

Effects of Nickel and Manganese on the Embrittlement of Low-Copper Pressure Vessel Steels



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To my loving parents,
Maureen and Michael Zelenty.

Chance favors only the prepared mind.
- Louis Pasteur

Abstract

Solute clustering is known to play a significant role in the embrittlement of reactor pressure vessel (RPV) steels. When precipitates form they impede the movement of dislocations, causing an increase in hardness and a shift in the ductile-brittle transition temperature. Over time this can cause the steel to become brittle and more susceptible to fracture. Thus, understanding precipitate formation is of great importance to the nuclear industry.

The first part of this thesis aims to isolate and better understand the thermal aging component of embrittlement in low copper, model RPV steels. Currently, relatively little is known about the effects of Ni and Mn in a low copper environment. Therefore, it is of interest to determine if Ni and Mn form precipitates under these conditions.

To this end, hardness measurements and atom probe tomography were utilized to link the mechanical properties to the microstructure. After 11,690 hours of thermal aging a statistically significant decrease in hardening was observed. Consistent with hardness measurements, no precipitates were present within the matrix of the thermally aged RPV steels. The local chemistry method was then applied to investigate the very early stages of solute clustering. Association was found to be statistically significant in both the thermally aged and as-received model RPV steels. Therefore, no apparent trends regarding the changes in solute association between the as-received and thermally aged RPV steels were identified.

Small, non-random clusters were observed at heterogeneous nucleation sites, such as carbide/matrix interfaces and grain boundaries, within the thermally aged material. The clusters found at the carbide/matrix interfaces were all rich in Mn and approximately 90-150 atoms in size. The clusters located along the observed low-angle grain boundary, however, were significantly larger (on the order of hundreds of atoms) and rich in Ni.

Lastly, copper-rich precipitates (CRPs) and Mn- and Ni-rich precipitates (MNPs) were observed within the cementite phase of a high copper and low copper RPV steel, respectively, following long term thermal aging. APT was used to characterize these precipitates and obtain more detailed chemical information. The presence of such precipitates indicates that a range of precipitation can take place within the cementite phase of thermally aged RPV steels.

The second part of this thesis aims to investigate the effects of ion irradiation on the microstructure of low copper RPV steels via APT. These steels were ion irradiated with 6.4 MeV Fe^{3+} ions with a dose rate of 1.5×10^{-4} dpa/s at 290°C. MNPs were observed in all five of the RPV steels analyzed. These precipitates were found to have nucleated within the matrix as well as at dislocations and grain boundaries. Using the maximum separation method these MNPs were extracted and characterized. Precipitate composition, size, volume fraction, and number density were determined for each of the five samples. Lastly, several grain boundaries were characterized.

Several emerging trends were observed within the samples: Ni content within the precipitates did not vary significantly once a threshold between 30-50% was reached; bulk Mn content appeared to dictate Si and Mn content within the precipitates; and samples low in bulk Ni content were characterized by a higher number density of smaller precipitates. Additionally, by regressing precipitate volume fraction against the interaction of Ni and Mn, a linear relationship was found to be statistically significant.

In the final part of this thesis, a new clustering algorithm is presented. This new technique (referred to as GEMA) utilizes a Gaussian mixture model to probabilistically distinguish clusters from random fluctuations in the matrix. This machine learning approach maximizes the data likelihood via expectation-maximization: given atomic positions, the algorithm learns the position, size, and width of each cluster. It was demonstrated that GEMA can outperform the maximum separation method in cluster detection accuracy when applied to realistically simulated data. Lastly, GEMA was successfully applied to real APT data.

Preface

The work presented in this doctoral thesis has been carried out at the Department of Materials, University of Oxford from October 2012 to August 2016, under the supervision of Prof. Michael Moody, Prof. George D. W. Smith 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:

Publications:

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Lastly, I would like to thank my partner, Andy Dahl. Thank you for your encouragement, patience, and love.

Acronyms

APT	Atom probe tomography
CCT	Continuous cooling transformation
CRP	Cu-rich precipitate
DBTT	Ductile-brittle transition temperature
dpa	Displacements per atom
EDX	Energy dispersive X-ray
FIB	Focused ion beam
ICF	Image compression factor
IVAS	Imago Visualization and Analysis Software
LBP	Late blooming phase
LEAP	Local electrode atom probe
LKMC	Lattice kinetic Monte Carlo
MC	Monte Carlo
MCP	Micro-channel plate
MNP	Mn- and Ni-rich precipitate
PAS	Positron annihilation spectroscopy
PWR	Pressurized water reactor
RPV	Reactor pressure vessel
SANS	Small angle neutron scattering
SSS	Solid solution strength
TEM	Transmission electron microscopy

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Chapter I

Introduction

In 2015, nuclear power plants (NPPs) provided 11.5% of the world's electricity (2,441 billion kWh) [1]. Due to population growth and improvements in standards of living, the demand for energy has been predicted to grow by 56% between 2010 and 2040 [2, 3]. Since nuclear power provides clean and reliable energy and is more resilient against international political tensions than oil, NPPs are an attractive way to fill the anticipated energy gap.

In recent years, there has been considerable opposition to the building of new nuclear power plants resulting in a decrease of new projects [4]. This opposition can, in part, be attributed to a decrease in public support, triggered by disasters such as the Fukushima incident in 2011. The skepticism of the general public is compounded by other safety concerns such as waste management. Due to the lack of NPP construction, the industry is focusing on extending the lifetime of existing reactors. Since the time needed to create new reactors is beginning to extend beyond the initial lifetime expectancy of many current reactors, this has become a necessity.

The reactor pressure vessel (RPV) is often considered the limiting factor in achieving long-term operation for commercial light water reactor (LWR) nuclear power plants. While other nuclear power plant components can be fixed or replaced with relative ease, RPVs are prohibitively expensive to replace.

Irradiation embrittlement is the leading cause of RPV degradation, thus limiting reactor lifetime [4]. There are several main factors that can influence the extent of this embrittlement, including: fluence, flux, and alloy composition [4]. Thermal aging is also known to exacerbate irradiation embrittlement [5, 6]. It is important to isolate the effects of thermal aging, as embrittlement resulting from thermal aging provides a zero-flux limit for irradiation embrittlement [6]. Additionally, isolating the effects of thermal aging is essential in order to fully understand any potential interaction effects that may be present. Lastly, significant portions of RPVs are located

within low irradiation environments. It is therefore essential to understand the effects of long-term thermal aging as it could potentially contribute significantly toward embrittlement in these regions.

This thesis is part of an ongoing collaboration with Rolls-Royce Plc. to analyze the microstructure and mechanical properties of low copper, model RPV steels that have been thermally aged. Currently, relatively little is known about the effects of nickel and manganese in the absence of copper. It is therefore of interest to determine if these solutes form precipitates under long-term thermal aging conditions in steels with low levels of copper. By systematically varying the amount of nickel and manganese in such steels, this research aims to determine the specific roles of these solutes in cluster formation. In this work a combination of hardness measurements and atom probe tomography (APT) are used to correlate the onset of clustering to changes in hardness, thus linking the microstructure and mechanical properties.

In parallel, in collaboration with University of California Santa Barbara (UCSB), an identical set of model RPV steels are analyzed using APT after being ion irradiated. The goal of this work is to characterize the manganese- and nickel-rich precipitates (MNPs) observed as well as to identify potential trends relating bulk composition to the resulting MNP composition.

This thesis is divided into eight chapters. **Chapter 2** reviews the current literature regarding RPV steels and potential causes of hardening embrittlement. As this work pertains entirely to new generation low copper RPV steels, the literature review focuses on manganese- and nickel-rich precipitates, their formation, and their presence in both thermally aged and irradiated materials.

Chapter 3 details the materials and methods utilized in this work. A strong emphasis is placed on atom probe tomography and current state-of-the-art cluster detection algorithms as one of the aims of the project is to detect the earliest stages of cluster formation within RPV steels.

Results regarding the long-term thermally aged model RPV steels are presented in **Chapter 4**. This chapter includes hardness measurements as well as atom probe analyses of the as-received and 11,690 hour thermally aged materials. Atom probe analyses were conducted within the matrix as well as at heterogeneous nucleation sites, such as carbide/matrix interfaces and grain boundaries. Chapter 4 concludes with the analysis of secondary precipitation within the cementite phase of RPV steels after thermal aging.

The atom probe analysis of low copper, ion irradiated RPV steels is discussed in **Chapter 5**. The goal of this work is to determine the effects of Ni and Mn content on MNP composition and equilibrium volume fraction.

Chapter 6 presents the development of a new cluster detection algorithm, GEMA, with the aim of standardizing cluster detection within the field of atom probe tomography. GEMA, a machine learning algorithm which utilizes a Gaussian mixture model, distinguishes clusters from random fluctuations in the matrix via expectation maximization (EM).

Finally, a summary is present in **Chapter 7** followed by a discussion of potential further research in **Chapter 8**.

Chapter II

Literature Review

1 Introduction

In a light water reactor, the reactor pressure vessel is a steel container that holds the coolant and reactor core (Figure 1). A properly functioning RPV is imperative for the safe operation of the nuclear reactor as it acts as the primary containment pressure boundary and encloses the reactor core. Since the RPV has direct safety significance, it must be closely monitored and maintained. Improper monitoring of an RPV may lead to ignoring the warning signs of a potentially catastrophic failure, resulting in the leakage of radioactive material to the surrounding environment.

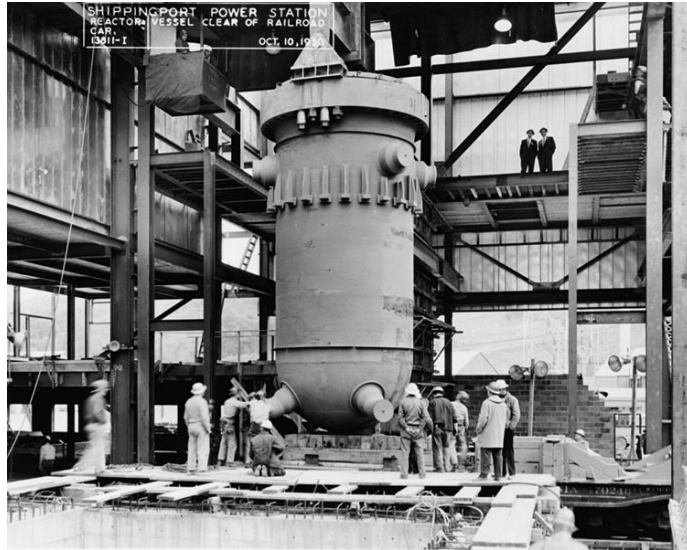


Figure 1: Reactor pressure vessel utilized in the first commercial light water nuclear power plant [7].

The RPV must be able to withstand pressures ranging from 7MPa to 17MPa, contain water coolant at a temperature of approximately 290°C, and survive exposure to high-energy neutrons

[8, 9]. The fluence at the end-of-life for a pressurized water reactor varies between specific vessels but typically is on the order of 10^{23} neutrons/m² [8]. Moreover, end-of-life fluences will become even greater as the lifetime of RPVs are extended. The reliable long-term operation of RPVs in such an extreme environment has proven to be a formidable challenge.

2 General RPV Microstructure

The effects of thermal aging are known to be very sensitive to variations in composition, microstructure, and heat treatments [6]. For this reason, Corwin et al. state “caution should be exercised in making conclusions regarding aging effects outside [an] existing data base.” Subtle differences in composition, microstructure, and heat treatments can significantly impact the embrittlement of RPVs.

2.1 Composition

In order to improve the initial properties of the steel, solutes, including nickel, silicon, and manganese, are added to the iron [10]. Ni is added to increase the toughness of the steel; Si is added at the molten stage of the steel-making process to de-oxidize the steel; Mn is added to form MnS which reduces the brittleness caused when free sulphur binds to iron [10]. Restrictions are also set on the amount of sulfur, phosphorus, and other trace impurity elements that can be incorporated into the steel. Solute ranges for a typical RPV steel are shown in Table 1. The addition of these solutes is essential to the structural integrity of the material. However, some strengthening solutes or unintentional solute impurities can have detrimental effects: copper is one such impurity.

C	Mn	Mo	Ni	Si	Cr	Cu
0.05-0.25%	0.3-1.5%	0.4-1.1%	0.2-1.4%	0.1-0.6%	0.05-0.5%	0.05-0.2%

Table 1: Solute percentages in at.% for typical RPV steels [11, 12].

The principal difference between older generation and contemporary RPV steels is the level of copper. Copper is an impurity found in older generation RPV steels due to the use of copper coated welding rods [11, 5]. In the late 1960s it was found that high impurity levels of copper (sometimes up to 0.4 at.%) lead to the formation of detrimental copper-rich precipitates (CRPs) at

typical reactor operating temperatures (on the order of 300°C) [13, 14, 15, 16, 17]. Studies have since shown that such CRPs form in RPV steels with greater than approximately 0.05 – 0.09 wt.% copper at 290°C [18, 19]. As a result, the new generation of RPVs have been engineered to contain less than 0.05 wt.% copper. Consequently, CRPs are no longer a main cause for concern regarding RPV structural integrity in new vessels. However, many high copper, older generation RPVs still remain in service.

2.2 Heat Treatments

Prior to service, RPV steels are generally subjected to several heat treatment stages as rolled plates or forgings [21]. The plates typically undergo austenitisation at approximately 900°C followed by an air cool [21, 22]. It is during this step in the heat treatment that carbides typically form. The plates are then tempered at approximately 600°C followed by a final air cool [21, 22].

After the RPV is welded together it is stress relieved. During this post weld treatment, the RPV is heated to approximately 600°C for a number of hours, the length of which depends on the wall thickness. This treatment allows for stress relaxation without a significant reduction of the mechanical properties.

2.3 Microstructure

RPV steels have a primarily tempered bainitic microstructure [11]. Varying proportions of ferrite and martensite are usually present as well. The proportions of these microstructures depends heavily on the fabrication and processing of the material. For a given composition and specimen thickness, these proportions can be determined via continuous cooling transformation (CCT) diagrams, such as the one shown in Figure 2. These diagrams are read top down for a specific initial temperature, specimen thickness, and quenching medium. For example, if a 100 mm plate of the steel specified at the top of Figure 2) was air cooled from 800°C, it will contain approximately 33% ferrite and 66% bainite. Details regarding the microstructure of the RPV steels utilized in this study can be found in Chapter 3.

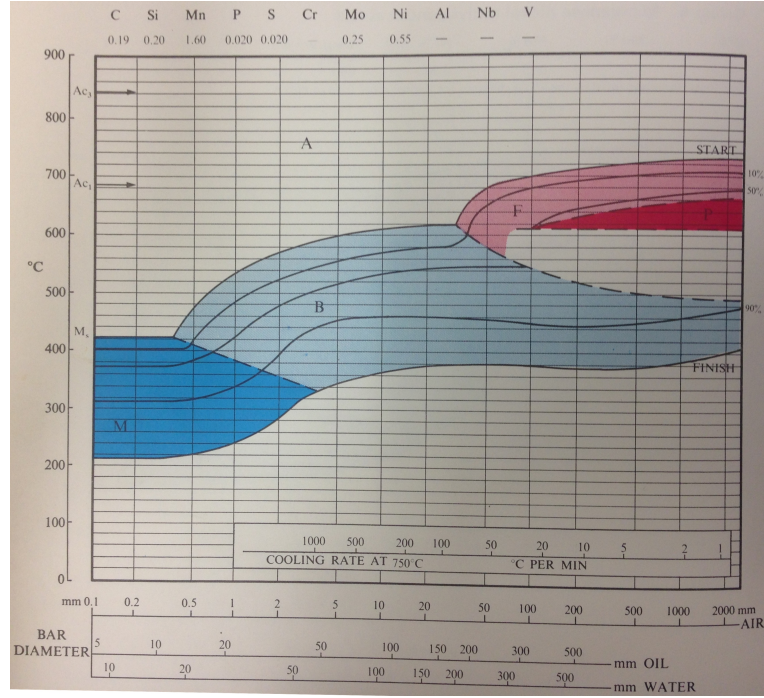


Figure 2: Continuous cooling transformation (CCT) diagram for a model RPV steel [23].

3 Embrittlement in RPV Steels

Embrittlement of an RPV alloy can be classified into two categories: non-hardening and hardening [24]. Both types of embrittlement have been shown to cause a shift in the ductile-brittle transition temperature (DBTT), which delineates the brittle and ductile fracture regimes [19]. An example of a DBTT shift due to irradiation and thermal aging is shown in Figure 3. A change in hardness reliably indicates that there has been a shift in the DBTT, i.e. there exists a strong correlation between hardness shifts and embrittlement [11]. Therefore, hardness testing can be combined with microstructural analysis techniques such as transmission electron microscopy (TEM) or atom probe tomography (APT), which can be used to characterize precipitates, to correlate changes in the microstructure to the mechanical properties of the steel.

3.1 Microstructure Causing Non-Hardening Embrittlement

Non-hardening embrittlement is mainly caused by the segregation of solutes, such as phosphorus, to grain boundaries. Prior to segregation interstitials and misfitting substitutional atoms located within the matrix impose a strain on the surrounding lattice structure. Grain

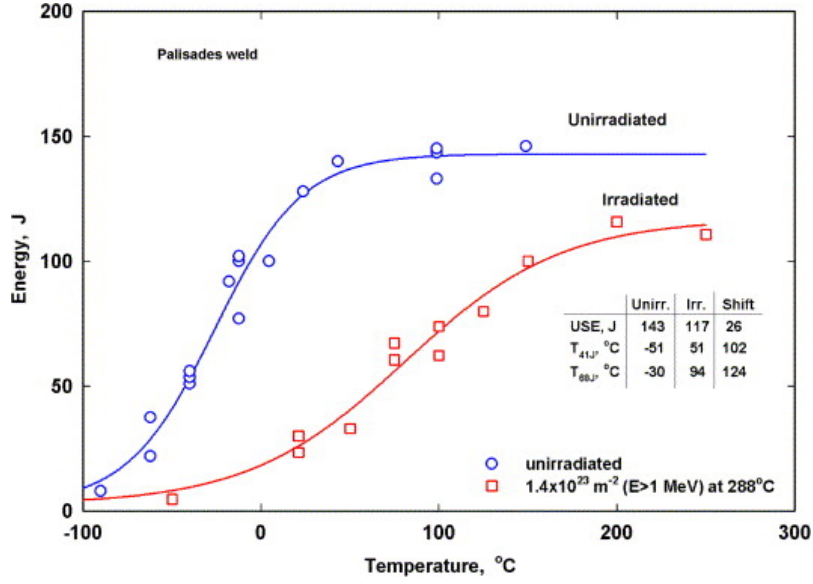


Figure 3: DBTT shift and lowering of upper shelf energy due to irradiation for a high Ni Palisades A 533B weld [25].

boundaries, which have lower atomic density, are therefore energetically favorable for such solute atoms. Thus, these solute atoms tend to segregate toward grain boundaries via diffusion. This effect can also be enhanced by irradiation.

In RPV steels phosphorus reduces grain boundary cohesion, elevating the DBTT and the probability of intergranular fracture [26]. Studies have indicated that irradiation increases phosphorus segregation to grain boundaries [27]. Phosphorous segregation was also found to increase with fluence, temperature¹, nickel content, and unsurprisingly, phosphorus content [26, 27].

Although solute segregation to grain boundaries used to play an important role in the embrittlement of RPV steels, modern impurity restrictions on phosphorus makes this concern less relevant. Therefore, the focus of this review has been placed on hardening embrittlement.

3.2 Microstructure Causing Hardening Embrittlement

There are two types of hardening that can cause RPV degradation via embrittlement: matrix hardening and precipitate hardening. Matrix hardening is caused by clusters of interstitials and vacancies, which block dislocation motion. Precipitate hardening, on the other hand, is caused by the precipitation of secondary phases hindering the passage of dislocations through the matrix.

¹Phosphorous segregation was found to increase with temperature, in the temperature regime of RPV operation, due to an increase in kinetics.

These precipitates can act as pinning points for dislocations via a number of mechanisms, including chemical strengthening, modulus hardening, and coherency strengthening [28]. Dislocations can pass through these particles in one of two ways: cutting through the precipitate or bowing around the precipitate. The latter mechanism is the most common and often referred to as the Orowan mechanism. In this case, the dislocation bows around the precipitate, eventually passing through it, leaving behind a dislocation loop.

In order to make accurate predictions of RPV lifetime, both of matrix and precipitate hardening must be fully understood. Neutron irradiation is known to cause both matrix and precipitate hardening. As neutrons bombard the material, interstitials and vacancies are formed. These defects cluster and act as heterogeneous nucleation sites where precipitates can form. The vacancies also accelerate precipitation by facilitating the diffusion of atoms within the system. Fluence, flux, and alloy composition influence the extent of irradiation embrittlement.

For thermally aged RPV steels, precipitation is the most prominent cause of hardening embrittlement. When precipitates form they impede the movement of dislocations, causing an increase in the hardness and a shift in the DBTT. Over time this can cause the steel to become brittle and more susceptible to fracture. Thus, understanding precipitate formation is of great importance to the nuclear industry.

3.2.1 Matrix Defects

Irradiation-induced changes in the microstructure, including matrix defects, can cause hardening and subsequent embrittlement [30]. Matrix defects (MDs) refer to a number of phenomena including vacancies, self-interstitial atoms, and interstitial solute atoms. Matrix defects are known to enhance solute diffusion, form defect-solute clusters, and aid in the formation of precipitates.

Hardening due to MDs was observed in an irradiation study performed by Kuramoto et al. Initial hardening due to the introduction of matrix defects was minimal compared to the subsequent hardening caused by the formation of copper-rich precipitates [30]. Based on APT characterization, the hardening due to CRPs was calculated using the Russell-Brown model [31]. This calculation was subsequently compared to the measured change in hardness. In the irradiated case, these two figures were in agreement. However, after annealing and re-irradiation it was found that the hardening observed could no longer be solely explained by CRPs, as the change in hardness was greater than

the estimated contribution from CRPs (Figure 4). It was determined via positron annihilation spectroscopy that newly formed matrix defects had significantly increased the hardness [30].

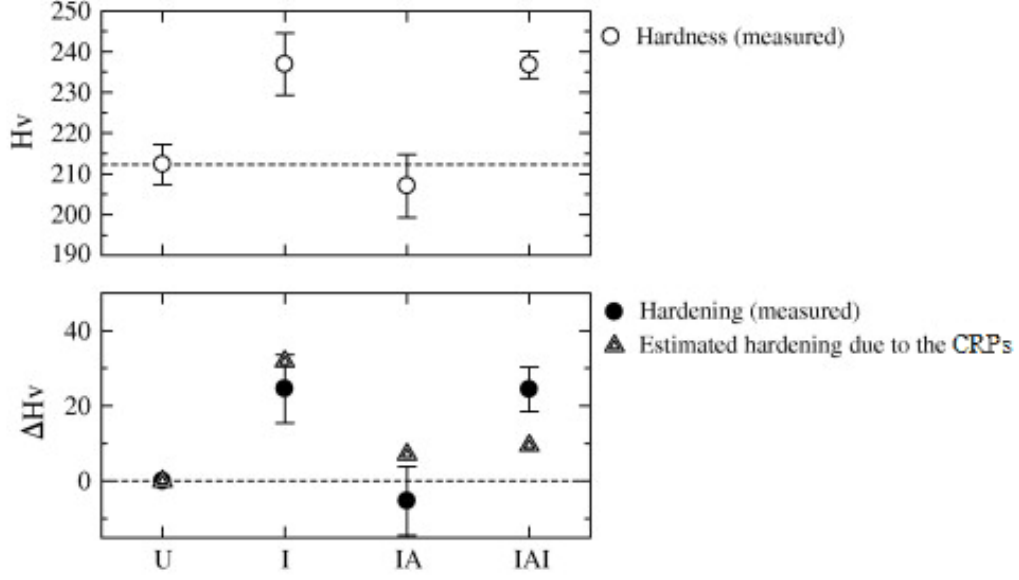


Figure 4: Vickers hardness measurements of the unirradiated (U), irradiated (I), irradiated-annealed (IA), irradiated-annealed-irradiated (IAI) states. The change in hardness illustrates the difference in the measured hardening and that estimated from the Russell-Brown model [30].

