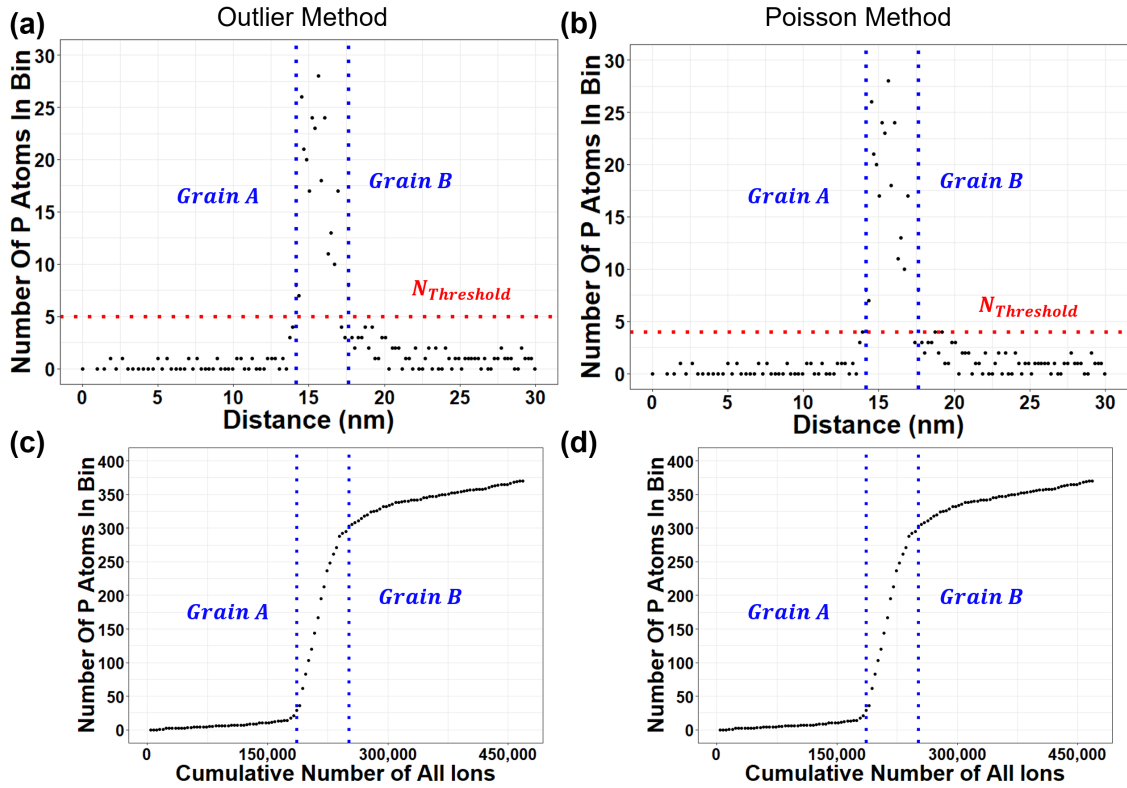


Figure 52: Plots showing Number of P atoms vs Distance along the region of interest and the determined start and end of the interface as calculated using (a) Outlier Method, (b) Poisson Method ($\alpha = 0.05$). (c) and (d) show cumulative count plots of P and the calculated interface position using the Outlier and Poisson Methods respectively.

Defining where the interface begins and ends when examining elements that exhibit low levels of segregation is more difficult. Figure 53 demonstrates the case of an element, Ni, weakly

segregating to a grain boundary in a separate dataset. Figure 53 (a) shows the OM fails to correctly identify the extents of the interface, whilst the PM with $\alpha = 0.05$ appears to correctly identify where the grain boundary starts and ends Figure 53 (b). This indicates that the PM is more sensitive in determining where enriched regions of solute begin and end.

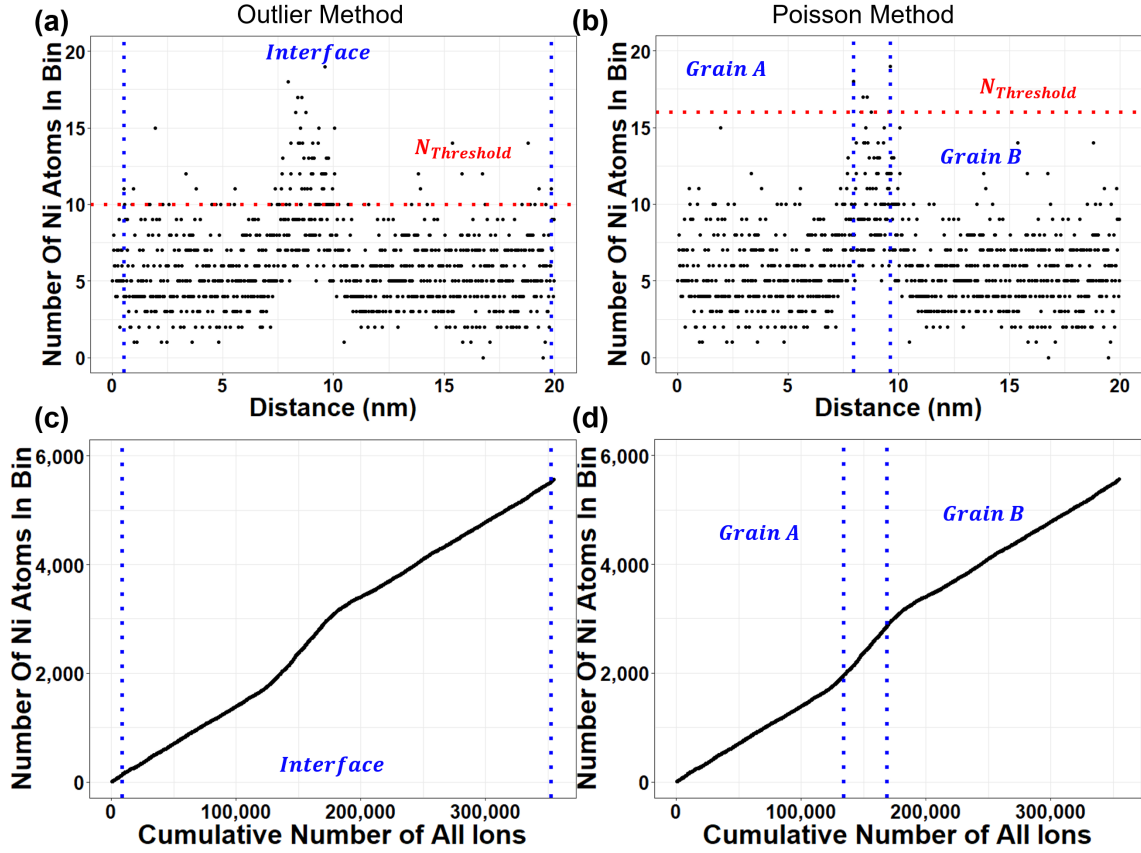


Figure 53: Plots showing Cumulative Number of Ni atoms vs Distance along a region of interest and the determined start and end of the interface as calculated using (a) Outlier Method, (b) Poisson Method ($\alpha = 0.05$). (c) and (d) show cumulative count plots of Ni and the calculated interface position using the Outlier and Poisson Methods respectively.

Therefore, it was decided that the PM method ($\alpha = 0.05$) should be used to calculate the extents of the interface region. This method can easily be extended to account for an interface between two phases that have very different compositions to one another. This may allow the Γ_i of interfaces, such as matrix-carbide interfaces, to be calculated.

4.5.2 Regions Used To Determine $C_{i(\alpha)}$ and $C_{i(\beta)}$

Once the location of the interface had been determined, Γ_i was then calculated using the method described above. $C_{i(\alpha)}$ and $C_{i(\beta)}$ were determined to be the composition of the region of interest before and after the interface, respectively.

4.5.3 Location of Gibbs Dividing Surface

As shown in Figure 45, it is possible to report upper and lower values of Γ_i by selecting different locations of the Gibbs dividing surface within the interface region. Therefore, Γ_i values were calculated for both of these cases. The reported values were the Γ_i value at the centre of the interface region $\pm$ the difference between this value and the lower limit of Γ_i .

4.5.4 Calculation of Gibbsian Interfacial Excess

Using the methods described above, values of Γ_i were calculated for each element at the interface in the region of interest in Figure 50. These are shown in Table 26. Si, Ni, Mn, and P have the highest Γ_i values, whilst Fe has the lowest Γ_i value and is negative. This indicates that, compared to the matrix, the interface is depleted in Fe but enriched in the majority of other elements.

Element	Γ_i (<i>atoms/nm²</i>)
Si	0.87 ± 0.03
Fe	-6.30 ± 0.25
Cu	0.04 ± 0.00
Ni	2.37 ± 0.05
Mn	1.15 ± 0.01
Mo	0.19 ± 0.00
C	0.19 ± 0.01
Cr	0.21 ± 0.18
P	1.31 ± 0.04
V	-0.01 ± 0.00

Table 26: Table showing the calculated Gibbsian interfacial excess values for the elements present in the region of interest in Figure 50.

4.6 Proposed New Method For Reporting Grain Boundary Analyses

Applying the method described in Section 4.5.1 allows the width of the interface to be determined. The distribution or clustering of elements within this volume can then be investigated.

The composition of this region can also be reported. However, before this can be done, a correction should be made to account for the difference in density of the interface region with respect to the matrix.

4.6.1 Calculating Composition of Interface

Blavette et al. proposed a correction for calculating the actual composition of a phase that is subjected to aberrant trajectory overlaps when analysed by APT [245]. They stated that physical concentration of an element ($C_i^{Overlap'}$) in a region affected by spatial overlaps is related to the observed concentration of the element in the phase ($C_i^{Overlap}$), the observed concentration of the element (C_i^{Matrix}) far from the interface in the phase adjacent to the interface, and the overlap rate (ψ) by the equation:

$$C_i^{Overlap'} = C_i^{Overlap} + \psi(C_i^{Overlap} - C_i^{Matrix}) \quad (22)$$

where the overlap rate is:

$$\psi = \delta n / n^{Overlap} \quad (23)$$

where δn is the excess number of atoms detected in the region and $n^{Overlap}$ is the number of atoms that are expected to be in the region.

Assuming that the interface region around a grain boundary has the same atomic density as the matrix of the material far from the interface, the corrected interface composition can be calculated as follows. Firstly, calculate the number of atoms detected in the interface region ($N^{Interface}$) and the volume of the interface region ($V^{Interface}$). Next, the number of atoms (N^{Matrix}) that are observed in the same volume in the matrix far from the interface (when the observed atomic density returns to its expected value) is calculated. ψ can then be calculated using the equation:

$$\psi = \frac{N^{Interface} - N^{Matrix}}{N^{Matrix}} \quad (24)$$

The composition for each element in the matrix and interface region can then be calculated using Equation 22.

4.6.2 Reporting Of Grain Boundary Analysis

The region of interest in Figure 50 was investigated using the proposed method. Phosphorus was used as the element for calculating the location of the start and end of the enriched zone since it displayed strong segregation behaviour. Using this approach, the enriched region was measured to have a width of 3.68 nm. It was determined that, due to spatial overlaps, $\psi = 0.103$. The corrected composition of the interface is shown in Table 27. The composition of Fe at the interface decreased after the correction was applied, whilst the composition of the majority of the other elements increased. This implies that the increased density observed at the boundary is the result of additional Fe ions.

Element	Uncorrected Composition (at.%)	Corrected Composition (at.%)
Si	0.49	0.51
Fe	95.03	94.85
Cu	0.06	0.06
Ni	2.04	2.11
Mn	0.74	0.78
Mo	0.17	0.18
C	0.09	0.10
Cr	0.99	0.99
P	0.39	0.43
V	0.00	0.00

Table 27: Table showing the composition of the interface, before and after correcting for spatial overlaps.

This volume enriched in phosphorus may be extracted and analysed to determine if the distribution of elements is non-uniform across the boundary when compared to a randomised case.

4.6.3 Limitations

There are some limitations to the reporting of interfaces described by a width, composition, and the uniformity of elements across the boundary.

Firstly, the observed width of the interface is likely to deviate from the true width. This is likely a result of evaporation effects that arise during the field evaporation of materials [238]. Another limitation is that there is no agreed upon way of quantifying the homogeneity of elemental distribution within APT data, despite recent qualitative methods being proposed [244]. Binomial

distribution analyses can indicate if an element is non-randomly distributed [246], whilst contingency tables can be used to determine whether co-segregation of elements is present [247]. However, χ^2 should not be applied to quantify if an element is more or less randomly distributed in one APT dataset compared to another [247]. The volume fraction of clusters may be quantified using clustering analyses, but each cluster analysis currently available requires user input and is subject to limitations [2].

4.7 Summary

A systematic way of calculating Gibbsian interfacial excesses has been proposed, removing the need for the user to choose where the interface starts and ends. The upper and lower values of Γ_i can be determined from within the interface region.

A novel way of reporting APT analyses of grain boundaries is presented. This method reports the composition of the interface, corrected for density artefacts, and the width of the interface. The volume fraction of non-randomly distributed elements at the interface may also be reported. Plotting composition maps of the boundary area may be used to qualitatively show the distribution of elements, but a quantitative method is yet to be developed.

Chapter VI

Thermally-Aged RPV Steels

This chapter presents hardness test results from a range of thermally-aged model RPV alloys. Thermal ageing was conducted at 330 °C, 365 °C, and 405 °C. APT analyses of two of these model alloys (Alloy F and Alloy I) are shown. Homogeneous precipitation was observed in Alloy F, which had a high nominal Cu composition (0.25 at.%). Mn-Ni-Si-rich precipitation was observed to occur in Alloy I. This alloy had a low nominal Cu level (0.04 at.%). Cluster searches were performed using the core-linkage method, and cluster calculations were carried out using the equations described in Chapter IV Section 3.6.3.

1 Hardness Measurements

Hardness tests were performed on the alloys after the times shown in Table 16. Hardness tests prior to 20,000 h of ageing were performed by Dr J. Zelenty [151]. The evolution of the measured hardness of each alloy after thermal ageing at 330 °C, 365 °C, and 405 °C is shown in Figure 54.

Alloy F was found to be the only alloy that displayed a significant increase in hardness from the as-received state after both the second and third ageing cycles had been conducted. Figure 55 displays the evolution in the measured hardness of Alloy F.

Alloy I exhibited a significant increase in hardness after the second and third ageing treatment at 330 °C (Figure 56). This alloy did not display a significant increase in hardness after any of the ageing times at 365 °C and 405 °C. However, since this alloy contained the highest nominal levels of the elements involved in the formation of MNSPs (Mn, Ni, and Si), it was prioritised for APT analysis.

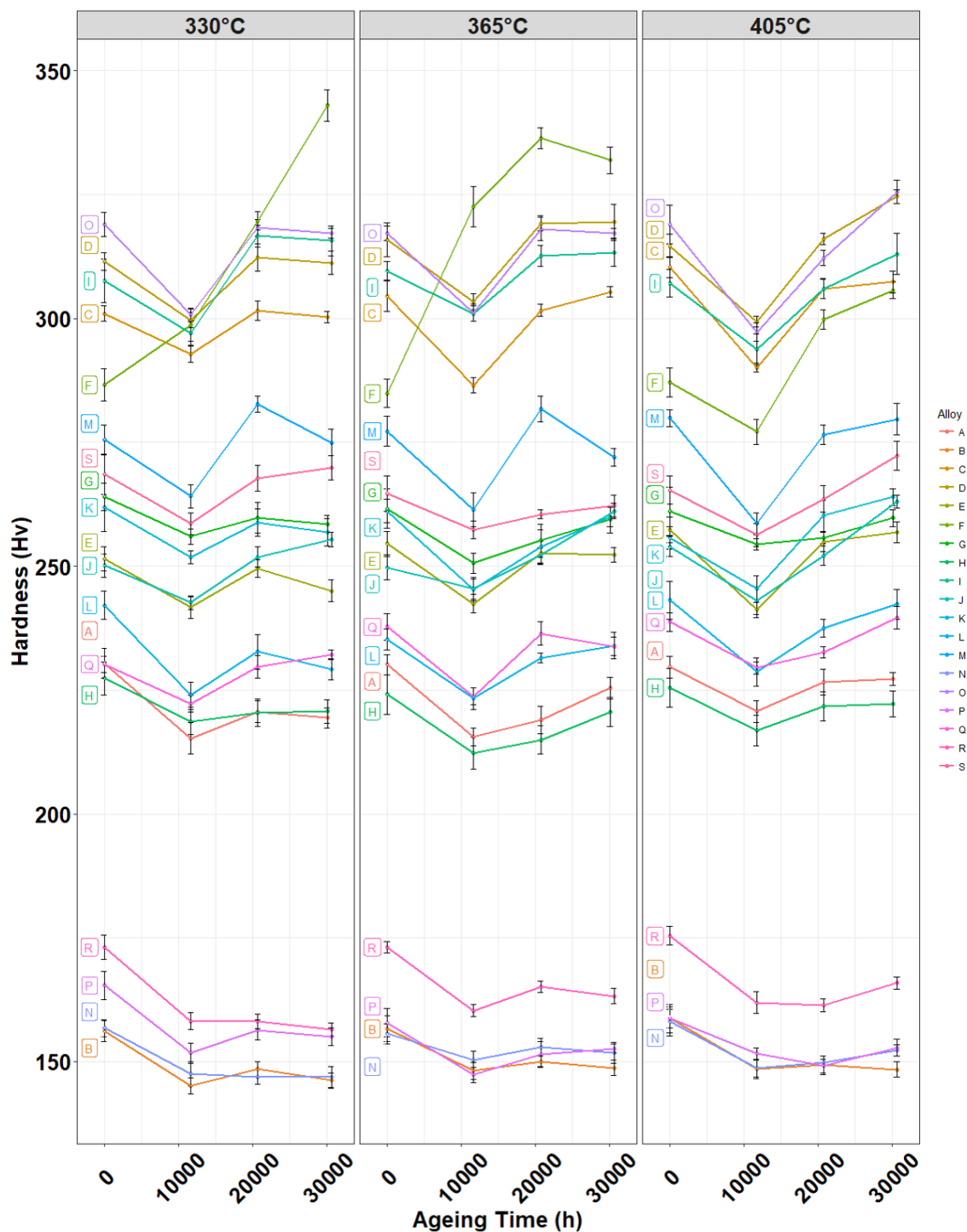


Figure 54: Graphs displaying the evolution in measured hardness with ageing time for each alloy during thermal ageing at 330 °C, 365 °C, and 405 °C. The error bars represent the standard error in the measurements.

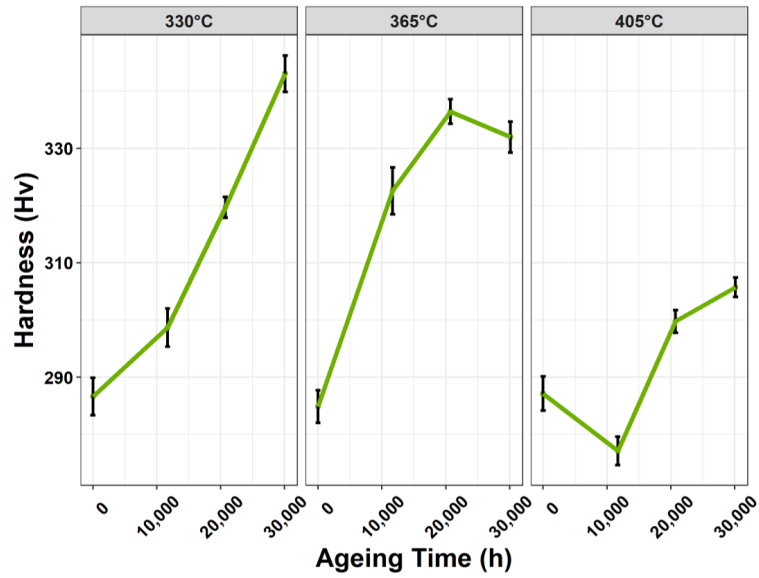


Figure 55: Graphs displaying the evolution in measured hardness with ageing time for Alloy F during thermal ageing at 330 °C, 365 °C, and 405 °C. The error bars represent the standard error in the measurements.

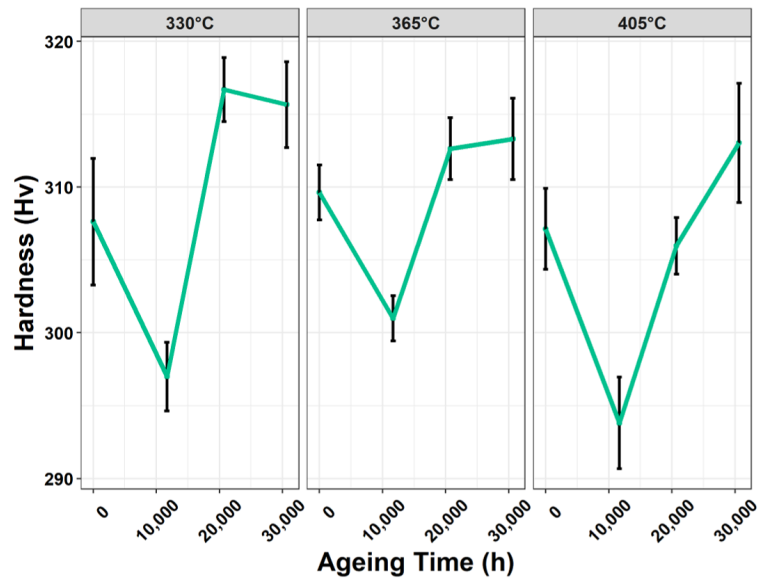


Figure 56: Graphs displaying the evolution in measured hardness with ageing time for Alloy I during thermal ageing at 330 °C, 365 °C, and 405 °C. The error bars represent the standard error in the measurements.

2 Alloy F - High Cu, High Ni, High Mn, Medium Si

Alloy F contained the highest nominal Cu level (0.25 at.%) of all the thermally-aged alloys. The steel also contained high levels of Ni (3.12 at.%), Mn (1.43 at.%), and medium levels of Si (0.37 at.%).

Atom probe analyses were performed on electropolished needles using the LEAP-3000X HR after 11,688 hours and 20,732 hours of ageing. From eleven atom probe experiments, only one run containing more than 500,000 ions was achieved for samples that had been thermally-aged at 330 °C for 11,688 hours. Multiple datasets were successfully obtained for all of the other ageing temperatures for times up to and including 20,732 hours.

2.1 Thermally-Aged For 11,688 Hours

2.1.1 Alloy F - Thermally-Aged At 330 °C

One APT dataset was collected for Alloy F after thermal ageing at 330 °C for 11,688 hours. Atom maps for this dataset are shown in Figure 57. The dataset contained three carbides, and a non-random distribution of Cu, Ni, Mn, and Si was observed in the matrix.

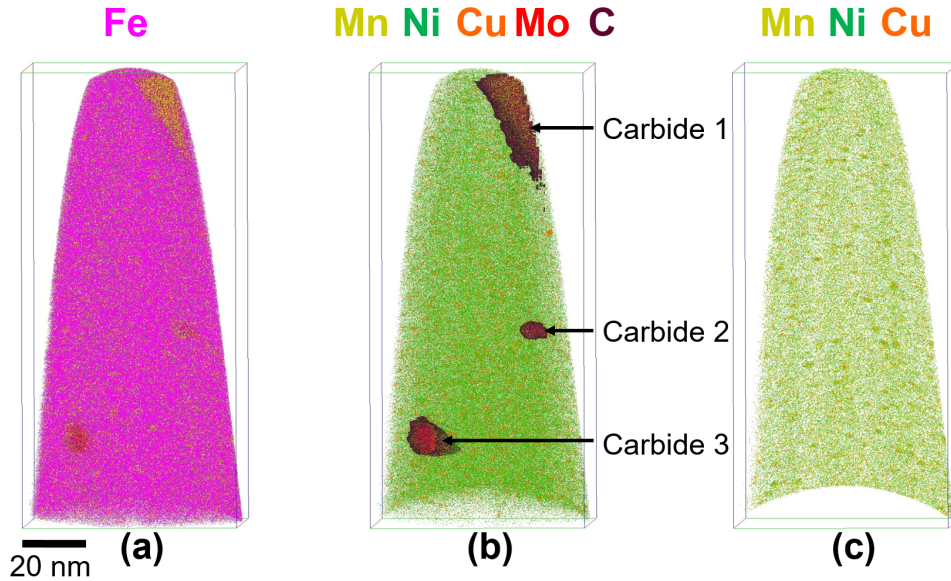


Figure 57: Atom maps of Alloy F specimen aged for 11,688 hours at 330 °C (Run 27511). The atom maps show (a) the distribution of all ions, (b) location of Mn, Ni, Cu, Mo, and C ions (isosurfaces of 2 at.% C are shown), (c) the distribution of Mn, Ni, and Cu through a 10 nm slice of the dataset.

Prior to performing cluster searches, the carbides were removed from the dataset using isosurfaces of 2 at.% C. The cluster searches detected features with a number density of $13.1 \times 10^{23} \text{ m}^{-3}$. The cluster volume fraction was 0.27 %, and the average diameter of the clusters was $1.5 \text{ nm} \pm 0.4 \text{ nm}$. The individual composition of each cluster is plotted in Figure 58.

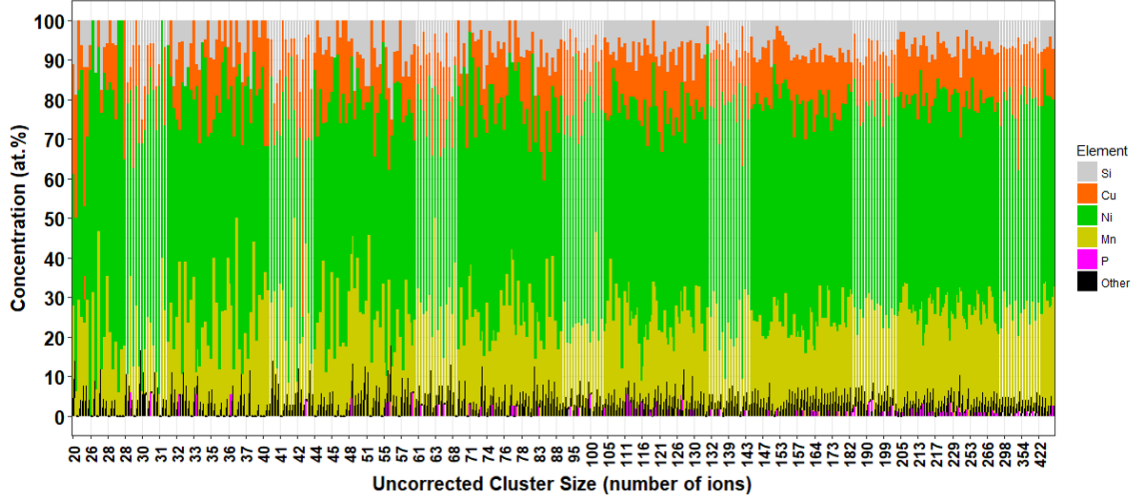


Figure 58: Composition of individual clusters detected in Alloy F specimen aged for 11,688 hours at 330 °C (Run 27511 - Figure 57).

It was not possible to accurately calculate the compositions of Carbide 1 or Carbide 2 as they were on the edge of the reconstructed dataset. However, the composition of a $5 \text{ nm} \times 5 \text{ nm} \times 5 \text{ nm}$ volume within Carbide 3 is shown in Table 28.

Element	Carbide 3 (at.%)
Si	0.55 ± 0.39
Fe	16.76 ± 2.24
Cu	0.00 ± 0.00
Ni	0.58 ± 0.45
Mn	3.73 ± 0.10
Mo	52.02 ± 2.97
C	24.23 ± 2.77
Cr	2.10 ± 0.81
P	0.00 ± 0.00

Table 28: Composition of Carbide 3 in Run 27511 (at.%). Alloy F sample aged for 11,688 hours at 330 °C (Figure 57).

2.1.2 Alloy F - Thermally-Aged At 365 °C

Two specimens of Alloy F were successfully analysed using APT. One of the reconstructions contained a grain boundary and three carbides. Regions enriched in Cu, Ni and Mn were visible in both datasets. Cluster searches detected features with a number density of $1.6 \times 10^{23} \text{ m}^{-3} \pm 0.1 \times 10^{23} \text{ m}^{-3}$. The volume fraction of these features was $0.64 \% \pm 0.11 \%$, and they had an average diameter of $3.3 \text{ nm} \pm 0.8 \text{ nm}$.

Visual inspection showed that Run 26355 contained clusters, a grain boundary, and three carbides (Figure 59). The compositions of the carbides, taken using a ROI away from the carbide-matrix interface, are shown in Table 29.

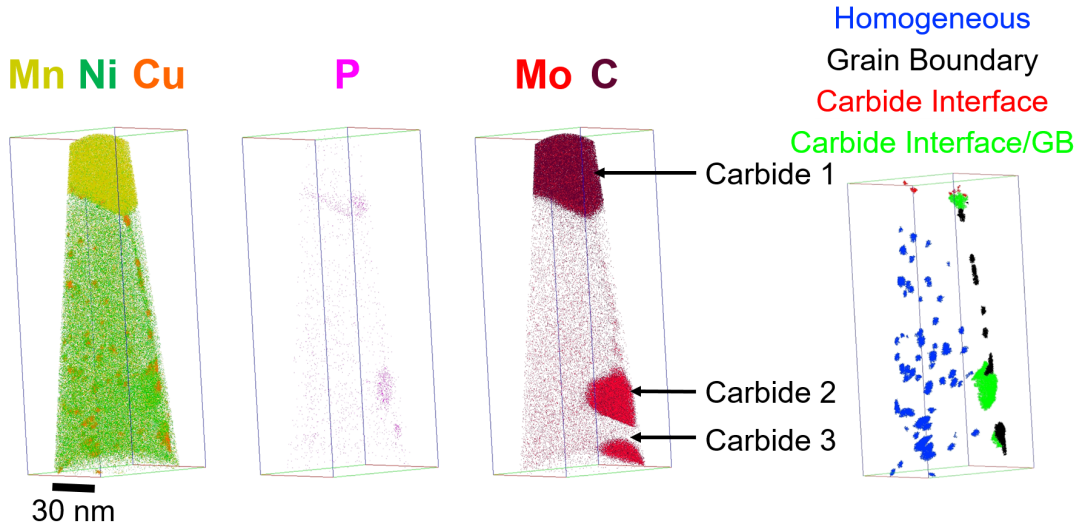


Figure 59: Atom maps for Alloy F sample aged for 11,688 hours at 365 °C (Run 26355). The distribution of Mn, Ni, Cu, P, Mo, and C atoms within the dataset are displayed. A map also shows the location of clusters designated as being nucleated on the following sites: “homogeneous”, “grain boundary”, “carbide interface”, and “carbide interface/grain boundary”.

Carbide 1 contains much higher levels of Fe and Mn than Carbide 2 and Carbide 3. Carbide 1 also contains a slightly lower C content in comparison to the other carbides. Atom probe measurements are known to underestimate C levels of carbides due to a combination of multiple events and detector dead time [185]. The ratio of metallic elements to C in Carbide 1 is $\sim \text{M}_3\text{C}$. As the majority of Carbide 1 is Fe, this region may be Fe_3C , or it may be an ϵ -carbide. Carbide 2 and Carbide 3 contain slightly less C than is required for the $\sim \text{M}_2\text{C}$ stoichiometry. However, assuming some C from within the carbides was not detected as a result of multiple events, Carbide 2 and

Carbide 3 may be Mo₂C type carbides.

Element	Carbide 1 (at.%)	Carbide 2 (at.%)	Carbide 3 (at.%)
Si	0.01 ± 0.00	0.56 ± 0.15	0.52 ± 0.19
Fe	56.92 ± 0.28	6.41 ± 0.42	6.58 ± 0.69
Cu	0.01 ± 0.00	0.01 ± 0.02	0.08 ± 0.09
Ni	0.71 ± 0.05	0.15 ± 0.07	0.20 ± 0.12
Mn	16.11 ± 0.20	5.35 ± 0.43	4.40 ± 0.57
Mo	1.32 ± 0.06	56.17 ± 0.92	56.51 ± 1.41
C	22.50 ± 0.26	28.83 ± 0.77	29.31 ± 1.37
Cr	2.42 ± 0.10	2.52 ± 0.28	2.32 ± 0.43
P	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00

Table 29: Carbide compositions (at.%) in Alloy F specimen aged for 11,688 hours at 365 °C (Run 26355 - Figure 59).

There was a large variance in the composition of the individual clusters that were detected in Run 26355. Figure 60 shows that some of the clusters contained very little Cu (< 5 at.%), whilst others comprised of more than 60 at.% Cu.

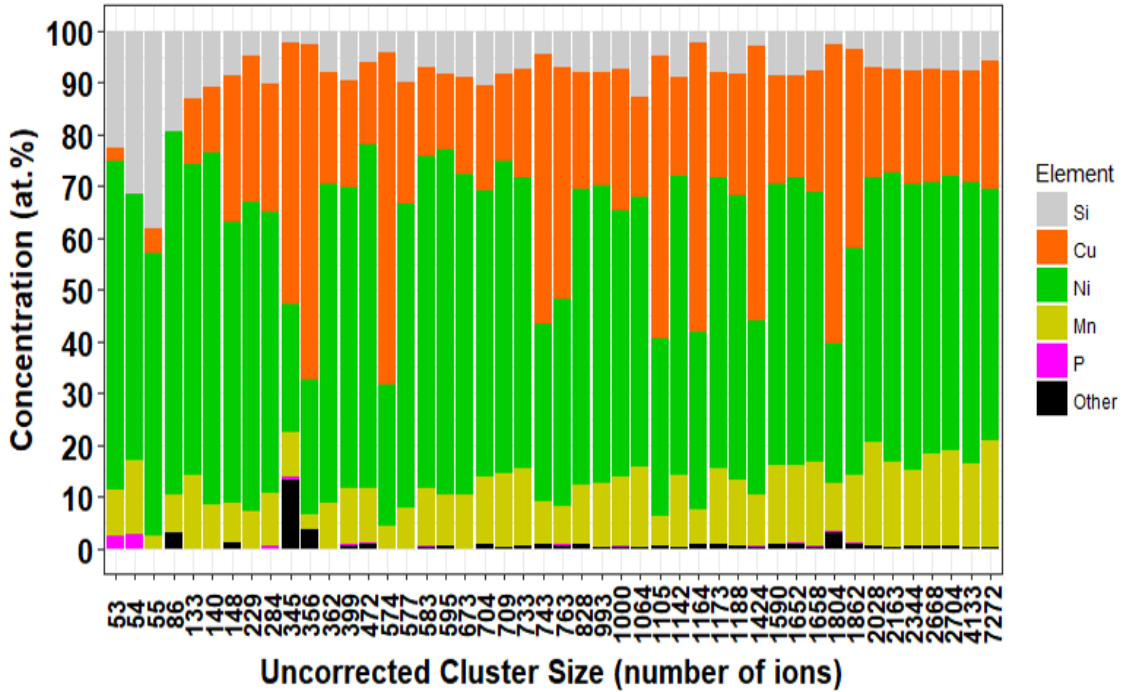


Figure 60: Composition of individual clusters identified in Alloy F specimen aged for 11,688 hours at 365 °C (Run 26355 - Figure 59).

To investigate the effect of nucleation site type on cluster composition, clusters were assigned

to categories based on their nucleation site. These categories included “homogeneous”, “grain boundary”, “carbide”, and “carbide interface”. In other specimens, the use of categories such as “dislocation” were necessary.

Comparisons of individual cluster compositions for clusters detected on homogeneous and heterogeneous nucleation sites are shown in Figure 61. The clusters that contained very low Cu levels (< 10 at.%) and high Si levels (> 10 at.%) were principally found to be on heterogeneous nucleation sites, more specifically at carbide-matrix interfaces. T-tests showed that clusters on heterogeneous nucleation sites contained significantly ($p < 0.05$) less Mn than clusters that were detected on homogeneous nucleation sites.

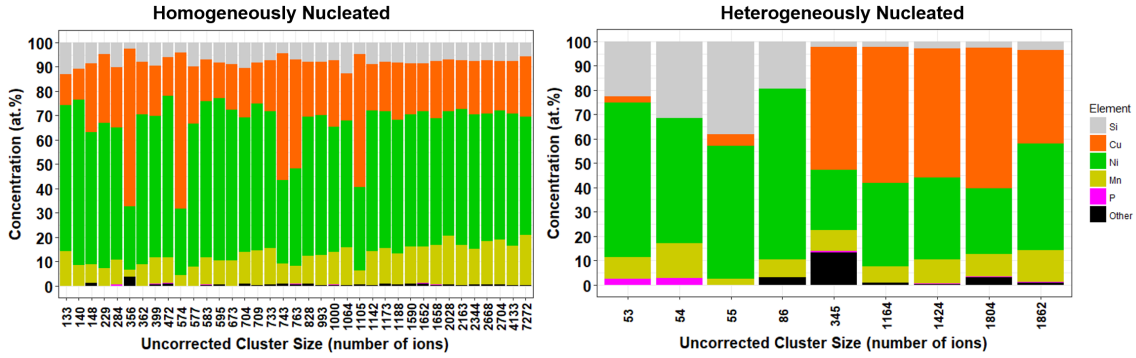


Figure 61: Comparison of individual cluster compositions that had nucleated homogeneously and heterogeneously in an Alloy F specimen aged for 11,688 hours at 365 °C (Run 26355 - Figure 59).

Some of the homogeneously nucleated clusters contained high levels of Cu. This is in contrast to the clusters that were detected in Run 26867 (Figure 62). In Run 26867, all clusters contained between 10 at.% - 25 at.% Cu. In contrast, only 78.4 % of the homogeneously nucleated clusters detected within Run 26355 contained this range of Cu. The average Cu composition of the other homogeneously nucleated clusters was 45.5 at.% $\pm$ 5.6 at.%.

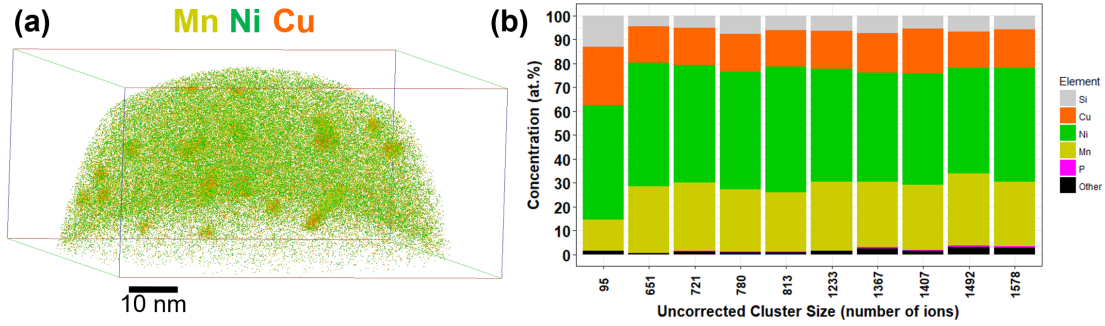


Figure 62: (a) Atom map showing distribution of Mn, Ni, and Cu in Alloy F specimen aged for 11,688 hours at 365 °C (Run 26867) and (b) plot of individual cluster compositions.

2.1.3 Alloy F - Thermally-Aged At 405 °C

APT was used to analyse two samples that had been aged for 11,688 hours at 405 °C. Figure 63 displays the atom maps of one of these specimens. Frequency distribution analyses revealed the distribution of Cu was not significantly different from that expected in a random solution. No non-random clustering was detected in both datasets when using the core-linkage search algorithm. The average Cu content of the tips was found to be 0.23 at.% $\pm$ 0.01 at.%. This is close to the nominal Cu composition of 0.25 at.%.

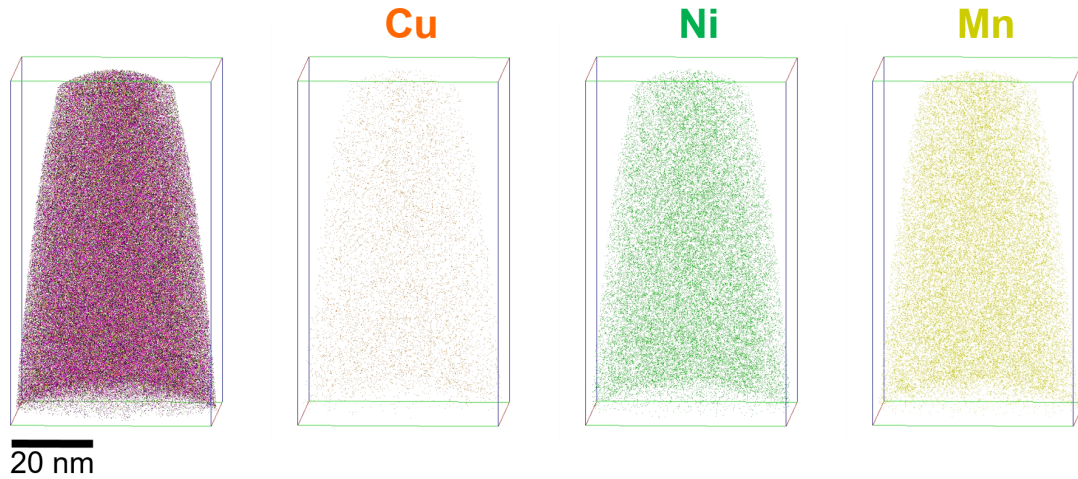


Figure 63: Atom maps showing distribution of Cu, Ni, and Mn in Alloy F after thermal ageing for 11,688 hours at 405 °C (Run 27121).

2.2 Thermally-Aged For 20,732 Hours

2.2.1 Alloy F - Thermally-Aged At 330 °C

APT was used to analyse two specimens that were aged at 330 °C for 20,732 hours. Regions enriched in Cu and Mn were observed during visual inspection. Core-linkage cluster searches revealed features with a number density of $13.6 \times 10^{23} \text{ m}^{-3} \pm 0.7 \times 10^{23} \text{ m}^{-3}$, a volume fraction of $0.62 \% \pm 0.11 \%$, and an average diameter of $1.9 \text{ nm} \pm 0.3 \text{ nm}$.

Figure 64 shows the distribution of Cu and Mn, as well as the distribution of Ni, Mo and C in one of the samples. The carbide and dislocation contained within the dataset acted as heterogeneous nucleation sites for precipitate formation. There was no significant ($\alpha = 0.05$) difference in composition between clusters found on homogeneous and heterogeneous nucleation sites. Figure 65 shows the composition of the clusters detected in this dataset.

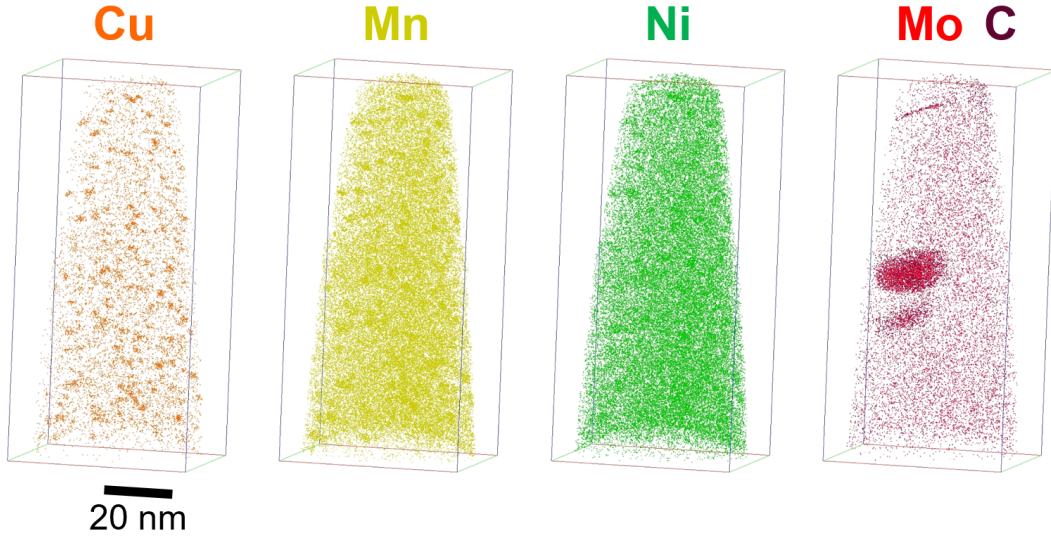


Figure 64: Atom maps showing distribution of Cu, Mn, Ni, Mo, and C in Alloy F after thermal ageing for 20,732 hours at 330 °C (Run 25971).

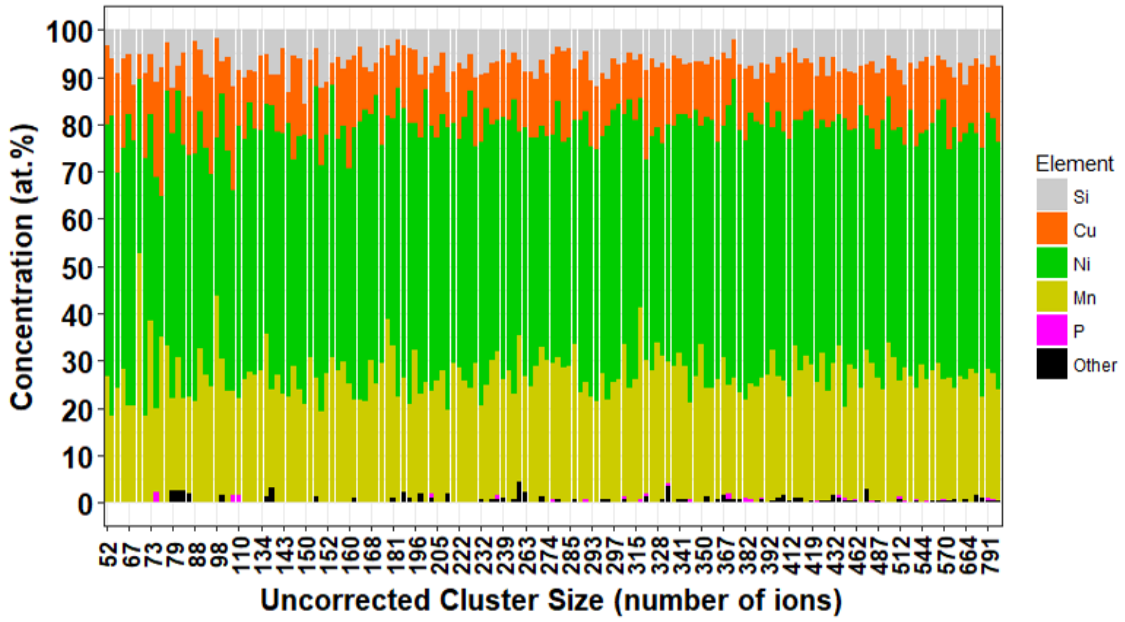


Figure 65: Individual cluster compositions for clusters detected in an Alloy F specimen aged for 20,732 hours at 330 °C (Run 25971 - Figure 64).

2.2.2 Alloy F - Thermally-Aged At 365 °C

APT datasets were collected for two specimens that were aged at 365 °C for 20,732 hours. Regions enriched in Cu, Ni and Mn were observed and core-linkage cluster searches detected features with a number density of $1.7 \times 10^{23} \text{ m}^{-3} \pm 0.1 \times 10^{23} \text{ m}^{-3}$, a volume fraction of $0.88 \% \pm 0.00 \%$, and an average diameter of $3.6 \text{ nm} \pm 1.0 \text{ nm}$.

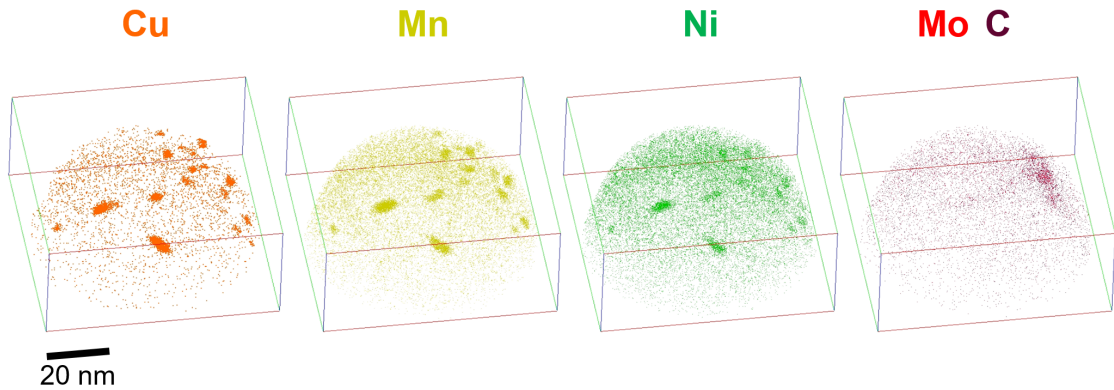


Figure 66: Atom maps for an Alloy F specimen aged for 20,732 hours at 365 °C (Run 25498). The locations of Cu, Mn, Ni, Mo, and C atoms are shown.

Figure 66 shows atom maps from one of the specimens. The non-random distribution of Cu, Ni, and Mn can be seen. Figure 67 shows the individual composition of each cluster detected APT analyses of Alloy F that had been thermal aged at 365 °C for 20,732 hours. The heterogeneously nucleated cluster that contained more than 40 at.% Cu was detected on a low-angle grain boundary. There was one homogeneously nucleated cluster that contained more Cu than the other homogeneously nucleated clusters.

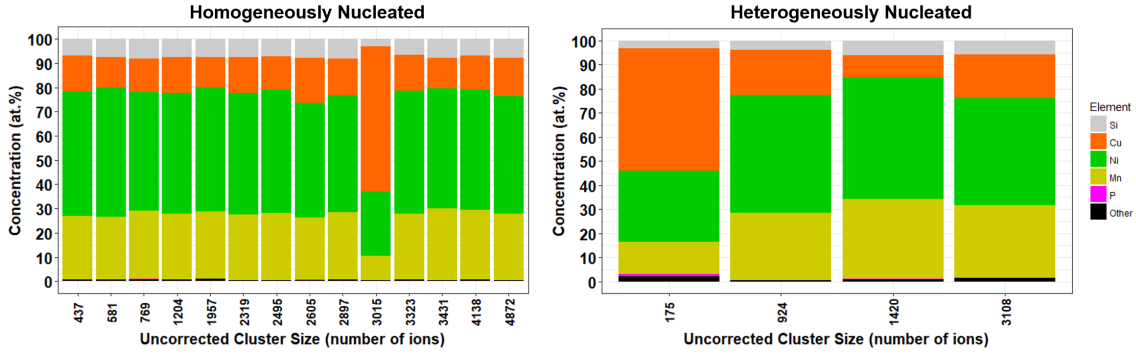


Figure 67: Individual cluster compositions for homogeneously and heterogeneously nucleated clusters detected in Alloy F after thermal ageing at 365 °C for 20,732 hours.

2.2.3 Alloy F - Thermally-Aged At 405 °C

Two specimens that had been aged at 405 °C for 20,732 hours were analysed using APT. Cu, Ni, and Mn were observed to be non-homogeneously distributed throughout both reconstructions. Core-linkage cluster searches revealed features with a number density of $0.3 \times 10^{23} \text{ m}^{-3} \pm 0.2 \times 10^{23} \text{ m}^{-3}$, a volume fraction of $0.48 \% \pm 0.25 \%$, and an average diameter of $5.2 \text{ nm} \pm 1.8 \text{ nm}$.

Figure 68 shows the distribution of selected elements in one dataset (Run 25872). This dataset contained a carbide and two sets of dislocations. Figure 69 shows the composition of each cluster detected in this dataset. A carbide and an array of dislocations can be seen in the atom map. The majority of the clusters detected within this dataset were found on these heterogeneous nucleation sites. The cluster, which was detected on a heterogeneous nucleation site and contained more than 20 at.% Si, was detected at the carbide-matrix interface.

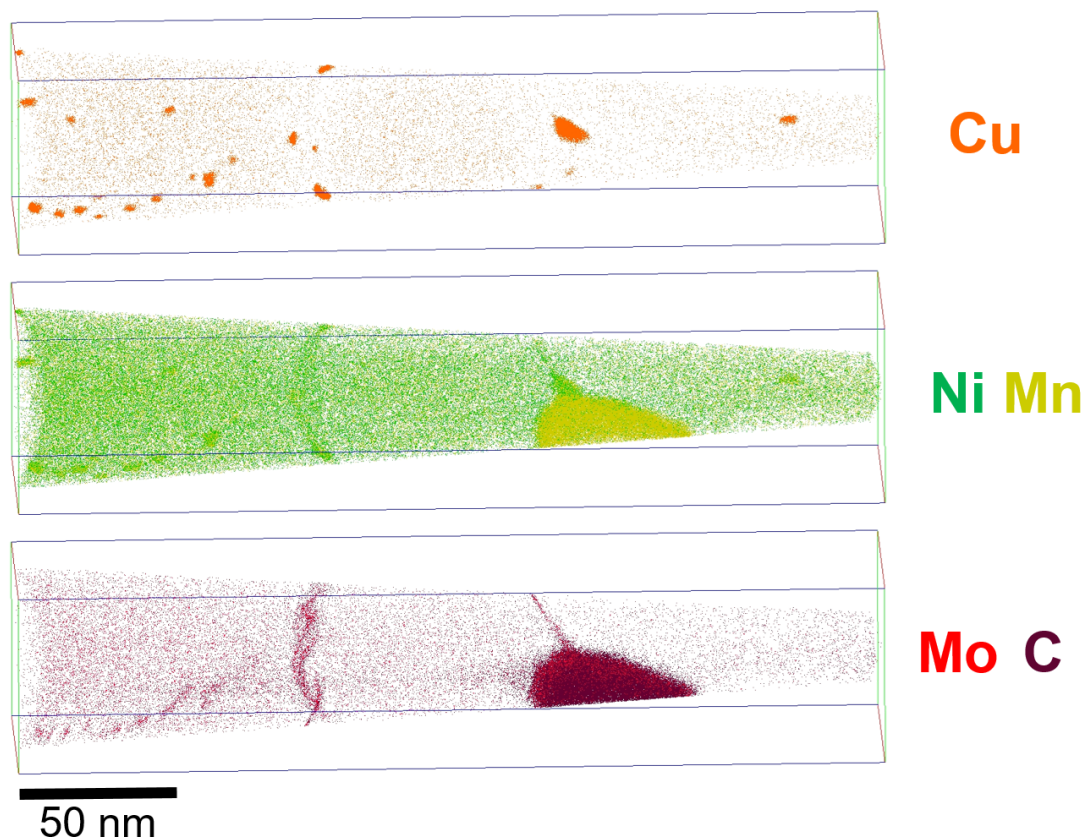


Figure 68: Atom maps showing distribution of Cu, Ni, Mn, Mo and C in Alloy F after thermal ageing for 20,732 hours at 405 °C (Run 25872).