In general, however, both MDs and CRPs contribute significantly to hardening [32]. The hardening response due to CRPs is known to increase rapidly with dose, but then eventually saturate [32]. In contrast, the hardening response from MDs increases approximately with the square root of dose [32, 33]. Thus, the hardening component due to CRPs tends to dominate at low doses and in high copper steels, whereas the MD component tends to dominate at higher doses and in low Cu steels [32].

3.2.2 Precipitation

There are several types of precipitates that contribute both directly and indirectly to the hardening and consequent embrittlement of RPV steels. In this review the term “precipitates” is used to describe solute clusters and thermodynamically stable precipitates alike. Specifically, the stability or size of a feature is not implied by the use of this terminology. The term embryo, however, is used to describe clusters of solute atoms that have not yet reached their critical size.

Carbides As a result of initial heat treatments, RPV steels generally contain carbides of the forms Mo_2C , M_3C , and M_7C_3 [20, 27]. These precipitates are relatively large (approximately 10nm to $1\mu\text{m}$) and generally do not change significantly during service [27]. Although carbides typically have a large effect on initial hardness, they do not significantly contribute to changes in hardness during service due to their static nature. However, their presence does have a significant effect on the distribution of other alloying elements. Phosphorus, for example, preferentially partitions to the boundaries of these precipitates (particularly Mo_2C) [5, 34]. This is generally regarded as beneficial because it reduces the amount of free phosphorus that can segregate to grain boundaries where it is far more deleterious.

Copper-rich Precipitates Copper-rich precipitates have been studied extensively and are known to cause hardening embrittlement [13, 14, 15, 16, 19, 18, 35, 36]. CRPs have been observed in both thermally aged and irradiated material. The details of such studies are beyond the scope of this literature review. However, two comprehensive reviews on RPV embrittlement due to CRPs have been provided by Miller [5, 37].

CRPs form at typical reactor operating temperatures (on the order of 300°C) when steels contain greater than approximately 0.05 – 0.09 wt.% Cu [18, 19]. CRPs continue to form until approximately 0.05 at.% Cu is left in the matrix [5]. Although these two findings seem slightly contradictory, it is plausible that a higher level of Cu is needed to begin the nucleation process, but once it is initiated precipitates continue to grow until the matrix is no longer supersaturated. A simple, albeit time consuming, study that systematically varied Cu would address this hypothesis.

Stable CRPs are known to form via two intermediate phases. Given a supersaturated solid solution, metastable body centered cubic (BCC) precipitates form [38, 39, 40]. These precipitates are coherent with the matrix and thus require less energy to form than face centered cubic (FCC) CRPs. CRPs characterized by a BCC structure are believed to be at their peak strength [40]. Once the precipitates reach a critical size, the coherence strain energy becomes too large and the precipitates transform into a 9R structure, characterized by a high density of twins [38, 39, 40]. At even larger sizes, the precipitates complete their transformation to a twin-free FCC structure.

Manganese-Nickel Enriched Precipitates The nuclear industry has shifted its focus to low Cu RPV steels due to the detrimental effects of CRPs. Consequently, manganese- and nickel-rich precipitates (MNPs) have arisen as a critical concern and as such represent the main

focus of this review. A detailed discussion of MNPs can be found in Section 4.

3.2.3 Hardening Mechanism Models

Several models have been developed to illustrate the hardening mechanism for precipitates; two prominent examples are the Russell-Brown Model and the Harry-Bacon Model.

Russell-Brown Model The first model describing the hardening mechanism behind RPV embrittlement due to precipitates blocking dislocation movement was proposed by Russell and Brown [31]. The Russell-Brown model utilizes a derived relationship for maximum yield strength to calculate the change in hardness caused by pure Cu precipitates. This equation for maximum yield strength was obtained from first principles and the equation for shear stress,

$$\tau = \frac{0.8Gb}{L} \cos(\phi/2), \quad (1)$$

where G is the shear modulus, b is the Burgers vector, L is the distance between obstacles, and ϕ is the angle between the arms of the bent dislocation. The derivation of the equation for shear stress can be found in the Appendix 1.

The Russell-Brown model,

$$\tau_{max} = 0.041Gb f^{1/2}/r_0, \quad (2)$$

where f is the precipitate volume fraction and r_0 is the inner cut-off radius, is still utilized in current studies [30, 40, 43] to determine the contribution of precipitates to hardening in a given system. Due to its frequent use, it is important to understand both the theory and the assumptions behind the Russell-Brown model.

The Russell-Brown model is based upon several key assumptions: the precipitates are spherical in shape; an equilibrium volume fraction has been precipitated; and the precipitates have a lower shear modulus than the matrix phase. These assumptions allow for the simplification of otherwise intractable equations detailing complex interactions between atoms. Although these assumptions are useful, one must ensure they are appropriate for the task at hand prior to applying the model.

In addition to the above assumptions, which are generally innocuous, several bold estimates are made for system dependent variables (e.g. the mean planar precipitate radius and Schmid

factor). Russell and Brown acknowledge that these estimates are “subject to considerable error; possibly as much as 50 per cent” [31].

When comparing the theoretical equation for maximum yield strength with the experimental data, Russell and Brown found that “theory and experiment can be brought into exact agreement if $r_0 = 2.5b$ ” [31]. However, there is limited theoretical justification for this parameterization. Moreover, although it is clearly acknowledged that r_0 is empirically determined, the downstream implication of this choice must be understood. For example, goodness of fit estimates are substantially biased when parameters are chosen adaptively.²

Furthermore, in their model Russell and Brown employ the FCC shear modulus of copper in order to calculate τ_{max} . This is troublesome as copper precipitates reach their peak hardness while they have a BCC structure and are coherent with the matrix.

Finally, the Russell-Brown model only addresses binary systems (in this case Cu precipitates in Fe), while, in practice, it is regularly applied to more complex systems. However, this is often overlooked as the model performs reasonably well outside of its intended scope.

Harry-Bacon Model A contradicting model was later proposed by Harry and Bacon [44]. In this model the structure of each precipitate and the energy of a screw dislocation are computed as the dislocation travels through the matrix [44]. Using this atomic-scale simulation the flow stress required by the dislocation to cut through the precipitates was calculated and compared to experimental results. It was found that the hardening observed experimentally was more accurately predicted by the effect of the screw dislocation on the BCC copper structure rather than elastic interactions, as postulated by Russell and Brown. Harry and Bacon argue that the reduction in energy observed is due to a dislocation induced transition of the copper precipitate from a BCC structure to an FCC or 9R structure [44].

²Although it is clearly stated that the value for r_0 is determined by fitting the experimental data to the theory, the gravity of this action is not properly emphasized. By using the experimental data to determine a value of r_0 they are ensuring a perfect fit of the experimental data to the theory. As a result of this action, the goodness of fit is no longer meaningful as it is dependent on the choice of r_0 .

4 Mn- and Ni-rich Precipitates in RPV Steels

4.1 Terminology and Classification

In 1995, the term “late blooming phases,” or LBPs, was coined by Odette to describe irradiation induced MNPs observed in RPV steels after exposure to significant fluence [8, 45]. However, recent studies indicate that these precipitates may not necessarily be late blooming nor thermodynamically stable phases [55, 46]. Therefore, Ni and Mn enriched precipitates are referred to as MNPs in this review, not LBPs.

4.2 Ni and Mn Enriched CRP Interface

Since the early 1990s, Ni and Mn clustering has been associated with CRPs in irradiated steels [5, 46, 47]. Langer-Schwartz simulations of Fe-Cu-Ni and Fe-Cu-Mn alloys indicate that the distribution of Ni and Mn within CRPs is not homogeneous but instead the concentrations of these solutes reach a maximum several nanometers away from the center [42]. These simulations, which were experimentally corroborated [27, 42, 48], demonstrate the existence of a Ni and Mn enriched interface.

This phenomenon can be theoretically explained via energy considerations [40, 49, 50, 51, 52]. Due to the insolubility of Cu in Fe, the interface energy for copper enriched clusters in an iron matrix is relatively high. Ni and Mn, however, are considerably more soluble in Fe. Ni and Mn also have energetically favorable interactions with Cu, further reducing the interface energy. Thus, a buffered Cu-Ni/Mn-Fe transition is energetically preferred over a stark Cu-Fe interface.

4.3 Heterogeneous Nucleation Sites for CRPs

Zhang et al. were able to illustrate the importance of Ni and Mn in the nucleation and growth of CRPs utilizing Langer-Schwartz simulations [42]. In this study binary alloy Fe-Cu simulations were compared to ternary Fe-Cu-Ni and Fe-Cu-Mn alloy simulations. The simulations indicated that the additions of both Ni and Mn decreased the work required to form a critical Cu nucleus as presented in Figure 5 [42]. It was also shown that the presence of both Ni and Mn increased the nucleation rate by a factor of 2-3 [42]. However, the absence of a quaternary Fe-Cu-Ni-Mn alloy simulation precludes the investigation of a potential interaction effect of Ni and Mn on the activation energy and nucleation rate. This could potentially be determined by creating

and analysing a fourth, quaternary alloy simulation.

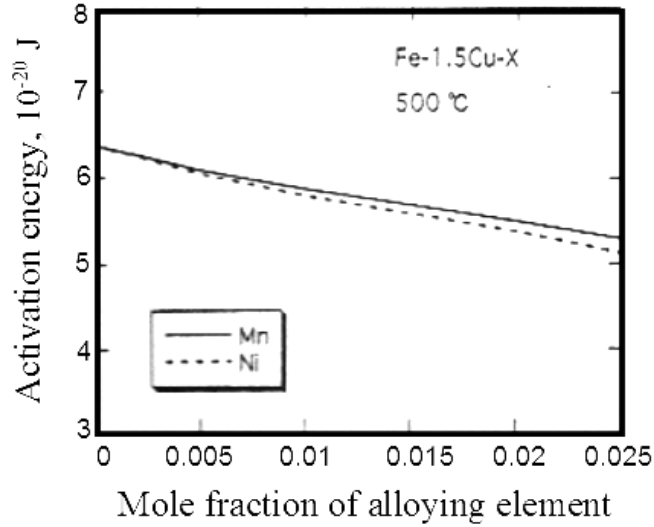


Figure 5: Plot of the activation energy required for the formation of a critical Cu nucleus with the additions of alloying elements Ni and Mn [42].

Numerous studies suggest that the presence of Ni and Mn significantly increase the number of Cu clusters present in a system [41, 53, 54]. In an investigation by Cerezo et al. an atomistic simulation was created using dynamical Ising models to analyze a Fe-Cu-Ni-Mn-Si system [41]. Through the use of modeling it was possible to examine the same precipitate at a range of simulated thermal aging time steps. This study found that prior to the formation a CRP, a Mn- and Ni-rich cluster formed in the region (Figure 6). It was concluded from the model that Mn- and Ni-rich clusters act as preferential, heterogeneous nucleation sites for CRPs, thus providing a possible explanation for the increased number of CRPs observed in the high Ni steels.

Since the majority of modern RPV steels contain less than 0.05 at.% Cu, it is now crucial to investigate the possibility of MNP formation via the sub-critical Ni-Mn nucleation sites observed via simulations by Cerezo et al. While this phenomenon has not been observed in high Cu steels due to the presence of Cu, it could potentially exist in low Cu RPV steels.

4.4 Potential Mechanisms for MNP Nucleation and Growth

MNPs, which are low in copper, were first reported by Pareige et al. [50]. The formation of MNPs in irradiated low Cu steels is a significant cause of hardening, particularly at high fluences [51, 55]. This new embrittlement mechanism which emerges only after long term irradiation is

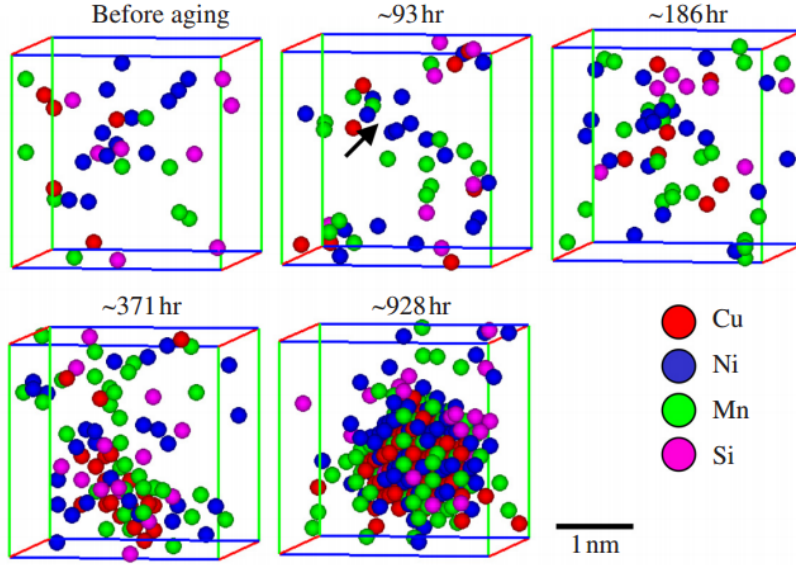


Figure 6: Region from the dynamical Ising model at different aging times illustrating the heterogeneous nucleation of a CRP at a pre-existing Mn- and Ni-rich cluster. [41].

concerning and could potentially invalidate some modern RPV end-of-life estimates [55].

There are two main conflicting theories regarding the development of MNPs:

1. MNPs are irradiation enhanced, i.e. thermodynamically favored but are difficult to nucleate.
2. MNPs are irradiation induced.

The former was first proposed by Odette in 1995 [8]. Odette et al. hypothesized that MNPs, although thermodynamically favored, were difficult to nucleate in the matrix and thus only observed after high fluences [52, 55, 56]. It was therefore suggested that MNPs form on heterogeneous nucleation sites provided by small Cu clusters. In a report from the Nuclear National Laboratory it was noted that if only a couple of Cu atoms were needed for a suitable nucleation site, then MNPs could form in RPV steels with as little as 0.01 at.% Cu [55]. Several years later, Liu et al. constructed a lattice Monte Carlo (LMC) simulation that supported this claim. The simulation, which was based on thermodynamic considerations, found evidence of MNPs with small Cu cores [49].

Through a comparison between ion and electron irradiation in low Cu and Cu-free alloys Radigue et al. found that Cu, Mn, and Ni clusters formed via heterogeneous precipitation on small point defect clusters such as dislocation loops [60]. Furthermore, it was observed that Ni and Mn

delayed the kinetic formation of Cu clusters. This was determined by comparing the Fe-Cu and Fe-Cu-Mn-Ni-P alloys in the study; clusters were larger and more numerous in the former.

The alternative theory that MNPs are irradiation induced is supported by a number of irradiation studies in which MNPs were found only after high fluences [52, 55, 56, 58]. Such studies, however, can also be interpreted to support the first theory: MNPs, although thermodynamically favored, are difficult to nucleate and thus only observed after high fluences. In a long-term thermal aging study conducted by Pareige et al. no significant changes in the mechanical properties or the microstructure were observed, thus supporting the theory that MNPs are irradiation induced [67].

Ngayam-Happy et al. suggest Mn dumbbells form and cluster via diffusion [46]. These dumbbell clusters act as sinks for additional Mn dumbbells as well as Ni solute atoms. Further simulations developed by Ngayam-Happy et al. support this theory, showing that although MNPs nucleate earlier than CRPs, which form via a vacancy driven mechanism, they grow at a much slower rate. This difference would explain why CRPs are experimentally observed to dominate in low dose regimes. Ngayam-Happy et. al. go on to suggest that these precipitates are not thermodynamically stable, citing their Metropolis Monte Carlo simulations, which show that Mn and Ni remain in solid solution at thermodynamic equilibrium for a range of temperatures (200°C, 300°C, and 400°C).

More recently, Bonny et al. utilized density functional theory calculations as well as Monte Carlo simulations to try and determine the thermodynamic stability of Mn- and Ni-rich clusters [57]. They concluded that while Mn-Ni pairs are unstable, larger clusters are held together by an attractive binding energy. However, this result comes with a caveat: the thermodynamic stability of the system will be extremely sensitive to small variations in temperature and bulk composition. Consequently, Bonny et al. hypothesized that the nucleation of MNPs, with volume fractions consistent with those observed experimentally, via thermodynamic considerations is highly improbable. Alternatively, they suggest that MNP nucleation and growth is made possible due to matrix defects.

Due to the large number of conflicting studies, a definitive answer regarding the mechanism for MNP nucleation as well as the thermodynamic stability of these precipitates has yet to be determined.

4.5 MNPs in Irradiated RPV Steels

Numerous studies have observed MNPs in irradiated RPV steels [32, 56, 61, 62, 63, 64, 65]. In an atom probe tomography study by Miller and Russell, a WWER1000 reactor weld was irradiated to a total fluence of $1.4 \times 10^{23} \text{ nm}^{-2}$ at 288°C [27]. This low Cu (0.05 at.% Cu) weld was found to contain MNPs approximately 1 – 2 nm in diameter. Atom maps containing these Ni-, Mn-, and Si-rich features are shown in Figure 7.

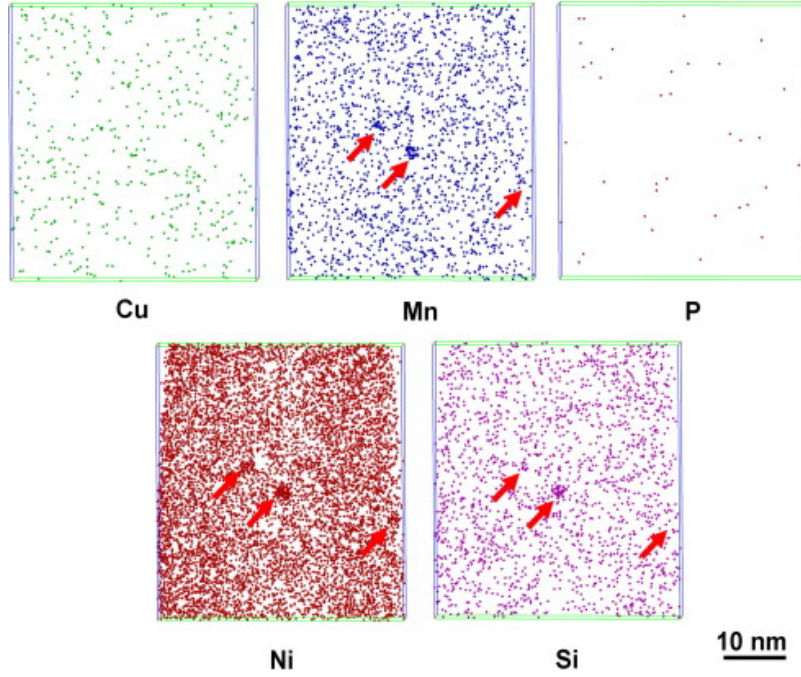


Figure 7: Atom probe tomography data showing MNPs in a low Cu, high Ni weld from a WWER1000 reactor [27].

In another study, Takeuchi et al. analysed the evolution of hardening in high Cu and low Cu steels after neutron irradiation. Both steels showed significant increases in hardness when irradiated [61]. This increase was attributed to the nucleation of CRPs and MNPs in the high and low Cu steels, respectively. Takeuchi et al. proposed that the dislocation pinning strength of both the CRPs and MNPs were accurately predicted by the Russell-Brown model. However, no formal evaluation of the model fit was presented.

In a study on composition and flux effects in irradiated RPV forging steels, Burke et al. provided evidence that Mn was the predominant solute responsible for the observed clustering behaviour [64]. In that APT study, statistical fluctuations in the spatial distribution were detected

using composition frequency distributions and contingency table analyses. The high Mn, high Ni steels were found to contain Ni and Mn solute distribution fluctuations as well as significant co-segregation. The low Mn, high Ni steel, however, was found only to contain Ni solute fluctuations. Hardness measurements indicated that no stable solute hardening occurred during neutron irradiation within the low Mn steel, though significant hardening was present in the high Mn steels even after annealing. Burke et al. conclude Mn plays a fundamental role in the irradiation induced development of stable solute-related hardening features. However, the possibility of a synergistic effect or interaction between Ni and Mn causing the observed clustering behavior cannot be ruled out. This possibility could be investigated, however, by characterizing an additional steel that was high in Mn and low in Ni. Although not a viable steel for service, analysing a high Mn, low Ni steel would shed light on the role of Mn and Ni in creating the observed hardening features.

4.6 MNPs in Thermally Aged RPV Steels

In a thermal aging study conducted by Styman, MNPs approximately 10nm in size were observed at heterogeneous nucleation sites (e.g. dislocations and grain boundaries) in steels aged as little as 50,000 hours at 365°C [36]. Styman also observed MNPs in a thermally aged high Cu steel. Each of the MNPs observed in that APT reconstruction (excluding those located at the edge of the analysis volume) were associated with CRPs (Figure 8). Styman hypothesized that existing CRPs acted as heterogeneous nucleation sites for the MNPs. Styman noted that this mechanism has been previously observed in neutron irradiated materials (low flux, high fluence) [58].

Styman also observed MNPs along a low angle grain boundary in a low Cu weld specimen after 100,000 hours of aging at 330°C (Figure 9) [36]. It was noted that these precipitates were not associated with any Cu-based precipitates. These features were much smaller than those observed in the steels with a higher copper content. Although the MNPs did not appear to be of a consistent stoichiometry, Styman suggests that these “phases” correspond to the LBPs predicted by Odette [8]. The very presence of such clusters in low copper, thermally aged steels strongly suggests that the mechanism for MNP nucleation is likely to be thermodynamic in origin.

Hardness tests performed on the low Cu steel in Styman’s study showed no evidence of precipitation hardening within the matrix [36]. This was confirmed via atom probe tomography: only random clustering was detected in the matrix. This null result was unsurprising considering the higher barrier for nucleation within the matrix when compared to heterogeneous nucleation

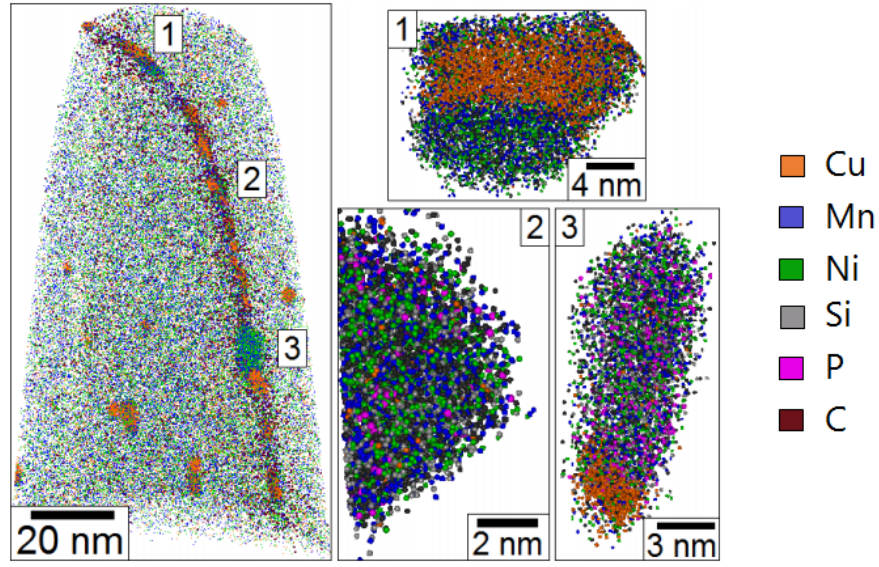


Figure 8: APT map of high Cu RPV steel aged for 50,000 hours at 365°C. A grain boundary containing CRPs and MNPs is shown [36]. Close-ups of three precipitates are shown.

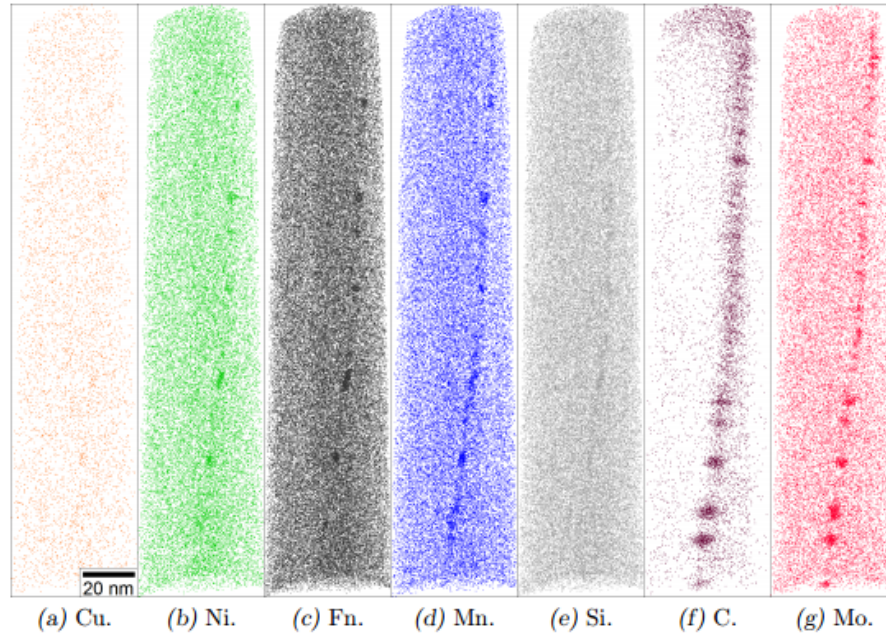


Figure 9: APT maps showing the distribution of Cu, Ni, "Fn" (overlapping Fe and Ni peak), Mn, Si, C, and Mo in a low Cu weld specimen aged for 100,000 hours at 330°C. A low angle grain boundary is shown and MNPs are visible [36]. Numerous Mo carbides are also visible along this grain boundary.

sites such as grain boundaries.

4.7 Summary

Embrittlement of RPV steels can occur via two mechanisms: non-hardening and hardening embrittlement. The first is primarily caused by segregation of solute to grain boundaries, which reduces grain boundary cohesion, subsequently increasing the likelihood of intergranular fracture. The second, hardening embrittlement, can be caused by either matrix or precipitate hardening, both of which block dislocation motion. In terms of precipitate hardening, CRPs have been extensively studied and are well understood. However, as the nuclear industry shifts its focus to low copper RPV steels, the need to better understand the mechanism behind the formation of MNPs has become increasingly clear.

It is in the author's opinion that these precipitates are thermodynamically favored, yet difficult to nucleate. The strongest evidence supporting this claim comes from [36], where MNPs were observed along a low angle grain boundary within a thermally aged, model RPV steel. Additionally, the majority of evidence in favor of the theory that MNPs are irradiation induced, does not preclude the theory that MNPs are simply radiation enhanced.

Therefore, the focus of this work is to study the effects of nickel and manganese in the absence of copper within model RPV steels. While the literature has provided valuable background for this research, there still remain open questions which have yet to be answered. In the absence of high levels of copper, do MNPs nucleate within the matrix of thermally aged RPV steels? If so, what is the mechanism by which this occurs? How does bulk nickel and manganese content affect MNP composition and volume fraction in irradiated steels? This research aims to begin answering these challenging questions.

Chapter III

Materials and Methods

1 Materials

1.1 Thermally Aged Model RPV Steels

In this study, hardness measurements were obtained for nineteen model RPV steels (Table 2). Subsequently, APT was utilized to characterize five of these new generation, low Cu samples which contained systematic variations in Ni and Mn content (Table 3). These alloys were targeted in order to isolate and better understand the clustering behavior of Ni and Mn. In this thesis, these five steels are categorized by their Ni and Mn content. For Ni there are three levels: low (0.19 at.%), medium (1.60-1.61 at.%), and high (3.31 at.%). For Mn there are two levels: low (0.25 at.%) and high (2.02 at.%).

Prior to thermal aging the steels had been subjected to heat treatments as 25 mm thick plates. The plates underwent austenitisation at approximately 920°C for 1 hour followed by an air cool. The plates were then tempered at approximately 600°C for 5 hours followed by a final air cool. At this point in the process – after the initial heat treatments but prior to thermal aging – the steels are referred to as “as-received.”

Following these initial heat treatments, the model RPV steels were thermally aged for 11,688 hours (approximately 1.3 years) in three furnaces. Prior to being placed in the furnaces, each set of steels was encapsulated in quartz tubing under vacuum to minimize oxidation. The furnaces were held at three temperatures: 330°C, 365°C, and 405°C ($\pm 2^\circ\text{C}$). Although RPV's typically operate at approximately 290°C, higher temperatures were utilized to expedite cluster formation in this investigation. Once removed from the furnaces, the steels were quenched in water.

The microstructure of a these steels was analysed by Titchmarsh using transmission electron microscopy (TEM) prior to thermal aging [20]. Due to variations in solute content, the

	Cu	Si	Ni	Mn	P	Cr	Mo	C
Sample Q	0.04	0.39	0.19	1.51	0.01	0.11	0.29	1.15
Sample E	0.04	1.18	0.19	1.50	0.01	0.11	0.29	1.15
Sample H	0.04	0.39	0.19	2.02	0.01	0.11	0.29	0.92
Sample P	0.04	0.39	0.24	0.25	0.01	0.11	0.29	1.15
Sample R	0.04	1.18	0.24	0.25	0.01	0.11	0.29	0.92
Sample B	0.04	0.39	0.24	0.25	0.05	0.11	0.29	0.92
Sample A	0.04	0.39	1.60	0.25	0.01	0.11	0.29	1.15
Sample L	0.04	0.39	1.60	0.76	0.01	0.11	0.29	1.15
Sample G	0.04	0.40	1.61	2.02	0.01	0.11	0.29	0.92
Sample K	0.04	0.39	3.31	0.25	0.01	0.11	0.29	1.15
Sample M	0.04	1.18	3.29	0.25	0.01	0.11	0.29	1.15
Sample S	0.04	0.39	3.31	0.76	0.01	0.11	0.29	1.15
Sample J	0.04	0.10	3.32	1.52	0.01	0.11	0.29	0.93
Sample O	0.04	0.40	3.31	1.52	0.05	0.11	0.29	0.92
Sample D	0.04	0.39	3.30	1.51	0.01	0.11	0.29	1.15
Sample I	0.04	1.18	3.30	1.51	0.01	0.11	0.29	0.92
Sample C	0.04	0.40	3.31	2.02	0.01	0.11	0.29	0.92
Sample N	0.17	0.39	0.24	0.25	0.01	0.11	0.29	0.92
Sample F	0.26	0.40	3.31	1.52	0.01	0.11	0.29	0.92
	Cu	Ni	Mn	Si	Mo	C	Cr	P

Table 2: Model RPV steel sample compositions in at.%. Nominal compositions were provided by Rolls-Royce Plc.

microstructures varied significantly. Samples which had lower concentrations of solute had greater amounts of ferrite/pearlite rather than bainite. As a result, these samples were much less tough and unsuitable for RPVs. All of the nineteen steels exhibited a banded microstructure, indicative of local variations in composition and precipitation [20]. An example of the banded microstructure observed is shown in Figure 10.

Several types of carbides were present within the microstructure, namely M_3C and Mo_2C . M_3C precipitates were typically found at prior austenite grain boundaries (Figure 11) [20]. Mo_2C was found in samples with a bainitic structure [20].

1.2 Ion Irradiated Model RPV Steels

Ion irradiation experiments were carried out on an identical set of model RPV steels (Table 2) led by researchers at University of California Santa Barbara (UCSB). These steels were subjected

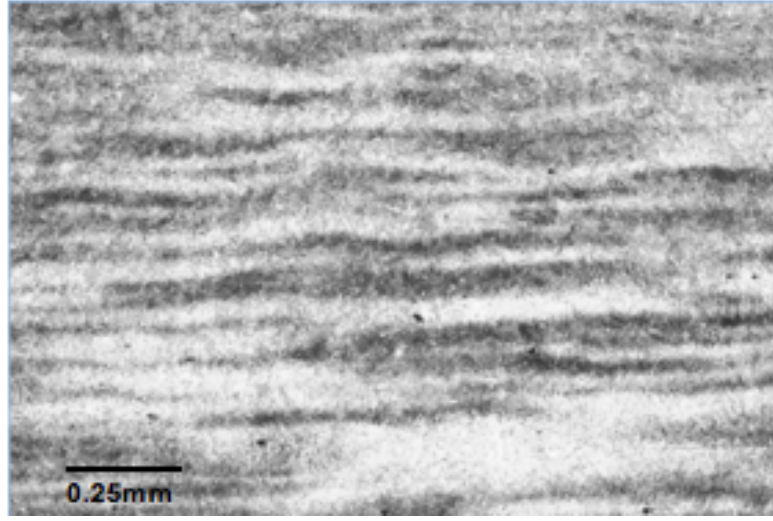


Figure 10: Optical micrograph image of a low Cu, high Ni RPV steel showing banded microstructure [20].

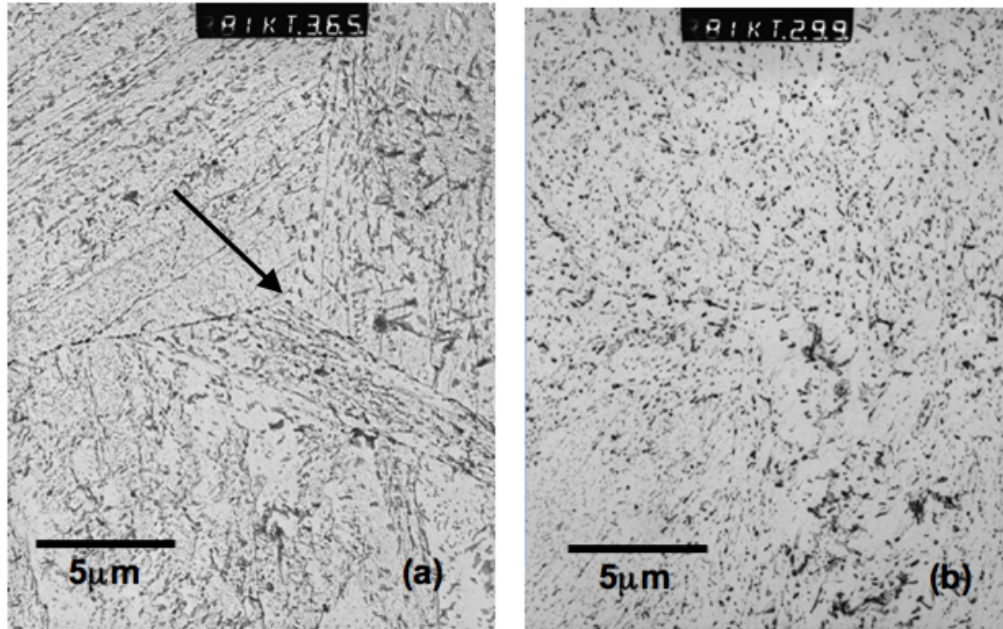


Figure 11: Carbon extraction replicas (CXRs) of (a) a prior austenite grain boundary triple point (arrow) and lath packets, (b) randomly distributed precipitates [20].

	Cu	Si	Ni	Mn	P	Cr	Mo	C
Sample H	0.04	0.39	0.19	2.02	0.01	0.11	0.29	0.92
Sample A	0.04	0.39	1.60	0.25	0.01	0.11	0.29	1.15
Sample G	0.04	0.40	1.61	2.02	0.01	0.11	0.29	0.92
Sample K	0.04	0.39	3.31	0.25	0.01	0.11	0.29	1.15
Sample C	0.04	0.40	3.31	2.02	0.01	0.11	0.29	0.92

Table 3: Model RPV steel sample compositions in at.%.

to the same initial heat treatments prior to ion irradiation: austenitisation at 920°C for 1 hour and tempering at 600°C for 5 hours, each followed by an air cool. Following these heat treatments, the steels were ion irradiated with 6.4 MeV Fe^{3+} ions at DUET in Kyoto, Japan. The samples were irradiated at 290°C with a dose rate of 1.5×10^{-4} dpa/s. A dose of approximately 4dpa was obtained 500nm below the surface (Figure 12).

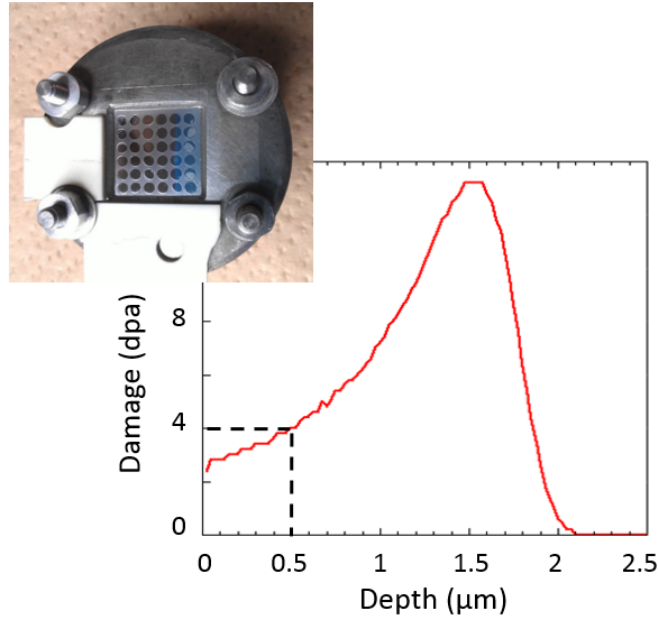


Figure 12: Simulation of damage from ion irradiation as a function of sample depth provided by UCSB. Image at top left shows physical samples prior to irradiation.

To compliment the thermal aging studies the same subset of five steels were selected for APT analysis (Table 3). Atom probe tomography samples were made via focused ion beam (FIB) lift-out, carried out on a FEI Helios FIB-SEM. The site-specific FIB lift-out technique is described in Section 4.2.

The damage depth profile for the samples, shown in Figure 12, was created at UCSB via

Stopping and Range of Ions in Matter (SRIM) simulations with a Kinchin-Pease displacement energy of 40 eV [66, 67]. In order to obtain APT specimens with a damage of approximately 4dpa, samples were created from material located 500nm below the surface. This was accomplished via site-specific FIB lift-out. Since APT samples were made from material located 500nm below the surface, regions with high levels of Fe implantation were avoided.

2 Hardness Measurements

Hardness measurements were undertaken for the as-received state, 0 hours, and thermally aged state, 11,690 hours, using a Vickers hardness machine (Figure 13). Prior to taking each set of measurements, the hardness machine, located in the furnace room of the Materials Department, was calibrated using a HV20 Vickers reference hardness block. The mean hardness of the reference block was certified as 195.7 HV, with a range of 3.2 HV. All calibration measurements conducted at the University of Oxford were within 4.3 HV of the average value, giving a maximum percent error of 2.2%. This level of error was considered acceptable.

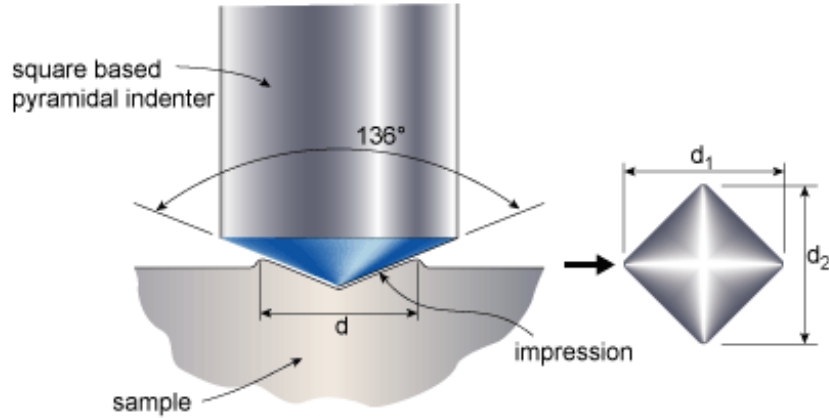


Figure 13: Schematic of Vickers hardness machine [68]. A load of 20kg was applied to the sample for a duration of 10 seconds. Measurements of the impression diagonals were taken via optical microscope. These dimensions were then converted to hardness measurements.

Prior to testing, the samples were polished using a series of silicon carbide grinding discs, ending with a grade of 1200, in order to remove any surface oxidation and provide a high quality surface finish. During the hardness test, a load of 20kg was applied to the sample for a duration of 10 seconds. Eight indents were made in each sample block (two per face, excluding the end faces).

Indents were made sufficiently far apart to ensure the effects of work hardening were negligible. Each indent comprised of two measurements, one for each diagonal of the square indent created by the pyramidal indenter. These measurements were averaged and converted to Vickers hardness using standard lookup tables. The Vickers hardness measurements from the eight indents were then averaged. The standard deviation was also calculated for each sample via the equation:

$$\sigma = \sqrt{\frac{1}{N} \sum_{i=1}^N (x_i - \mu)^2} \quad (3)$$

where σ is the standard deviation, x_i is the i th hardness measurement, μ is the average hardness, and N is the total number of measurements taken for that sample. The average standard deviation was 5.03, with a range of 7.78.

3 Atom Probe Tomography

The microstructures of the model RPV steels were characterized using atom probe tomography (APT). APT enables atomic-scale studies of the microstructure, solute clustering, and grain boundary segregation within a material. This is made possible due to APT's unique combination of mass and 3D spatial resolution. A schematic of an atom probe is shown in Figure 14. In APT ions are field evaporated from the surface of a very sharp, needle-shaped specimen. The intense electric field required for field evaporation is acquired through the superposition of a standing DC voltage, which generates an electric field just below that required for field evaporation, and high voltage (HV) pulses. In order to achieve evaporation at a relatively low voltage, it is essential that the specimen tip be sharpened. This is because the electric field, E , is inversely proportional to the tip radius, R , as shown in the equation,

$$E = \frac{V}{k_f R}, \quad (4)$$

where V is the voltage and k_f is the field factor, a parameter accounting for the geometry of the specimen [70, 71]. During this process, the goal is to achieve highly controlled evaporation where, ideally, no more than one atom is ionized per pulse.

After the ions are field evaporated from the surface of the specimen, they are projected by the applied electric field onto a position-sensitive detector and their time-of-flight is recorded via a

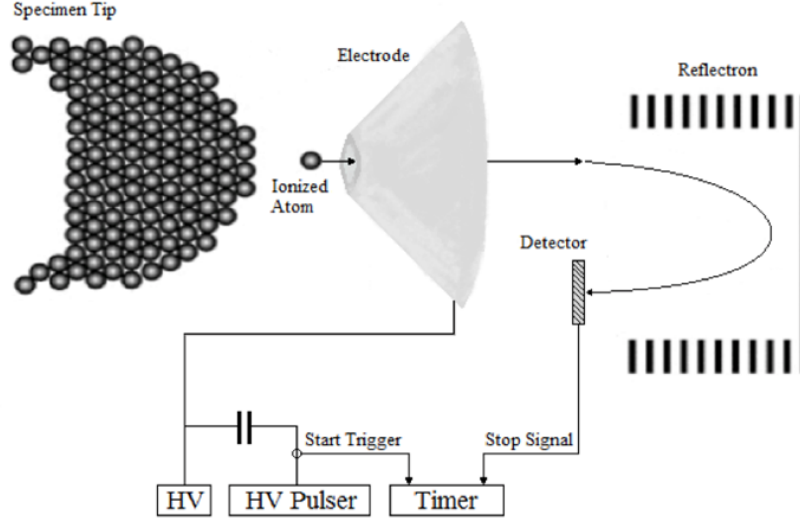


Figure 14: Schematic of Local Electrode Atom Probe (LEAP) [69]. Not drawn to scale.

time-to-digital converter. Timing begins as the HV pulse is delivered to the specimen and ends when the ion(s) hits the detector. In order to decrease the amount of background noise, flight time measurements are restricted to a timing window, the duration of which is based on the flight distance, d , and the expected range of mass-to-charge-state ratios [72]. From the time-of-flight data, the ions' mass-to-charge-state ratios are determined and chemical identities are assigned.

The conversion from time-of-flight to mass-to-charge-ratio-state is relatively straightforward. During field evaporation the electric potential energy, qV , of the ion is converted into kinetic energy, $\frac{1}{2}mv^2$. In the equation for kinetic energy v is approximated to be constant. This is considered to be a reasonable approximation because x , the distance at which the ion is accelerated to terminal velocity, is much less than d , the distance between the specimen and the detector. By relating kinetic energy to the energy gained via electric potential it is possible to determine the mass-to-charge-state ratio of the ion:

$$qV = \frac{1}{2}mv^2 \quad (5)$$

$$v = \frac{d}{t} \quad (6)$$

$$\Rightarrow \frac{m}{q} = 2V \left(\frac{t}{d} \right)^2, \quad (7)$$

where m is the mass of the ion, q is the charge of the ion, V is the total voltage applied to the specimen³, and t is the time it takes for the ion to reach the detector.

As ions are field evaporated from the specimen, the full potential energy from the voltage pulse is not necessarily transferred into kinetic energy [72, 73]. This is often the result of ions being field evaporated during the HV pulse decay time (in practice pulses are imperfectly square). As a result of these energy deficits, the peaks within the mass spectrum are broadened [72]. In modern atom probes, a reflectron is often added prior to the detector in order improve mass resolution [73]. The reflectron is comprised of a series of electrostatic or reflectron lenses which deflect the ions back toward the detector utilizing an electric field. Due to the reflectron, ions which are higher in energy have a longer flight path, and therefore take longer to reach the detector. As a result, the time-of-flight differences between ions within a given peak are shortened, thus improving mass resolution.

Once the data has been collected, using an assumed model of the specimen's geometry (i.e. hemispherical cap on a shank), the ions are reverse projected using their X and Y detector-hit positions to estimate their relative lateral coordinates (x and y) within the specimen [74, 75]. The sequence of evaporation forms the basis of the estimate of the z-coordinate, combined with a correction based on the radius. The resulting product is an atomic 3D reconstruction of the original specimen. Several assumptions are made regarding specimen geometry during this process. Most notably, it is assumed that the tip apex is hemispherical in shape with a radius that increases as the tip is evaporated [74, 75, 71]. This assumption allows the tip radius to be estimated as atoms are removed from the surface.

In this thesis, APT reconstructions were performed using the IVAS software. The image compression factor (ICF) was held constant across all analyses at a value of 1.65. In order to calibrate the reconstruction, the crystallographic plane spacing was calculated for a given pole and used to adjust the initial radius. Typically, between 10^6 and 10^7 atoms were detected and volumes with dimensions of approximately 60 x 60 x 100 nm were analyzed.

In this work, a Local Electrode Atom Probe (LEAP) was utilized. The LEAP 3000X HR is

³In reality the value for V is not precisely known. This is due to the presence of reflections of the voltage pulse in the tip-electrode structure. Voltage is often modelled by the equation, $V = V_{DC} + \alpha V_{pulse}$, where α is the pulse factor. The pulse factor in the LEAP 3000X HR is assumed to be 1.

equipped with a reflectron lens and has a wide-field-of-view [72]. The model used in this study has a flight path of approximately 40 cm and has a resolution of $\Delta m/m = 1/600$ full-width at half-maximum (FWHM). The LEAP 3000X HR is also capable of replacing the HV pulsing with laser pulsing, which is preferable for brittle and less conductive materials [70]. However, laser pulsing is known to introduce unwanted artefacts into the reconstruction. Additionally, samples run using voltage mode typically have a better mass resolution. As all of the samples analyzed in this thesis were highly conductive and not very brittle, voltage mode was utilized.