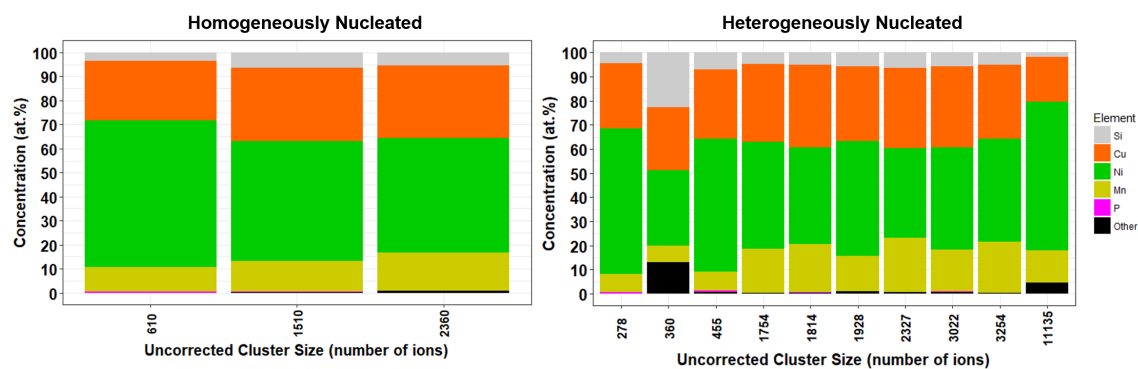


Figure 69: Individual cluster compositions for homogeneously and heterogeneously nucleated clusters detected in an Alloy F specimen aged for 20,732 hours at 405 °C (Run 25872 - Figure 68).

3 Alloy I - Low Cu, High Ni, High Mn, High Si

Alloy I had a low nominal Cu level (0.04 at.%). However, it contained high levels of Ni (3.11 at.%), Mn (1.42 at.%), and Si (1.11 at.%).

FIB lift-out was used to prepare site-specific samples of Alloy I that had been thermally-aged for 20,733 hours. Site-specific sample preparation was used to incorporate grain boundaries or other features, such as dislocations, that could act as heterogeneous nucleation sites in the final specimens.

APT analyses were conducted using a LEAP-5000XR. Clustering analyses indicated that no homogeneous clustering was present in the matrix of the majority of specimens. Multiple datasets that contained heterogeneous nucleation sites were collected for each ageing condition.

Since these specimens were prepared using site-specific sample preparation, detected cluster number densities, volume fractions, and sizes are unlikely to be representative of the specimen as a whole.

3.1 Thermally-Aged For 20,733 Hours

3.1.1 Alloy I - Thermally-Aged At 330 °C

14 samples were analysed using APT. Clustering was detected in four datasets. The majority of the precipitates were observed to have formed on heterogeneous nucleation sites, such as grain boundaries and dislocations. Two reconstructions contained grain boundaries.

Figure 70 shows a dataset (Run 4073) that contains a carbide and a grain boundary. Segregation of Mo, C, Si, P, and Ni can be seen to the grain boundary. The calculated Gibbsian interfacial excess of each element at the boundary is shown in Table 30. Table 30 also shows the composition of the enriched volume around the grain boundary, which was measured to have a width of 4.2 nm. Clustering of Mn, Ni and Si ions was detected at the grain boundary and at the carbide-matrix interface.

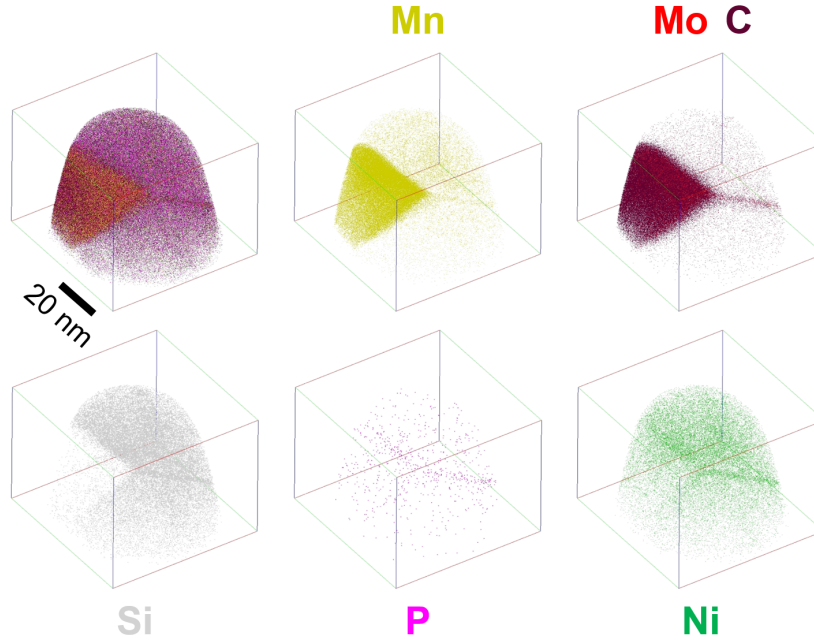


Figure 70: Atom maps for a specimen of Alloy I that had been thermally-aged at 330 °C for 20,733 hours (Run 4073).

Element	Γ_i (<i>atoms/nm²</i>)	Composition (at.%)
C	3.65 ± 0.12	1.44
Cr	-0.04 ± 0.02	0.06
Cu	0.04 ± 0.03	0.08
Fe	-9.65 ± 0.15	90.28
Mn	-0.19 ± 0.19	0.95
Mo	1.60 ± 0.04	0.69
Ni	3.57 ± 0.16	4.72
O	-0.02 ± 0.01	0.01
P	0.23 ± 0.03	0.08
Si	0.81 ± 0.09	1.68

Table 30: The calculated Gibbsian interfacial excess values for the elements present at a grain boundary in Alloy I after thermal ageing for 20,733 hours at 330 °C (Run 4073 - Figure 70). The composition of the grain boundary is also reported.

The composition of all clusters detected in this dataset are shown in Figure 71. The clusters detected on the carbide interface contained significantly ($p < 0.05$) more “other” elements than the clusters detected on the grain boundary.

A grain boundary was also observed in Run 4108. Atom maps of this experiment are shown

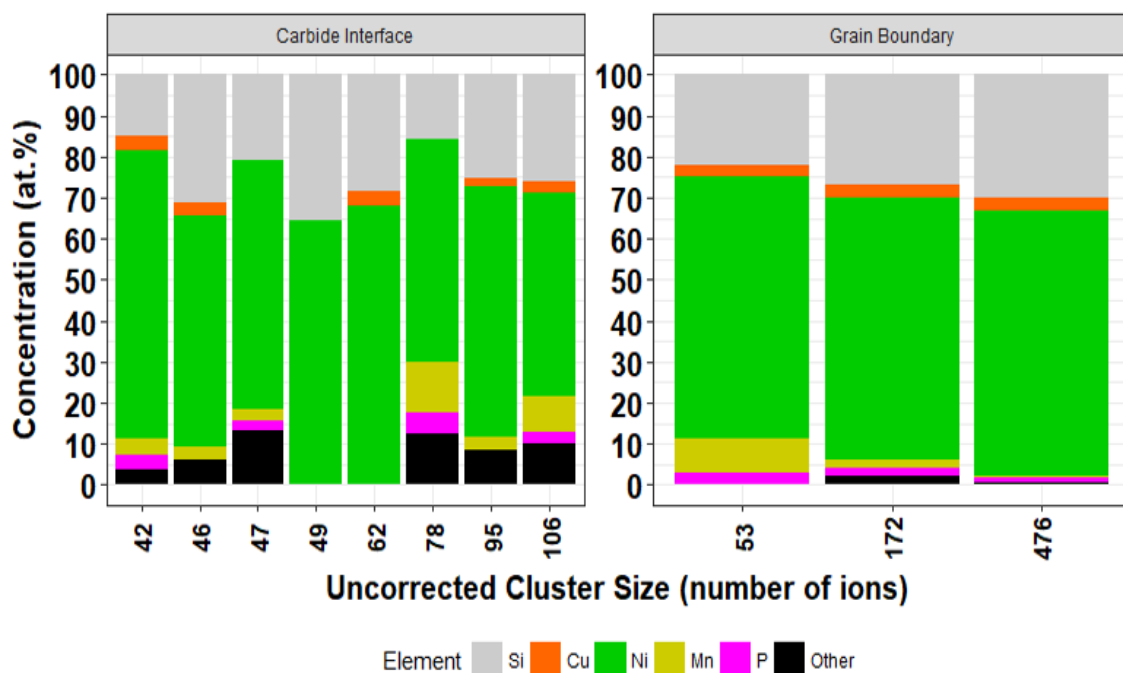


Figure 71: Individual composition of clusters detected in a specimen of Alloy I that had been thermally-aged at 330 °C for 20,733 hours (Run 4073 - Figure 70).

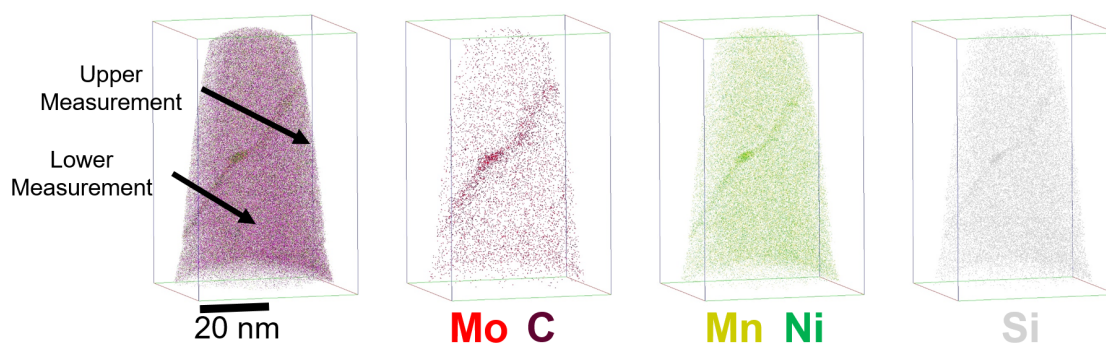


Figure 72: Atom maps for a specimen of Alloy I that had been thermally-aged at 330 °C for 20,733 hours (Run 4108).

in Figure 72. There appears to be a kink in the boundary, with high levels of Mn and Ni segregated to this part of the boundary. The Gibbsian interfacial excess and composition of the “upper” and “lower” region of this grain boundary were calculated (Table 31). The composition of each cluster detected in this dataset is shown in Figure 73 along with the composition of all the other clusters detected in Alloy I after ageing at 330 °C for 20,733 hours.

Element	Γ_i (<i>atoms/nm²</i>)		Composition (at.%)	
	Upper	Lower	Upper	Lower
C	0.63 ± 0.17	1.36 ± 0.01	0.39	0.47
Cr	-0.11 ± 0.01	-0.07 ± 0.02	0.06	0.06
Cu	0.12 ± 0.00	0.08 ± 0.04	0.11	0.11
Fe	-7.14 ± 0.12	-4.96 ± 0.81	90.77	92.24
Mn	1.57 ± 0.17	-0.09 ± 0.36	1.61	0.95
Mo	0.95 ± 0.02	0.63 ± 0.05	0.45	0.39
Ni	2.71 ± 0.02	2.73 ± 0.57	4.72	4.20
P	0.09 ± 0.00	0.05 ± 0.00	0.03	0.02
Si	1.16 ± 0.10	0.27 ± 0.00	1.85	1.56

Table 31: The calculated Gibbsian interfacial excess values for the elements present at the Upper and Lower regions of a grain boundary in Alloy I after ageing at 330 °C for 20,733 hours (Run 4108 - Figure 72). The compositions of these regions are also shown.

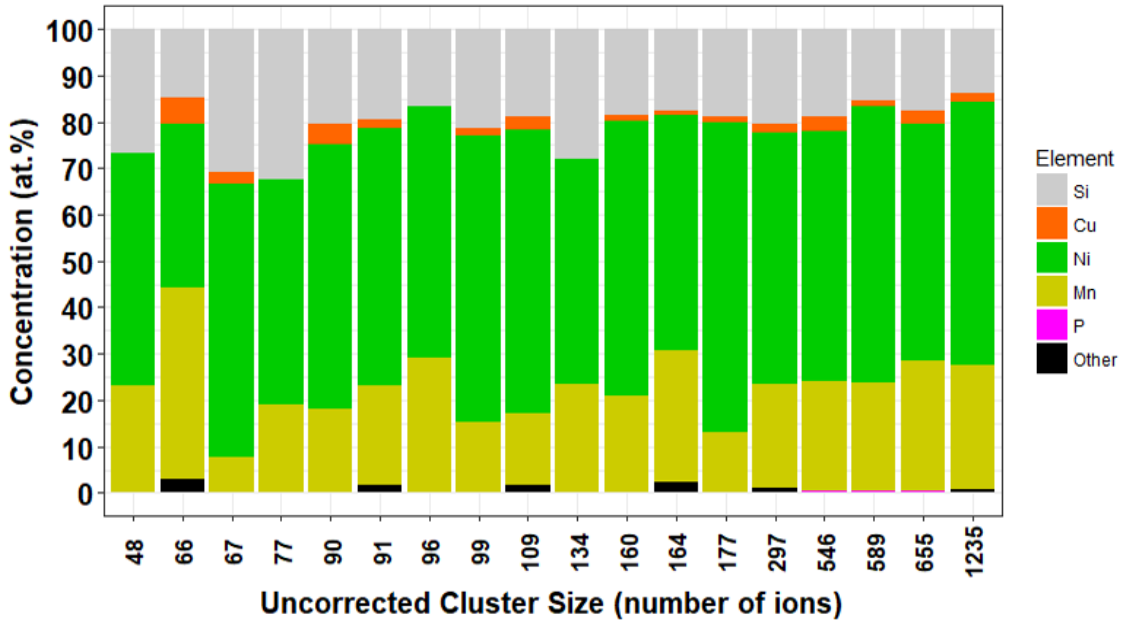


Figure 73: Cluster compositions for all clusters detected in Alloy I after 20,733 hours of ageing at 330 °C. Clusters from Run 4073 are not included in this plot.

3.1.2 Alloy I - Thermally-Aged At 365 °C

Five specimens were successfully analysed and a uniform solute distribution was observed in three datasets. However, frequency distribution analyses revealed non-uniform distribution of Ni and Mn in two datasets and core-linkage cluster searches found clusters in both of these datasets.

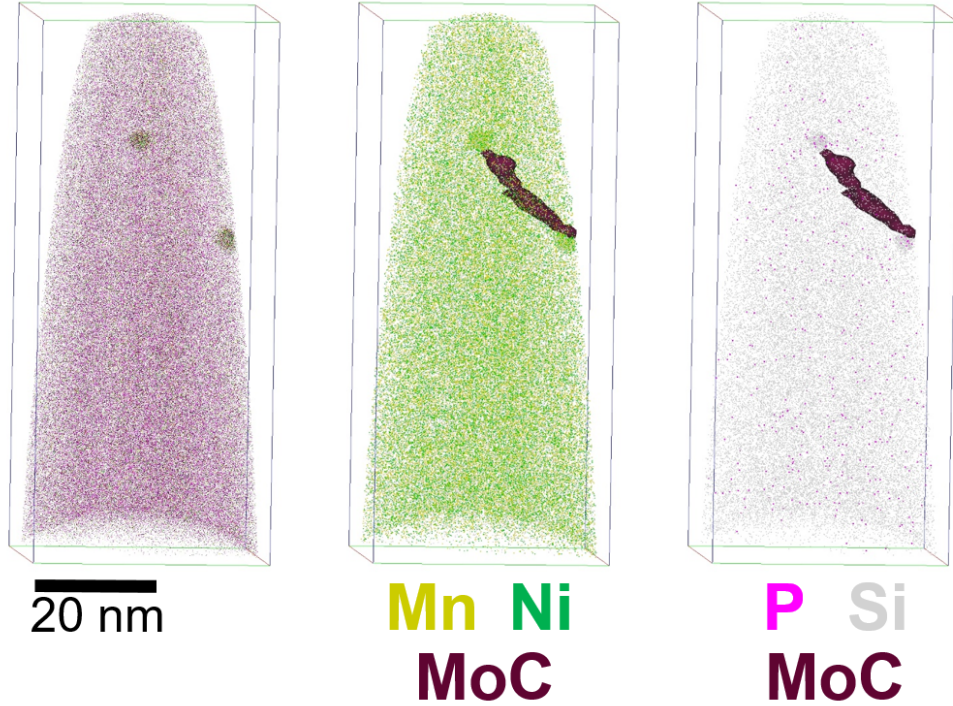


Figure 74: Atom maps of Alloy I specimen after ageing at 365 °C for 20,733 hours (Run 4386). The distribution of Mn, Ni, Si, and P atoms are shown alongside a 1.4 at.% isosurface for Mo and C.

All detected clusters appeared to have formed on dislocations and were on the edge of the analysis volume. An isosurface for Mo and C in Figure 74 reveals a region enriched in Mo and C that is likely to be a dislocation. Two Mn-Ni-Si-rich features can be seen along this dislocation. The composition for all clusters detected in Alloy I after thermal ageing at 365 °C for 20,733 hours are shown in Figure 75.

Two other datasets contained grain boundaries but no clustering above levels expected in a random solution was observed. The results of grain boundary analyses are shown in Table 32.

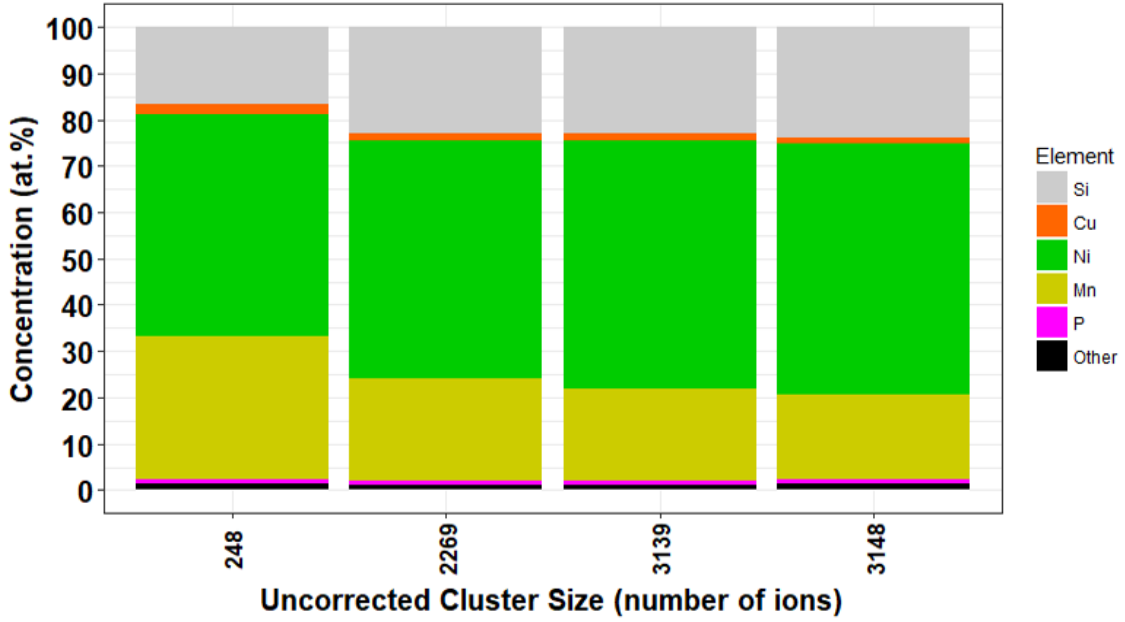


Figure 75: Cluster compositions for all clusters detected in Alloy I after 20,733 hours of ageing at 365 °C. All clusters were detected on dislocations and on the edge of the analysis volume.

Element	Γ_i (atoms/nm ²)		Composition (at.%)	
	Run 4384	Run 4890	Run 4384	Run 4890
C	1.27 ± 0.06	5.95 ± 0.17	0.70	7.56
Cr	0.05 ± 0.01	0.67 ± 0.05	0.09	0.95
Cu	-0.06 ± 0.03	0.02 ± 0.02	0.08	0.13
Fe	-3.91 ± 0.44	-14.44 ± 6.17	92.72	65.47
Mn	1.38 ± 0.16	1.95 ± 2.88	1.17	8.76
Mo	1.00 ± 0.02	3.24 ± 0.01	0.57	4.00
Ni	0.67 ± 0.19	2.14 ± 3.01	3.55	11.21
P	-0.02 ± 0.00	0.06 ± 0.00	0.00	0.08
Si	-0.38 ± 0.09	0.41 ± 0.01	1.12	1.84

Table 32: Comparison of the calculated Gibbsian interfacial excess values for grain boundaries detected in Alloy I after ageing at 365 °C for 20,733 hours (Run 4384 - Figure 74 and Run 4890). The compositions of these grain boundaries are also shown.

3.1.3 Alloy I - Thermally-Aged At 405 °C

Two APT datasets (out of 8 successful analyses) contained non-random distributions of solute ions. Precipitates were detected in both datasets. In one dataset, the precipitate was clearly on a dislocation (Figure 76). The precipitates in the other dataset were detected immediately prior to specimen fracture. Therefore, it was not possible to directly determine if these precipitates had

nucleated homogeneously or heterogeneously.

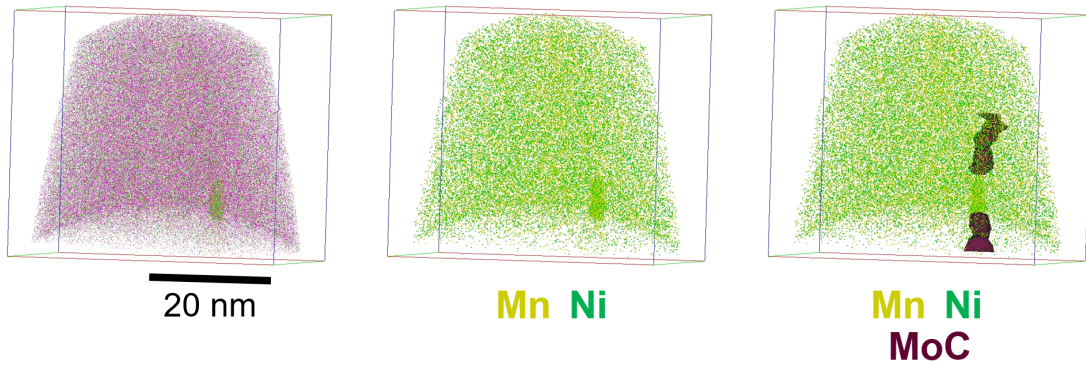


Figure 76: Atom maps of Alloy I specimen after ageing at 405 °C for 20,733 hours (Run 3397). Distribution of Mn and Ni atoms is shown, along with a 3.0 at.% isosurface for Mo and C.

Figure 77 shows the composition of all of the precipitates detected in Alloy I after thermal ageing for 20,733 hours at 405 °C.

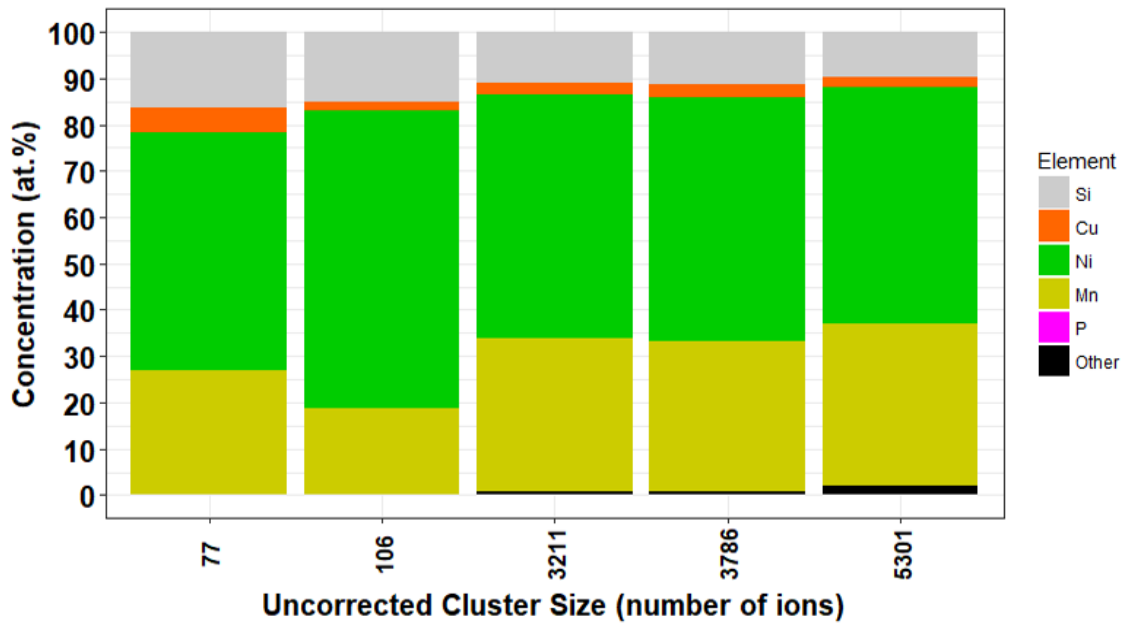


Figure 77: Cluster compositions for all clusters detected in Alloy I after 20,733 hours of ageing at 405 °C. All clusters were detected on the edge of the analysis volume.

4 Discussion

4.1 Hardness Measurements

Table 33 shows which alloys experienced a significant ($\alpha = 0.05$) increase in hardness from their as-received state after each ageing cycle.

Ageing Temperature ($^{\circ}\text{C}$)	Ageing Treatment		
	First	Second	Third
330	F	F, I, M	F, I, J
365	F	F	F, J
405		F	F, D, K, J, O, S

Table 33: Matrix displaying which alloys had experienced a significant increase in hardness from their as-received state after ageing treatments at each temperature.

All of the alloys, excluding Alloy F, showed a decrease in hardness from their as-received state after thermal ageing for 11,688 hours at the three different temperatures. It has been suggested that this may be due to a reduction in the amount of solid solution strengthening present in the alloys [151]. However, Alloy F only displayed a significant decrease in hardness after the first ageing cycle at 405 $^{\circ}\text{C}$.

The measured increase in the hardness of Alloy F is likely to due the formation of precipitates that inhibit dislocation motion. Larger increases in hardness are indicative of a higher volume fraction of precipitate formation [21]. Since the kinetics of precipitate formation are likely to be increased at higher temperatures, it is peculiar that the measured hardness of Alloy F was greater after ageing at 330 $^{\circ}\text{C}$ and 365 $^{\circ}\text{C}$ than at 405 $^{\circ}\text{C}$. A possible explanation for this is that, at 405 $^{\circ}\text{C}$, the solubility of Cu in Fe is higher than at 330 $^{\circ}\text{C}$ and 365 $^{\circ}\text{C}$. Therefore, there would be a lower driving force for Cu to form precipitates [31]. If this is true, the validity of using temperatures as high as 405 $^{\circ}\text{C}$ to simulate the conditions experienced by high-Cu steels during operation at ~ 290 $^{\circ}\text{C}$ is questioned.

Alloy I did not display a significant increase in hardness from its as-received state after $\sim 30,650$ hours of thermal ageing at 365 $^{\circ}\text{C}$ and 405 $^{\circ}\text{C}$. However, it did display a significant increase in hardness at all three ageing temperatures between the end of ageing at 11,688 hours and future ageing times. This is indicative of precipitate formation after 11,688 hours of ageing.

Alloy J contains nominally low levels of Cu (0.05 wt.%) and Si (0.05 wt.%). However, this

alloy displayed a significant increase in hardness at all three temperatures after the third ageing cycle. This may be a result of clustering or precipitation in the matrix of this alloy. However, APT analyses should be carried out to confirm this.

Several alloys showed a significant increase in hardness exclusively after the third ageing treatment at 405 °C. Alloys D, K, O, and S all contain high nominal levels of Ni (3.5 wt.%), low levels of Cu (0.05 wt.%) and medium Si (0.2 wt.%) content. They contain a variety of Mn and P levels. As a result, these alloys can potentially be used in the future to determine the role of Mn in measured hardness changes during thermal ageing.

Alloy M displayed a significant increase in hardness after the second ageing cycle at 330 °C. However, after the third ageing treatment, its measured hardness was the same as its as-received hardness.

4.2 Alloy F

4.2.1 Relationship Between Clustering And Hardness Measurements

It has been suggested that the hardness change that alloys experience is proportional to the square root of cluster volume fraction ($\sqrt{V_f}$) [21, 248, 249]. Figure 78 shows the relationship between hardness changes and measured $\sqrt{V_f}$ for clusters in Alloy F. A trend for increasing hardness changes with increasing cluster $\sqrt{V_f}$ can be seen. However, there are too few data points to confidently determine whether this trend is linear in nature.

4.2.2 Observation of Carbides in the Microstructure

Carbides were observed in several datasets from Alloy F. The presence of carbides affected the composition of detected clusters.

Cluster compositions fluctuated greatly within some of the datasets. Figure 61 shows that some of this variation may be attributed to the nucleation site of the cluster. All of the clusters that contained more than 10 at.% Si were observed to have formed at the carbide-matrix interface. Si is known to have a low solubility in cementite [250]. Therefore, the Si may diffuse out of the carbide and into the matrix during processing treatments or thermal ageing. This would lead to an enrichment in Si of the local composition around the carbides, leading to more Si being available to form precipitates.

The Mn content of clusters detected at carbide interfaces was found to be significantly lower

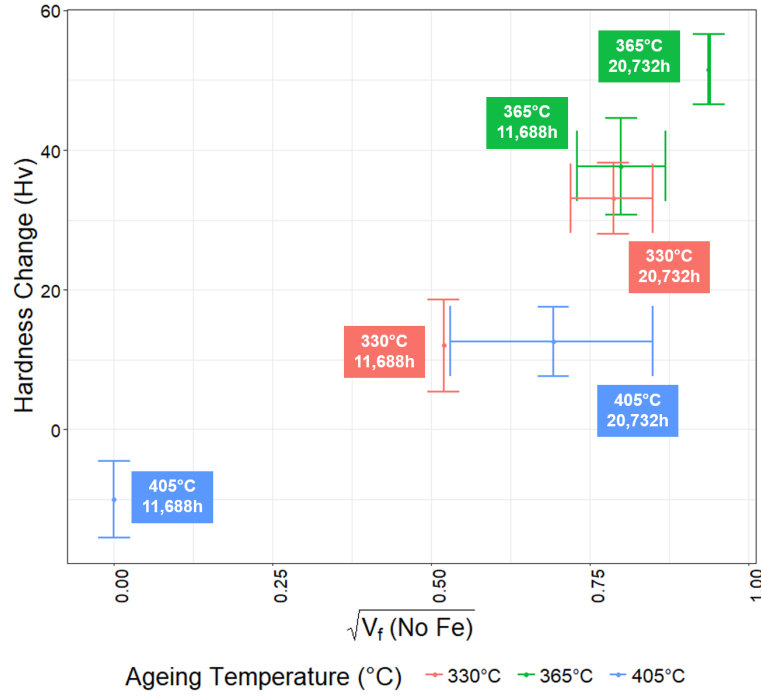


Figure 78: Plot of $\sqrt{V_f}$ vs measured change in hardness (Hv) for Alloy F after 11,688 hours and 20,732 hours of ageing. Error bars represent the standard error in the measurements*.

*Only one dataset was collected for Alloy F after 11,688 hours of ageing at 330 °C, therefore it was not possible to calculate a standard error of the mean.

($p < 0.05$) than in homogeneously nucleated clusters. Mn is a known carbide former, with Carbide 1 in Run 26355 containing $16.1 \text{ at.\%} \pm 0.2 \text{ at.\%}$ Mn (Table 29). This is likely to result in volumes surrounding carbides being depleted in Mn, reducing the amount of Mn available during cluster formation.

As a result of these clusters having a different compositions to clusters detected elsewhere in the specimen, they were not included in mean cluster composition calculations.

4.2.3 Effect of Ageing Time And Temperature

Table 34 summarises the measured cluster number densities, volume fractions, and sizes for each of the conditions analysed for Alloy F. No clustering was detected in the datasets obtained from Alloy F after thermal ageing at 405 °C for 11,688 hours. As the Cu composition of the analysed regions was very similar to the nominal composition of the alloy, and no hardness increase was observed from the as-received stated, it is unlikely that there is precipitation occurring in regions not analysed via APT. Therefore, the cluster number density, size and volume fraction were

determined to be negligible in this state.

Ageing Temperature (°C)	Ageing Time (h)	Number Density ($\times 10^{23} \text{ m}^{-3}$)	Volume Fraction (%)	Diameter (nm)
330	11,688	$13.1 \pm 0.8^*$	0.27	1.5 ± 0.4
	20,732	13.6 ± 0.7	0.62 ± 0.11	1.9 ± 0.3
365	11,688	1.6 ± 0.1	0.64 ± 0.11	3.3 ± 0.8
	20,732	1.7 ± 0.1	0.88 ± 0.00	3.6 ± 1.0
405	11,688	0	0	0
	20,732	0.3 ± 0.2	0.48 ± 0.25	5.2 ± 1.8

Table 34: Measured cluster number density, volume fraction, and mean size of clusters detected in Alloy F. The errors represent the standard error of the mean.

*Only one dataset was collected for this alloy and condition, so the error in the number density value was estimated as described in Chapter IV Section 3.6.3.

The number density of clusters detected in Alloy F varied with ageing temperature. After each ageing cycle there was a trend for higher cluster number densities but smaller mean cluster size at lower ageing temperatures (Table 34). At lower temperatures, the driving force for Cu to precipitate out of the matrix will be higher. As a result of this higher driving force, it is to be expected that the nucleation rate of precipitates in the 330 °C samples will be exponentially higher than the nucleation rate in the 365 °C and 405 °C samples [31]. This trend is visible in Table 34 and may explain the absence of detected clustering in the 405 °C aged samples after 11,688 hours. At lower temperatures, diffusion distances will be shorter; this may explain why the mean precipitate size increases with increasing ageing temperature in the 20,732 hour aged specimens. These data indicate that, were this alloy subjected to service temperatures of ~ 290 °C, a very high number density of small solute clusters may form after 10,000 hours to 20,000 hours.

In the 330 °C and 365 °C specimens, there was an increase in cluster volume fraction between 11,688 hours and 20,732 hours. This may explain the increase in hardening observed in this condition. The increase in volume fraction is likely the result of precipitate growth as the number density of clusters appeared to remain relatively stable at each ageing temperature.

Table 35 shows the mean compositions of non-edge clusters that had not nucleated on carbide interfaces in these alloys. For the samples aged at 365 °C, there is a large increase in the Mn content of the precipitates from 11,688 hours to 20,732 hours. This is likely a result of sampling a region near a carbide and grain boundary in Run 26355 (Figure 59).

Ageing Temperature (°C)	Ageing Time (h)	Average Composition (at.%)					
		Cu	Ni	Mn	Si	P	Other
330	11,688	13.58 ± 0.37	53.48 ± 0.52	24.70 ± 0.43	7.58 ± 0.24	0.18 ± 0.04	0.49 ± 0.06
	20,732	12.85 ± 0.29	52.05 ± 0.39	27.15 ± 0.36	7.30 ± 0.19	0.14 ± 0.03	0.05 ± 0.06
365	11,688	25.67 ± 1.98	51.31 ± 1.43	14.80 ± 1.01	7.34 ± 0.35	0.11 ± 0.02	0.76 ± 0.12
	20,732	19.17 ± 3.17	47.12 ± 1.69	26.12 ± 1.31	6.69 ± 0.40	0.11 ± 0.06	0.80 ± 0.10
405	11,688	-	-	-	-	-	-
	20,732	30.67 ± 0.87	48.01 ± 2.39	15.30 ± 1.56	5.34 ± 0.3	0.2 ± 0.07	0.46 ± 0.09

Table 35: Measured mean composition and standard error for clusters detected in Alloy F.

As Run 26355 contained a Mn-rich carbide, the volume around this carbide is likely to be depleted in Mn. Therefore, there would be less Mn able to enter the clusters forming in this region. After 11,688 hours of ageing at 365 °C, the clusters in Run 26867 (Figure 62) contained significantly more ($p < 0.001$) Mn than the clusters in Run 26355 (Figure 61). Indeed the mean Mn level of clusters detected in Run 26867 was 27.79 at.% ± 0.19 at.%, very similar to the cluster compositions calculated after 20,732 hours of ageing at 330 °C and 365 °C.

A similar effect may be responsible for the mean measured Mn content for the clusters in the 405 °C samples aged for 20,732 hours of ageing. The mean Mn composition of the clusters detected in the specimen containing carbides is 15.68 at.% ± 0.27 at.%, whilst the clusters in the dataset that does not contain a carbide are 28.67 at.% ± 0.52 at.% Mn.

If the presence of carbides is responsible for the reduced Mn cluster composition, then ageing time and temperature appear to have very little effect on cluster composition.

4.2.4 Appendage Clusters

Some of the clusters detected in the 365 °C specimens were found to have a Cu-rich section appended to a Mn-Ni-rich section. Figure 79 shows a precipitate from Run 26867. One end of the precipitate contains most of the Cu, whilst the other end of the precipitate mainly consists of Mn, Ni, and Si. Ni, Mn, and Si appendages on Cu precipitates have been observed in neutron-irradiated steels [40] and have been shown to form in kinetic Monte Carlo simulations [251].

There was large variance in the Cu content of the clusters detected after Alloy F had been aged at 365 °C for 11,688 hours and 20,732 hours (Figure 62 and Figure 67). The cluster compositions appeared to be split into two classes, those that contained very high Cu levels (> 40 at.%), and others that contained ~ 10 at.% Cu. The cause of this division is unknown, but

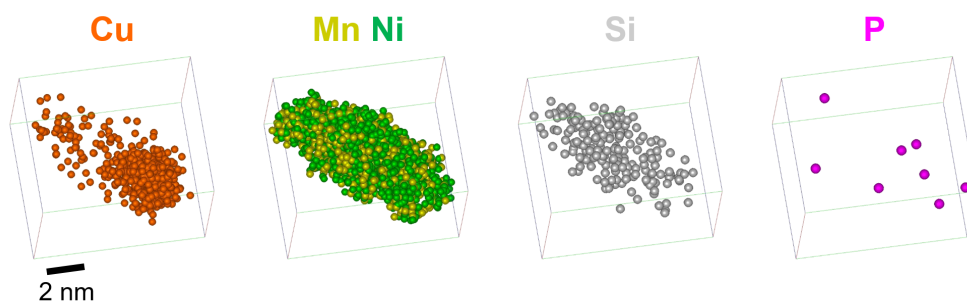


Figure 79: Atom maps for a cluster detected in an Alloy F specimen aged for 11,688 hours at 365 °C (Run 26867).

did not appear to be related to the presence of appendage clusters and was not observed at the other ageing temperatures.

4.3 Alloy I

4.3.1 Grain Boundary Analyses

Gibbsian interfacial excess values were calculated for two grain boundaries in samples that had been aged at 330 °C.

The grain boundary analysed in Run 4073 had more C, Mo and Ni than the boundary in Run 4108. However, the boundary analysed in Run 4108 contained more Mn than the boundary in Run 4073. This variation between the two boundaries may be a result of the boundary in Run 4073 being close to a carbide, or may be a result of the boundaries being of a different misorientation angle or plane [62]. Complementary TKD, which was not available at the time of these analyses, would have allowed the misorientation angle and plane of each grain boundary to be determined.

There was a large variation in the measured excess values of some elements at the boundary in Run 4108 between the upper and lower regions of the boundary (Figure 72 and Table 31). This shows the distribution of elements across this grain boundary is non-uniform. The reason for this is not known, however, it demonstrates an issue in reporting a single Gibbsian interfacial excess value to describe a grain boundary. The compositions of the upper and lower grain boundary regions were also different to one another. Therefore, maps which display the variation in segregation/composition across a boundary would be a better way to qualitatively report data [244].

Grain boundaries were also analysed in Alloy I after ageing at 365 °C. Table 32 shows that

there were large differences in the Gibbsian excess values and compositions between the two boundaries. The boundary in Run 4890 was at the very start of the dataset. It is not possible to say what caused the differences in the measured elemental excesses and boundary compositions.

These differences in grain boundary composition and segregation behaviour in samples that have undergone the same thermal ageing treatment highlight the importance of complementary characterisation techniques, such as TKD. TKD data would have enabled the structure of the grain boundary to be determined. Whether the differences in grain boundary composition were a result of grain boundary structure could then have been revealed. Due to the large number of different possible grain boundary structures in an in-service RPV, understanding the relationship between grain boundary structure and segregation behaviour is desired. If certain grain boundary types are found to be more susceptible to solute segregation and, therefore, non-hardening embrittlement, it may be possible to process the alloys in a way that reduces the amount of these types of boundary in the final component.

4.3.2 Observation of Mn-Ni-Si-Rich Precipitates

Mn-Ni-Si-rich clusters were observed in Alloy I after 20,733 hours of ageing. The mean cluster number densities, volume fractions, and diameters for each ageing temperature are shown in Table 36. These mean values were calculated using only datasets that contained heterogeneous nucleation sites. Therefore, they are unlikely to be entirely representative of the material. However, there appears to be a higher volume fraction of Mn-Ni-Si-rich clusters in the vicinity of heterogeneous nucleation sites after 20,733 hours of ageing at 405 °C when compared to the other ageing temperatures.

Ageing Temperature (°C)	Number Density ($\times 10^{23} \text{ m}^{-3}$)	Volume Fraction (%)	Diameter (nm)
330	1.0 ± 0.3	0.05 ± 0.02	1.5 ± 0.5
365	0.2 ± 0.1	0.12 ± 0.03	3.6 ± 0.9
405	0.5 ± 0.3	0.24 ± 0.06	3.8 ± 1.2

Table 36: Measured cluster number density, volume fraction, and mean size of clusters detected in Alloy I after 20,733 hours of ageing. N.B. These values were calculated using only datasets that contained heterogeneous nucleation sites and are, therefore, unlikely to be representative of the material as a whole.

Some of the clusters detected in Alloy I after 20,733 hours of ageing at 330 °C were found to

have nucleated homogeneously, whilst others had formed at heterogeneous nucleation sites. However, all of the clusters that were detected in specimens that were aged at 365 °C and 405 °C were likely to have nucleated on heterogeneous nucleation sites. As some of the features observed after ageing at 405 °C were located on the edge of the analysed volumes, it was not possible to determine if heterogeneous nucleation sites were in the vicinity of the features. However, due to the aspect ratio of the precipitates being similar to the feature observed in Run 3397 (Figure 76), and the fact that no clusters were observed to have formed heterogeneously in six other datasets, it is likely that these features did form on heterogeneous nucleation sites. Crystallographic defects, such as dislocations and grain boundaries may act as fast diffusion pathways. The nucleation rate, therefore, is likely to be higher at these features than in the matrix.

Clusters determined to have nucleated on carbide-matrix interfaces and grain boundaries were not included in average cluster composition calculations. Clusters from Run 4073 were not included in mean composition calculations as the Mn-rich carbide in the analysis is likely to have depleted the Mn in the surrounding matrix. The average composition of the features is shown in Table 37. All clusters detected in the 365 °C samples were on the edge of the analysed volume. However, as none of the features detected in Alloy I appeared to have a core-shell or appendage structure, it was deemed that the inclusion of edge clusters would not bias compositional calculations.

Element	Ageing Temperature (°C)		
	330	365	405
Cu	1.77 ± 0.40	1.68 ± 0.21	2.92 ± 0.65
Ni	53.90 ± 1.70	51.78 ± 1.35	54.44 ± 2.51
Mn	23.86 ± 2.02	22.77 ± 2.80	29.21 ± 2.95
Si	19.77 ± 1.32	21.62 ± 1.71	12.71 ± 1.27
P	0.04 ± 0.03	0.88 ± 0.05	0.04 ± 0.02
Other	0.67 ± 0.23	1.27 ± 0.12	0.68 ± 0.35

Table 37: Comparison of composition for clusters detected in Alloy I after 20,733 hours of ageing.

The clusters contained very little Cu, P, or other elements, and the composition of the clusters was very similar across the three temperatures. However, t-tests revealed that there was a significant ($p < 0.01$) difference in the Si content of the clusters detected in 405 °C samples compared to other two temperatures. This reason for this difference is not known. However, these compositional differences should be considered when performing thermal ageing experiments at

temperatures far in excess of those experienced by the alloy during service.

The average cluster composition for the 330 °C and 365 °C samples is very close to the composition of the G-phase ($\text{Mn}_6\text{Ni}_{16}\text{Si}_7$). CALPHAD models have predicted that the G-phase is thermodynamically stable in alloys with similar nominal compositions [129]. Wells et al. have observed clusters in neutron-irradiated steels that have compositions very similar to the G-Phase [40].

The observation of Mn-Ni-Si-rich precipitates in a low-Cu alloy after only 20,733 hours indicates that these features are thermodynamically stable at 330 °C, 365 °C, and 405 °C. This observation demonstrates that hardening embrittlement is still a concern in low-Cu alloys. This information supports the work by [129] on the thermodynamic stability of these phases. It is important that the formation of these features is incorporated in models that predict the development of mechanical properties of RPV alloys. Whether these features are the “Late Blooming Phases” (LBP) described in [12] is still debatable. However, as the volume fraction of these LBP’s is predicted to rapidly increase [252], the development of Alloy I’s hardness and microstructure at further ageing times should be closely monitored.

5 Summary

Hardness measurements revealed that, after $\sim 30,000$ hours of ageing at 405 °C, some alloys have shown a significant increase in hardening. The alloys all have high nominal Ni contents.

Alloy F is high in Cu and displayed the largest increases in hardness of all the alloys. This increase in hardness is likely the result of precipitate formation. APT was used to characterise these precipitates, with the degree of hardening increasing with the square root of the measured precipitate volume fraction.

The measured composition of the precipitates sampled in Alloy F was found to vary depending on nucleation site. The presence of carbides near precipitates was found to reduce the amount of Mn present in the precipitates. When these variations were accounted for, the clusters had very similar compositions across the three ageing temperatures.

Lower ageing temperatures were observed to lead to a higher measured cluster number density and lower mean size in Alloy F.

Some Cu-rich clusters observed in Alloy F were observed to have Ni-Mn-rich appendage structures attached to them.

Grain boundary analyses of Alloy I displayed large variations in measured Gibbsian interfacial excess values between different specimens. Differences were also observed within specimens.

The formation of Mn-Ni-Si-rich precipitates was observed in Alloy I after 20,733 hours of ageing. These precipitates had a very similar composition to the predicted G-phase.

Chapter VII

Neutron-Irradiated RPV Steels

Results from APT analyses of four neutron-irradiated alloys are presented. Three of the alloys (C, G, K) had the same composition and processing route as three of the thermally-aged alloys, whilst RX12 was a cross-reference alloy. All four alloys were analysed at the Centre for Advanced Energy Studies (CAES), Idaho National Laboratory, USA. The steels had been irradiated to a fluence of 1.4×10^{20} n/cm² at 290 °C and a flux of 3.6×10^{12} n/cm²s in the Advanced Test Reactor 2 (ATR-2) experiment by the University of California, Santa Barbara (UCSB). All specimens were prepared via FIB lift-out and analysed using a LEAP-4000X HR.

Cluster searches were performed on the APT data using the core-linkage cluster search method. Cluster number densities, volume fractions, and sizes were calculated using the equations presented in Chapter IV Section 3.6.3. To investigate whether nucleation site had an impact of cluster size or composition, the nucleation site type of each cluster was determined.

1 Atom Probe Analyses

1.1 Alloy C - High Ni, High Mn, Medium Si

Alloy C had high nominal levels of Ni (3.11 at.%) and Mn (1.90 at.%). The alloy had a nominal Si content of 0.37 at.%. Seven APT datasets were collected for Alloy C, five of these contained grain boundaries and five contained carbides. Core-linkage cluster searches detected non-random clustering in all of the datasets. The clusters had a number density of $15.9 \times 10^{23} \text{ m}^{-3} \pm 1.0 \times 10^{23} \text{ m}^{-3}$, an average diameter of $2.38 \text{ nm} \pm 0.03 \text{ nm}$, and a volume fraction of $1.85 \% \pm 0.07 \%$.

If all of the Fe in the clusters is assumed to be the result of trajectory aberrations, the average cluster composition for the homogeneously nucleated clusters was 1.3 at.% Cu, 59.3 at.%

Ni, 25.3 at.% Mn, 0.1 at.% P, 13.2 at.% Si, and 0.8 at.% other elements. As the clusters consisted of mainly Mn, Ni, and Si, the ratio of these elements to one another in each cluster was plotted on a Gibbs triangle (Figure 80). The colour of each point represents the type of nucleation site the cluster was determined to have formed on, whilst the shape of each point depicts the dataset in which the cluster was detected.

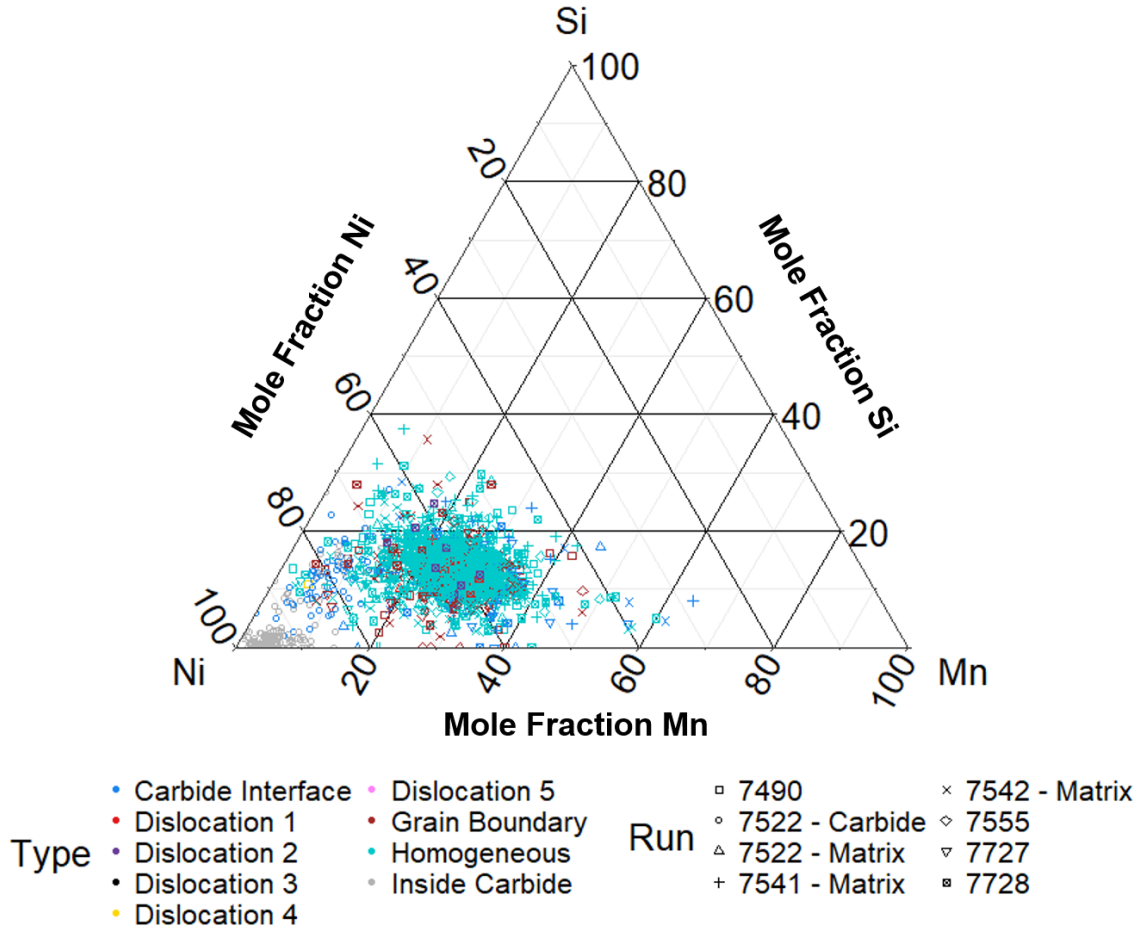


Figure 80: Gibbs triangle displaying cluster compositions for each cluster detected in Alloy C. The colour of each point represents the type of nucleation site, whilst the shape of each point depicts in which dataset the cluster was observed.

1.1.1 Grain Boundary Analyses

Figure 81 shows a neutron-irradiated sample of Alloy C. Mn, Ni, Si and P segregation was observed to be on a planar feature, likely to be a grain boundary. Multiple regions of interest (ROIs) were extracted from the grain boundary. Each ROI was taken perpendicularly to the grain

boundary and contained different sections of the grain boundary. These regions were then analysed using the methods described in Chapter V Sections 4.5 and 4.6.

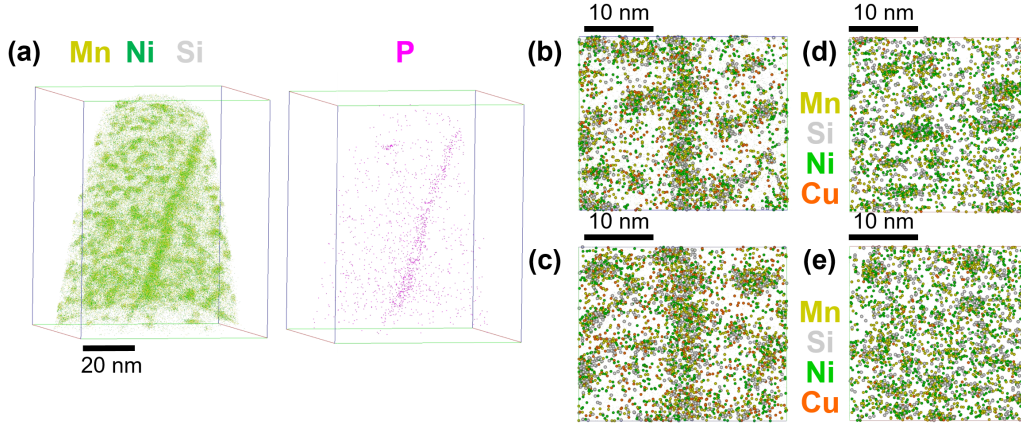


Figure 81: Atom maps from Alloy C, Run 7490 showing (a) distribution of Mn, Ni, Si, and P atoms throughout the entire specimen. (b) and (c) show the distribution of Mn, Si, Ni and Cu atoms in ROIs containing different sections of the grain boundary (y - z plane). (d) and (e) display the Mn, Si, Ni and Cu atom locations across the enriched region of ROIs in (b) and (c) respectively (x - y plane).

Table 38 displays the Gibbsian interfacial excess values calculated for each of the grain boundary regions shown in Figures 81 (b) and (c). The composition of the volumes determined to be the grain boundary regions (d) and (e) are also reported. The enriched region in Figure 81 (b) had a width of 2.6 nm and a cluster V_f of 5.7 %, whilst the enriched region in Figure 81 (c) was found to have a width of 3.2 nm and a cluster V_f of 3.6 %.

Element	Γ_i (atoms/nm ²)		Composition (at.%)	
	GB (b)	GB (c)	GB (b)	GB (c)
C	0.76 ± 0.01	0.72 ± 0.06	0.44	0.34
Cr	0.07 ± 0.01	0.08 ± 0.00	0.09	0.07
Cu	0.18 ± 0.01	0.17 ± 0.02	0.11	0.08
Fe	-20.46 ± 0.61	-18.91 ± 0.01	87.03	89.51
Mn	5.11 ± 0.22	4.29 ± 0.04	3.14	2.36
Mo	0.53 ± 0.02	0.69 ± 0.02	0.39	0.32
Ni	11.16 ± 0.36	10.65 ± 0.12	7.37	6.17
P	0.23 ± 0.02	0.25 ± 0.01	0.11	0.09
Si	2.41 ± 0.08	2.06 ± 0.02	1.33	1.04

Table 38: Comparison of the calculated Gibbsian interfacial excess values for the grain boundary regions sampled from Run 7490 (Figure 81). The compositions of these regions are also shown.