All of the atom probe analyses in this thesis were carried out at 50 K with a pulse repetition rate of 200,000 Hz and pulse fraction of 20%. These experimental parameters were previously optimized for similar RPV steels by Styman [36].

It should be noted that techniques such as transmission electron microscopy (TEM) could theoretically provide comparable lateral resolution ($\sim 0.5\text{-}2$ nm) to atom probe tomography. However, TEM images are integrated through the specimen's thickness, which is often on the order of tens of nanometers [72]. Atom probe tomography, on the other hand, can provide sub 0.3 nm resolution on all three axes⁴ [70, 72]. Furthermore, APT enables atomic-scale studies of three-dimensional features such as solute clustering and precipitates. The 3D spatial resolution offered through APT is essential to this investigation, as it focuses on identifying and characterizing the very early stages of solute clustering.

3.1 Background Noise

In atom probe analyses, there exists noise within the mass spectra due to ions within the chamber striking the detector. Although the analysis chamber is kept under ultra-high vacuum, there still remains residual gas within the chamber. Background events are created when these gas molecules pass near the specimen surface, become polarized, and are then attracted to the specimen. Once on the surface, these molecules become ionized and are propelled toward the detector via the same mechanism as atoms from the specimen.

Background noise within the mass spectrum can also be caused by the dark current of the detector. The dark current is a small electric current present within the detector which attracts residual gas toward the detector when the timing gate is initially opened.

⁴Trajectory aberrations and local magnification effects can cause degradation of the x and y resolution [70].

3.2 Mass Spectrum and Ranging

A mass spectrum is created by plotting a histogram of the mass-to-charge-state ratios for each ion detected by the atom probe in a given sample. The peaks in these mass spectra are subsequently identified and labeled; this process is called “ranging” (Figure 15). There exists two components in the process of ranging mass spectra: peak identification and defining peak extents.

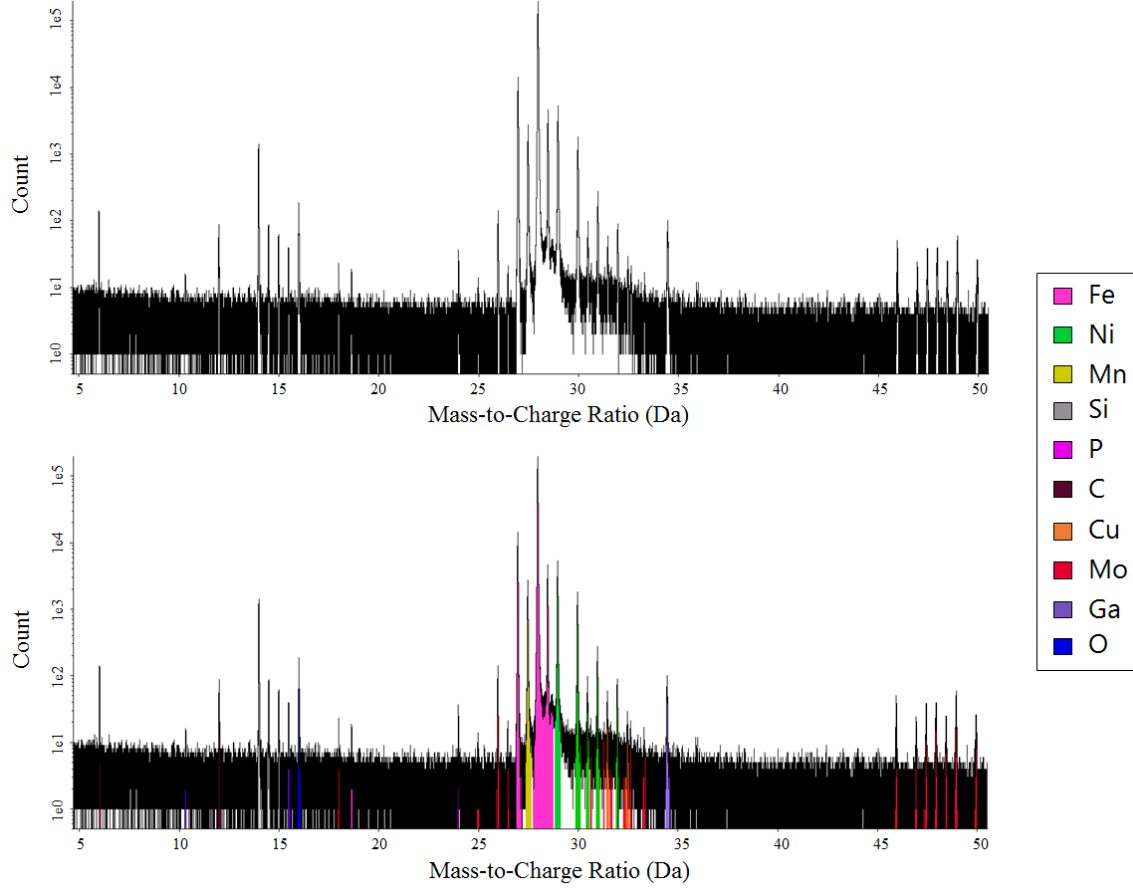


Figure 15: Mass spectrum before (above) and after (below) ranging.

Correct peak identification is essential to atom probe analysis. For RPV steels, peak identification is relatively straightforward as only several peak overlaps, i.e. two or more ions with the same mass-to-charge-state ratio, are present in the spectra. The deconvolution of these overlapping peaks is discussed in Section 3.1.1. Correctly identifying and deconvoluting peaks is extremely important as peak misidentification can be a significant source of error. Misidentification directly affects composition analyses, cluster analyses, identification of phases, and the general

interpretation of the data.

There exists a number of methods to range mass spectra, or to define the extents of each peak. In this work the background-to-background method was utilized. Methodical and consistent ranging assists in maximizing the signal-to-noise ratio within the data. For the background-to-background method, ranges begin at the start of each peak and end when the peak's ion count returns to the background level (Figure 16). If tails are present, the ranges are cut-off at the local background level. The background-to-background method was utilized in this thesis as it enabled consistent ranging without peak fitting. Ranging methods such as full width at half maximum (FWHM) require such fitting to obtain consistent, reliable results.

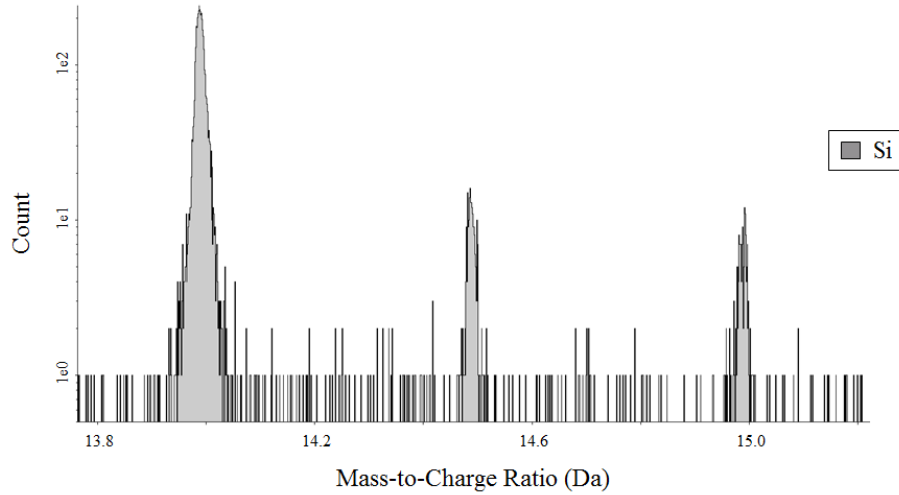


Figure 16: A portion of a mass spectrum illustrating the background-to-background method of ranging.

Additionally, prior to all analyses background subtraction was performed on each of the mass spectra. This was done using IVAS, a software package for creating and analyzing APT reconstructions. To do this, IVAS fits a model to the background and then subtracts this from the mass spectrum.

3.2.1 Peak Overlaps

APT analysis is complicated by the fact that the mass spectra of RPV steels can contain several peak overlaps, the most prominent being due to $^{58}\text{Ni}^{2+}$ and $^{58}\text{Fe}^{2+}$ ions. Common peak overlaps in the mass spectra of RPV steels are listed in Table 4. Typically, the relative contributions to these peaks are deconvoluted using known natural isotopic abundances and the heights of

adjacent non-overlapping isotope peaks. Using this information, the expected contribution of each element to the overlapping peak can be determined. This process is illustrated in Figure 17. In this example the $\text{Ni}58^{2+}$ and $\text{Fe}58^{2+}$ peak overlap is addressed. From isotopic abundances it can be determined that the overlapping peak at 29 Da is expected to contain 0.28% of the total Fe and 68.08% of the total Ni in the system. These totals can be calculated via the Fe and Ni peaks located at 28.5 and 30 Da, respectively. Finally, the expected number of counts for each element within the overlapping peak can be calculated. These counts are then normalized, as the two numbers typically do not exactly add up to the total number of counts observed within the peak in question. However, the sum is typically within 100 atoms of the number of counts observed in the overlapping peak.

Generally, deconvolution is applied to the entire dataset. However, in this thesis peak deconvolution depended heavily on the local chemistry and was therefore carried out separately for precipitates and the matrix.

Mass-to-Charge Ratio (Da)	Element 1	Element 2	Peak Assignment
12	$^{12}\text{C}^+$	$^{12}\text{C}_2^{2+}$	Considered to be $^{12}\text{C}^+$
14	$^{14}\text{N}^+$	$^{28}\text{Si}^{2+}$	Considered to be $^{28}\text{Si}^{2+}$
27	$^{54}\text{Cr}^{2+}$	$^{54}\text{Fe}^{2+}$	Considered to be $^{54}\text{Fe}^{2+}$
28	$^{28}\text{Si}^+$	$^{56}\text{Fe}^{2+}$	Considered to be $^{56}\text{Fe}^{2+}$
29	$^{58}\text{Fe}^{2+}$	$^{58}\text{Ni}^{2+}$	Deconvolved
31	$^{31}\text{P}^+$	$^{62}\text{Ni}^{2+}$	Considered to be $^{62}\text{Ni}^{2+}$
32	$^{96}\text{Mo}^{3+}$	$^{64}\text{Ni}^{2+}$	Considered to be $^{64}\text{Ni}^{2+}$

Table 4: Common peak overlaps in the mass spectra of RPV steels.

Another potential peak overlap is $\text{Si}28^{2+}$ and $\text{N}14^+$. However, the nitrogen content in these model RPV steels is very low. Furthermore, the limited amount of nitrogen that does exist is most likely located within aluminum nitride particles and molybdenum carbo-nitrides. Regardless, it is possible to calculate the expected Si contribution to the relevant overlapping peaks (14 Da and 15 Da) using isotope abundances. From these calculations it was confirmed that the free nitrogen content was negligible in the atom probe analyses presented.

Additional peak overlaps commonly present in RPV mass spectra and their treatment are listed in Table 4. In several cases peak deconvolution was not possible due to the lack of isotopic peaks for particular elements. In these cases the peak in question was ranged as the more prominent element out of the two.

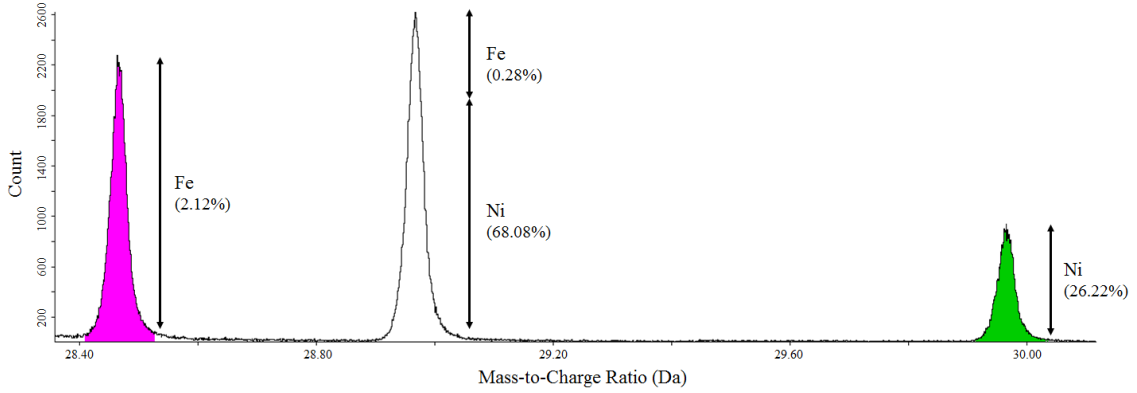


Figure 17: Ni⁵⁸²⁺ and Fe⁵⁸²⁺ peak overlap is addressed. From isotopic abundances it can be determined that the overlapping peak at 29 Da is expected to contain 0.28% of the total Fe and 68.08% of the total Ni in the system.

3.3 Trajectory Aberrations

Trajectory aberrations and local magnification effects are known to degrade the x and y resolution of atom probe reconstructions [70, 72, 76]. Trajectory aberrations are typically caused by precipitates which have an evaporation field different from that of the matrix. Due to differences in the applied electric field needed to evaporate different elements, these precipitates can have significant effects on the local curvature of the specimen surface. When the evaporation field of the precipitates is higher than the matrix, the precipitate is preferentially retained. As a result, the precipitate protrudes from the surface, creating a localized region of higher curvature. Thus, when the ions from these high-field precipitates are evaporated from the surface, they are erroneously directed outward, causing an apparent decrease in the atomic density. Conversely, low-field precipitates, i.e. precipitates incorporating elements prone to evaporation at a less intense electric field, increase the apparent density (Figure 18).

3.4 Surface Migration

Surface migration in APT refers to the movement of atoms across the surface of the specimen prior to field evaporation [103, 78, 79, 80, 81]. These atoms move along the surface due to the presence of inhomogeneities in the electric field. This phenomenon is a thermally activated process. Typically, solute atoms with higher field evaporations are more prone to these surface migration effects, as they spend significantly more time on the surface of the specimen.

In RPV steels, surface migration, specifically segregation of solute to the poles, is commonly

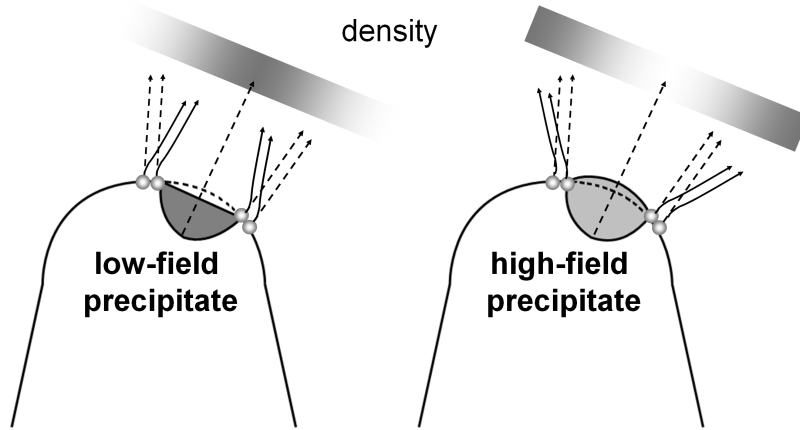


Figure 18: Trajectory aberrations, due to changes in the curvature of the specimen surface, have a significant impact on the perceived density of precipitates. The diagram illustrates the origins of these artificial changes in apparent density for a low-field and high-field precipitate.

observed. Poles are due to crystallographic planes that protrude from the surface of the specimen. Areas around these poles are generally characterized by relatively high electric field gradients. Therefore, when solute atoms traveling along the surface of the specimen reach these regions they field evaporate. This causes an increase in solute density around the pole within the reconstruction and can therefore be easily identified and removed if necessary.

3.5 Detector and Efficiency

Current atom probes typically incorporate a detector that is comprised of a series of micro-channel plates (MCPs) [70]. This stack of MCPs is responsible for converting each ion that strikes the detector into an amplified electron signal. This amplified signal is then projected onto a delay-line detector. The delay-line detector contains two or more conductive lines along which the signal travels. The time each signal takes to reach the end of the line is then utilized to triangulate its point of origin, thus providing the x and y coordinate of the detector hit.

Due to this configuration and the presence of the reflectron, the LEAP 3000-HR has a detector efficiency of approximately 37%. This is a stochastic process, independent of ionic identity and therefore does not affect chemical compositions. This loss of atoms is due to a combination of the geometry of the channels on the MCP as well as the design of the reflectron. As a result, a cluster that contains a 100 atoms will be observed, on average, to contain only 37 atoms. The significance of this is discussed further in Section 7.1. In addition to clusters appearing to contain fewer atoms, small clusters could potentially not be detected at all. Furthermore, even if these

clusters are detected they will often be too small to distinguish from randomly occurring clusters.

It should also be noted that as the physical cluster size decreases, the error of this measurement increases. In the case of very small clusters, removing just a few atoms can drastically change the observed composition and size. For example, if one less atoms is observed for a 100 atom cluster, its size only changes by 1%, whereas for a 10 atom cluster, its size would change by 10%. A cluster's observed composition would be similarly affected.

4 APT Sample Preparation

Two methods were utilized in APT sample preparation: electropolishing and focused ion beam (FIB) lift-out. Electropolishing was used to produce the majority of the samples in this thesis. However, in order to create APT samples from the ion irradiated material, FIB lift-outs were conducted. Site-specific FIB lift-outs were also necessary in order to incorporate grain boundaries or carbides within an APT sample.

4.1 Electropolishing

For electropolishing, 0.5mm x 0.5mm x 10mm “matchsticks” were created from bulk samples using a Buehler Isomet 5000 diamond saw. These matchsticks were then sharpened using a standard two-stage electropolishing technique. In the first stage, the specimens were polished using a solution of 25% perchloric acid (60%) and 75% acetic acid using an applied voltage between 6V-18V (Figure 19a). During the second stage a 2% perchloric acid (60%) and 98% butoxyethanol solution was used to sharpen the specimens with a voltage between 2V-6V (Figure 19b). This final sharpening was accomplished using an optical microscope, producing specimens with a tip diameter of approximately 100nm. After electropolishing was complete the samples were rinsed in ethanol to remove any residual acid and minimize oxidation prior to analysis.

4.2 Focused Ion Beam Lift-Out

A focused ion beam (FIB) was used to create APT samples from ion irradiated material as well as samples which incorporated grain boundaries or carbides. This was achieved by specifically selecting a region of interest (ROI) in the FIB, a capability not accessible when using the electropolishing technique. The site-specific lift-outs were carried out on two machines: the Zeiss

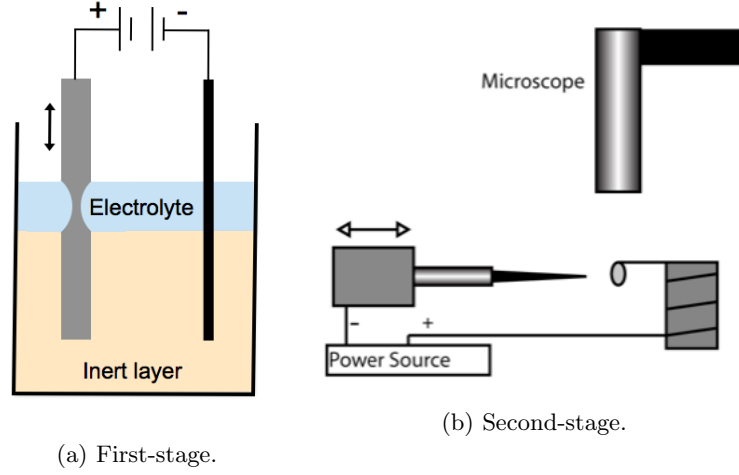


Figure 19: First- and second-stage electropolishing of atom probe samples [70].

Auriga FIB-SEM at the University of Oxford or the Helios NanoLab 600i at the Culham Centre for Fusion Energy. At UCSB a FEI Helios Dualbeam Nanolab 650 was utilized to make all of the ion irradiated APT specimens.

There exist many variants of the FIB liftout technique, the most common of which is detailed in [82]. However, a brief overview of the technique is presented here (Figure 20). First, a ROI is identified and covered with a platinum capping layer, typically $3\mu\text{m} \times 20\mu\text{m}$ and approximately 100nm thick. This capping layer limits the amount of gallium ion damage to the sample. This is particularly important when the ROI is a grain boundary, as Ga damage can be more prominent in these regions. Next, a wedge containing the ROI is created by removing adjacent rectangular sections of material via FIB. After attaching the micromanipulator, this wedge is lifted out from the bulk and used to create several atom probe specimens. Each specimen is created by attaching a portion of the wedge to a prefabricated microtip via platinum deposition.

The specimens are then sharpened using a series of annular milling patterns. The first mill was typically performed at 3-5nA and 30kV; subsequent millings were performed with progressively lower ion currents and smaller inner radii until the desired tip radius was acquired. Lastly, a low energy “solid” mill was performed at 5kV in order to remove a layer of material, minimizing the amount of Ga damage at the surface as well as implanted Ga present in the specimen.

For the ion irradiated specimens a damage of about 4dpa was obtained at the apex of the samples by FIBing approximately 500nm below the capping layer. FIBing samples at a consistent depth was made possible through the use of the capping layer as a marker for the surface.

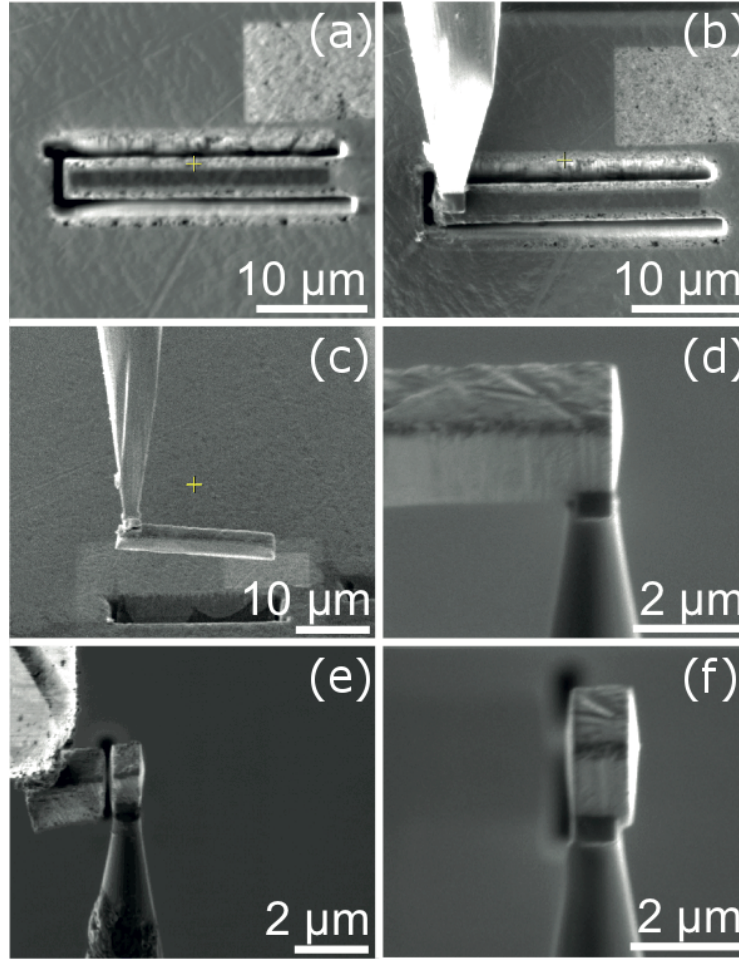


Figure 20: Images showing the various stages of the FIB lift-out process [70]: (a) shows the wedge after it has been cut free from the sample on all but one side; (b) shows the wedge after being welded to the micromanipulator; (c) illustrates the physical lift-out of the wedge from the bulk; (d) shows the mounting process of the wedge to a prefabricated microtip; (e) and (f) illustrate the cutting and removal of the remainder of the wedge. Steps (d), (e), and (f) can be repeated to make multiple APT samples on additional microtips.