Grain boundaries were also observed in reconstructions from Run 7542, Run 7555, Run 7727,

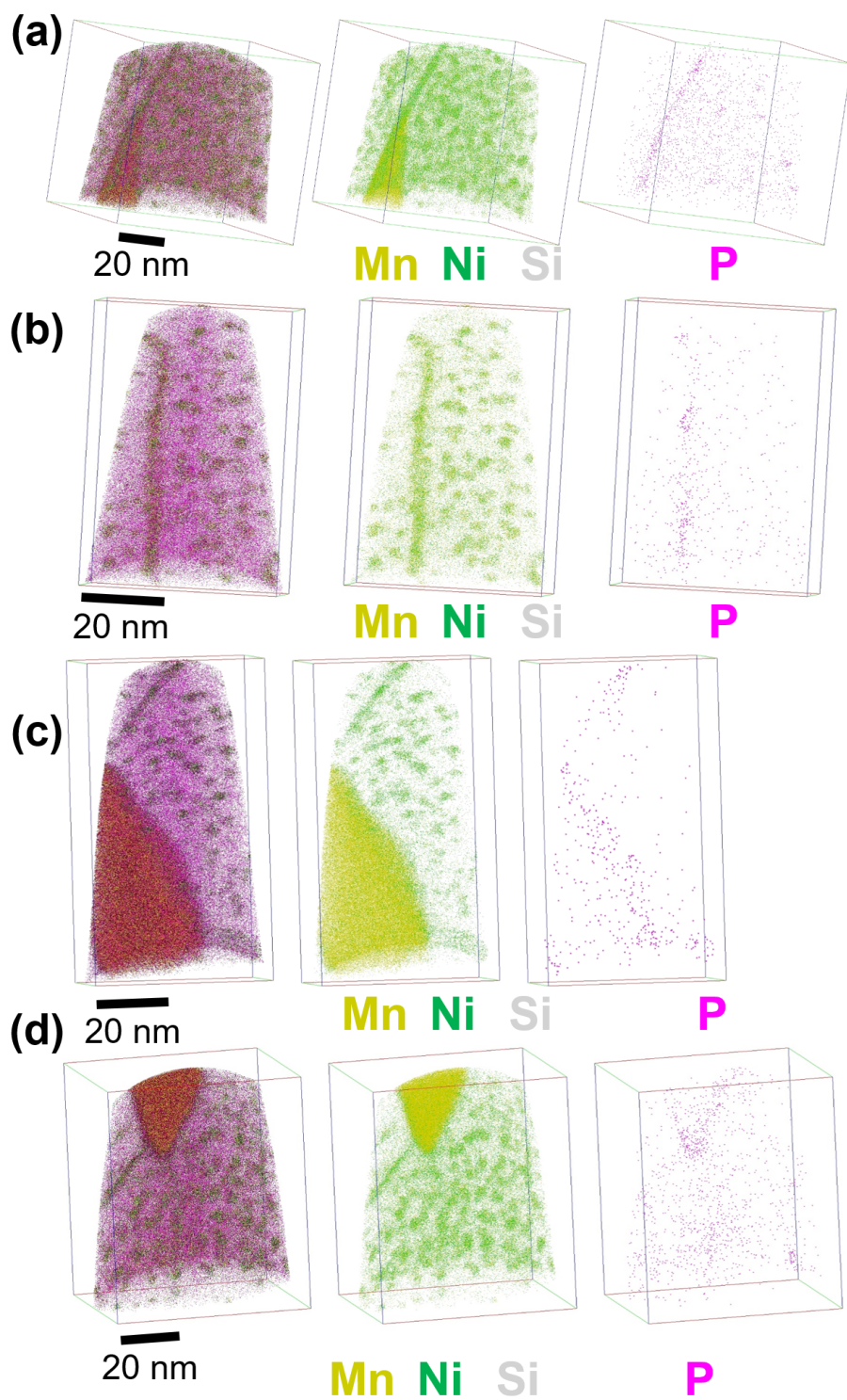


Figure 82: Atom maps showing the distribution of Mn, Ni, Si, and P atoms in Alloy C from (a) Run 7542, (b) Run 7555 (c) Run 7727, and (d) Run 7728.

and Run 7728 (Figure 82). The grain boundaries were typically decorated with Ni atoms. Runs 7542, 7727, and 7728 also contained carbides. The carbides can be seen as the regions enriched in Mn in Figure 82.

Table 39 summarises the Gibbsian interfacial excess values calculated for the grain boundaries detected in Runs 7542, 7555, 7727, and 7728.

Element	Γ_i (<i>atoms/nm²</i>)			
	Run 7542	Run 7555	Run 7727	Run 7728
C	-0.11 $\pm$ 0.12	0.97 $\pm$ 0.01	0.36 $\pm$ 0.1	0.06 $\pm$ 0.07
Cr	-0.07 $\pm$ 0.04	0.19 $\pm$ 0.02	0.06 $\pm$ 0.01	0.04 $\pm$ 0.00
Cu	0.07 $\pm$ 0.05	0.14 $\pm$ 0.03	0.40 $\pm$ 0.00	0.30 $\pm$ 0.01
Fe	-6.52 $\pm$ 0.42	-21.88 $\pm$ 0.86	-19.55 $\pm$ 0.12	-15.37 $\pm$ 0.68
Mn	0.89 $\pm$ 0.45	6.12 $\pm$ 0.18	4.31 $\pm$ 0.01	2.73 $\pm$ 0.59
Mo	-0.05 $\pm$ 0.06	0.71 $\pm$ 0.05	0.34 $\pm$ 0.02	0.11 $\pm$ 0.10
Ni	4.19 $\pm$ 0.29	11.24 $\pm$ 0.53	11.73 $\pm$ 0.03	10.07 $\pm$ 0.05
P	0.16 $\pm$ 0.01	0.22 $\pm$ 0.01	0.10 $\pm$ 0.01	0.03 $\pm$ 0.00
Si	1.46 $\pm$ 0.07	2.28 $\pm$ 0.12	2.25 $\pm$ 0.04	2.04 $\pm$ 0.22

Table 39: Calculated Gibbsian interfacial excess values for grain boundaries detected in Runs 7542, 7555, 7727, and 7728.

The enriched region of Run 7542 had an average width of 1.3 nm $\pm$ 0.1 nm and a cluster V_f of 1.6 % $\pm$ 0.6 %. Run 7555's grain boundary was found to have a width of 2.6 nm $\pm$ 0.0 nm and a cluster V_f of 5.4 % $\pm$ 0.2 %. The enriched volume in Run 7727 was determined to have a width of 2.0 nm $\pm$ 0.0 nm and a cluster V_f of 7.6 % $\pm$ 0.3 %, whilst the grain boundary in Run 7728 was 2.5 nm $\pm$ 0.1 nm wide and had a cluster V_f of 5.5 % $\pm$ 0.2 %.

The composition of the grain boundary volumes detected in each of these runs is shown in Table 40.

Element	Composition (at.%)			
	Run 7542	Run 7555	Run 7727	Run 7728
C	0.27 ± 0.03	0.53 ± 0.02	0.27 ± 0.08	0.16 ± 0.07
Cr	0.06 ± 0.02	0.15 ± 0.01	0.10 ± 0.04	0.07 ± 0.03
Cu	0.11 ± 0.03	0.10 ± 0.01	0.21 ± 0.05	0.14 ± 0.05
Fe	90.75 ± 0.67	87.38 ± 0.13	87.25 ± 0.44	89.54 ± 0.35
Mn	1.64 ± 0.35	3.49 ± 0.05	2.93 ± 0.21	2.18 ± 0.18
Mo	0.23 ± 0.04	0.49 ± 0.00	0.27 ± 0.07	0.11 ± 0.05
Ni	5.57 ± 0.19	6.59 ± 0.07	7.58 ± 0.40	6.59 ± 0.34
P	0.11 ± 0.01	0.09 ± 0.01	0.04 ± 0.03	0.02 ± 0.02
Si	1.25 ± 0.06	1.19 ± 0.01	1.36 ± 0.16	1.17 ± 0.14

Table 40: Calculated compositions (at.%) for grain boundary regions extracted from Runs 7542, 7555, 7727, and 7728.

1.1.2 Carbide Analyses

Carbides were present in five datasets from Alloy C. ROIs from within each carbide were extracted and the composition of these volumes was calculated. The composition of each carbide is shown in Table 41.

Element	Composition (at.%)				
	Run 7522	Run 7541	Run 7542	Run 7727	Run 7728
C	24.47 ± 0.05	15.07 ± 0.26	17.11 ± 0.34	26.45 ± 0.29	20.48 ± 0.11
Cr	0.42 ± 0.01	0.62 ± 0.04	1.78 ± 0.10	2.25 ± 0.07	2.38 ± 0.03
Cu	0.01 ± 0.00	0.01 ± 0.01	0.02 ± 0.01	0.00 ± 0.00	0.01 ± 0.00
Fe	65.20 ± 0.05	70.41 ± 0.25	61.10 ± 0.39	48.59 ± 0.27	57.22 ± 0.12
Mn	7.76 ± 0.02	12.83 ± 0.17	18.04 ± 0.32	20.12 ± 0.20	16.03 ± 0.08
Mo	0.45 ± 0.01	0.22 ± 0.03	0.54 ± 0.05	1.99 ± 0.06	1.59 ± 0.03
Ni	1.61 ± 0.01	0.82 ± 0.05	1.26 ± 0.08	0.59 ± 0.04	1.99 ± 0.03
P	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.01	0.00 ± 0.00	0.03 ± 0.00
Si	0.07 ± 0.00	0.01 ± 0.00	0.15 ± 0.03	0.01 ± 0.00	0.26 ± 0.01

Table 41: Compositions (at.%) of the carbides present in each dataset obtained from Alloy C.

1.1.2.1 Clustering Within Carbides

Mn, Ni, and Si were found to be non-randomly distributed within the matrix of all the datasets that contained carbides. However, Run 7522 (Figure 83) was the sole Alloy C dataset in which Ni and Si atoms were found to be non-randomly distributed within the carbide. Separate cluster searches were performed for the carbide and matrix regions of this dataset.

The composition, excluding Fe, of each cluster detected within the carbide is shown in

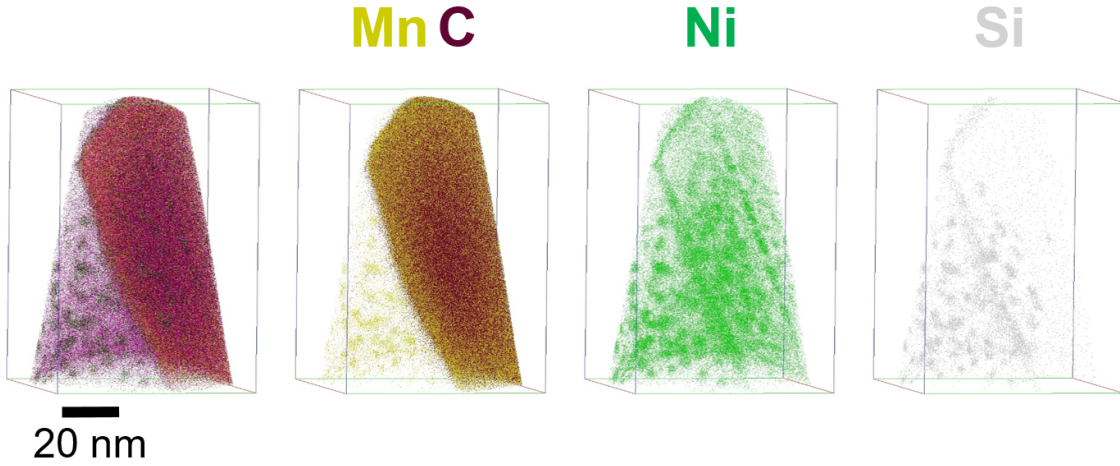


Figure 83: Atom maps showing the distribution of Mn, C, Ni, and Si atoms in a specimen of Alloy C (Run 7522).

Figure 84. The mean cluster composition was 72.0 at.% Ni, 5.2 at.% Mn, 5.5 at.% Si, 1.5 at.% Cu, 0.4 at.% P, 15.4 at.% other elements. The majority of the “other” atoms (> 95 %) were C atoms.

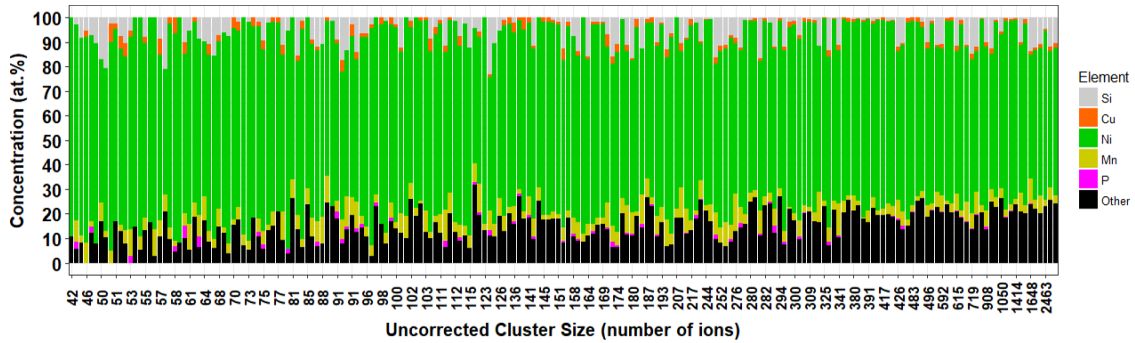


Figure 84: Composition (at.%) of each cluster detected within the carbide in Run 7522 (Alloy C - Figure 84).

1.2 Alloy G - Medium Ni, High Mn, Medium Si

Alloy G had medium nominal levels of Ni (1.54 at.%) and Si (0.38 at.%), and high levels of Mn (1.93 at.%). Core-linkage cluster searches detected clustering in each of the three datasets analysed via APT. The clusters were found to have a number density of $6.4 \times 10^{23} \text{ m}^{-3} \pm 0.9 \times 10^{23} \text{ m}^{-3}$, a volume fraction of $0.55 \% \pm 0.10 \%$, and a mean diameter of $2.16 \text{ nm} \pm 0.10 \text{ nm}$. A carbide was observed in one of the datasets.

The average cluster composition for the homogeneously nucleated clusters (excluding Fe) was 2.0 at.% Cu, 51.7 at.% Ni, 26.9 at.% Mn, 0.1 at.% P, 18.6 at.% Si, and 0.7 at.% other elements. The ratio of Mn:Ni:Si in each cluster is shown in Figure 85.

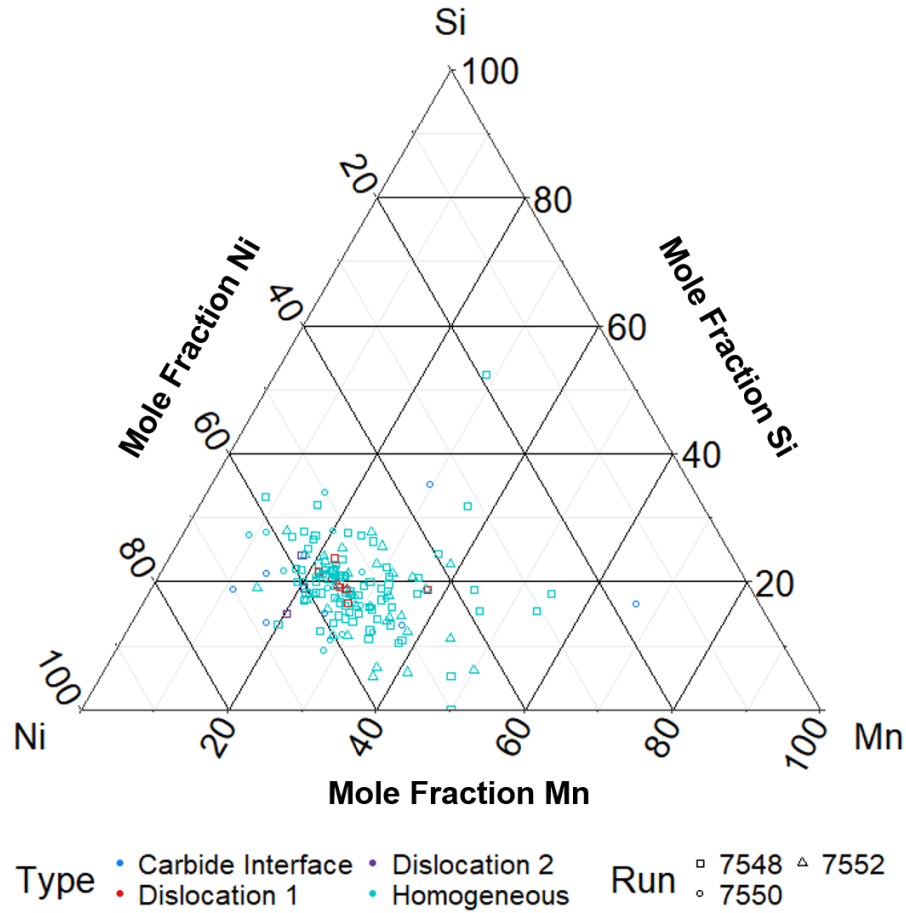


Figure 85: Gibbs triangle displaying cluster compositions for each cluster detected in Alloy G. The colour of each point represents the type of nucleation site, whilst the shape of each point depicts in which dataset the cluster was observed.

Figure 86 shows a typical atom map for a neutron-irradiated sample of Alloy G. Clustering of Mn, Ni, Si, and P atoms can be seen. The majority of P atoms were observed to be segregated to a dislocation.

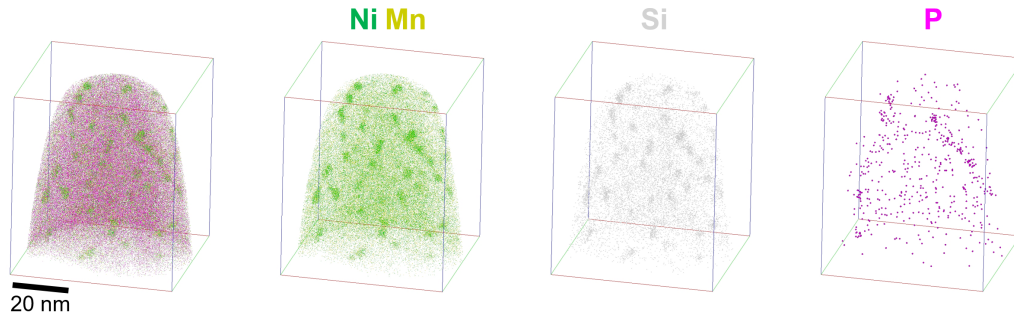


Figure 86: Atom maps showing the distribution of Ni, Mn, Si, and P atoms from a specimen of Alloy G (Run 7548).

1.2.1 Carbide Analyses

A carbide in Alloy G was observed in Run 7550. Atom maps from this dataset are shown in Figure 87. Table 42 presents the composition of this carbide. Solute atoms were observed to be randomly distributed within the carbide.

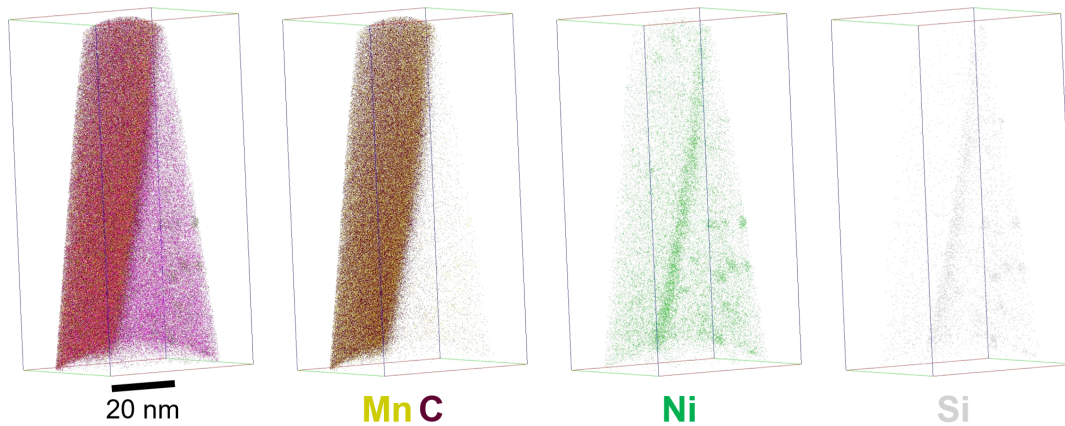


Figure 87: Atom maps showing the distribution of Mn, C, Ni, and Si atoms from a specimen of Alloy G (Run 7550).

Element	Composition (at.%) Run 7550
C	24.59 ± 0.14
Cr	1.25 ± 0.03
Cu	0.00 ± 0.00
Fe	58.01 ± 0.14
Mn	14.28 ± 0.09
Mo	1.39 ± 0.03
Ni	0.47 ± 0.02
P	0.01 ± 0.00
Si	0.02 ± 0.00

Table 42: Compositions (at.%) of the carbide present in Run 7550 (Alloy G).

1.3 Alloy K - High Ni, Low Mn, Medium Si

Alloy K had high nominal levels of Ni (3.16 at.%), a nominal Si content of 0.38 at.%, and low levels of Mn (0.24 at.%). 12 specimens were successfully analysed via APT. Clustering was observed in all 12 datasets, and one dataset contained a grain boundary. The clusters were observed to have a number density of $9.2 \times 10^{23} \text{ m}^{-3} \pm 0.5 \times 10^{23} \text{ m}^{-3}$, a volume fraction of $0.73 \% \pm 0.03 \%$, and an average diameter of $2.08 \text{ nm} \pm 0.04 \text{ nm}$.

The average cluster composition for the homogeneously nucleated clusters in Alloy K was 1.9 at.% Cu, 73.6 at.% Ni, 5.1 at.% Mn, 0.1 at.% P, 18.5 at.% Si, and 0.8 at.% other elements. The Ni:Mn:Si ratio present in each cluster is shown in Figure 88.

Figure 89 shows the atom maps observed for the dataset from Run 7488. Ni, Mn, and Si are all non-randomly distributed.

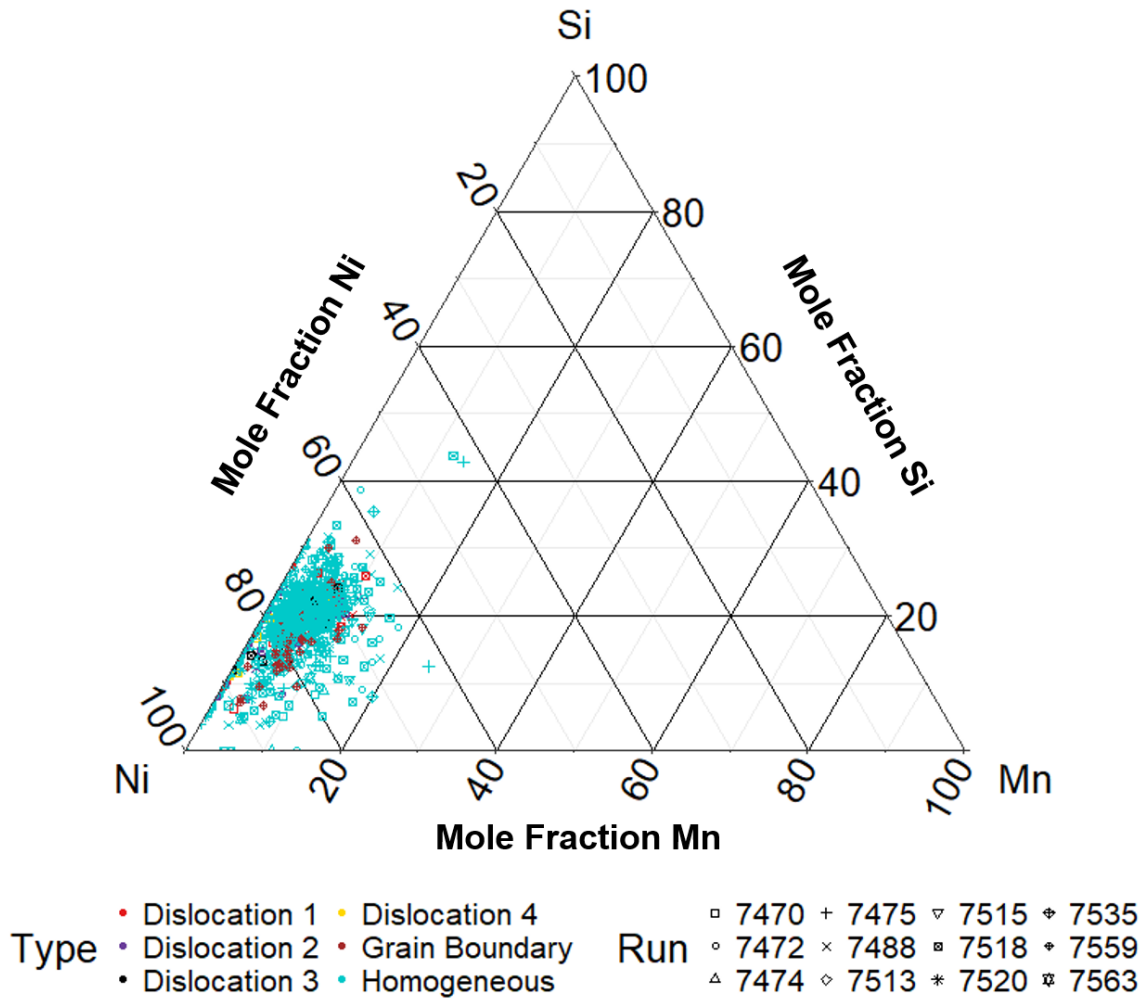


Figure 88: Gibbs triangle displaying cluster compositions for each cluster detected in Alloy K. The colour of each point represents the type of nucleation site, whilst the shape of each point depicts in which dataset the cluster was observed.

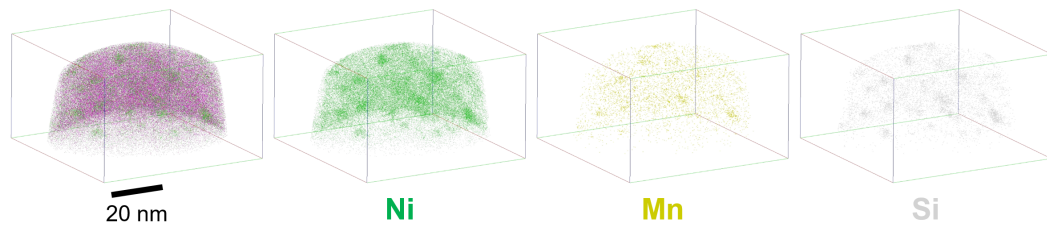


Figure 89: Atom maps showing the distribution of Ni, Mn, and Si atoms in a sample of Alloy K (Run 7488).

1.3.1 Grain Boundary Analyses

A grain boundary was observed in the dataset from Run 7559 (Figure 90). Multiple ROIs containing the grain boundary were extracted and grain boundary analyses were performed. The calculated Gibbsian interfacial excess values and composition of the grain boundary are shown in Table 43. The grain boundary was observed to have an average width of $2.0 \text{ nm} \pm 0.2 \text{ nm}$. The clustering V_f within the boundary region was observed to be $5.0 \% \pm 0.9 \%$.

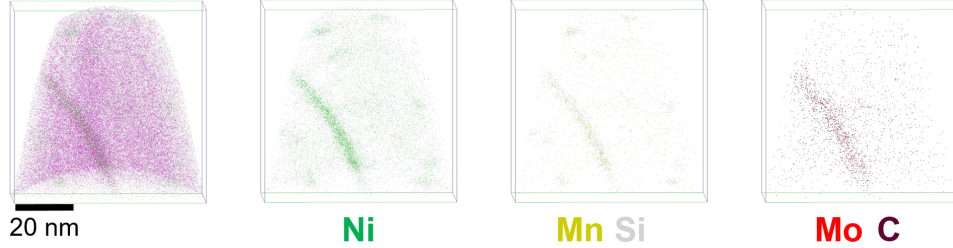


Figure 90: Atom maps showing the distribution of Ni, Mn, Si, Mo, and C atoms in an Alloy K specimen (Run 7559).

Element	Γ_i (<i>atoms/nm²</i>)	Composition (at.%)
C	3.61 ± 0.07	1.89 ± 0.08
Cr	0.07 ± 0.01	0.09 ± 0.01
Cu	0.26 ± 0.00	0.11 ± 0.00
Fe	-27.05 ± 0.73	86.08 ± 0.56
Mn	0.80 ± 0.10	0.46 ± 0.04
Mo	1.72 ± 0.03	0.91 ± 0.03
Ni	16.97 ± 0.34	8.82 ± 0.30
P	0.07 ± 0.01	0.03 ± 0.00
Si	3.55 ± 0.2	1.6 ± 0.11

Table 43: The calculated Gibbsian interfacial excess values for the grain boundary regions sampled from Run 7559 (Figure 90). The composition of this grain boundary is also shown.

1.4 Alloy RX12 - High Ni, Very Low Mn, Low Si

Alloy RX12 had high nominal levels of Ni (3.42 at.%), but very low levels of Mn (0.04 at.%) and Si (0.06 at.%). Two datasets were analysed, and non-random clustering was detected in both after using core-linkage cluster search algorithm. The clusters were found to have a number density of $6.8 \times 10^{23} \text{ m}^{-3} \pm 4.1 \times 10^{23} \text{ m}^{-3}$, a volume fraction of $0.65 \% \pm 0.23 \%$, and an average diameter of $2.26 \text{ nm} \pm 0.19 \text{ nm}$. However, the majority of clusters were found on dislocations. Since

both datasets contained dislocations, the number density, volume fraction, and size calculations may not be representative of the sample as a whole.

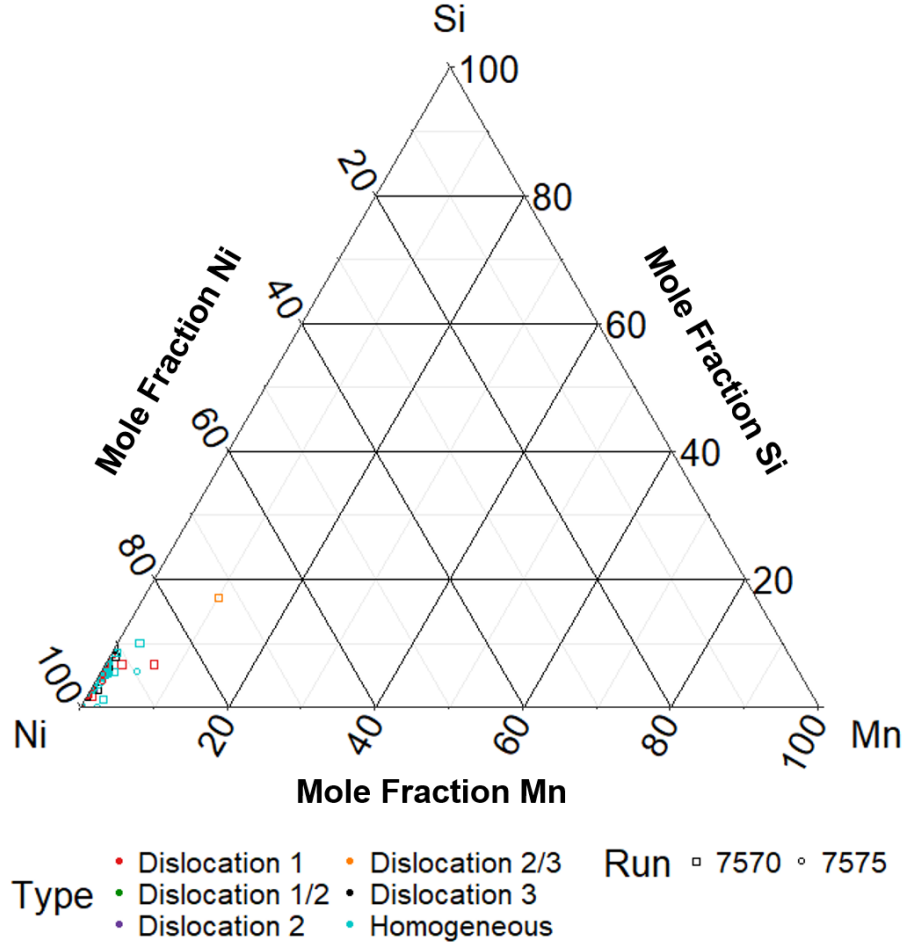


Figure 91: Gibbs triangle displaying cluster compositions for each cluster detected in Alloy RX12. The colour of each point represents the type of nucleation site, whilst the shape of each point depicts in which dataset the cluster was observed.

Excluding Fe, the average cluster composition for all detected clusters in Alloy RX12 was 0.8 at.% Cu, 94.6 at.% Ni, 0.4 at.% Mn, 0.0 at.% P, 2.9 at.% Si, and 1.3 at.% other elements. The ratio of Ni:Mn:Si is shown in Figure 91 for each cluster detected in Alloy RX12. In some of the datasets, such as Figure 92, there were dislocations that appeared to intersect with one another. Nucleation site types “Dislocation x/y ” indicates a cluster that was detected at the intersection point between Dislocation x and Dislocation y .

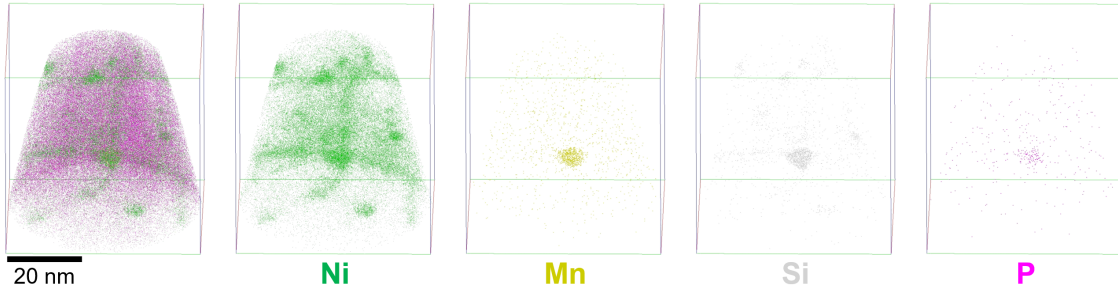


Figure 92: Atom maps showing the distribution of Ni, Mn, Si, and P atoms in a specimen of RX12 (Run 7570).

2 Discussion

2.1 Grain Boundary Analyses

Five grain boundaries were analysed from Alloy C, and one grain boundary was contained in the datasets from Alloy K.

2.1.1 Alloy C

The segregation behaviour of each element, described by the Gibbsian interfacial excess values, was observed to vary from dataset to dataset in Alloy C. This may be a result of differing grain boundary misorientations and grain boundary planes in each of these datasets. However, a trend can be seen between datasets containing grain boundaries and carbides, and those just containing grain boundaries.

Mn and C were found to have higher Γ_i values at grain boundaries in datasets (Run 7490 & Run 7555) that did not also contain carbides. This may be a result of Mn and C segregating to the carbides in Run 7542, Run 7727, and Run 7728. Segregation of Mn and C to carbides could deplete the grain boundary in the immediate vicinity of the carbide. As a result of this reduced Mn and C segregation to grain boundary sections near grain boundaries, the magnitude of Fe depletion at these grain boundaries was reduced.

The grain boundary regions in datasets not containing carbides had higher at.% of Mo, Mn, and C. These elements are known carbide formers and may have segregated to the carbides, reducing the amount of these elements present at the grain boundary.

Ni was observed to be the most strongly segregated element to each grain boundary analysed

from Alloy C. The reason for the segregation strength of Ni being lower in Run 7542 than the other datasets is unknown. However, the grain boundary region in Run 7542 also had a lower Ni composition (at.%) than the grain boundary regions in the other runs. This decrease in Ni composition indicates there were lower absolute levels of Ni at this boundary compared to the other observed boundaries, not just less strong segregation of Ni to the boundary from the surrounding matrix.

2.1.2 Alloy K

C, Mn, Mo, Ni, and Si had positive values of Γ_i at the grain boundary observed in Alloy K. Ni was observed to have the strongest segregation behaviour of all of the elements at this section of the observed grain boundary.

The Ni content at this section of the grain boundary was $8.82 \text{ at.\%} \pm 0.30 \text{ at.\%}$. This is more than twice the value of the nominal Ni content ($3.16 \text{ at.\%}$).

2.1.3 Comparison With Nominal Compositions

Care must be taken when making comparisons between grain boundaries of unknown misorientation or grain boundary plane. However, it is interesting to note that the grain boundary in Alloy K was found to have much higher values of Γ_i for Ni and Si, and lower Γ_i values for Mn, than the grain boundaries tested in Alloy C.

When comparing the nominal compositions of the two alloys, the main difference is that Alloy K contains 1.66 at.% less Mn than Alloy C. This may explain the lower Γ_{Mn} value observed in Alloy K. The Fe composition of the grain boundary in Alloy K was also found to be lower than that of all the grain boundaries observed in Alloy C. This is despite Alloy K containing nominally more Fe than Alloy C.

2.2 Carbide Analyses

Carbides were present in five datasets from Alloy C and one dataset from Alloy G. Clustering of Ni and Si atoms was observed in one of the carbides in Alloy C. As APT datasets typically only sample a fraction of a carbide's entire volume, it is not possible to definitely determine whether or not there was clustering present within the other carbides. It can only be stated that no clustering was observed in the carbide regions that were sampled during APT experiments.

The carbide in Alloy G had a stoichiometry of $\sim \text{M}_3\text{C}$ and may be either an Fe_3C lath, or an ϵ -carbide. No clustering was observed in the carbide in this dataset.

The five carbides in Alloy C were found to have different compositions from one another. This is likely because the carbides are of different types to one another. The approximate stoichiometry and possible types of each carbide is shown in Table 44.

	Run 7522	Run 7541	Run 7542	Run 7727	Run 7728
C (at.%)	24.47 ± 0.05	15.07 ± 0.26	17.11 ± 0.34	26.45 ± 0.29	20.48 ± 0.11
Stoichiometry	$\sim \text{Fe}_3\text{C}$	$\sim \text{Fe}_5\text{Mn}_5\text{C}$	$\sim \text{Fe}_{18}\text{Mn}_5\text{C}_6$	$\sim \text{Fe}_{10}\text{Mn}_4\text{C}_5$	$\sim \text{Fe}_{18}\text{Mn}_5\text{C}_6$
Carbide Type	Fe_3C or M_3C	M_6C	M_{23}C_6	Fe_3C or ϵ -carbide	M_{23}C_6

Table 44: Stoichiometry of each carbide present in Alloy C and possible carbide type.

Clustering was observed within the carbide in Run 7522. The clusters consisted of mainly Ni and Si. This indicates that Ni and Si have low solubility in this carbide. Clusters that were detected at the carbide-matrix interface had significantly ($p < 0.001$) higher Si and Mn contents than clusters detected elsewhere within the carbide (Figure 93).

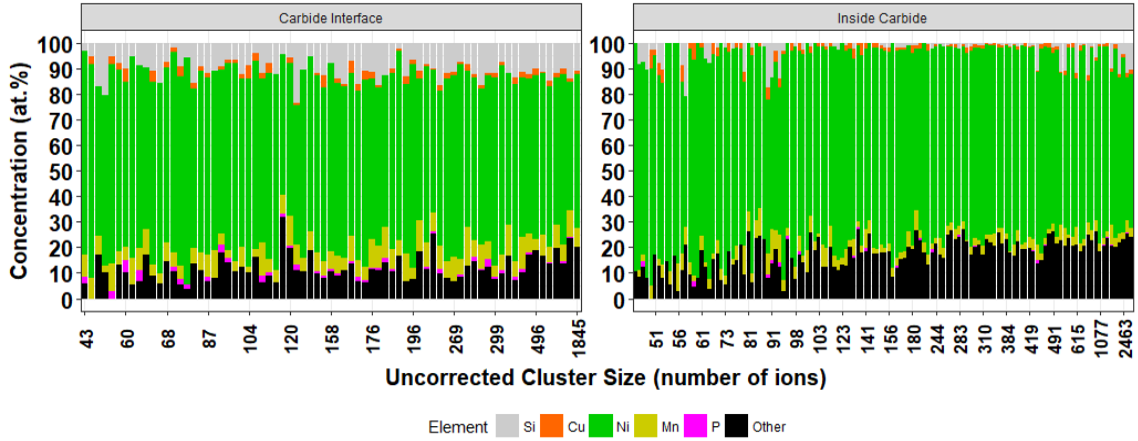


Figure 93: Composition (at.%) of individual clusters detected within the carbide in Run 7522 (Alloy C). One plot shows the composition of clusters detected at the carbide-matrix interface, the other shows the composition of clusters detected within the carbide.

2.3 Cluster Compositions

2.3.1 Fe Content Of Clusters

Previous work indicates that APT overestimates the Fe content of Cu-rich precipitates [113]. This is due to the local magnification effects introduced as a result of the different evaporation fields of Cu (30 Vnm^{-1}) and Fe (35 Vnm^{-1}). The calculated evaporation fields of Mn (30 Vnm^{-1}) and Si (33 Vnm^{-1}) are also lower than Fe [157]. Therefore, clusters enriched in these elements may also be susceptible to similar aberrations during APT experiments, as discussed in Chapter IV Section 3.3. It has been reported that Mn-Ni-Si-rich clusters contain, on average, 6.0 at.% Fe [126].

Excluding Fe, the clusters in Alloy C contained 59.3 at.% Ni and were observed to have a higher density than the surrounding matrix (Figure 94 (a)). Meanwhile, the clusters detected in RX12 were nearly pure Ni (94.6 at.%) when Fe was excluded from cluster composition calculations. The density of these clusters was very similar to that of the surrounding matrix (Figure 94 (b)). As the RX12 clusters contained very little Mn (0.4 at.%) and Si (2.9 at.%), they may not be influenced by trajectory aberrations. If this is true, the Fe detected within these clusters is likely to be real and should be included in cluster composition, size and volume fraction calculations.

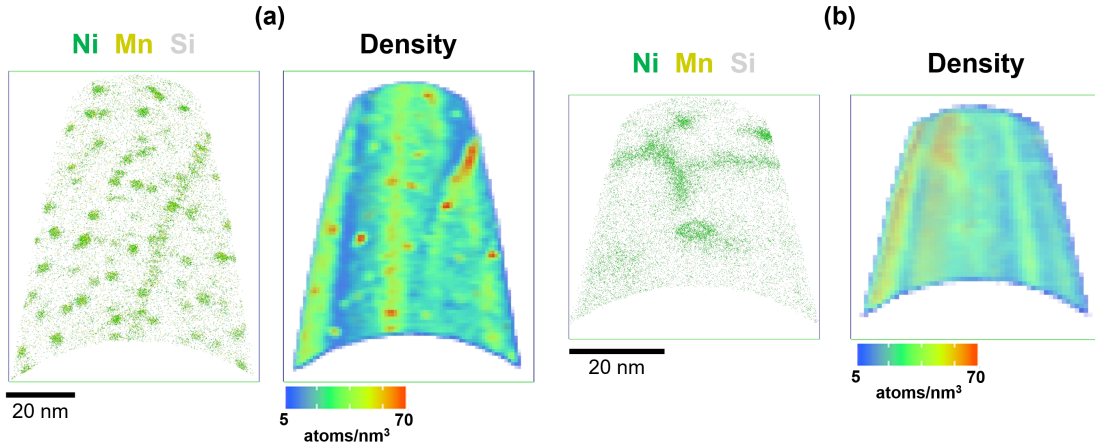


Figure 94: (a) Atom maps of Ni, Mn and Si atoms and density plot of atom map in Alloy C (Run 7490). (b) Atom maps of Ni, Mn and Si atoms and density plot of atom map in Alloy RX12 (Run 7570).

Table 45 shows the effect that including Fe has on the calculated cluster composition, size, and volume fraction for Alloy RX12.

	Mean Composition (at.%)							Diameter (nm)	V_f (%)
	Fe	Ni	Mn	Si	P	Cu	Other		
Excluding Fe	-	94.6	0.4	2.9	0.0	0.8	1.3	2.26 ± 0.19	0.65 ± 0.23
Including Fe	40.1	56.7	0.3	1.7	0.0	0.5	0.8	2.73 ± 0.23	1.08 ± 0.32

Table 45: Table detailing how including and excluding Fe affects the calculated cluster attributes for Alloy RX12.

If the Fe in the clusters is not an artefact, then plotting the cluster compositions on a ternary Mn-Ni-Si plot is unsuitable. The compositions of each cluster detected in Alloy RX12 are shown plotted on a bar chart in Figure 95.

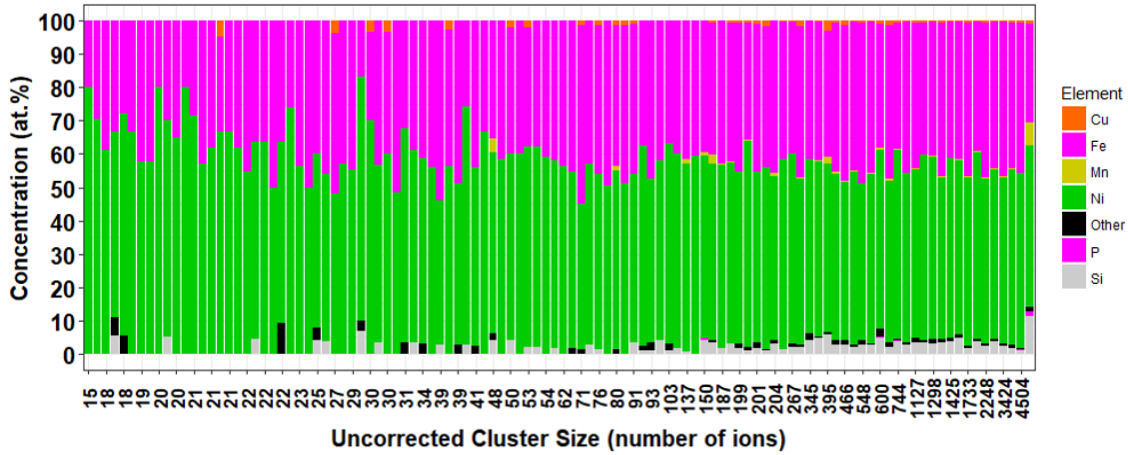


Figure 95: Compositions (at.%) of each cluster detected in Alloy RX12. Fe is included.

The average composition of these clusters is ~ 40 Fe-60 Ni (at.%). The Fe-Ni binary phase diagram in Figure 96 shows that this composition is around the transition between the FeNi, Fe₃Ni and γ phase fields at 290 °C. TEM and APT studies have observed that Fe₃Ni precipitates formed in binary Fe-Ni alloys after ion-irradiation [253]. However, the precipitates observed in [253] were far larger than the clusters observed in this study.

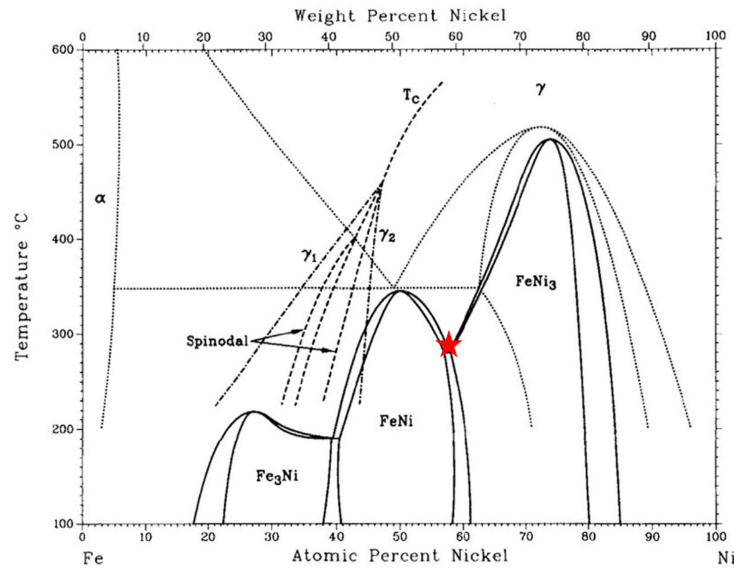


Figure 96: Fe-Ni binary phase diagram. The red star represents the mean composition of the clusters detected in alloy RX12 after irradiation at 290 °C. Reproduced with permission from [254]. Copyright © 1991 Published by Springer Nature.

2.3.2 Dependence on Nucleation Site

The Gibbs triangles plotted in Figure 97 show the average ratio of Mn, Ni, and Si detected in the clusters on each nucleation site type in Alloys C, G, and K. As no appendage clusters, or core-shell type clusters were detected in these alloys, edge clusters were included for these average composition calculations.

The clusters that were detected inside the carbide in Alloy C contained a significantly higher Ni to Si/Mn ratio than the other clusters detected in Alloy C. The clusters that were detected on “Dislocation 4” contained a lower ratio of Mn than the homogeneously nucleated clusters in Alloy C. However, there was a large variance in the calculated composition of the clusters detected on this dislocation. Clusters detected on grain boundaries Alloy C had a very similar composition to clusters that were observed to have formed homogeneously.

One of the dislocations in Alloy G had clusters present on it which contained less Mn than the other clusters detected in this alloy. The composition of clusters that were observed to have formed homogeneously in this alloy had similar compositions to clusters detected at the carbide-matrix interface.

The clusters detected in Alloy K were found to have very similar compositions, regardless of

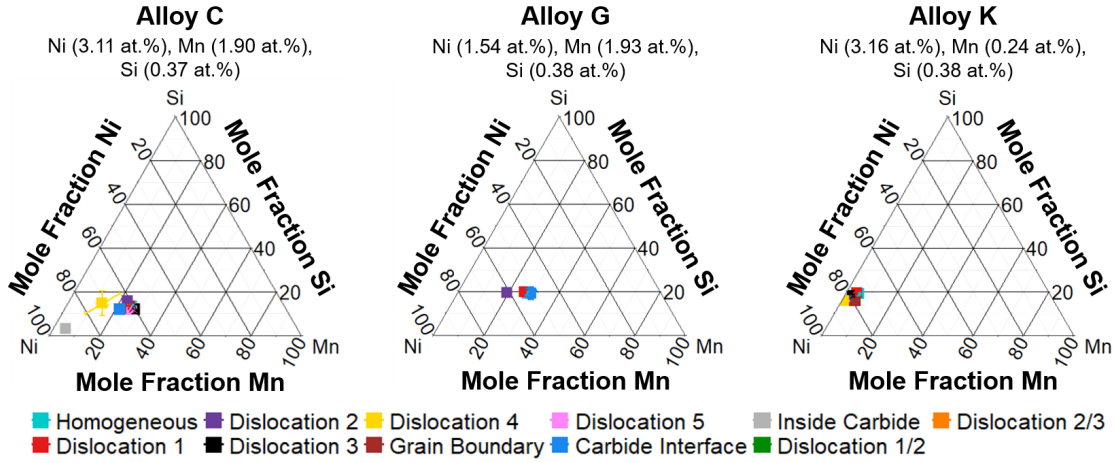


Figure 97: Average composition for clusters detected on each nucleation site in Alloy C, G, and K. Error bars represent standard error of the mean for each class of cluster. Nominal Ni, Mn, and Si compositions for each alloy are displayed above each plot.

whether they had formed homogeneously, on dislocations, or on grain boundaries.

In RX12, the largest detected cluster had formed at the intersection between two dislocations (Figure 92). This cluster contained may more non-Ni atoms than other clusters detected in Alloy RX12. The cluster composition (including Fe) was: 29.8 at.% Fe, 11.3 at.% Si, 0.9 at.% Cu, 48.4 at.% Ni, 6.8 at.% Mn, 1.3 at.% P, and 1.6 at.% other elements. The intersection point between two dislocations is subject to two fast diffusion pathways, along which atoms may diffuse. This may explain why this cluster was larger than the other clusters observed in this alloy. The higher levels of Si, P, and Mn in this cluster may also be a result of the cluster being present at the intersection point of two dislocations.

2.3.3 Variation of Cluster Composition With Size

To investigate whether cluster composition changed as the clusters increased in size, the clusters detected in each alloy were split into quartiles based on size. The mean Mn:Ni:Si ratios of these quartiles was found and plotted (Figure 98). As the clusters grew larger, there was less variance in their compositions.

T-tests revealed that the composition of the smallest 25 % of clusters in Alloy C (not including clusters that nucleated within carbides) contained significantly ($p < 0.001$) less Mn than the largest 25 % of clusters. This increase in Mn content came at the expense of Ni ($p < 0.001$) and

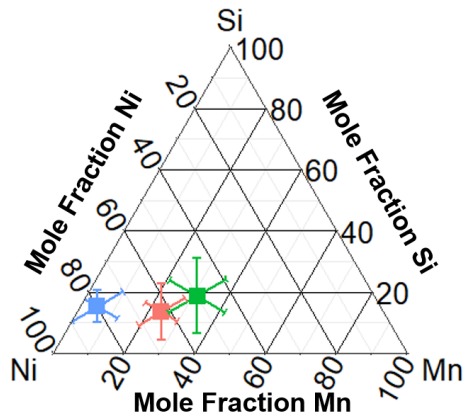
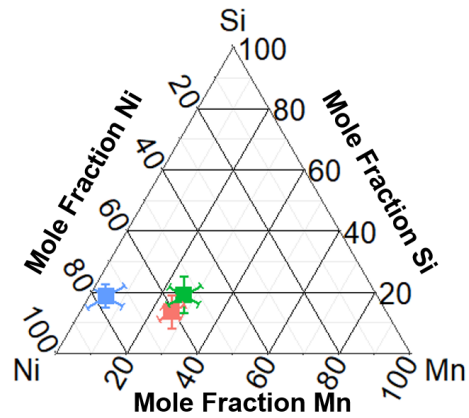
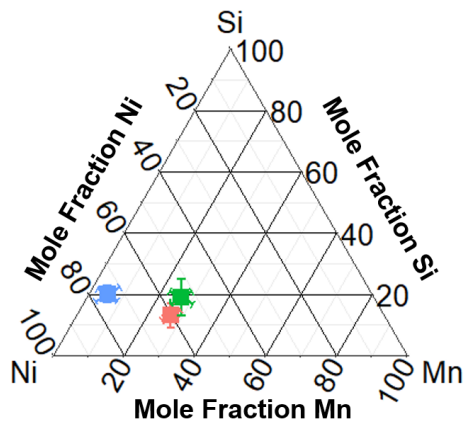
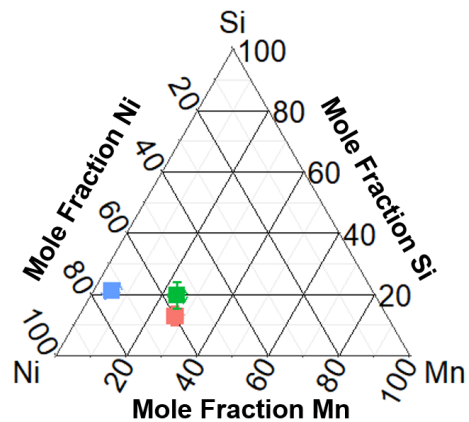
Average Cluster Composition
Cluster Size Percentile 0-25%Average Cluster Composition
Cluster Size Percentile 25-50%Alloy
C
G
KAverage Cluster Composition
Cluster Size Percentile 50-75%Average Cluster Composition
Cluster Size Percentile 75-100%Alloy
C
G
K

Figure 98: Evolution of average cluster composition with cluster size. Error bars represent the standard error of the mean.