5 Detecting the Presence of Clusters

In order to detect the presence of non-random clusters, first the term “random cluster” must be defined. In a hypothetical, unaged RPV steel, solute atoms are distributed randomly within the matrix. Perhaps counterintuitively, some of this solute will appear to be clustered, i.e. it is statistically likely that some solute atoms will be adjacent to one or more other solute atoms, forming clusters. These random occurrences are referred to as “random clusters” and defined as clusters that are statistically likely to be observed in a randomly distributed system. Logically,

large random clusters are statistically unlikely. Determining whether or not non-random clusters are present in a dataset can be very challenging, particularly if the clusters are very small or poorly defined.

Various statistical methods can be utilized to determine if non-random clusters are present within an APT reconstruction, including frequency distributions, k-nearest neighbor analysis, contingency tables, cluster size distributions, radial distribution functions, and the local chemistry method [83, 84, 85]. Three of the most commonly used – frequency distributions, k-nearest neighbor analysis, and the local chemistry method – are discussed in the following sections.

5.1 Frequency Distributions

To create a frequency distribution an APT dataset is divided into small voxels, or cubic volumes, each of which contain a set number of atoms, typically on the order of 100 [86]. This analysis tool compares the frequency with which an element occurs in each voxel to that expected from a binomial distribution. A binomial distribution is the expected distribution of solutes in a random solid solution. Using a χ^2 test statistic, the significance of the deviation of the distribution from randomness can be determined. If an element’s p-value is below a predetermined significance level, α , typically chosen to be 0.01, it is considered to have a non-random distribution of solute.

One disadvantage of frequency distribution analyses is that information is lost as a result of statistical sampling. This is due to the fact that neighboring atoms are often assigned to different voxels. For this method it is imperative to select an appropriate voxel size. If the number of atoms in each voxel is too large, small compositional fluctuations will be averaged out [87]. If the number of atoms is too small, the distribution will not contain meaningful results. Furthermore, the results can often be difficult to interpret in terms of the extent of clustering present. This is because frequency distributions do not identify individual clusters or offer any insight into possible spatial-chemical associations between elements.

5.2 k-Nearest Neighbor Analysis

k-nearest neighbor analysis is based on the distribution of solute-solute k-NN distances in a sample, i.e. the distance between a solute and its closest k solute neighbors [88, 89]. One advantage of k-NN analyses is that, unlike other methods, no statistical sampling is introduced; only the raw data is utilized [87]. Furthermore, k-NN analyses are computationally simple and fast.

Considering first nearest neighbors, the theoretical density probability, $P(r)$, can be calculated,

$$P(r) = 4\pi r^2 Q C_0 \exp\left(-\frac{4}{3}\pi Q C_0 r^3\right), \quad (8)$$

where r is the distance between solute atoms, Q is the detection efficiency, and C_0 is the nominal composition [89]. This distribution is determined using the assumption that the solute atoms are randomly distributed throughout the matrix. The experimental distribution, $P(r)$, is determined by calculating the distance, r , between every solute atom and its nearest neighboring solute atoms [89]. The actual and theoretical distributions are then compared ⁵. Although the probability density for 1NNs is presented here, the approach can be extended to higher order NN analyses, e.g. 5NN, 10NN, etc. This can be particularly effective in systems with higher solute concentrations.

One disadvantage of the k-NN approach is that it is strongly affected by local magnification effects [90, 87]. This poses a problem for systems that include elements with very different field evaporations (e.g. Fe and Cu). Extreme differences in field evaporation can lead to large local magnification effects and thus significantly affect the experimental k-NN distribution [87, 89].

Furthermore, implementation of this technique in the current version of IVAS is misleading, as the experimental distribution is only compared to a single random distribution. This random distribution could be highly improbable and not representative of a typical random distribution. Therefore, one way to further improve this method would be to choose a statistical test that enabled the user to compare the experimental distribution to a large sample of random distributions.

5.3 Local Chemistry Method

The methods mentioned previously are often not sensitive enough to reveal the subtle fluctuations in solute distributions at the earliest stages of solute clustering. Therefore, the local chemistry method, a more sensitive technique developed by Hyde et. al., was utilized in this thesis [84].

The local chemistry method determines spatial correlations between atoms types. This is done by selecting a base element, for example Ni, and analyzing the solutes found within a fixed number of nearest neighbors (NN) of every Ni atom as illustrated in Figure 21. The observed

⁵It is also commonplace to compare the experimental NN distribution to the NN distribution obtained from a randomized dataset.

number of a particular solute, for example Mn, found within this fixed number of NN for each Ni atom is tallied. This observed value is compared to the expected number of Mn atoms: at.% Mn in the sample times the total number of NN atoms. A ratio of the observed number of atoms to expected number of atoms is then calculated. Interpreting the results is intuitive: a ratio of 1 indicates no solute association, a ratio of less than 1 indicates less solute association than expected, and a ratio of more than 1 indicates more solute association than expected. Assuming Poisson statistics a test statistic is generated and the p-value is determined. This p-value indicates the probability of obtaining a result at least as extreme as the one that was observed.

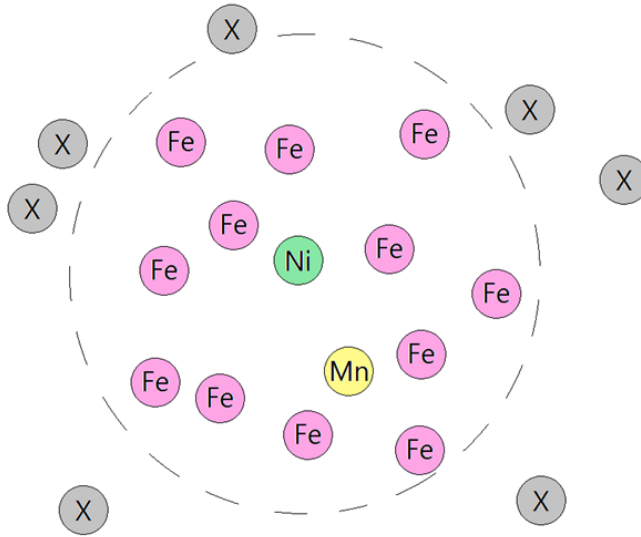


Figure 21: Schematic of the local chemistry method. The case of association between Ni and Mn is considered in this example.

The local chemistry method essentially aggregates fluctuations over the entire dataset and therefore can detect association of elements on the atomic scale. The local chemistry method can, in theory, identify statistically significant association between two elements using only the first nearest neighbor. However this depends heavily on the size of the dataset and the severity of the association between the two elements.

There is no formal upper limit regarding cluster size for which the local chemistry method ceases to be effective. However, for sufficiently large clusters, essential information, such as cluster size and cluster count, is not provided. Therefore, alternative methods, such as the maximum separation method, are more suitable for larger clusters.

5.3.1 P-values and Bonferroni Correction

A conservative significance level of 0.01 was chosen for all t-tests. Thus, only p-values below 0.01 were considered to be statistically significant. For each sample 49 t-tests were carried out (there are 7 solutes of interest and association between all solute types was tested). If multiple t-tests are performed in parallel in this way the chance of an unlikely event increases. Therefore, a Bonferroni correction was used in order to avoid type I errors (i.e. incorrectly rejecting the null hypothesis, which, in this case, is that there is no solute association). The Bonferroni correction is a simple and conservative way to avoid false positives. The Bonferroni correction divides the significance level by the number of tests conducted in order to compensate for this increased chance of an improbable event occurring. In this case, the significance level was set to 0.01 and 49 tests were conducted; therefore, the significance level was corrected to 0.0002.

6 Extracting Individual Clusters

It is often of interest to identify, extract, and characterize non-random clusters within an APT reconstruction. Identifying individual clusters, however, is both ontologically and practically challenging as there is no established definition of a cluster and APT data is imperfect [70]. The imperfect detection efficiency and spatial resolution of an APT reconstruction becomes extremely significant on the atomic scale. As clusters of interest can sometimes contain only a few atoms, this can be a challenging problem. In order to meet this challenge, a range of clustering identification algorithms have been developed, which identify clusters using a variety of definitions (atomic separations, local densities, etc.) [70]. These algorithms include the maximum separation method [92], local concentration-based metrics [93], the core-linkage algorithm [88], and Voronoi partitioning [94]. Several of these methods, namely the maximum separation method, the envelope method, and the core-linkage clustering algorithm, are described in detail below. However, an authoritative review on this subject is provided by Marquis and Hyde [87].

6.1 Maximum Separation Method

The most commonly used cluster identification algorithm in APT is the maximum separation method. The maximum separation method utilizes the fact that a pair of adjacent solute atoms within the same cluster will be in closer proximity to one another than any corresponding pair of

solute located within the matrix [87, 83]. A schematic of this method is shown in Figure 22.

The maximum separation method requires the user to select the solute elements within the dataset. Following this selection, a maximum separation distance, D_{max} , is then defined. D_{max} is typically chosen to be between 0.4 - 0.7 nm but depends on several variables such as the expected spacing between atoms, solute concentration, and the approximate size of the clusters. A recursive search algorithm is then utilized to identify groups of solute atoms that are within D_{max} of at least one other solute atom in the cluster (Figure 22a-b). Solute atoms selected in this step are referred to as core atoms.

In the next step, matrix atoms are incorporated in the clusters if they are within a distance L of the core atoms (Figure 22c-d) [85]. This is known as enveloping and often inherently results in the inclusion of a shell of matrix atoms around the cluster [87]. This shell is removed through the erosion step; atoms within a distance E of matrix atoms are removed from the clusters (Figure 22e-f). Lastly, clusters incorporating less atoms than the user defined parameter N_{min} are removed. This is done in order to remove the contributions of false positives; naturally occurring fluctuations of solute atoms are also identified as clusters by the cluster search algorithm. Once individual clusters have been identified via the maximum separation method, various information can also be extracted, including cluster sizes, chemistry, and morphology.

6.1.1 Maximum Separation Method Parameter Selection

The most important parameter of the maximum separation method is D_{max} . While there is no unique, correct choice for D_{max} , it is often said that there are plenty of wrong ones [87]. If D_{max} is too small, dilute clusters will be overlooked. If D_{max} is too large, many random, insignificant clusters will be included and adjacent clusters may be identified as a single cluster [87, 96].

Hyde et al. have conducted a series of simulations in order to determine the sensitivity of the maximum separation input parameters, including D_{max} [96]. It was concluded that in order to identify clusters (containing $> 50\%$ solute atoms) between 1.5 and 2.5 nm in diameter in a BCC Fe matrix with a detection efficiency of 37% the optimal value for D_{max} is 0.5 nm. This optimal D_{max} value was reaffirmed by Styman et al. specifically for reactor pressure vessel steels [97]. Styman found that the optimal parameter values they put forth are equally applicable to both large and small clusters.

The maximum separation method was used to identify clusters within the ion irradiated

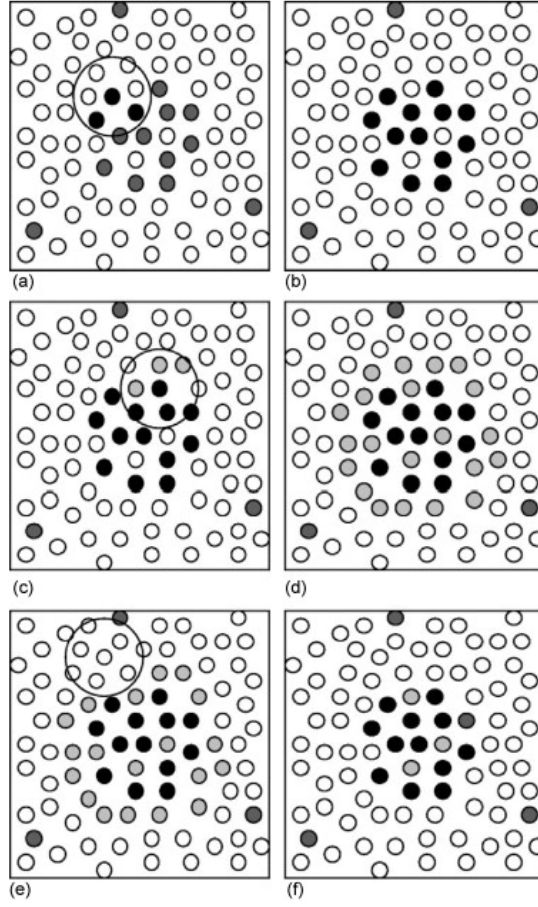


Figure 22: Schematic diagram the maximum separation method: (a) and (b) show solute atom selection; solute atoms (dark grey) within D_{max} of each other are selected as core atoms (black). (c) and (d) show matrix atom selection; matrix atoms (white) are selected (light grey) if they are within a distance L of the core atoms. (e) and (f) illustrate erosion; atoms within a distance E of matrix atoms are removed [96, 87].

RPV steels analyzed in Chapter 5 of this thesis. Within the ion irradiated steels, Ni segregation to grain boundaries and dislocations made it particularly difficult to identify individual clusters. The maximum separation algorithm would often join multiple clusters together, thus artificially decreasing the number density and increasing the cluster size. Therefore a compromise was made; Ni was not included in the cluster search as a solute atom. Additionally, in order to ensure the inclusion of any Ni shell present, the erosion step was also eliminated. The application of this technique enabled the identification of individual clusters even in the presence of grain boundaries and dislocations (Figure 23). The parameters used were as follows: $D_{max} = 0.45 - 0.65$ nm; N_{min} = number of atoms where the random cluster size distribution was equal to zero; $L = D_{max}$; and

$E = 0$.

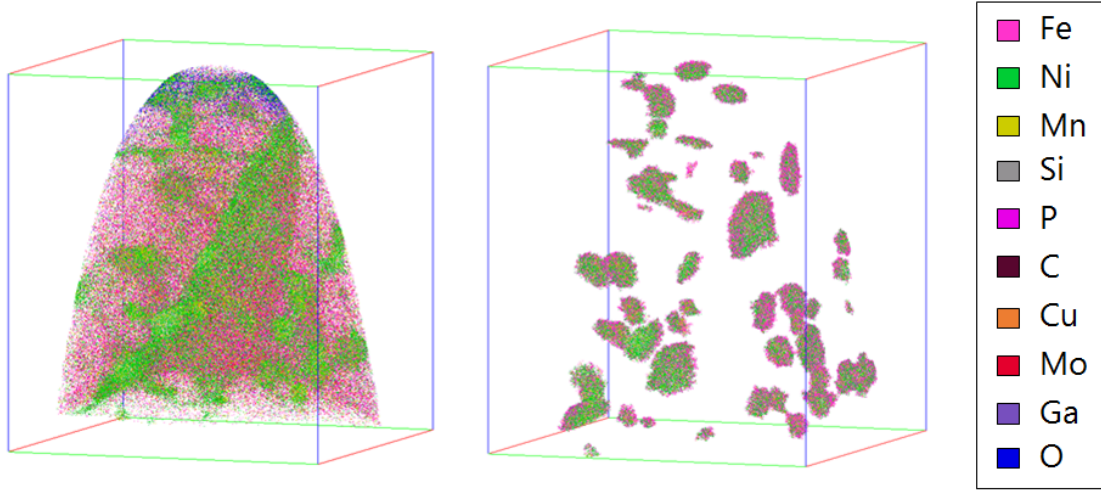


Figure 23: Atom probe reconstruction of sample C before (left) and after (right) the application of the maximum separation method. Precipitates located along the grain boundary have been successfully identified as individual clusters.

7 Characterizing Clusters

7.1 Estimating Physical Cluster Size Distribution

Due to the microchannel plate and reflectron, the LEAP 3000X HR has an efficiency of approximately 37% [70]. This is usually assumed to be a random process, independent of chemical identity. This has several important implications; for instance, the cluster size distribution will be significantly altered⁶. However, using statistics it is possible to estimate this lost information. Although the affect of efficiency cannot be reversed on an individual cluster basis, physical cluster size distributions can be estimated from efficiency degraded distributions quite effectively [98].

Imperfect detector efficiency introduces uncertainty in the distribution of cluster sizes [98]. For example, a cluster that contains 100 atoms in the specimen will not necessarily be identified as a cluster of 37 atoms in the APT data, but rather can appear in the reconstruction consisting of anywhere between 0 and 100 atoms. Therefore it is desirable to be able to recover the original physical cluster-size distribution. Stephenson et al. utilize an expectation-maximization (EM)

⁶This only occurs if cluster size is based on the number of atoms found within the cluster.

algorithm in order to obtain a physical distribution of cluster-size from an efficiency-degraded distribution [98]. This approach estimates the probability of a y -atom cluster, where x atoms are actually detected, as binomial. Since Stephenson et al. estimate the probability as binomial they are making the assumption that whether or not an atom is detected is an independent process. This assumption is often made in the field of atom probe tomography and accepted as a reasonable claim.

According to this model, the efficiency degraded cluster-size distribution can be expressed as

$$f_{\epsilon}(x) = \sum_{y=x}^{\infty} \binom{y}{x} \epsilon^x (1 - \epsilon)^{y-x} g(y), \quad (9)$$

where $g(y)$ is the physical cluster-size distribution, ϵ is the detector efficiency, y is the physical cluster size, and x is the detected cluster size [98]. The EM algorithm is then utilized in order to fit the probability distribution to the measured data. Stephenson et al. demonstrated using simulations that the restorative EM algorithm they developed was adequately able to restore several test functions [98].

When estimating the physical cluster size distribution from the degraded cluster size distribution, there exist three levels of complexity based on the constraints placed on the detection efficiency, θ : *a priori* known, uniform unknown, random unknown. For atom probe data only the first of these is applicable as the detection efficiency is assumed to be constant and is *a priori* known.

In Stephenson's work, the physical cluster size distribution is calculated from the degraded cluster size distribution using an expectation-maximization (EM) algorithm [98]. However, in the case where θ is *a priori* known, there exists an analytical solution to the maximum likelihood estimate (presented in the Appendix 2), thus obviating the need for EM. EM provides an estimate of the solution and in some cases outputs a local maximum instead of the global maximum. Therefore, EM should only be used when an analytical solution is not practical or impossible to obtain.

8 Transmission Electron Microscopy

The TEM experiments conducted in this thesis were carried out on a Jeol 2100 at the University of Oxford. Transmission electron microscopy (TEM) is a microscopy technique in which a beam of electrons is passed through a very thin sample. Electrons are emitted from an emission source or electron gun and accelerated toward the sample. Prior to reaching the sample the

electrons are passed through a series of lenses. Condenser lenses are responsible for focusing the electron beam onto the specimen such that sufficient image intensity is obtained [99]. The apertures are responsible for eliminating the high angle electrons from the beam. The electrons then come into contact with the sample and are scattered as they pass through the material. The objective lens collects and focuses these scattered rays after they have passed through the sample. The back-focal plane of the objective lens is where the diffraction pattern of the sample is formed. The projector lenses then magnify and place the beam onto an imaging device, such as a florescent screen. A more detailed description of TEM can be found in [100].

Specimens for TEM were prepared from 3 mm disks, which were ground down to a thickness of approximately 90 μm using a series of silicon carbide grinding discs followed by diamond paper. The specimens were then electropolished using 90% perchloric acid with a TenuPol Electropolisher.

Chapter IV

Thermally Aged RPV Steels

First, hardness measurements are presented followed by atom probe analyses of five low copper steels which contained systematic variations in Ni and Mn. The level of solute clustering within the matrix is determined via the local chemistry method for the steels in both as-received and thermally aged states. Next, clusters which have formed at heterogeneous nucleation sites are analyzed. Finally, work on secondary precipitates found within the cementite phase of both high and low copper steels is presented.

1 Hardness Measurements

Hardness measurements of the samples were taken in the as-received state (0 hours) and after approximately 11,690 hours of thermal aging. Hardness measurements for samples C, K, G, A, and H are shown in Figure 24. Complete tables of hardness measurements can be found in the Appendix. Typically, RPV steels are expected to undergo hardening after thermal aging due to the pinning of dislocations by precipitates. Such hardness increases are observed in sample F, an RPV steel high in copper (Figure 25). However, in the low copper steels a statistically significant decrease in hardness was observed after 11,690 hours of thermal aging.

In order to statistically verify the apparent decrease, a multiple linear regression model was utilized. These models aim to describe a dependent variable, in this case hardness, via one or more independent variables. When fitting data with a linear model, the assumption is made that the dependent variable is linear dependent on the various regressors, or independent variables. While this claim might not necessarily be true for this data, the hardness measurements were only collected at two points in time, and therefore fitting a more complicated model would result in drastic overfitting. Furthermore, the aim here is simply to determine if there exists a statistically significant change in hardness (increase or decrease) due to time or temperature. Thus, the

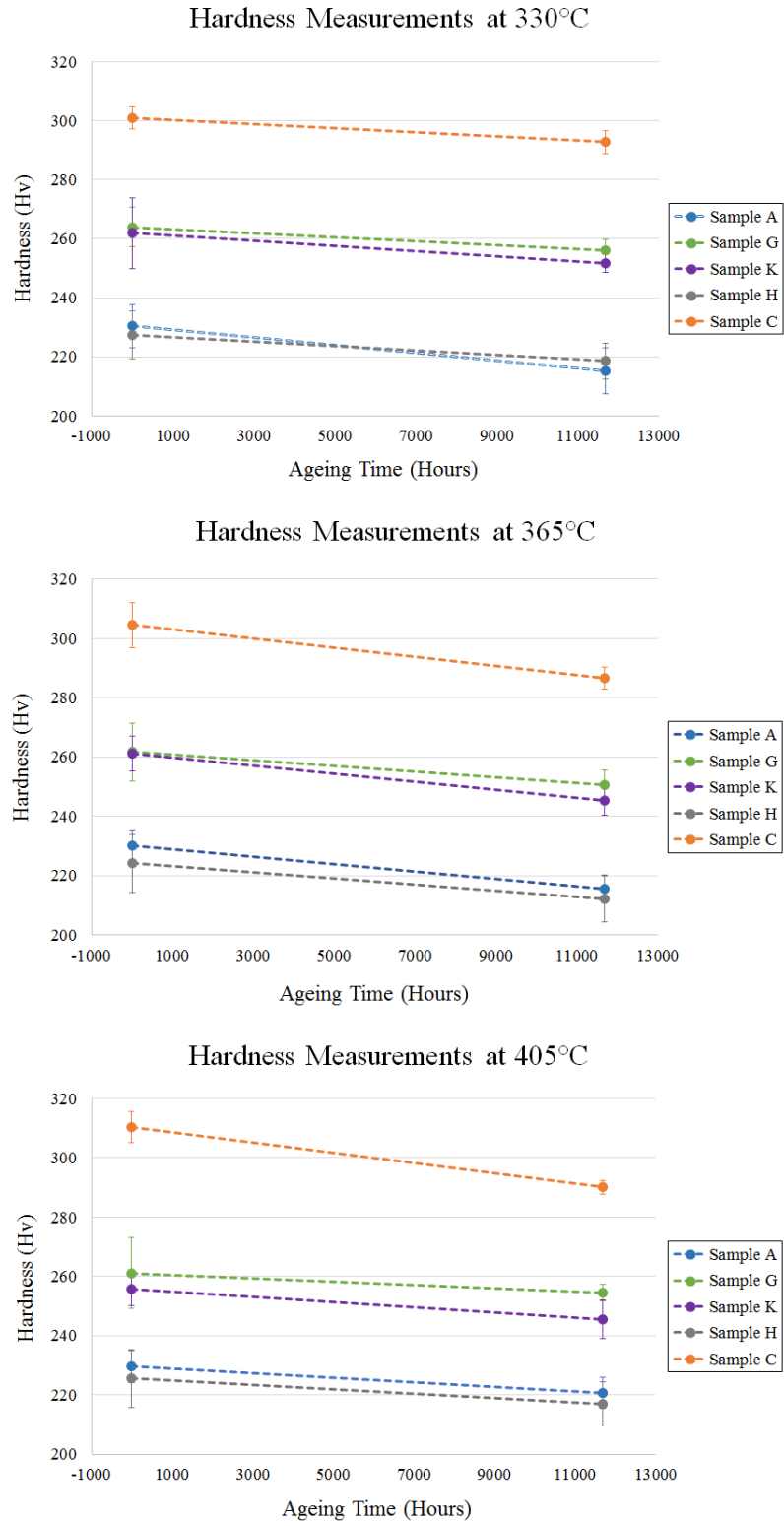


Figure 24: Hardness measurements for RPV steels after 11,690 hours of thermal aging at 330°C, 365°C, and 405°C.

following equation was used to model hardness:

$$\text{Hardness} = \beta_0 + \beta_1 \text{Time} + \beta_2 \text{Temperature} + \beta_3 C + \beta_4 G + \beta_5 H + \beta_6 K + \epsilon \quad (10)$$

where C, G, H, and K are indicator variables and ϵ is an error term. Indicator variables take on either a value of 0 or 1, depending on the steel. For sample C, the indicator variables G, H, and K would be set equal to 0 and the indicator variable C would be set equal to 1. Therefore, for sample C the model would simplify to the following equation:

$$\text{Hardness} = \beta_0 + \beta_1 \text{Time} + \beta_2 \text{Temperature} + \beta_3 C + \epsilon \quad (11)$$

Modeling hardness using a multiple linear model made it possible to determine the effect of each variable on hardness while the remaining predictor variables were held constant. By regressing on time, temperature, and steel type it was determined that there is a statistically significant decrease in hardness due to time. The R output for this regression is shown in Table 5.

For each variable included in the model a t-test was performed in order to determine the probability (p-value) that the observed effect on hardness was due to random chance. The t-values and p-values are both shown in Table 5. Predictor variables were considered statistically significant if their p-values were less than 0.05, a predetermined significance level (α). Thus, the variable “time” was considered statistically significant, while the variable “temperature,” with a p-value of 0.89, was not considered statistically significant. Examining the coefficient of time one can determine the effect of one unit of time (1 hour) on hardness. By multiplying this coefficient by the number of hours the samples underwent thermal aging (11,688 hours), it is possible to determine the total estimated effect of time on hardness. Additionally, time’s negative coefficient indicates that there was a decrease in hardness due to time. Thus, hardness is expected to decrease by 11.6 Hv after 11,690 hours of thermal aging after taking steel type into account.

It should also be noted that the intercept coefficient in this table (β_0 in the model) is representative of the initial hardness for sample A, the only sample without an indicator variable. The coefficient for Steel C (β_3 in the model) is representative of the difference in initial hardness between samples A and C. Similarly, the coefficient for Steel G represents the difference in initial hardness between samples A and G and so on. For the indicator variables listed, their low p-values are indicative of significant differences in initial hardness between the steel in question and steel A.

Variable	Coefficient	Std. Error	T-value	P-value
Intercept	229.20	6.35	36.11	<2e-16
Time	-9.94e-4	8.89e-5	-11.18	<2e-16
Temperature	2.25e-3	1.70e-2	0.13	0.89
Steel C	73.31	1.64	44.62	<2e-16
Steel G	32.92	1.64	20.03	<2e-16
Steel H	-3.43	1.64	-2.09	0.04
Steel K	29.50	1.64	17.96	<2e-16

Table 5: Table of the R output from multiple linear regression on hardness displaying variables, coefficients, errors, t-values, and p-values.

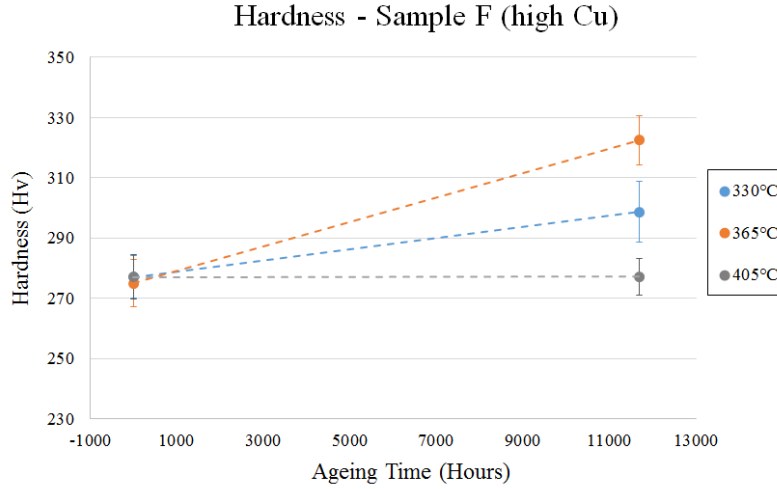


Figure 25: Hardness measurements for high copper RPV steel (sample F) after 11,690 hours of thermal aging at 330°C, 365°C, and 405°C.

2 Detecting the Presence of Clustering within the Matrix

Atom probe reconstructions for each of the five low copper samples were analyzed via the local chemistry method with the aim of determining if non-random clustering was present within the matrix after 11,690 hours of thermal aging. In order to ensure that any clustering observed after 11,690 hours was in fact due to thermal ageing, samples were analyzed before and after thermal ageing.

Prior to applying the local chemistry method, several other cluster detection analyses were explored, including frequency distributions and NN analyses. However no clustering was detected using these methods, and therefore the more sensitive local chemistry method was adopted.

As stated in Chapter 3, the local chemistry method was applied to regions of interest (ROIs) within the matrix of each sample in order to avoid incorporating dislocations and grain boundaries in the analysis. Additionally, in order to avoid sampling areas where surface migration was present, pole structures were avoided or removed.

It should be noted that for several of the samples the table of p-values was non-symmetric about the diagonal. At first, this lack of symmetry seems counterintuitive. It might be expected that if there is Ni-Si association then Si-Ni association should also be statistically significant. However, due to the nature of the local chemistry method algorithm, this is not necessarily the case. Simply explained, if a Si atom has a Ni atom as one of its 13 nearest neighbors, the converse is not necessarily true.

2.1 As-Received Steels

Prior to analyzing the thermally aged steels, the as-received steels were analyzed using the local chemistry method; thus providing baseline samples to compare the thermally aged steels. The results for samples K and C are shown below, as examples; details regarding the three other steels can be found in the Appendix.

Statistically significant solute association was found in all but one (sample H) of the as-received RPV steels. This solute association is likely due to the diffusion of solute during cooling after tempering. A table summarizing the statistically significant solute association found within each of the five steels is shown in Table 21.

2.1.1 Sample K: High Ni, Low Mn

The as-received sample K atom probe reconstruction contained three dislocations highlighted by molybdenum and carbon. Although dislocations are not directly observable in atom probe data due to detection efficiency and limited spatial resolution, their presence within an APT reconstruction can be highlighted by solute segregation. Carbon, characterized by a relatively high diffusion rate, segregates readily to features such as dislocations and grain boundaries. In sample K, the molybdenum diffusion was likely secondary as molybdenum is known to be a strong carbide former. Isosurfaces are used in Figure 26 to highlight the segregation of both elements to the three dislocations observed in sample K.

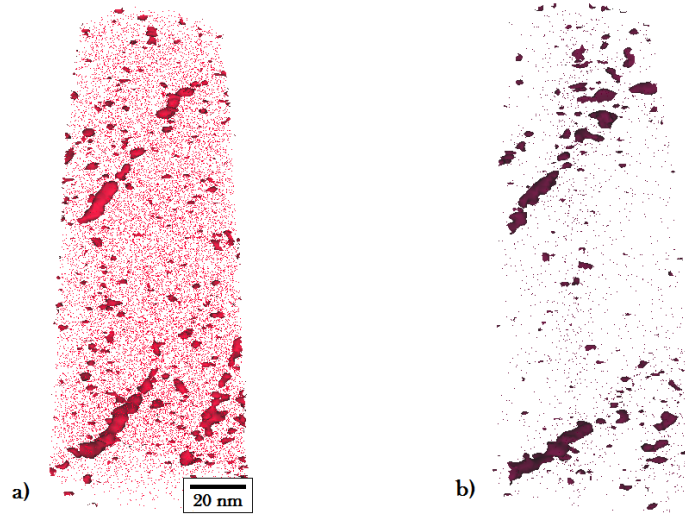


Figure 26: Atom maps of as-received sample K. Isosurfaces were used to highlight the three dislocations present. Molybdenum atoms (a), shown in red, as well as carbon atoms (b), shown in maroon, have segregated to these dislocations.

The local chemistry method was applied to a ROI within the matrix (in order to avoid analysing the dislocations). Ni-Si, Si-Ni, Ni-Ni, and C-C association was found to be statistically significant. A table of p-values is shown in Table 6; statistically significant entries are shown in bold. As discussed in Chapter 3, C-C association is regarded as an atom probe artifact. Ni and Si are, therefore, not considered to be randomly distributed in this as-received sample K atom probe reconstruction.

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	20.9	44.43	< 0.001	39.36	5.05	32.64	21.19
Cu	34.09	47.61	0.016	11.12	38.97	1.04	21.48
Ni	0.007	1.66	< 0.001	0.13	10.93	7.78	1.13
Mn	26.43	1.92	0.023	28.77	10.75	35.2	3.51
Mo	22.06	45.22	4.75	20.9	1.46	12.71	21.77
C	9.34	21.77	0.12	33.36	1.79	< 0.001	9.68
Cr	20.61	20.33	0.49	10.93	23.58	12.71	19.49

Table 6: P-value table for association within the matrix of sample K in the as-received state. Ni-Si, Si-Ni, Ni-Ni, and C-C association was found to be statistically significant.

2.1.2 Sample C: High Ni, High Mn

Sample C was noted for its prominent crystallographic pole structure. Atom maps from this reconstruction are shown in Figure 27. For this sample, the average atomic density within the reconstruction was approximately 30 atoms/nm³. In order to avoid analysing areas where surface migration was clearly present, regions of high atomic density were removed (greater than 45 atoms/nm³). The crystallographic planes from the extracted pole are shown in Figure 28. The stereographic projection of a BCC lattice and the detector event histogram from the reconstruction are also shown [101]. This pole was removed in order to avoid false positives, due to the presence of atom probe artefacts, when searching for solute association.

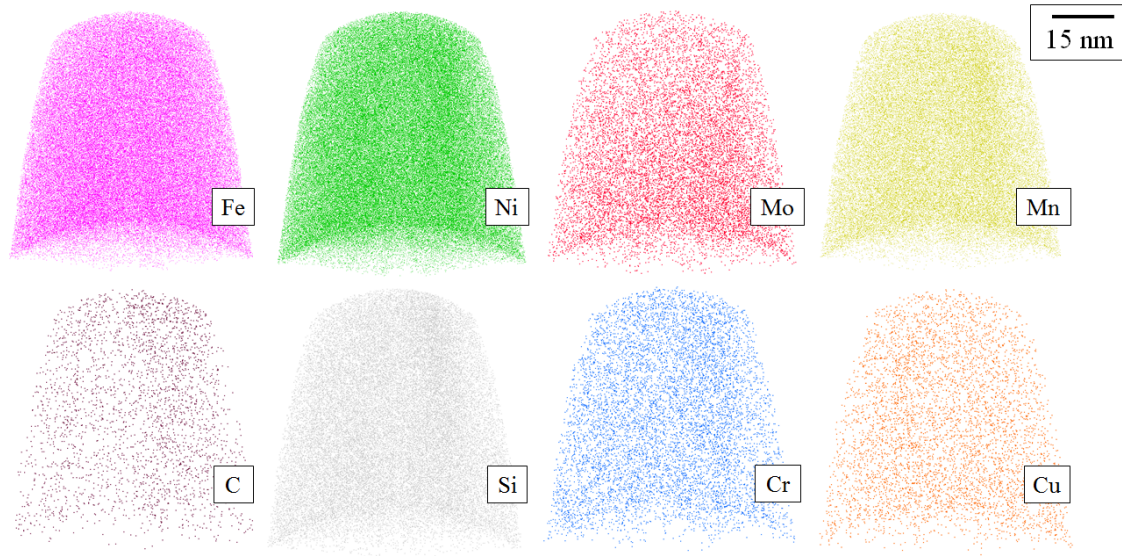


Figure 27: Atom maps of as-received sample C. Apparent segregation to the (110) pole (right hand side of the reconstruction) can be seen in the majority of elements.

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	0.097	16.85	<0.001	0.016	40.52	23.58	11.31
Cu	20.61	8.23	0.32	7.21	6.43	37.07	22.06
Ni	<0.001	4.27	<0.001	<0.001	13.57	22.66	34.46
Mn	0.069	38.21	<0.001	<0.001	31.92	31.21	8.38
Mo	46.81	1.22	19.49	24.2	10.2	26.11	47.61
C	22.36	36.69	21.77	19.77	15.39	<0.001	2.56
Cr	47.61	48.4	24.83	0.87	48.01	4.46	48.8

Table 7: P-value table for association within the matrix of sample C in the as-received state. Bold entries are considered statistically significant.

However, the observed solute association varied significantly between the thermally aged and as-received for all samples, except A.

2.2.1 Sample K: High Ni, Low Mn

Sample K contained several identifying features: two dislocations and a grain boundary. The atom maps of this sample is shown in Figure 29. The inset in Figure 29 illustrates the lack of visually apparent clustering within the matrix. The results from the local chemistry method are shown in Table 8. In this sample association of Si-Ni, Cu-Ni, Ni-Ni and C-C was found to be statistically significant. Cu-Ni association, which was not seen in the as-received sample, indicates that the distribution of Cu and Ni within the sample has potentially undergone a change due to thermal aging.

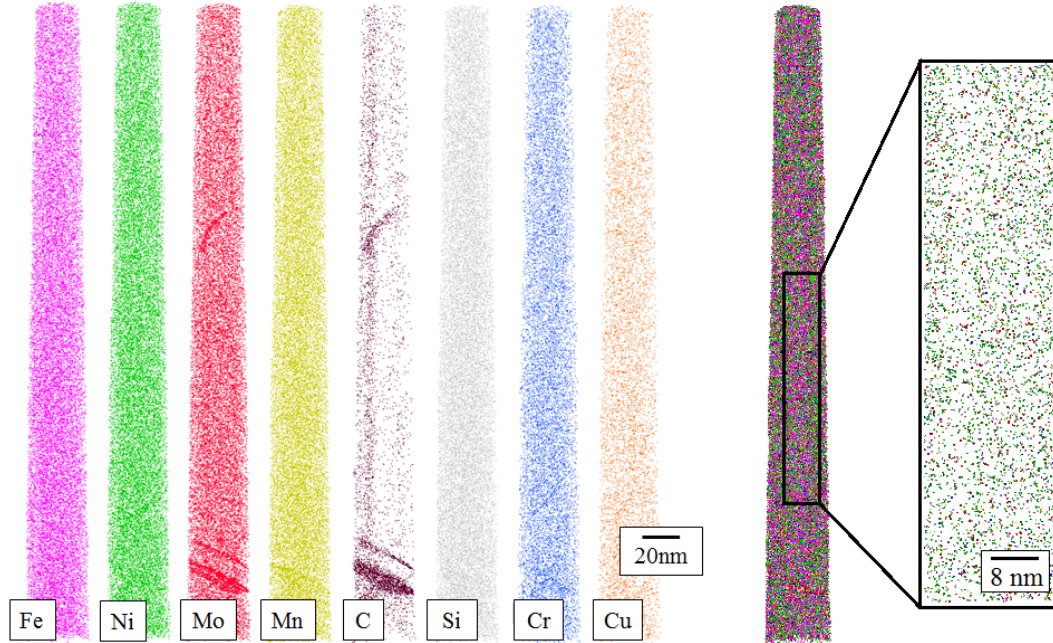


Figure 29: Atom maps of sample K, aged for 11,690 hours at 405°C. Insert shows a slice of the reconstruction; by visual inspection there is no apparent clustering present.

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	18.41	2.87	<0.001	5.82	5.82	38.97	17.88
Cu	20.61	34.83	<0.001	3.75	21.19	31.56	29.81
Ni	0.023	0.069	<0.001	7.64	28.77	17.62	19.77
Mn	5.94	15.62	5.05	0.2	9.34	11.51	44.83
Mo	1.58	14.01	13.35	8.23	9.01	40.9	15.87
C	15.15	26.76	6.06	27.09	29.46	<0.001	9.85
Cr	18.94	18.67	37.83	31.92	5.59	5.82	10.2

Table 8: P-value table for association within the matrix of thermally aged sample K. Bold entries are considered statistically significant.

2.2.2 Sample C: High Ni, High Mn

Thermally aged sample C contained a low-angle grain boundary decorated by various solutes, namely Ni, Mo, Mn, C, and Cu (Figure 30). After a region of the matrix was extracted, the local chemistry method was applied. Ni-Ni and Mn-Mn association was found to be statistically significant (Table 9). Comparing sample C before and after thermal aging, there was considerably less association in the thermally aged material than in the as-received material.

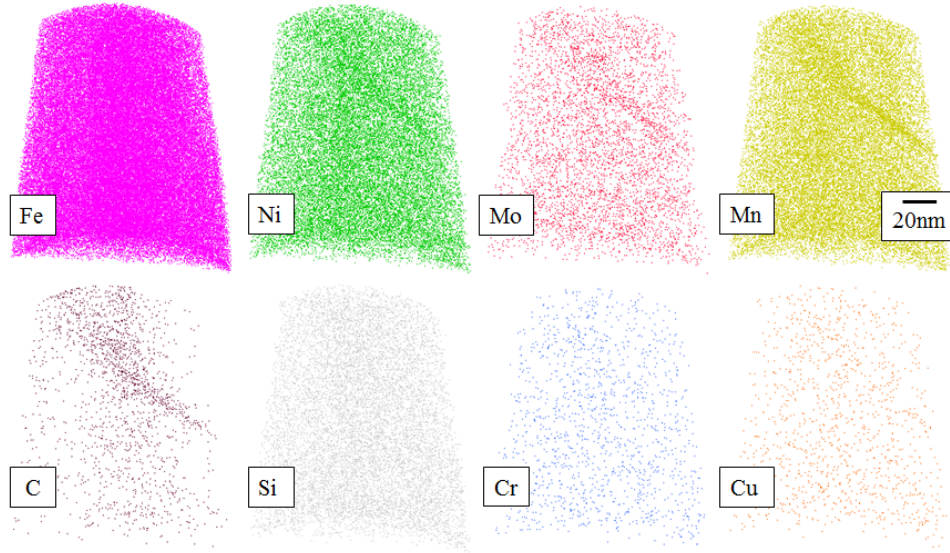


Figure 30: Atom maps of thermally aged sample C. The sample was aged for 11,690 hours at 405°C.

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	24.2	10.93	2.5	1.58	30.85	9.51	12.92
Cu	22.36	N/A	46.02	41.68	25.14	4.55	8.53
Ni	7.64	24.83	<0.001	6.06	1.29	16.11	42.86
Mn	10.03	47.61	3.07	<0.001	43.25	7.08	44.43
Mo	33	47.61	0.54	42.86	41.68	33.72	39.74
C	13.14	N/A	2.33	3.22	35.94	N/A	45.22
Cr	16.85	8.53	48.4	27.09	28.77	31.92	24.2

Table 9: P-value table for association within the matrix of thermally aged sample C. Bold entries are considered statistically significant. Entries labeled N/A did not have enough solute to complete the local chemistry method analysis.

3 Clustering and Segregation at Grain Boundaries and Carbide Interfaces

In the following sections, clusters which have nucleated at heterogeneous nucleation sites, such as carbide interfaces and grain boundaries, within the thermally aged RPV steels are identified and analyzed.

3.1 Clusters at Carbide Interfaces

An atom probe reconstruction of sample K, thermally aged at 405°C, contained several large molybdenum carbides. These carbides are clearly visible in the atom maps shown in Figure 31. A region of interest was created in order to analyze the distribution of solute around two of the carbides. The ROI, shown in blue on the left hand side of Figure 32, was a 2 nm thick slice of the data that extended across the entire specimen in two dimensions. A 2D density map of the solute distribution was created using this ROI (Figure 32).

The 2D density map has two notable features. Two rings of increased solute density are present around the carbide/matrix interfaces. These rings outline the two carbides that the ROI intersects and are likely caused by trajectory aberrations due to the differences in field evaporation between Mo_2C and Fe. The other notable feature, marked by a red arrow in Figure 32, is a dense region of solute found at one of the matrix/carbide interfaces. Several of these dense regions are observed within the specimen at various carbide/matrix interfaces. As these features are considerably denser than the solute rings outlining the carbides, they are believed to be clusters which have formed at carbide/matrix interfaces.

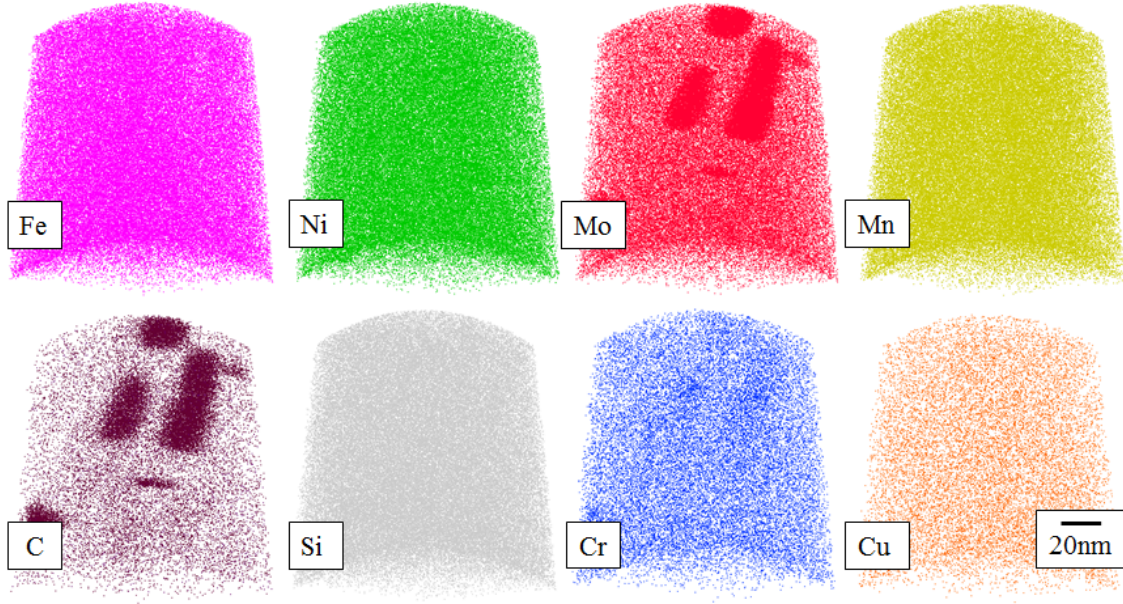


Figure 31: Atom maps of sample K. Aged for 11,690 hours at 405°C.