Si ($p < 0.01$) which were both found to be present in significantly lower levels in the larger clusters.

The clusters in Alloy G were observed to contain significantly ($p < 0.01$) less Mn as they became larger in size. The Ni content of the clusters was found to significantly increase ($p < 0.01$) between the lower and upper quartile of cluster size. The largest quartile of clusters in Alloy G contained, on average, $27.0 \text{ at.\%} \pm 0.4 \text{ at.\%}$ (95 % CI) Mn whilst the smallest quartile of clusters contained $34.2 \text{ at.\%} \pm 0.8 \text{ at.\%}$ (95 % CI) Mn.

The average compositions of the smallest 25 % of clusters in Alloy K was determined to be significantly different to the average compositions of the largest 25 % of clusters in Alloy K. Whilst

the Mn content did not undergo a significant change, there was a significant increase ($p < 0.001$) in the Si content between the smallest and largest clusters. Ni was found to be present in significantly ($p < 0.001$) lower quantities in the larger clusters than in the smallest 25 % of clusters.

Figure 99 summarises the evolution of the mean cluster composition for Alloys C, G, and K for the smallest to largest quartile of clusters.

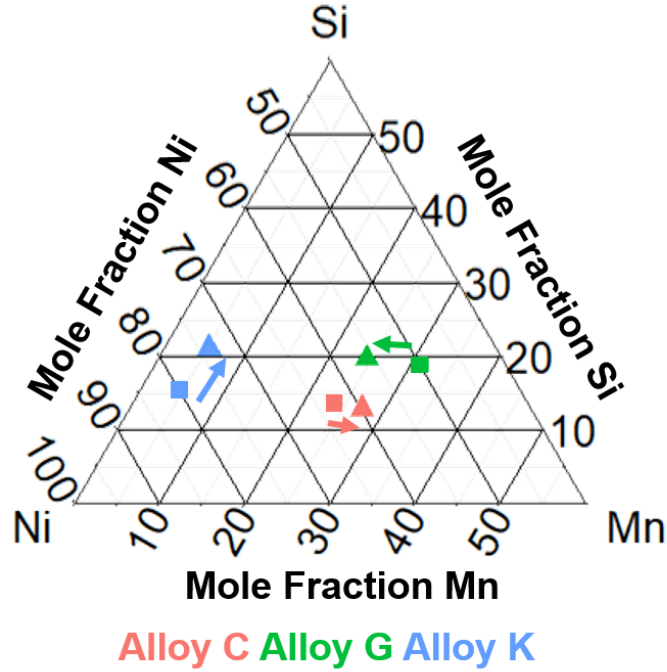


Figure 99: Development of average cluster composition with cluster size. Squares represent the mean composition of the smallest 25 % of clusters, whilst triangles represent the mean composition of the largest 25 % of clusters.

2.3.4 Comparison Of Compositions To Known Phases

Table 46 shows the average cluster composition for the largest 25 % of clusters in each of the irradiated alloys. The mean compositions of the clusters were compared to the phases predicted to be thermodynamically stable by Xiong et al. [129] (Figure 100).

Alloy	Note	Composition (at.%)						
		Fe	Ni	Mn	Si	P	Cu	Other
C	-	-	58.6	25.7	12.2	0.2	1.4	1.9
G	-	-	54.2	23.5	19.0	0.8	1.6	0.9
K	-	-	70.6	5.4	20.6	0.5	1.7	1.3
RX12	Excluding Fe	-	90.8	1.0	5.8	0.2	0.7	1.5
	Including Fe	42.3	52.4	0.6	3.3	0.1	0.4	0.9

Table 46: Mean composition of the largest 25 % of clusters in Alloys C, G, K, and RX12.

The authors in [129] predicted that, amongst others, the G ($\text{Mn}_6\text{Ni}_{16}\text{Si}_7$) and T6 ($\text{Mn}_2\text{Ni}_3\text{Si}$) phases are thermodynamically stable in similar alloy systems. None of the alloys in this study were found to have clusters that had average compositions which matched the stoichiometry of these phases. However, this may be because the simulations assumed thermodynamic equilibrium and a system that only contained Fe, Mn, Ni, Si, and Cu. The clusters in Alloy K had a stoichiometry that is approximately $\text{Ni}_3\text{Si}/\text{Mn}$. The L_{12} type structure is a crystal structure which is known to have a stoichiometry of A_3B and was predicted to be thermodynamically stable in the Ni and Si-rich region of the Ni-Mn-Si ternary phase diagram by [129]. If the measured level of Fe within the clusters from RX12 is accurate, the clusters have a stoichiometry that is similar to FeNi .

2.3.5 Effect of Nominal Alloy Composition

The systematic variations in the nominal compositions of the alloys allowed the effects of nominal composition on cluster composition to be investigated. Alloys C and G had the same nominal composition of most elements, but Alloy G contained 1.57 at.% less Ni than Alloy C. The effect this change in nominal composition had on detected cluster composition was that the clusters in Alloy C contained higher levels of Ni and lower levels of Si than the clusters detected in Alloy G.

Alloy K contained a much lower nominal level of Mn (0.24 at.%) than Alloy C (1.90 at.%). The Mn content of the clusters in Alloy K were found to contain much less (~ 20 at.%) Mn than the clusters that were detected in Alloy C. Both the Ni and Si content of clusters in Alloy K was observed to increase from the Ni and Si levels calculated in clusters in Alloy C.

2.4 Mechanical Property Changes

The square root of measured cluster volume fraction of each alloy was plotted against the hardness change measured in each alloy after irradiation (Figure 101). There is a trend for

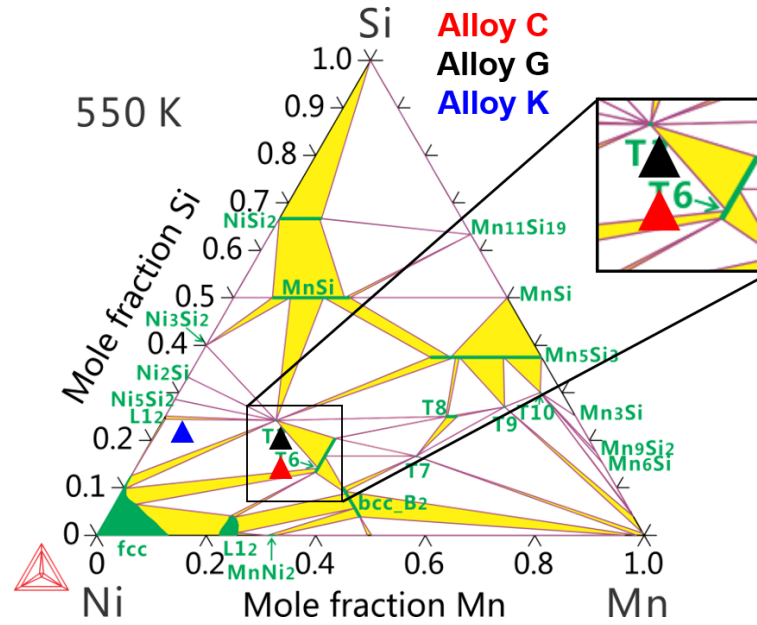


Figure 100: Gibbs triangle showing the mean composition of the largest quartile of clusters detected in Alloys C, G, and K. The figure was adapted from [129] and shows the phases that are predicted to be thermodynamically stable at 550 K. Adapted and reproduced with permission from [129]. Copyright © 2014 Published by Cambridge University Press.

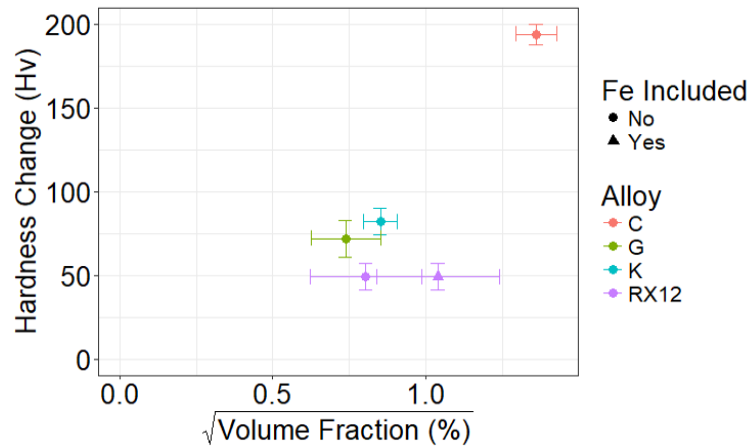


Figure 101: Plot of hardness change vs. $\sqrt{V_f}$ of clusters detected in neutron-irradiated Alloys C, G, K, and RX12. The calculated $\sqrt{V_f}$ is shown for RX12 both including and excluding Fe in the cluster calculations. Hardness data were supplied by collaborators at UCSB.

increasing observed hardness changes with increasing detected cluster $\sqrt{V_f}$ for Alloys C, G, and K. Alloy RX12 does not appear to follow this trend and had a higher measured cluster $\sqrt{V_f}$ than Alloys G and K. However, the majority of clusters detected in Alloy RX12 had formed on heterogeneous nucleation sites. Since both datasets for RX12 contained dislocations, a sampling bias may have led to a calculated cluster $\sqrt{V_f}$ for this alloy that is an overestimate of the true cluster $\sqrt{V_f}$ present.

2.5 Effect of Tip Composition On Cluster Volume Fraction

To investigate whether tip-to-tip compositional variations had an effect on detected cluster volume fraction, measured tip composition was plotted against detected cluster V_f (Figure 102). Increasing tip composition of Mn ($p < 0.001$) and P ($p < 0.001$) were found to significantly predict linear increases in the detected cluster V_f .

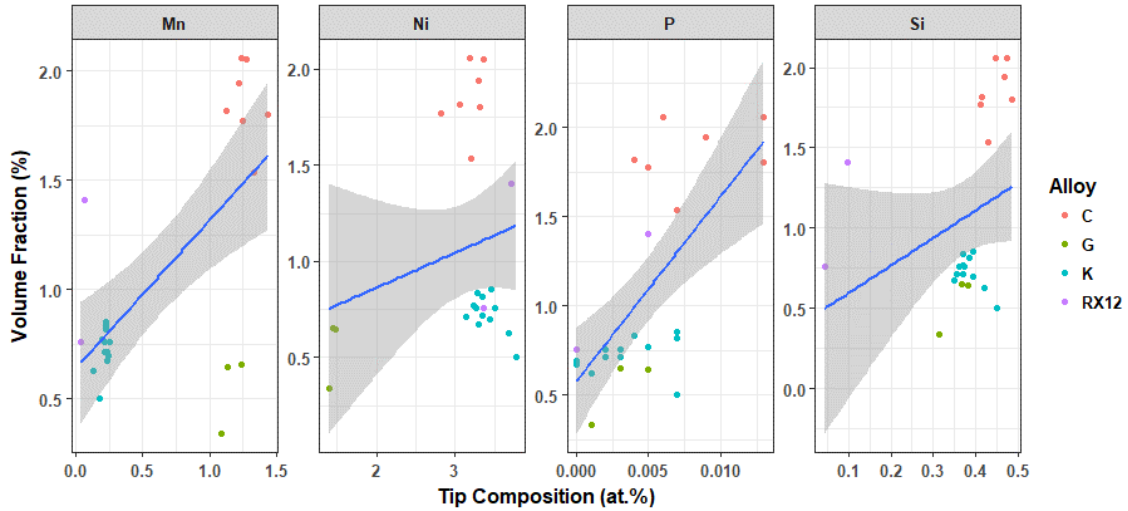


Figure 102: Plot of Mn, Ni, P, and Si tip composition vs measured cluster V_f . Linear models with 95 % confidence intervals are also shown.

However, plotting tip “Ni + Mn” and “Ni + Mn + Si” composition against detected cluster volume fraction were both found to improve the fit of the linear model (Figure 103).

The dependence of detected cluster volume fraction on tip composition indicates that, not only does composition vary from tip-to-tip, but that the clustering behaviour also varies from tip-to-tip.

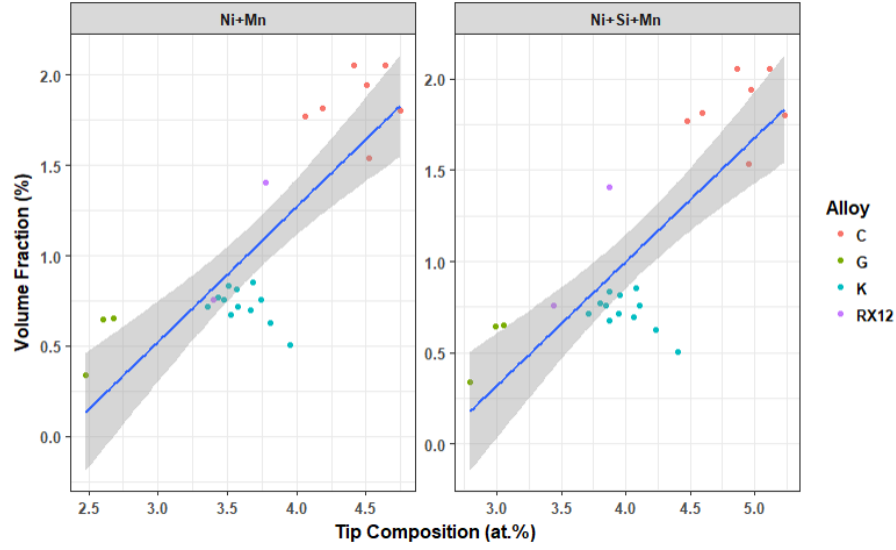


Figure 103: Plot of tip Ni + Mn and Ni + Mn + Si composition vs measured cluster V_f . Linear models with 95 % confidence intervals are also shown.

3 Summary

Grain boundaries in neutron-irradiated steels were analysed via atom probe tomography. The levels of segregation were found to vary from grain boundary to grain boundary within Alloy C. The grain boundary in Alloy K was found to have a higher Γ_{Ni} level than the grain boundaries in Alloy C despite both alloys containing the same nominal Ni level.

Clusters enriched in Ni, Mn, and Si were detected in all four alloys that had been subjected to neutron irradiation, despite some alloys containing very low levels of Mn and Si. The composition of the detected clusters was found to vary with the nominal composition of the alloys.

The hardness change observed for each alloy appeared to have a dependence of the measured cluster $\sqrt{V_f}$. The cluster volume fraction was found to be dependent on “Ni + Mn + Si” composition.

The clusters detected in RX12 are believed to contain Fe, whilst the Fe in the clusters detected in Alloys C, G, and K is believed to be the result of trajectory aberrations.

Chapter VIII

Complementary Grain Boundary Analyses

This chapter shows how complementary use of transmission Kikuchi diffraction (TKD) and atom probe tomography (APT) can provide a more holistic description of a grain boundary. It is demonstrated how the five macroscopic degrees of freedom of a grain boundary can, in theory, be determined from TKD data alone. The necessary assumptions and methodology for determining the five degrees of freedom from the TKD data are discussed.

This method is then applied to determine the five macroscopic degrees of freedom of a grain boundary from an alloy (Alloy C) that had been irradiated to a fluence of 1.4×10^{20} n/cm² at 290 °C and a flux of 3.6×10^{12} n/cm²s in the Advanced Test Reactor 2 (ATR-2) experiment by the University of California, Santa Barbara (UCSB). This grain boundary is then analysed using a LEAP-4000X HR and the chemistry of the interface is studied. The samples were prepared at the Centre for Advanced Energy Studies (CAES), Idaho National Laboratory, USA.

1 Calculating A Grain Boundary's Five Degrees Of Freedom

The five macroscopic degrees of freedom of a grain boundary completely describe the structure of the grain boundary [255]. The five degrees of freedom of a grain boundary in a model steel have previously been determined using a combination of TKD and APT [77]. However, this method requires the use of a specialist specimen holder. If some assumptions are made regarding the specimen, all five macroscopic degrees of freedom of the grain boundary can be determined from the TKD data alone.

1.1 Determining Misorientation Angle And Rotation Axis

The misorientation angle and rotation axis of the grain boundary can be calculated from the TKD data using the same methods that are commonly used on EBSD data. This can routinely be performed with software such as the open source MTEX.

1.2 Calculating Grain Boundary Plane

Determining the plane of the grain boundary in each crystal in a TKD map is possible if it is assumed that the grain boundary does not deviate through the length of the lift-out section that TKD is performed on. If a lift-out bar contains a continuous, straight section of a grain boundary approximately $20\ \mu\text{m}$ - $25\ \mu\text{m}$ in length, it is reasonable to assume that the grain boundary is straight in the z -direction of a thinned ($200\ \text{nm}$ - $750\ \text{nm}$) section of the bar (Figure 104). If this assumption is made, and the crystal is cubic in nature, the plane of the boundary normal in each crystal can be determined.

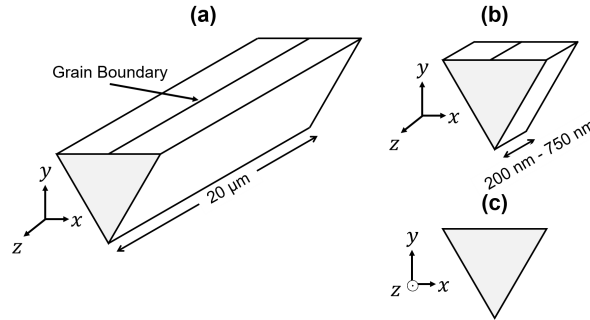


Figure 104: Schematic diagrams of (a) a lift-out bar containing a section of a grain boundary that appears straight on the polished surface of the material, (b) a thinned section of the lift-out bar containing the grain boundary, and (c) the section from (b) viewed end on.

To determine the plane normal of the grain boundary in each grain, it is first necessary to ascertain the crystallographic directions in Grains A ($\vec{v}_A$) and B ($\vec{v}_B$) which correspond to the y -direction in the TKD map (Figure 105 (a)). Once these directions have been determined, the grain boundary plane normals of Grain A ($\vec{v}'_A$) and Grain B ($\vec{v}'_B$) can be calculated by applying rotation matrices to the original vectors (Figure 105 (b) & (c)). As it is assumed that the grain boundary does not deviate in the z -direction, this component of $\vec{v}_A$ and $\vec{v}_B$ does not change, so the rotation can be applied around the z -axis.

When $0 < \theta \leq 90$ and Grain A is the uppermost grain in the TKD map, the equations and

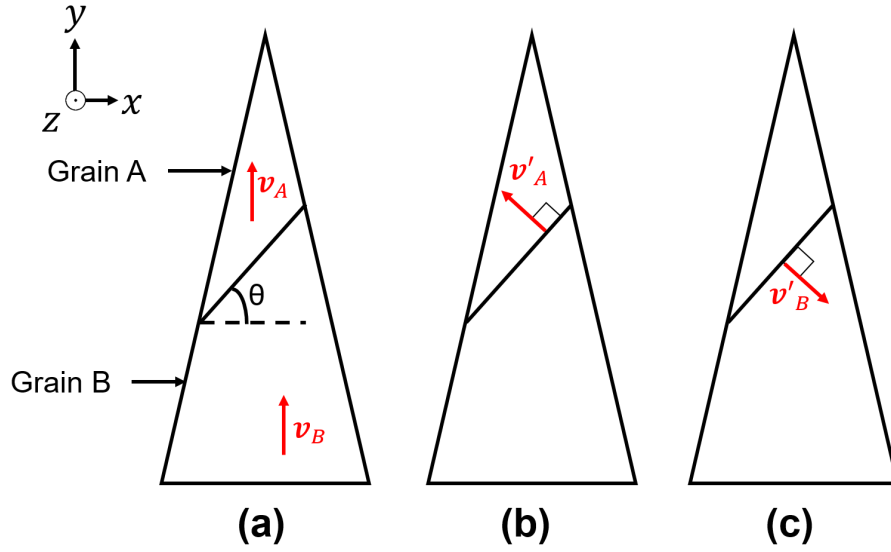


Figure 105: Schematic diagram showing (a) the vectors which describe the crystallographic directions in Grain A and Grain B with respect to the y -axis in the TKD map, (b) the grain boundary plane normal in Grain A ($\vec{v}'_A$) and (c) the grain boundary plane normal in Grain B ($\vec{v}'_B$).

rotation matrices used to calculate $\vec{v}'_A$ and $\vec{v}'_B$ are:

$$\vec{v}'_A = \mathbf{R}(\theta)\vec{v}_A = \begin{bmatrix} \cos \theta & -\sin \theta & 0 \\ \sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_A \\ y_A \\ z_A \end{bmatrix} = \begin{bmatrix} x'_A \\ y'_A \\ z'_A \end{bmatrix} \quad (25)$$

$$\vec{v}'_B = \mathbf{R}(\theta + 180)\vec{v}_B = \begin{bmatrix} \cos(\theta + 180) & -\sin(\theta + 180) & 0 \\ \sin(\theta + 180) & \cos(\theta + 180) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_B \\ y_B \\ z_B \end{bmatrix} = \begin{bmatrix} x'_B \\ y'_B \\ z'_B \end{bmatrix} \quad (26)$$

however, when $90 < \theta \leq 180$, the equations used are:

$$\vec{v}'_A = \mathbf{R}(\theta + 180)\vec{v}_A = \begin{bmatrix} \cos(\theta + 180) & -\sin(\theta + 180) & 0 \\ \sin(\theta + 180) & \cos(\theta + 180) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_A \\ y_A \\ z_A \end{bmatrix} = \begin{bmatrix} x'_A \\ y'_A \\ z'_A \end{bmatrix} \quad (27)$$

$$\vec{v}'_B = \mathbf{R}(\theta) \vec{v}_B = \begin{bmatrix} \cos(\theta) & -\sin(\theta) & 0 \\ \sin(\theta) & \cos(\theta) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_B \\ y_B \\ z_B \end{bmatrix} = \begin{bmatrix} x'_B \\ y'_B \\ z'_B \end{bmatrix} \quad (28)$$

where θ is the angle between the grain boundary and the x -axis of the TKD map (Figure 105 (a)).

1.3 Application To Theoretical TKD Data

To demonstrate the feasibility of the above method, the theoretical case in Figure 106 is considered. The angle (θ) between the grain boundary and the x -axis in Figure 106 is 45° . $\vec{v}_A$, the crystallographic direction in Grain A which corresponds to the y -axis in the TKD map, is $\begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix}$, whilst $\vec{v}_B$ is $\begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix}$.

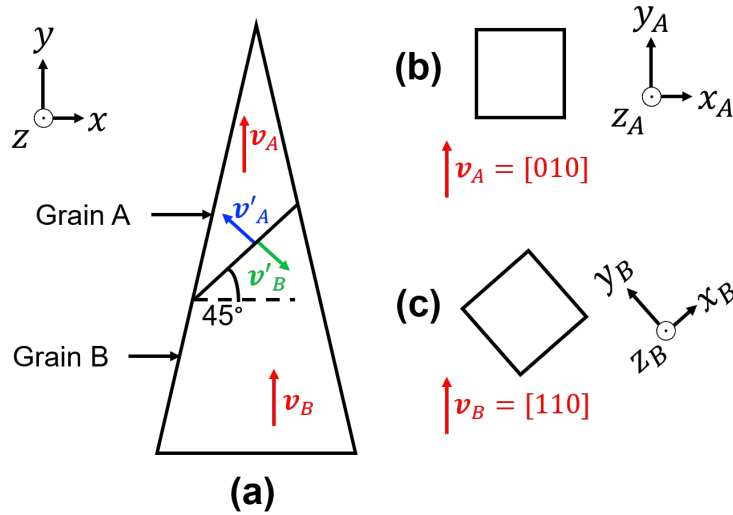


Figure 106: Schematic diagram showing (a) the sample that TKD was performed on, including the vectors $\vec{v}_A$, $\vec{v}_B$, $\vec{v}'_A$, and $\vec{v}'_B$. (b) the orientation of the unit cell of Grain A along with the crystallographic axes which define the coordinate system of the unit cell and (c) the orientation of the unit cell along with the crystallographic axes which define the coordinate system of the unit cell of Grain B.

The misorientation angle and rotation axis were calculated to be 45° and $\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$, respectively. Meanwhile, as $\theta = 45^\circ$, the vectors $\vec{v}'_A$ and $\vec{v}'_B$ were calculated by applying Equations 25 and 26. Equations 29 and 30 show that the $\vec{v}'_A$ was determined to be $\frac{-\sqrt{2}}{2} \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix}$ and $\vec{v}'_B$ was calculated to be $\frac{-\sqrt{2}}{2} \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix}$. These are equivalent to the $[\bar{1} \ 1 \ 0]$ and $[0 \ \bar{1} \ 0]$ directions, respectively.

$$\vec{v}'_A = \mathbf{R}(45)\vec{v}_A = \begin{bmatrix} \cos(45) & -\sin(45) & 0 \\ \sin(45) & \cos(45) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} = \begin{bmatrix} -\frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} \\ 0 \end{bmatrix} = \frac{\sqrt{2}}{2} \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix} \quad (29)$$

$$\vec{v}'_B = \mathbf{R}(45 + 180)\vec{v}_B = \begin{bmatrix} \cos(225) & -\sin(225) & 0 \\ \sin(225) & \cos(225) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 \\ -\frac{\sqrt{2}}{2} \\ 0 \end{bmatrix} = \frac{\sqrt{2}}{2} \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix} \quad (30)$$

In a cubic crystal, lattice planes described by the Miller indices (hkl) will have a plane normal of $[hkl]$ [256]. The grain boundary in Figure 106 is parallel to the plane $(\bar{1} 1 0)$ in Grain A and parallel to the $(0 \bar{1} 0)$ plane in Grain B. Since these planes are equivalent to the plane normals $\vec{v}'_A$ and $\vec{v}'_B$ that were calculated by applying the rotation matrices to $\vec{v}_A$ and $\vec{v}_B$ (Equation 29 and Equation 30), the applicability of the above method is demonstrated.

2 Application To A Real Grain Boundary

2.1 TKD Data

Figure 107 (a) shows a TKD map from a thinned section of a lift-out bar. A grain boundary, indicated by change in the misorientation between regions in the map, can be seen. FIB milling was used to incorporate the grain boundary at the centre of a volume (Figure 107 (b)). Annular milling was then used to position the grain boundary within a volume that could undergo APT analysis. TKD maps were taken of this final specimen to ensure that the grain boundary was contained within the volume (Figure 107 (c)).

To demonstrate how the method outlined above can be applied to determine the five macroscopic degrees of freedom of a real grain boundary, the grain boundary in Figure 107 (c) was used. However, as the axes of the TKD map are orientated differently with respect to the sample when compared to example above (Figure 106), the rotation matrices that are required to calculate $\vec{v}'_A$ and $\vec{v}'_B$ are slightly different.

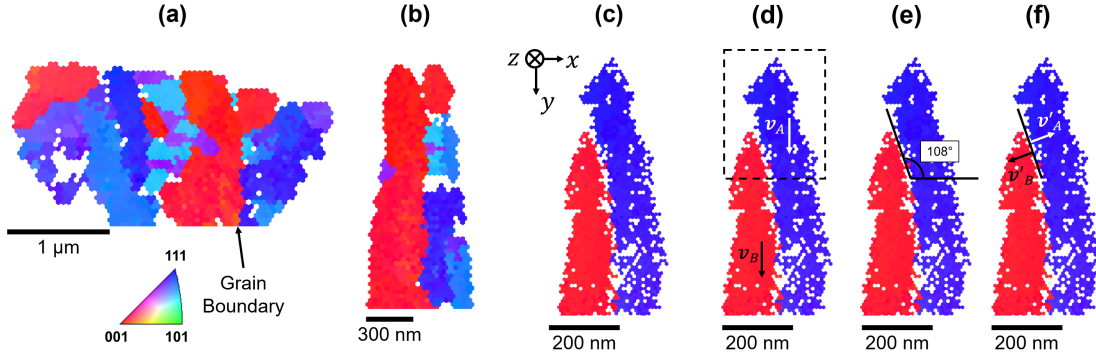


Figure 107: Diagram showing TKD maps for (a) thinned region of a FIB lift-out bar, (b) section of the lift-out containing a grain boundary, (c) the final tip shape prior to APT, (d) the region of the grain boundary for which the grain boundary plane was calculated, (e) the measured angle for θ and (f) the vectors $\vec{v}_A$ and $\vec{v}_B$ that describe the grain boundary plane normal in each grain.

2.2 Determining Misorientation Angle and Rotation Axis

The misorientation angle was determined to be 55.1° and rotation axis was found to be $[1, \bar{10}, 0]$.

2.3 Determining Grain Boundary Plane in Each Crystal

The plane of the boundary was determined for the region shown in Figure 107 (d), since this is the part that would be first characterised during the APT experiment. First, the angle between this section of the grain boundary and the x -axis was determined to be $108^\circ \pm 1^\circ$ (Figure 107 (e)).

Secondly, $\vec{v}_A$ and $\vec{v}_B$ were determined using MTEX 5.0.3. As the axes are with respect to the sample as shown in Figure 107 (c), $\vec{v}_A$ and $\vec{v}_B$ are orientated as shown in Figure 107 (d). The unit vector for $\vec{v}_A = [-0.7363, -0.0895, 0.6707]$, whilst the unit vector for $\vec{v}_B = [-0.0161, 0.6297, -0.7767]$. When rounded to the greatest divisor, these correspond to the Miller indices $\vec{v}_A = [\bar{10}, \bar{1}, 9]$ and $\vec{v}_B = [0, 9, \bar{11}]$.

Finally, a rotation matrix was applied to $\vec{v}_A$ and $\vec{v}_B$ to calculate $\vec{v}'_A$ and $\vec{v}'_B$, respectively. As $90 < \theta \leq 180$, $\vec{v}'_A = \vec{v}_A \mathbf{R}(-\theta)$ and $\vec{v}'_B = \vec{v}_B \mathbf{R}(180 - \theta)$ for the axes system in Figure 107 (c), with $\theta = 108^\circ$. The unit vectors were found to be $\vec{v}'_A = [0.1424, 0.7279, 0.6707]$ and $\vec{v}'_B = [-0.6039, 0.1792, -0.7767]$. When rounded to the greatest common divisor, the Miller indices were found to be $\vec{v}'_A = [2, 11, 10]$ and $\vec{v}'_B = [\bar{7}, 2, 9]$.

Combining this information with the misorientation angle and rotation axis that had been

previously calculated, means that all five macroscopic degrees of freedom of the grain boundary have been determined. The grain boundary structure can be defined as $55.1^\circ [1, \bar{10}, 0], (2, 11, 10)$ and $(\bar{7}, 2, \bar{9})$.

3 Atom Probe Analysis

After TKD, the specimen in Figure 107 (f) was successfully analysed via APT. Atom maps for this dataset are shown in Figure 108. The segregation of Mn, Ni, Si, and P to a planar feature indicates the presence of a grain boundary.

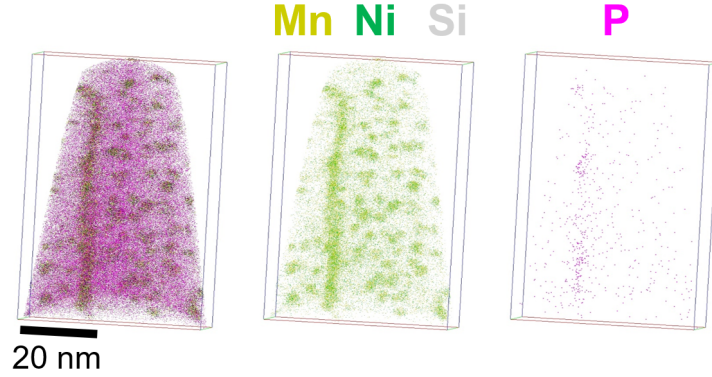


Figure 108: Atom maps for the the needle shown in Figure 107 (f). Mn, Ni, Si, and P segregation can be observed to a planar feature (Run 7555).

Several regions of the boundary were extracted and the methods described in Chapter V Section 4.6 were applied to each volume. Ni was used as the element for calculating the threshold values used to define the start and end of the grain boundary. The grain boundary was found to have a width of $2.6 \text{ nm} \pm 0.0 \text{ nm}$. The grain boundary regions defined by the Poisson Method were then extracted and cluster searches were carried out within these sub-volumes. Cluster searches determined a cluster V_f of $5.4 \% \pm 0.2 \%$. The calculated Gibbsian interfacial excess values and composition of the grain boundary is shown in Table 47.

Element	Γ_i (<i>atoms/nm²</i>)	Composition (at.%)
C	0.97 ± 0.01	0.53 ± 0.02
Cr	0.19 ± 0.02	0.15 ± 0.01
Cu	0.14 ± 0.03	0.10 ± 0.01
Fe	-21.88 ± 0.86	87.38 ± 0.13
Mn	6.12 ± 0.18	3.49 ± 0.05
Mo	0.71 ± 0.05	0.49 ± 0.00
Ni	11.24 ± 0.53	6.59 ± 0.07
P	0.22 ± 0.01	0.09 ± 0.01
Si	2.28 ± 0.12	1.19 ± 0.01

Table 47: Calculated Gibbsian interfacial and grain boundary composition (at.%) for the grain boundary region.

4 Discussion

Combining TKD with APT allows for a more holistic description of the grain boundary. The five macroscopic degrees of freedom describe the grain boundary's structure, whilst APT allows the chemistry of the boundary and the spatial distribution of elements to be determined.

4.1 Limitations

One of the main limitations of the method used to determine the grain boundary structure is the difficulty in determining the error in the grain boundary plane calculations. The angular resolution of each measurement in a TKD image is around 1° [225]. However, each grain will contain many measurements that may be slightly different to one another. These slight differences can be accounted for by averaging the measurements across the grain. Once the measurements have been averaged, the Miller index that corresponds to the average orientation can be determined. It has been suggested that doing this with a maximum Miller index of 6 leads to an error of about 4° in the Miller indices that are used to describe each grain [77]. However, the authors do not describe how they came to such a conclusion.

Increasing the maximum Miller index is likely to increase the precision and accuracy of the measurement, reducing the error. Therefore, a maximum Miller index of 11 was used to describe the orientation each grain in this study. However, as it is not clear by how much the error will be reduced, it is assumed that the error in measured orientation of each grain is 4° . If the error in each grain's orientation is 4° , then the error of the plane calculation in each grain will be double this.

This error should be combined with the error in the measurement of the angle between the grain boundary and the x -axis in the TKD map; this is estimated to be $\pm 1^\circ$. This results in an approximate error of $\pm 10^\circ$ in the calculated grain boundary plane normal in each crystal.

4.2 Grain Boundary Plane Orientation

Grain boundaries may, in order to reduce their associated surface energy, display a preference for low index planes [257, 258]. Whilst the grain boundary planes determined in the specimen above are not known low index planes, one of the grain boundary planes (2, 11, 10) is misorientated from the low index (0,1,1) plane by around 8° , which is within the estimated error of the measurement. However, the $(\bar{7}, 2, \bar{9})$ plane is misorientated from the $(\bar{1}, 0, \bar{1})$ plane by 12° which is larger than the estimated error of the measurement. It may be that this plane is orientated along another plane that is associated with low energy, such as (3,1,3), or this grain boundary may not be along a low index plane in this crystal.

5 Summary

A novel method, which allows determination of all five macroscopic degrees of freedom that describe a grain boundary, has been described. This methodology is unique in that only TKD data is used to determine the grain boundary's structure. The method was applied to a neutron-irradiated steel specimen that contained a grain boundary. Firstly, the macroscopic degrees of freedom of the boundary were determined from a TKD map. Atom probe analysis of the grain boundary was then performed. This complementary approach allowed the chemical and structural properties of a grain boundary from a neutron-irradiated steel to be found.

Chapter IX

Conclusions

The work presented in this thesis focuses on the use of APT to characterise a series of model RPV alloys. In an attempt to investigate the effect of systematic compositional variations, 19 model alloys were thermally-aged for over 30,000 hours; in addition, a subset of these alloys were exposed to neutron irradiation. The effect that nominal composition had on mechanical property changes was studied, and correlated to the effect of composition on nanostructural developments. The main conclusions of this work are outlined as follows:

Quantitative Literature Comparison

By carefully assessing data from the peer-reviewed literature, using a variety of statistical analysis techniques, increased levels of Cu, Ni, Si, and P were found to be correlated with larger deleterious changes in mechanical properties in high-Cu alloys that were subjected to neutron irradiation. However, because of the more recent implementation of low-Cu alloys, there is currently a scarcity of available data from these materials within the literature. There were also a shortage of studies which systematically varied alloy composition, and there was a lack of consistency as to which experimental parameters were reported within the peer-reviewed literature.

Analysis of RPV Steels Using LEAP-5000 XR Atom Probe

A series of experiments were conducted to ensure that data collected using the LEAP-5000XR was directly comparable to data which was gathered using the LEAP-3000X HR. Solute cluster distributions detected in data collected using the LEAP-5000XR were observed to have comparable compositions and volume fractions to the clusters detected in LEAP-3000X HR data. However, due to the enhanced detection of small clusters, a slightly higher overall number density of features were observed in LEAP-5000XR data. This indicates that the LEAP-5000XR is more sensitive at detecting early stage clustering, and that number density measurements are not

directly comparable between the two instruments, particularly when a high number density of very small clusters are present.

In an attempt to determine the experimental conditions which would maximise data quality collected using the LEAP-5000XR, a range of experimental conditions were applied to analyse a model RPV steel. Laser mode was found to lead to poor data quality. Meanwhile, when voltage-pulsing mode was used, higher pulse fractions and lower operating temperatures were found to improve the accuracy of compositional measurements of Cu and P. However, these operating conditions also increased the likelihood of specimen failure prior to 1,000,000 ions being detected. In this study, the benefits of higher quality data was deemed to outweigh the additional time required to prepare specimens.

Automated Detection of Edge Clusters

A new method implementing the α -hull algorithm was developed for automatically and reproducibly identifying clusters intersected by the edge of the volume analysed during atom probe experiments. Simulations highlighted the importance of accounting for edge clusters in calculations. The α -hull method enables edge clusters to be identified in real datasets that are complex in shape. This approach is readily implementable and significantly improves the accuracy of solute cluster analyses.

Reporting Grain Boundary Segregation Observed Using Atom Probe Tomography

A systematic method was developed to calculate Gibbsian interfacial excess values. The method defines the beginning and end of the interface region based on the distribution of solute within the grains adjacent to the interface. This has reduced the number of user inputs required to perform these calculations, making measurements more easily reproducible.

However, issues were observed in using Gibbsian interfacial excess measurements to describe grain boundary segregation in complex systems. In neutron-irradiated alloys, segregation was found to be non-homogeneous across the interface. An alternative procedure was developed to report APT analyses of grain boundary in RPV steels. The potential benefits of this method are that some of the shortcomings of the Gibbsian interfacial excess method are overcome, and that a quantitative measure of solute clustering on the interface can be reported.

Thermally-Aged Alloys

Vickers Hardness tests revealed there was no significant hardness increase in the majority of model alloys after over 30,000 hours of thermal ageing. However, hardening was observed in Alloy F after just 11,688 hours of ageing. Alloy F contained high nominal levels of Cu. After the third ageing cycle, several alloys did display a significant increase in hardness from their as-received state. All of these alloys had high nominal Ni contents.

APT data revealed that precipitates were present in the Alloy F samples which had exhibited an increase in Vickers hardness. Ageing temperature was observed to affect the number densities and sizes of the precipitates, with higher number densities of smaller precipitates present at lower ageing temperatures. Ageing temperature was not found to significantly affect mean precipitate composition. However, a dependence of composition on precipitate nucleation site was displayed.

Alloy I had high nominal levels of Ni, Mn, and Si. APT revealed the formation of Mn-Ni-Si-rich precipitates at heterogeneous nucleation sites after 20,733 hours of thermal ageing. This is evidence that these features are thermodynamically stable at the temperatures used in this study. These precipitates had a composition that was similar to the G-phase, but also reflected the initial matrix concentrations of Ni, Mn, and Si. Increasing ageing temperature was correlated with a reduction in the Si content of the precipitate compositions.

Neutron-Irradiated Alloys

Four alloys with low nominal Cu contents were characterised with APT after exposure to neutron irradiation. All four alloys exhibited a large increase in hardness after neutron irradiation and clustering was observed in all four alloys. However, three of these alloys (C, G, K) that were subjected to thermal ageing did not display a significant increase in hardness after over 30,000 hours of ageing at 330°C.

Cluster nucleation site was not observed to have a strong effect on precipitate composition, apart from clusters nucleated in carbides. However, nominal alloy composition was found to affect cluster composition, with a lower nominal composition of Mn resulting in clusters which contained lower Mn levels.

The measured cluster compositions were compared with those predicted by thermodynamic models in [129]. The measured compositions differed from the predicted compositions, indicating that the thermodynamic state used in the models is different to that experienced during the

irradiation conditions used in this study.

Multiple grain boundary analyses were conducted on Alloy C. These revealed that Mn, Ni, Si, and P segregated to the grain boundaries. However, the magnitude of these elements at the interface varied from dataset-to-dataset. The magnitude of Mn and C at grain boundaries was influenced by the proximity of carbides to the analysed regions. Meanwhile, Ni was observed to exhibit stronger segregation to grain boundaries in Alloy K than in Alloy C, despite Alloy C containing higher nominal levels of Ni.

There was evidence that the clusters detected in RX12 were not as significantly affected by the trajectory aberrations present during the evaporation of clusters as the other irradiated alloys. If true, the clusters in RX12 had a similar composition to Fe-Ni.

Complementary GB Analyses

An original sample preparation method for consistently preparing grain boundaries within a specimen ready for APT analysis was presented. The use of a novel FIB lift-out/milling protocol, combined with iterative TKD/FIB milling, also allowed the orientation of the grains to be determined. A technique that utilises the TKD data to calculate all five macroscopic degrees of freedom of a grain boundary was presented. This information was combined with APT analysis of the interface to provide a more complete description of the grain boundary. To enhance the understanding of grain boundary segregation phenomena in complex systems, this more detailed description is required.

Chapter X

Future Work

Despite the work conducted in this thesis, there are several unresolved issues which should be investigated in the future.

Effect of Thermal Ageing and Neutron Irradiation on Low-Cu Alloys

The quantitative analysis of the literature revealed a lack of available data for low-Cu alloys that had been subject to long-term thermal ageing or neutron irradiation. The effect of systematically exposing low-Cu alloys to elevated temperatures and a variety of neutron fluxes and fluence needs to be investigated in order to create and validate models that accurately predict mechanical property changes.

A study which exposes two alloys, of the same composition, to thermal ageing and neutron irradiation may be used to determine how similar the features which form during neutron irradiation are to the phases which form in the thermally-aged experiments. These results may be used to inform predictive thermodynamic models.

Mn-Ni-Si Precipitate Development in Thermally-Aged RPV Steels

Mn-Ni-Si-rich precipitates were observed in a low-Cu alloy after 20,733 hours. It remains to be seen whether the “late-blooming” effect of a rapid increase in the volume fraction of these features will occur. The evolution in the hardness of Alloy I should be closely monitored in the future.

APT analyses of Alloy J, which exhibited an increase in hardness after the third ageing cycle, should be conducted to determine if Mn-Ni-Si-rich solute clusters are responsible from this increase.

The determination of whether Mn-Ni-Si-rich precipitates form an ordered structure may be possible from APT datasets if enough crystallographic information is present. TEM studies may also be conducted to investigate the structure of Mn-Ni-Si-rich precipitates. Data from these

experiments could then be utilised to further notify predictive models.

Effect of Grain Boundary Structure on Segregation

A systematic study of the effect of grain boundary structure on segregation could be undertaken in an alloy which has undergone a shift in its ductile-to-brittle-transition temperature as a result of thermal ageing. The use of complementary TKD and APT would permit the effects of grain boundary plane and misorientation on interfacial segregation to be investigated, and possibly differentiated, at multiple time-points.

Energy dispersive X-ray studies within a high resolution scanning transmission electron microscope may permit the width of the region subjected to solute enrichment around a grain boundary to be accurately determined.

Improvements in The Detection of Edge Clusters

Whilst an automated way to identify edge clusters has been developed, there is scope for improvement. One of the shortcomings of the method is the incorrect identification of some non-edge clusters as edge. It may be possible to reduce the rate of this phenomena by modelling the clusters as non-cuboidal in shape. The modelling of the clusters as cuboids overestimates their volume, particularly in the case of non-spherical clusters.

Reporting Grain Boundary Segregation Observed Using Atom Probe Tomography

The complexity of segregation to interfaces in irradiated alloys has highlighted the weaknesses in the use of Gibbsian interfacial excess as a parameter to describe grain boundary segregation. A quantitative method for describing non-homogeneous segregation to an interface, which is readily reproducible and requires limited user input, would be highly desirable.

Chapter XI

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Chapter XII

Appendix

1 Hardness Measurements

Alloy	Temp. (°C)	Ageing Time (h)	Avg. Hardness (Hv)	Standard Dev.
A	330	20732	220.6	5.4
A	365	20732	219.0	6.8
A	405	20732	226.6	6.3
B	330	20733	148.5	3.5
B	365	20733	150.0	2.6
B	405	20733	149.3	4.7
C	330	20732	301.6	4.8
C	365	20732	301.7	3.1
C	405	20732	306.0	5.0
D	330	20733	312.3	6.6
D	365	20733	319.2	3.6
D	405	20733	316.0	2.8
E	330	20733	249.5	4.2
E	365	20733	252.6	5.7
E	405	20733	254.9	4.7
F	330	20732	319.7	4.4
F	365	20732	336.4	5.3
F	405	20732	299.8	4.8
G	330	20732	259.8	7.7
G	365	20732	255.2	8.2
G	405	20732	255.8	3.0
H	330	20732	220.4	6.9
H	365	20732	214.9	7.0
H	405	20732	221.7	7.2
I	330	20733	316.7	5.4
I	365	20733	312.6	5.2
I	405	20733	306.0	4.8
J	330	20733	251.9	4.8
J	365	20733	252.2	4.0
J	405	20733	252.2	4.7
K	330	20732	258.8	6.7
K	365	20732	253.9	8.3
K	405	20732	260.2	7.9

Table 48: Hardness measurements for thermally-aged RPV steels. The average hardness was based on eight indents.

Alloy	Temp. (°C)	Ageing Time (h)	Avg. Hardness (Hv)	Standard Dev.
L	330	20733	232.7	8.7
L	365	20733	231.5	2.3
L	405	20733	237.5	4.4
M	330	20733	282.7	4.0
M	365	20733	281.8	6.3
M	405	20733	276.6	4.8
N	330	20733	146.9	3.7
N	365	20733	152.9	4.4
N	405	20733	149.8	1.6
O	330	20733	318.3	4.1
O	365	20733	318.0	5.8
O	405	20733	312.2	3.7
P	330	20733	156.4	4.9
P	365	20733	151.4	6.4
P	405	20733	149.1	3.4
Q	330	20733	229.7	5.6
Q	365	20733	236.4	5.6
Q	405	20733	232.6	2.9
R	330	20733	158.1	3.7
R	365	20733	165.1	2.8
R	405	20733	161.4	3.1
S	330	20733	267.8	6.3
S	365	20733	260.5	2.3
S	405	20733	263.6	6.5

Table 49: Hardness measurements for thermally-aged RPV steels. The average hardness was based on eight indents.

Alloy	Temp. (°C)	Ageing Time (h)	Avg. Hardness (Hv)	Standard Dev.
A	330	30116	219.4	5.0
A	365	30116	225.4	5.3
A	405	30116	227.3	3.2
B	330	30646	146.2	3.9
B	365	30646	148.7	3.7
B	405	30646	148.4	3.8
C	330	30116	300.3	2.8
C	365	30116	305.4	2.7
C	405	30116	307.4	5.5
D	330	30646	311.2	5.8
D	365	30646	319.4	9.0
D	405	30646	324.6	3.2
E	330	30646	245.0	5.5
E	365	30646	252.3	3.5
E	405	30646	256.9	5.2
F	330	30116	343.0	7.8
F	365	30116	331.9	6.7
F	405	30116	305.7	4.1
G	330	30116	258.5	4.2
G	365	30116	259.4	6.4
G	405	30116	259.7	4.2
H	330	30116	220.7	5.7
H	365	30116	220.5	7.2
H	405	30116	222.2	6.5
I	330	30646	315.7	7.2
I	365	30646	313.3	6.8
I	405	30646	313.0	10.0
J	330	30646	255.4	3.7
J	365	30646	261.2	3.7
J	405	30646	263.1	3.1
K	330	30116	256.9	6.9
K	365	30116	260.0	4.7
K	405	30116	264.0	4.1
L	330	30646	229.2	5.4
L	365	30646	233.9	6.5
L	405	30646	242.3	7.4

Table 50: Hardness measurements for thermally-aged RPV steels. The average hardness was based on eight indents.

Alloy	Temp. (°C)	Ageing Time (h)	Avg. Hardness (Hv)	Standard Dev.
M	330	30646	275.0	6.7
M	365	30646	271.9	4.4
M	405	30646	279.7	7.9
N	330	30646	146.9	5.2
N	365	30646	151.8	5.1
N	405	30646	152.3	2.7
O	330	30646	317.2	2.3
O	365	30646	317.2	2.4
O	405	30646	325.5	5.8
P	330	30646	155.1	4.4
P	365	30646	152.6	2.2
P	405	30646	152.8	4.2
Q	330	30646	232.1	2.5
Q	365	30646	233.8	4.5
Q	405	30646	239.7	5.6
R	330	30646	156.4	3.2
R	365	30646	163.2	3.8
R	405	30646	165.9	3.0
S	330	30646	269.8	6.0
S	365	30646	262.2	5.3
S	405	30646	272.3	7.3

Table 51: Hardness measurements for thermally-aged RPV steels. The average hardness was based on eight indents.

2 Experimental, Reconstruction, and Cluster Search Parameters

2.1 Thermally-Aged Specimens

Run	LEAP	Operating Temperature (K)	Pulse Fraction (%)	Pulse Frequency (kHz)	η	K_f	ICF	Ions	D_{max} (nm)	Order	N_{min}	L (nm)	E (nm)
3390	5000XR	50	25	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	7	30	0.25	0.25
3397	5000XR	50	25	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	8	30	0.25	0.25
3989	5000XR	50	25	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	7	33	0.25	0.25
4073	5000XR	50	25	200	0.37	4.5	1.65	Si Cu Ni Fm P	0.5	5	24	0.25	0.25
4076	5000XR	50	25	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	7	23	0.25	0.25
4108	5000XR	50	25	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	7	32	0.25	0.25
4386	5000XR	50	25	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	6	40	0.25	0.25
4388	5000XR	50	25	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	7	30	0.25	0.25
25498	3000X HR	50	25	200	0.37	4.6	1.65	Si Cu Ni Fm Mn P	0.5	7	20	0.25	0.25
25500	3000X HR	50	25	200	0.37	4.3	1.65	Si Cu Ni Fm Mn P	0.5	7	60	0.255	0.25
25827	3000X HR	50	20	200	0.37	5.1	1.65	Si Cu Ni Fm Mn P	0.5	5	17	0.25	0.25
25872	3000X HR	50	20	200	0.37	4.5	1.65	Si Cu Ni Fm P	0.5	7	70	0.25	0.25
25967	3000X HR	50	20	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	5	23	0.25	0.25
25971	3000X HR	50	20	200	0.37	5.1	1.65	Si Cu Ni Fm Mn P	0.6	7	30	0.3	0.3
26355	3000X HR	50	20	200	0.37	4.5	1.65	Si Cu Ni Fm P	0.5	7	30	0.25	0.25
26577	3000X HR	50	20	200	0.37	4.3	1.65	Si Cu Ni Fm Mn P	0.5	8	30	0.255	0.25
26867	3000X HR	50	20	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.5	7	30	0.25	0.25
27511	3000X HR	50	20	200	0.37	4.5	1.65	Si Cu Ni Fm Mn P	0.65	10	15	0.325	0.325

Table 52: Experimental conditions, reconstruction and cluster search parameters used in cluster searches in thermally-aged specimens. η is the detection efficiency of the instrument, k_f is the field factor, and ICF is the image compression factor. Fm is the name assigned to the Fe and Ni overlap peak at 29 Da.

2.2 Neutron-Irradiated Specimens

Run	LEAP	Operating Temperature (K)	Pulse Fraction (%)	Pulse Frequency (kHz)	η	K_f	ICF	Ions	D_{max} (nm)	Order	N_{min}	L (nm)	E (nm)
7470	4000X HR	55	20	200	0.37	4.3	1.65	Si Cu Ni Mn Fm	0.45	1	20	0.225	0.225
7472	4000X HR	55	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm	0.65	10	10	0.325	0.32
7474	4000X HR	55	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.55	3	35	0.275	0.275
7475	4000X HR	55	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.5	4	20	0.25	0.25
7488	4000X HR	55	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.5	3	19	0.25	0.25
7490	4000X HR	55	20	200	0.37	4.3	1.65	Si Cu Ni Mn Fm P	0.55	6	30	0.275	0.275
7513	4000X HR	55	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.55	3	40	0.275	0.275
7515	4000X HR	55	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.55	4	18	0.275	0.275
7518	4000X HR	55	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.6	6	16	0.3	0.3
7520	4000X HR	50	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.55	4	28	0.275	0.275
7535	4000X HR	50	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.5	3	20	0.25	0.25
7548	4000X HR	50	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.55	5	11	0.275	0.275
7550	4000X HR	55	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.6	4	11	0.3	0.3
7552	4000X HR	55	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.55	3	17	0.275	0.275
7555	4000X HR	55	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.6	10	17	0.3	0.3
7559	4000X HR	55	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.6	8	15	0.3	0.3
7563	4000X HR	55	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.55	5	20	0.275	0.275
7570	4000X HR	55	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.5	6	11	0.25	0.25
7575	4000X HR	50	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.55	2	30	0.275	0.275
7727	4000X HR	50	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.55	5	25	0.275	0.275
7728	4000X HR	50	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.5	5	20	0.25	0.25
7522 -Carbide	4000X HR	50	20	200	0.37	4.4	1.65	Si Cu Ni Fm P	0.7	4	35	0.35	0.35
7522 - Matrix	4000X HR	50	20	200	0.37	4.4	1.65	Si Cu Ni Mn Fm P	0.6	4	20	0.3	0.3
7541 - Matrix	4000X HR	50	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.6	7	18	0.3	0.3
7542 - Matrix	4000X HR	50	20	200	0.37	4.5	1.65	Si Cu Ni Mn Fm P	0.6	8	23	0.3	0.3

Table 53: Experimental conditions, reconstruction and cluster search parameters used in cluster searches in neutron-irradiated specimens. η is the detection efficiency of the instrument, k_f is the field factor, and ICF is the image compression factor. Fm is the name assigned to the Fe and Ni overlap peak at 29 Da.