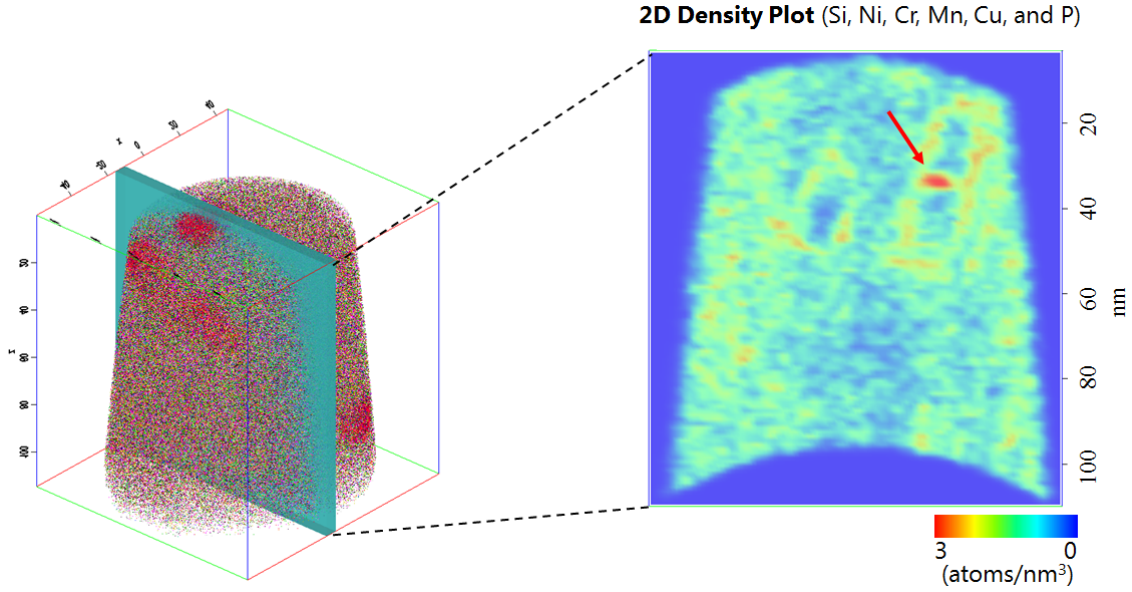


Figure 32: 2D density plot of the solutes within sample K (excluding C and Mo). Red arrow points to a particularly high density region.

In order to further investigate these potential clusters, the carbides themselves were removed from the analysis and a cluster count distribution was created selecting the following solute elements: Mn, Ni, Si, and Cu. Through analyzing the experimental and randomized cluster count distributions for various D_{max} , it was determined that a D_{max} of 0.5 nm maximized the number of

non-random clusters. Using this D_{max} selection, a cluster size distribution was created. The cluster size distribution, shown in Figure 33, indicated that it was statistically unlikely for clusters greater than 28 atoms to be the result of random clustering. Therefore, an N_{min} of 28 was chosen for cluster analysis. Examining the experimental cluster size distribution, five clusters were observed with a size greater than N_{min} . In order to analyze these features, a cluster search was conducted via the maximum separation method.

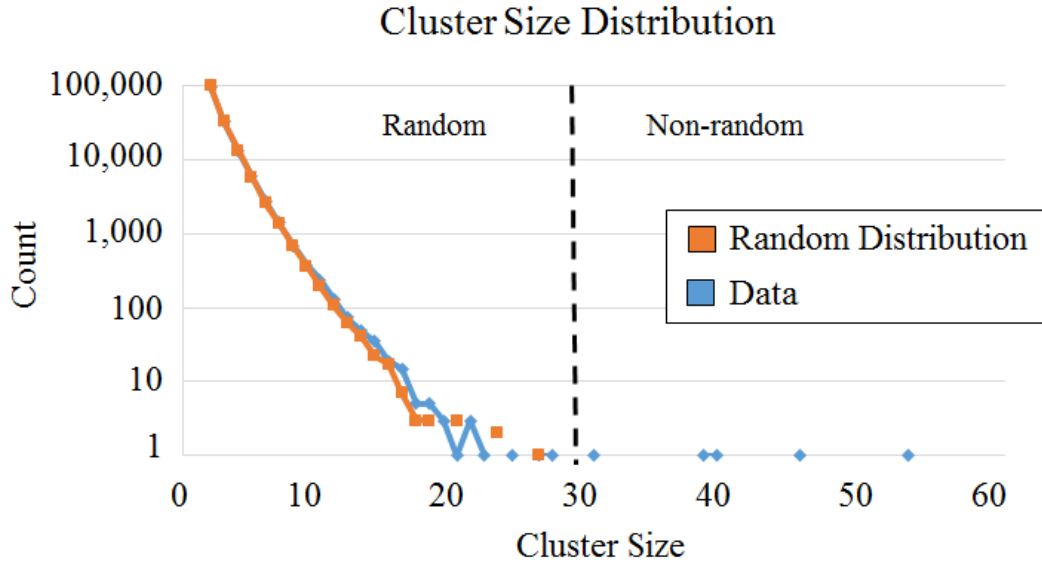


Figure 33: Cluster size distribution for sample K. C and Mo were excluded from the cluster search as these elements are found within carbides. A conservative cutoff of $N_{min} = 28$ was chosen in order to include only non-random clusters in the cluster search.

As indicated by the cluster size distribution, five non-random clusters were detected via the maximum separation method. Using their spatial coordinates it was determined that these clusters were all located at carbide/matrix interfaces. One such cluster is highlighted in Figure 34. Additionally, the cluster in question from Figure 32 was identified as one of the five non-random clusters in the sample. These clusters were approximately 100-300 atoms in size after detection efficiency was taken into account. Although the clusters' composition varied significantly, one unifying feature was the Mn content: all five clusters had a large fraction of Mn (greater than 25 at.%) as shown in Table 10.

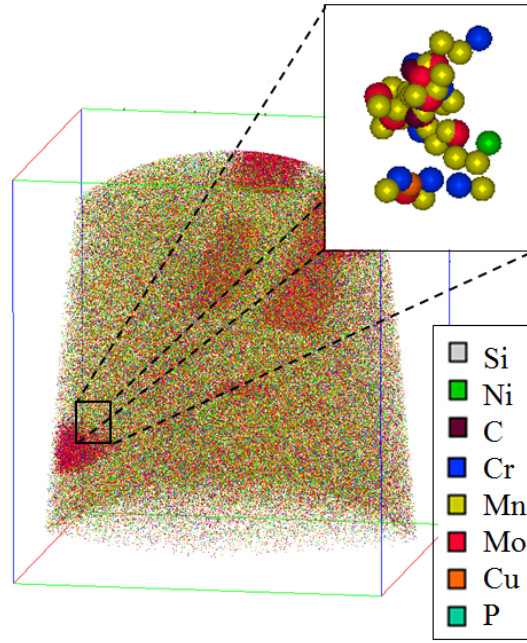


Figure 34: Atom map of sample K highlighting a cluster found at a carbide/matrix interface.

Cluster	Cluster Size (atoms; corrected)	Fe (%)	Si (%)	Cu (%)	Ni (%)	Mn (%)	C (%)	Cr (%)	Mo (%)
1	268	39.4	5.1	0.0	11.1	29.3	2.0	9.1	4.0
2	138	2.0	0.0	2.0	9.8	51.0	9.8	11.8	11.8
3	205	32.9	5.3	0.0	14.5	36.8	1.3	3.9	5.3
4	105	20.5	5.1	2.6	7.7	41.0	2.6	20.5	0.0
5	149	7.3	0.0	1.8	3.6	49.1	3.6	18.2	16.4
Average	173	20.4	3.1	1.3	9.3	41.4	3.9	12.7	7.5

Table 10: Cluster compositions for the five clusters identified in Figure 33. All of the clusters contained large amounts of Mn, with an average of approximately 40 at.%.

3.2 Clusters at Grain Boundaries

3.2.1 Low-Angle Grain Boundary in Sample C

A low-angle grain boundary was observed in sample C after 11,690 hours of thermal aging at 405°C. The dislocation network, which indicated the presence of this boundary, was notably enriched in Ni, Mo, Mn, and C. Atom maps showing the distribution of these elements are shown in Figure 30. In order to better illustrate the presence of these dislocations, an isodensity of 3.5 solute atoms/nm³ was created within the atom probe reconstruction. This isodensity is shown in grey and the dislocations are highlighted by black dashed lines in Figure 35.

A cuboid ROI (5 nm x 10 nm x 40 nm) was placed parallel to the grain boundary,

perpendicular to the dislocations, and a 1D concentration profile was extracted (Figure 35). This 1D concentration profile illustrates the peaks in total solute concentration due to segregation to the dislocations.

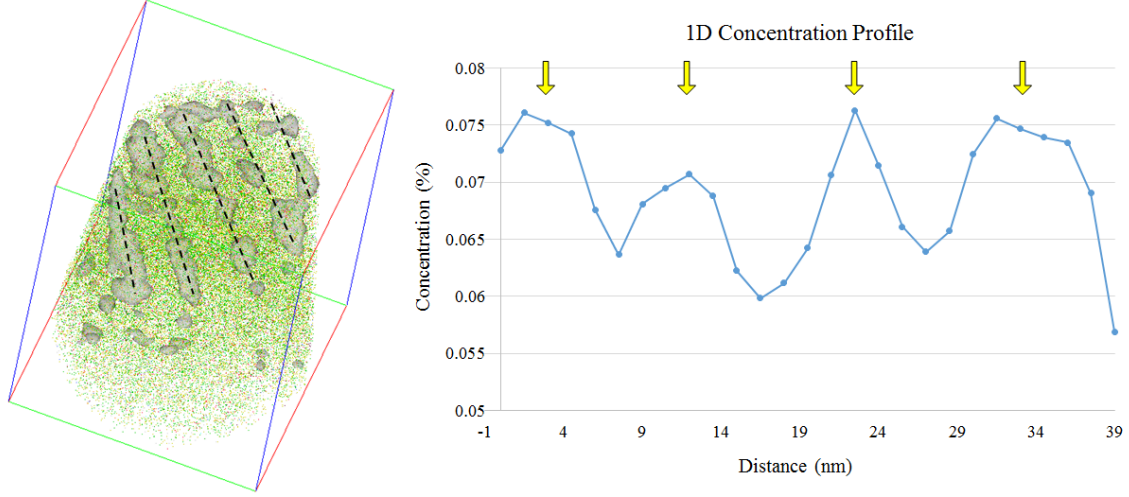


Figure 35: The atom probe reconstruction of thermally aged sample C is shown on the left. An isodensity of 3.5 atoms/nm³ is shown in grey to highlight the segregation of solute to the dislocations. The dislocations are individually marked by dotted black lines. The 1D concentration profile on the right shows increases in overall solute concentration for four of the five dislocations, the position of which are marked by yellow arrows.

A cuboid ROI (10 nm x 10 nm x 15 nm) spanning across the grain boundary, i.e. perpendicular to the grain boundary, was created in order to obtain a 1D concentration profile and calculate the Gibbs interfacial excess of each element. The 1D concentration profile, shown in Figure 36, reveals increased levels of Ni, Mn, Mo, and C at this low angle grain boundary. Plots of the cumulative ion count across the ROI are also shown for the following elements: C, Ni, Mn, and Si (Figure 37). These plots illustrate segregation to the grain boundary and enable the visualization of the Gibbs interfacial excess for these elements.

The Gibbs interfacial excess was calculated for each solute element via the equation:

$$\Gamma_i = \frac{N_{i(excess)}}{V} \quad (12)$$

where Γ_i is the Gibbs interfacial excess of element i , $N_{i(excess)}$ is the number of excess solute atoms at the interface, and V is the interfacial volume utilized to determine the interfacial excess [102, 103]. These calculations are shown in Table 11.

A 2D density plot of the solutes Ni, Mn, Si, and Cu was created using a ROI across the grain

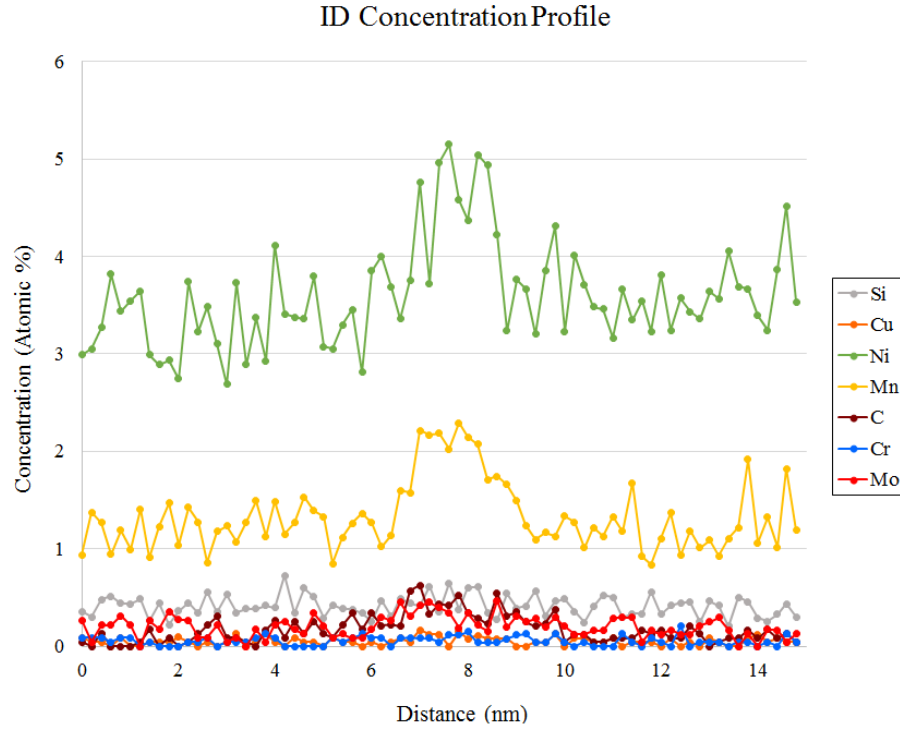


Figure 36: A 1D concentration profile for the ROI that spans across the low-angle grain boundary in thermally aged sample C. This 1D concentration profile reveals increased levels of Ni, Mn, Mo, and C.

Element	Gibbs interfacial excess (atoms/nm ³)
Ni	4.33
Mn	2.23
C	0.64
Si	0.29
Mo	0.23
Cu	0.12
Cr	0.09

Table 11: Calculated Gibbs interfacial excess for various elements at the observed low-angle grain boundary in sample C aged for 11,690 hours at 405°C.

boundary (Figure 38). From the density plot, solute segregation to the grain boundary is clear. However, it was also noted that this solute appears to be clustered; regions of very high density (red) alternate with regions of medium atomic density (orange) along the grain boundary.

After picking an appropriate D_{max} , through maximizing the number of non-random clusters within the cluster count distribution, a cluster size distribution was created. The value for N_{min}

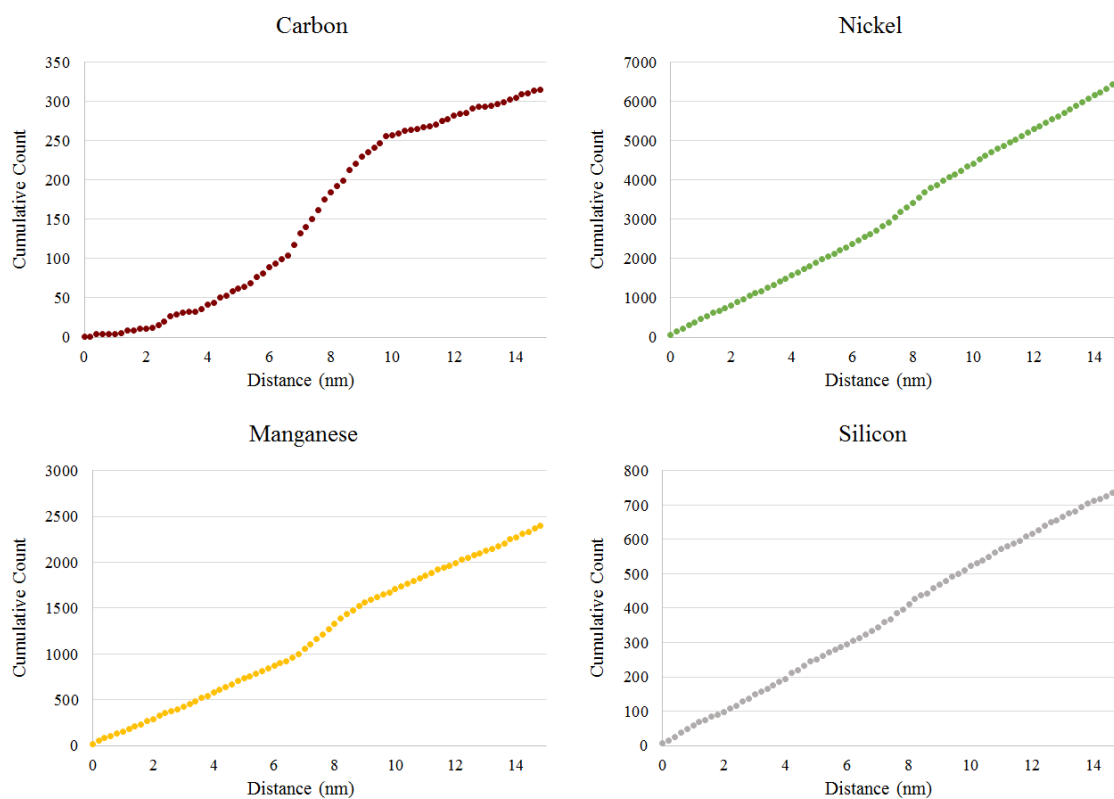


Figure 37: Plots of the cumulative ion count for C, Ni, Mn, and Si across the low-angle grain boundary in thermally aged sample C.

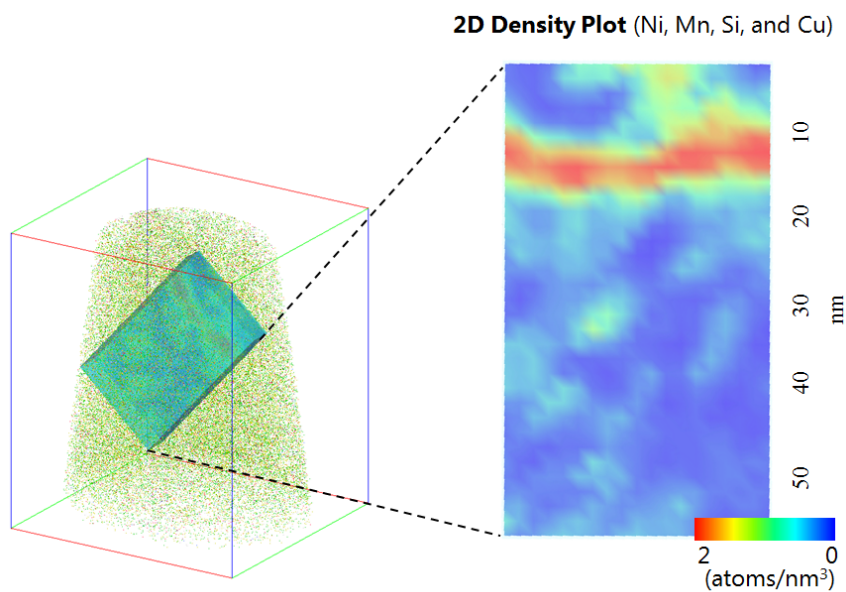


Figure 38: 2D density plot of Ni, Mn, Si, and Cu in thermally aged sample C.

was chosen by visual inspection of the cluster size distribution. For $N_{min} = 50$ only non-random clusters were expected to be present. Using these parameters, a cluster search was conducted using the maximum separation method, where Ni, Mn, Si, and Cu were chosen as core atoms. The clusters from this search can be seen in the atom map shown in Figure 39. It should be noted that these clusters lie along the low-angle grain boundary. These clusters ranged in size from 350-650 atoms, with an average of 425 atoms, after detection efficiency was taken into account. Cluster compositions are shown in Table 12.

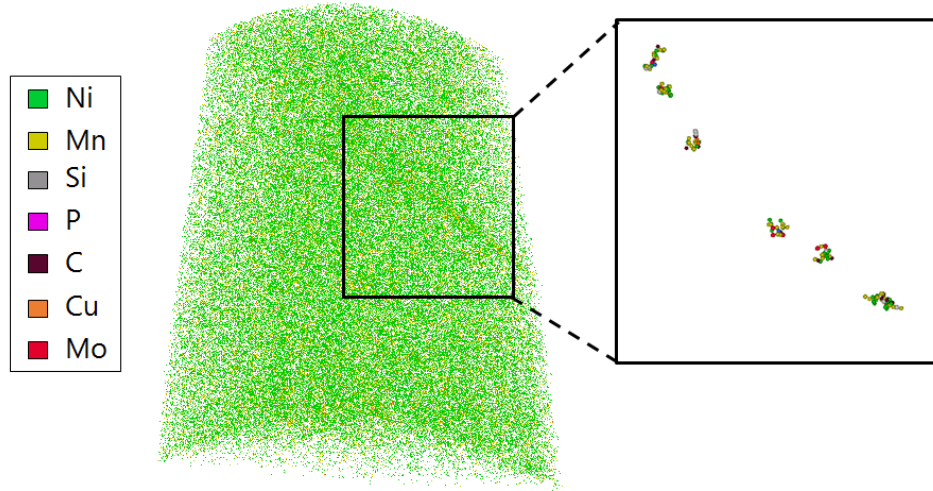


Figure 39: Atom map of sample C highlighting the clusters found at the grain boundary.

Cluster	Cluster Size (atoms; corrected)	Fe (%)	Si (%)	Cu (%)	Ni (%)	Mn (%)	C (%)
1	386	59.4	2.1	0.7	25.9	11.2	0.7
2	368	60.3	3.7	0.7	22.1	13.2	0.0
3	451	63.5	2.4	1.2	22.8	8.4	1.8
4	373	57.2	3.6	0.0	23.9	15.2	0.0
5	616	65.4	1.3	0.0	24.1	9.2	0.0
6	357	58.3	0.8	2.3	23.5	15.2	0.0
Average	425	60.7	2.3	0.8	23.7	12.1	0.4

Table 12: Cluster sizes and compositions for the clusters identified in thermally aged sample C.

3.2.2 Grain Boundary in Sample K

A grain boundary was observed in sample K after 11,690 hours of thermal aging at 405°C. Atom maps from the reconstruction are shown in Figure 29. A cuboid ROI (10 nm x 10 nm x 18

nm) was placed across the grain boundary in order to obtain a 1D concentration profile and calculate the Gibbs interfacial excess for elements of interest. The 1D concentration profile, shown in Figure 40, highlights increased levels of Ni, C, Mn, and Cr at the grain boundary.

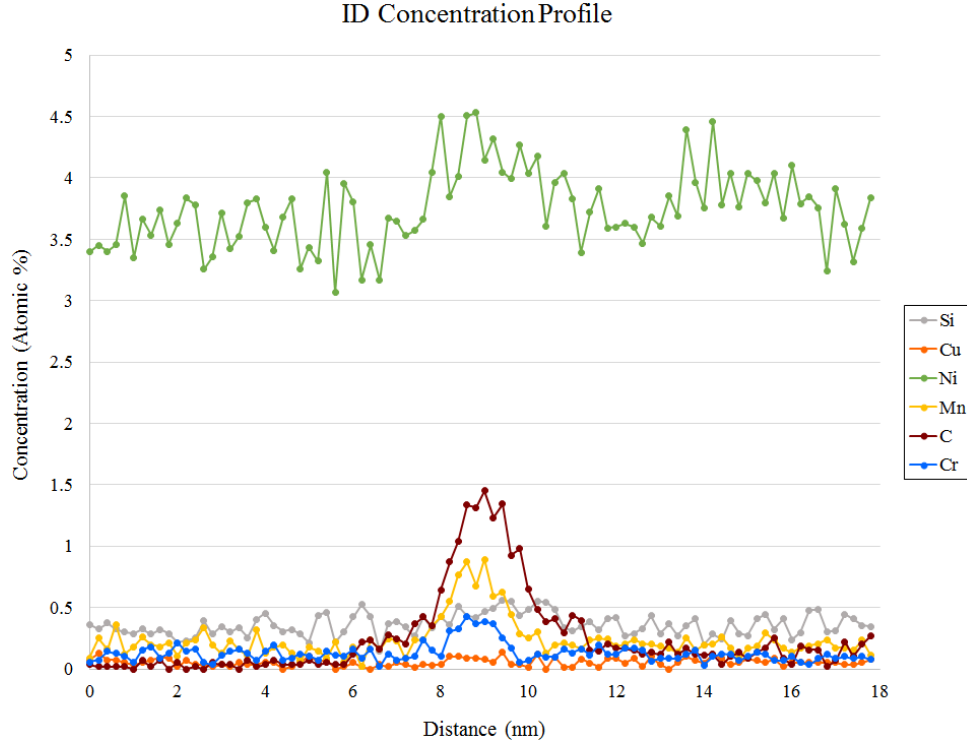


Figure 40: A 1D concentration profile for the ROI that spans across the grain boundary in thermally aged sample K. This 1D concentration profile reveals increased levels of Ni, Mn, Cr, and C.

Plots of the cumulative ion count vs. distance along the ROI are shown in Figure 41 for C, Ni, Mn, Si, Mo, and P. As stated previously, these plots illustrate segregation to the grain boundary as well enable the visualization of the Gibbs interfacial excess. The Gibbs interfacial excess was then calculated for each solute element, the results of which are shown in Table 13.

Lastly, a cluster search was performed via the maximum separation method. As before, a cluster count distribution was utilized to pick D_{max} . D_{max} was chosen such that the number of non-random clusters was maximized. Using this D_{max} , a cluster size distribution was created. From this plot, N_{min} was set equal to the number of atoms where the random cluster size distribution was equal to zero. After setting N_{min} , it was determined that no non-random clusters were present along the grain boundary. Although the observed cluster size distribution was slightly above the randomized cluster size distribution, no clusters were present above the N_{min} threshold. The deviation of the observed cluster size distribution from the randomized distribution is believed to be

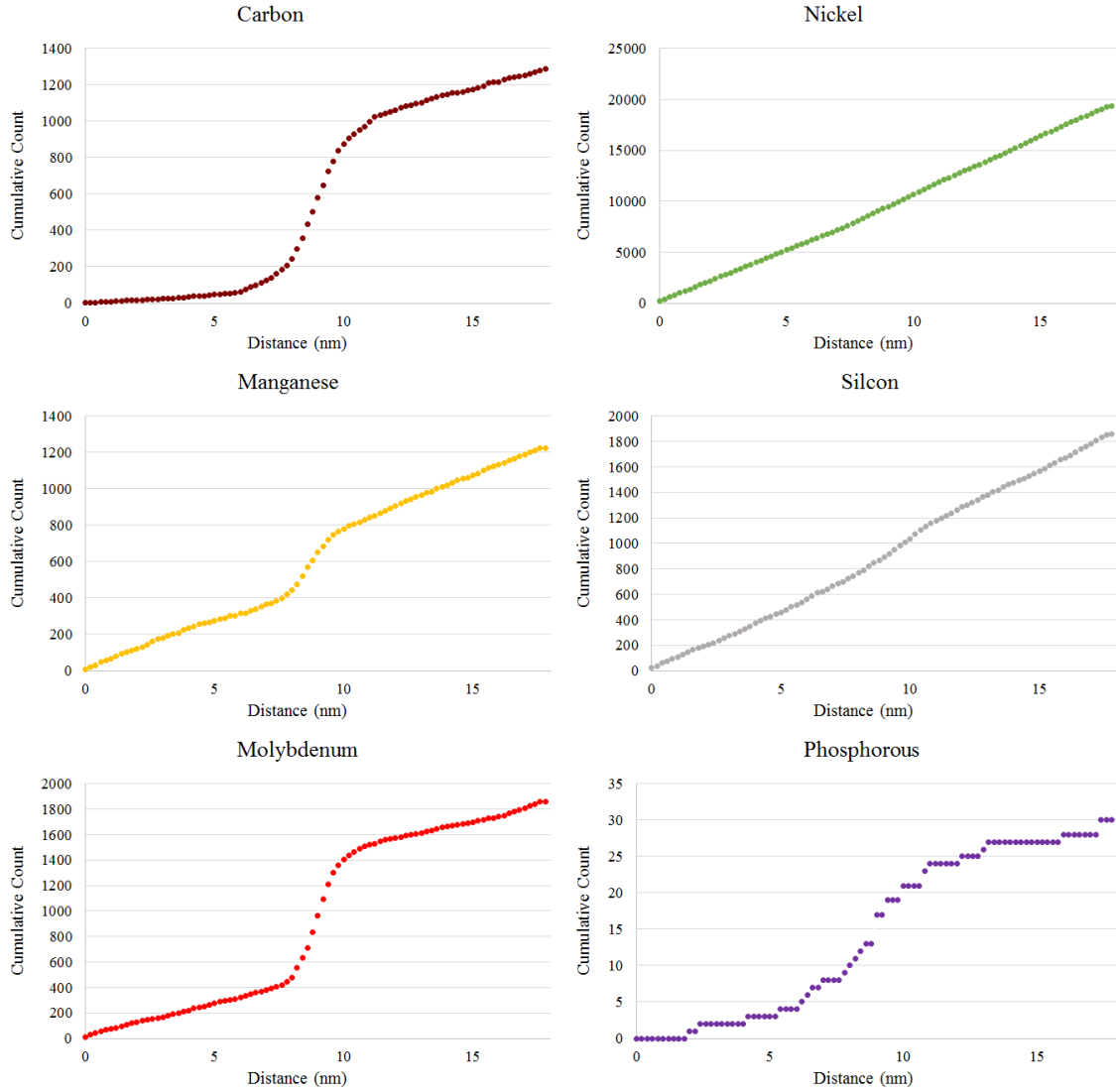


Figure 41: Plots of the cumulative ion count for C, Ni, Mn, Si, Mo, and C across the grain boundary in thermally aged sample K.

due to the segregation of solute to the grain boundary instead of clustering.

4 Secondary Precipitates within Cementite

CRPs within the matrix of RPV steels have been extensively studied [36, 19, 18, 5, 40, 39]. However, there is relatively little in the published literature regarding CRPs within carbides. Copper-rich solute clusters located within carbides were first reported by Khalid and Edmonds utilizing TEM [105, 106]. The material analyzed in that study was a high-alloy hypereutectoid steel

Element	Gibbs interfacial excess (atoms/nm ³)
Mo	2.93
C	2.09
Ni	1.19
Mn	0.87
Cr	0.36
Si	0.32
Cu	0.03
P	0.03

Table 13: Calculated Gibbs interfacial excess for various elements at the observed the grain boundary in sample K aged for 11,690 hours at 405°C.

containing large amounts of Mn and thus significantly different from the model RPV steels investigated in this thesis. Through the use of scanning transmission electron microscopy-energy-dispersive spectrometry (STEM-EDS) they showed that these precipitates were high in copper. However, an extensive chemical characterization was not conducted.

MNPs located within the matrix of RPV steels have also been extensively studied [50, 47, 49, 48, 51], and although MNPs have been observed at heterogeneous nucleation sites after thermal aging [36], previous work has not revealed any secondary MNPs located within carbides in the new generation RPV steels. In this work, CRPs and MNPs were observed within the cementite phase of a high copper and low copper RPV steel, respectively, following long term thermal aging (Table 14).

	Cu	Ni	Mn	Si	Mo	C	Cr	P	Fe
High Cu Steel (Sample F)	0.3	3.3	1.5	0.4	0.3	0.9	0.1	0.01	93.3
Low Cu Steel (Sample K)	0.04	3.3	0.3	0.4	0.3	1.2	0.1	0.01	94.4

Table 14: Nominal chemical compositions of high and low copper RPV steels in at.%.

4.1 TEM Analysis of Secondary Precipitates

In this work, CRPs were observed within the cementite phase of thermally aged high copper RPV steels. In order to confirm that these particles were located within the cementite, rather than above or below, a series of under-, in-, and, over-focus TEM images were obtained. Since the precipitates came in and out of focus with the carbide, it was determined that they were in fact

located within this phase. One of the in-focus TEM images is shown in Figure 42(a). By visual inspection the precipitates appear to be randomly distributed throughout the cementite as well as the iron matrix.

TEM analyses of the as-received high copper steel, shown in Figure 42(b), as well as the low copper steels showed no evidence of precipitates within the cementite phase [20]. This suggests that these features formed during thermal aging.

Additionally, previous work determined that M_3C (the metallic constituent of this phase being predominantly Fe) was the most common carbide in both the high and low copper steels [20]. These results are consistent with the APT data obtained in this study (detailed below) as all three of the carbides observed were cementite (Fe_3C).

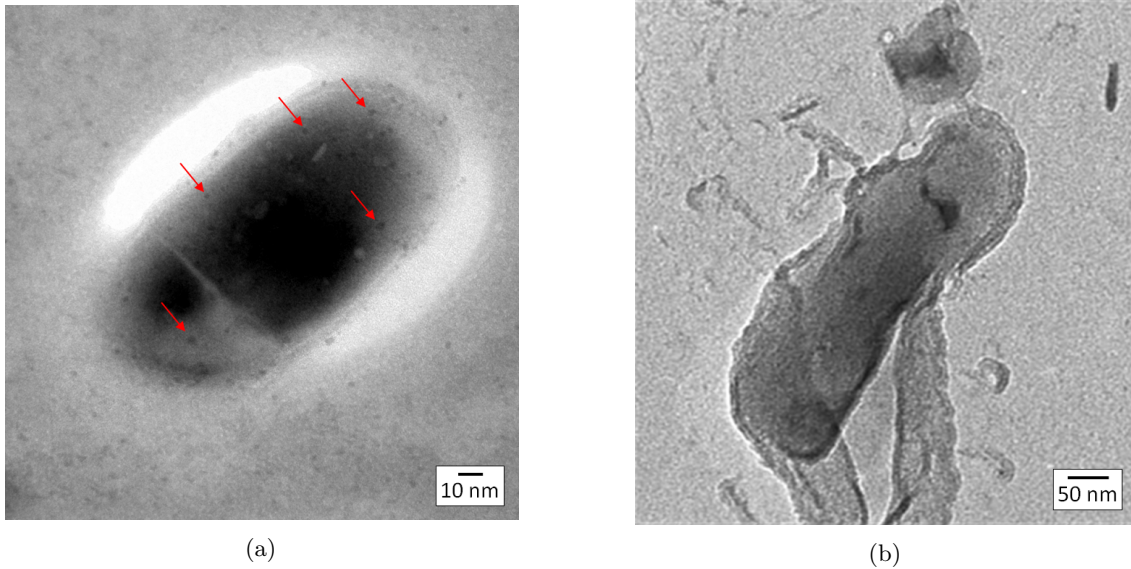


Figure 42: a) TEM image of copper-rich precipitates (highlighted by red arrows) dispersed randomly within the cementite phase of the high copper RPV steel after thermal aging. b) TEM image of cementite within a ferrite matrix prior to thermal aging.

4.2 APT Analysis of Secondary Precipitates

APT was utilized to obtain a more detailed chemical characterization of the CRPs found in the thermally aged high copper sample. In agreement with the TEM results, APT analyses showed CRPs within the cementite phase of the thermally aged high copper RPV steel (Figure 43). These precipitates were approximately 5 nm in diameter and found in manganese-rich cementite.

The average composition of the CRPs, the matrix, and the carbide are shown in Table 15.

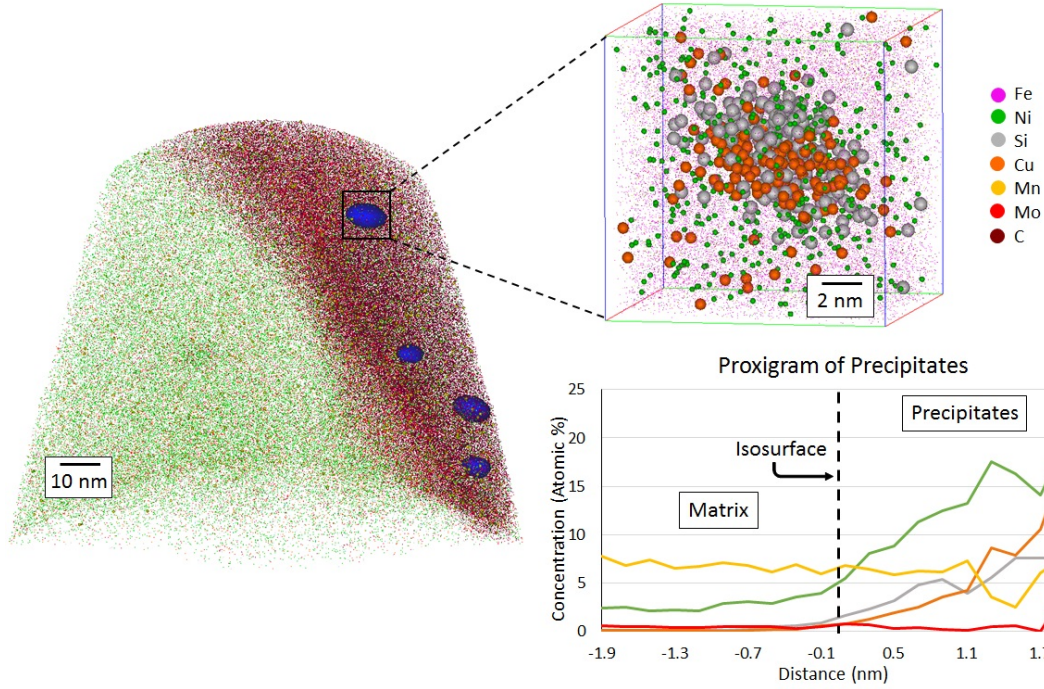


Figure 43: Atom probe tomography reconstruction of the high copper RPV steel. Four CRPs are present in the cementite phase. An isodensity surface is used to emphasize the precipitates (Blue - Cu, Ni, and Si). A proxigram of a single cluster is used to highlight how its composition varies across the isodensity surface.

The secondary precipitates contain elevated levels of copper, nickel, and silicon. This is illustrated by a proxigram analysis, which plots the chemical distribution as a function of distance from the isodensity surface, in Figure 43. Since trajectory aberrations can significantly influence matrix element levels within precipitates, the average composition for CRPs without the cementite matrix elements, Fe and C, is also provided.

	Cu	Ni	Mn	Si	Mo	C	Cr	Fe
Matrix	0.26	3.59	1.00	0.45	0.15	0.14	0.08	94.33
Carbide	0.05	1.85	9.70	0.03	0.78	20.16	0.76	66.68
Precipitates within Carbides	3.00	10.22	5.80	3.99	0.37	20.82	0.13	55.68
Precipitates within Carbides (w/out matrix elements)	12.78	43.48	24.67	16.96	1.56	-	0.55	-

Table 15: Phase compositions of the high copper RPV steel (at.%). Error is estimated to be $\pm 0.01\%$.

In the thermally aged low copper RPV steel, MNPs were observed in two APT analyses, one of which is shown in Figure 44. These precipitates were approximately 5 nm in diameter and found in Mo- and Mn-rich cementite phases. A single MNP is highlighted in Figure 44 in order to measure

its composition using a 1D concentration profile. The average composition of the precipitates, as well as the matrix and carbide compositions, are shown in Table 16. The compositions are a weighted average of the two atom probe analyses of the low copper steel. Forty precipitates were analyzed in total; eight and thirty-two precipitates, respectively, in the two APT reconstructions.

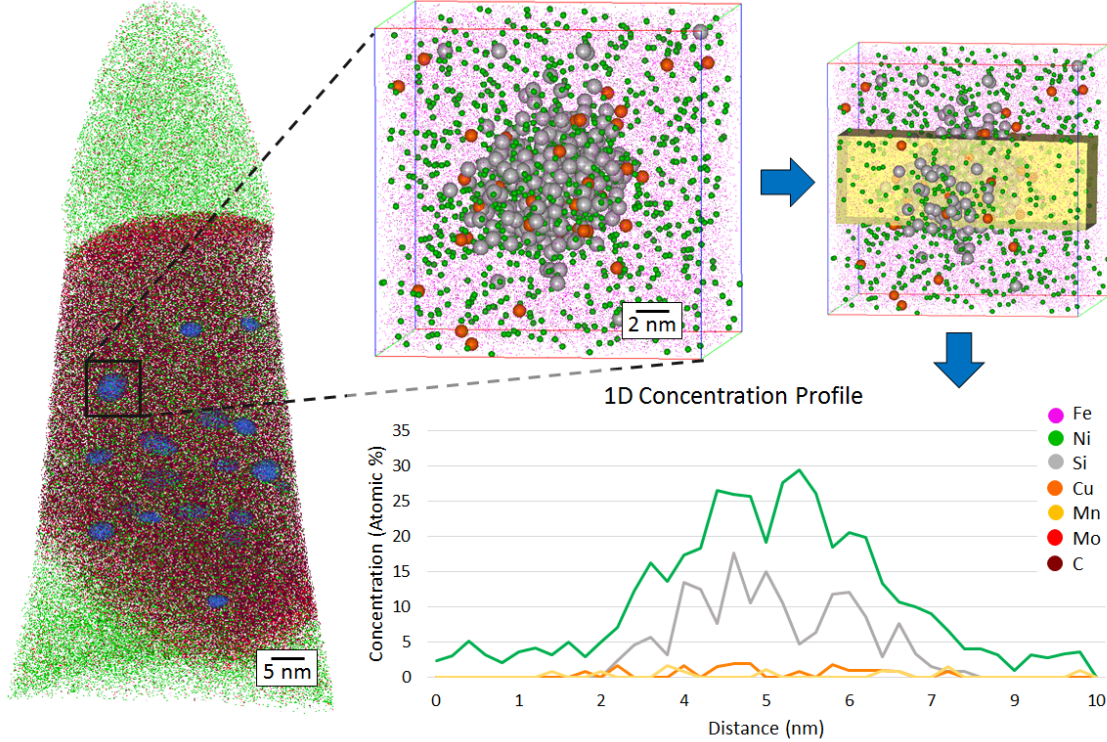


Figure 44: Atom probe tomography reconstruction of the low copper steel. Twenty-four Si- and Ni-rich precipitates are present in the cementite. Isodensities are used to highlight the precipitates (Blue - Ni and Si). A single cluster is highlighted to enable analysis of its composition via a 1D concentration profile.

	Cu	Ni	Mn	Si	Mo	C	Cr	Fe
Matrix	0.05	4.07	0.11	0.51	0.20	0.39	0.04	94.68
Carbide	0.03	2.67	1.00	0.04	0.89	27.47	0.44	69.66
Carbide Precipitates	1.11	27.52	0.47	13.95	0.39	17.62	0.18	41.30
Carbide Precipitates (w/out matrix elements)	2.55	63.08	1.07	31.98	0.90	-	0.42	-

Table 16: Phase compositions of the low copper RPV steel (at.%). Error is estimated to be ± 0.01 .

The MNP solute compositions from the two analyses were consistent except for Si, which varied significantly between the two datasets (16.5 at.% and 8.2 at.%). Similarly, it was observed that the Si content within the cementite phase of the two samples was also different. This variation

in Si content is likely due to the fact that cementite plates form at different times in the cooling process and therefore at different temperatures. At lower temperatures more Si becomes trapped within the quickly forming cementite phase, while at higher temperatures more Si is able to diffuse into the matrix. The Si content of the MNPs was strongly correlated to the Si levels in the cementite phases in which they were located: higher Si content within the cementite phase led to MNPs higher in Si and vice versa.

Additionally, the observed MNPs contained relatively small amounts of Mn. Since Mn is a strong carbide former, it is hypothesized that the Fe_3C matrix retains much of the Mn, leaving the MNPs deficient. Ni and Si, however, are weak carbide formers and thus are the predominant species found within the precipitates.

Cementite forms rapidly at large supersaturations in pearlitic and bainitic steels [108]. It is therefore proposed that during cooling after austenitisation, when carbides typically form, solute becomes trapped within the quickly forming phase. Driving forces for precipitation come into play during thermal aging when the kinetics of the system are increased considerably. Solutes, such as Ni, Cu, and Si, which have a low solubility in cementite, readily precipitate out of solution. Conversely, elements which have a high solubility, such as Mn and Mo, remain in solid solution within the cementite. This hypothesis explains the observed chemical compositions as well as the absence of precipitates in the as-received material prior to thermal aging.

4.3 Quantifying Solute within Secondary Precipitates

In order to obtain a full characterization, the amount of solute confined within these secondary precipitates was estimated. An upper bound of the carbide volume fraction can be obtained by assuming that all of the carbon is consumed to form cementite and all atoms occupy the same volume regardless of chemical identity. Using these approximations, upper bounds for the carbide volume fraction were 3.6 at.% and 4.8 at.% in the high and low copper steels, respectively.

This estimate can be refined for the low copper steel by comparing the nominal, matrix, and cementite compositions for each element. Specifically, the difference between matrix and nominal compositions has been plotted against the difference between matrix and cementite compositions to create the Lever rule plot shown in Figure 45. The resulting points were then fitted with a line, the slope of which was used to estimate the volume fraction of cementite, giving approximately 4.5 at.% for the low copper steel. In the reconstruction of the high copper steel, only a portion of the carbide

was observed as it was located at the edge of the analysis volume. As compositions typically vary near interfaces, such as the carbide/matrix interface observed, this volume was deemed insufficient to accurately determine the composition of the cementite. Therefore, a more precise estimate of the volume fraction for the high copper steel was not obtained.

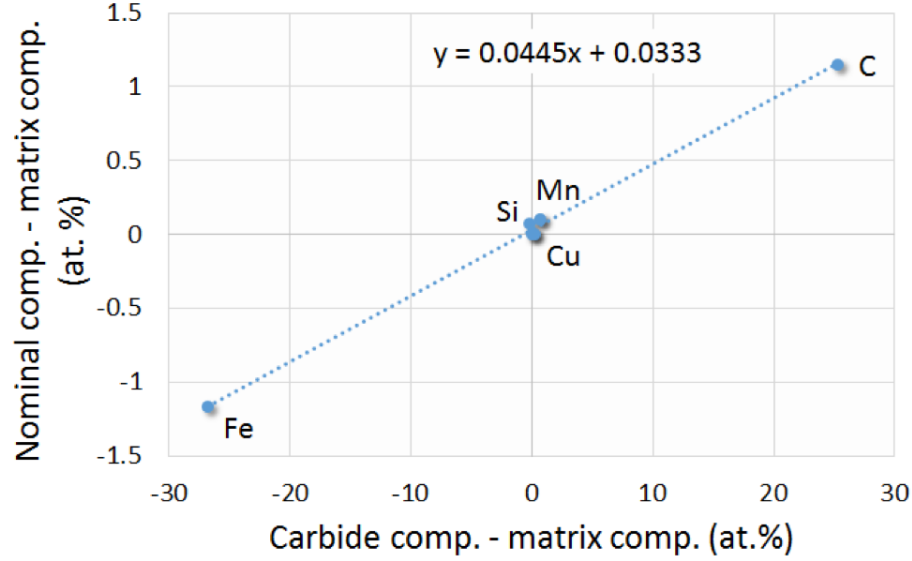


Figure 45: Plot quantifying the percentage of cementite in the low copper RPV steel.

From these volume fractions (3.6 at.% and 4.5 at.%) and the chemical compositions obtained from APT it was possible to estimate the amount of solute trapped within cementite for both the high and low copper steels. The percent of total solute estimated to be trapped within cementite is shown Table 17 for each element. For example, in the low copper steel 30.1at.% of the total manganese in the steel is expected to be trapped within carbides. It should be noted, however, that any significant effects on the microstructure will already have been implicitly accounted for in estimates of RPV lifetime as all RPV steels contain carbides and thus presumably these secondary precipitates.

	Cu	Ni	Mn	Si	Mo
High Cu Steel	0.8	1.8	25.2	0.4	14.1
Low Cu Steel	3.5	3.1	30.1	1.2	17.5

Table 17: Proportion of solute located within cementite in high and low copper RPV steels.

5 Discussion

5.1 Hardness Measurements

A statistically significant decrease in hardness was observed in the low copper RPV steels analyzed in this study. A similar decrease in hardness was observed in the two low copper RPV steels analyzed by Styman [36]. Again, this subtle decrease occurred after 11,690 hours of thermal aging. However, after 20,000 hours of thermal aging Styman observed the more distinct, expected increase in hardening.

One potential explanation for the observed decrease in hardness is a reduction in solid solution strengthening (SSS). If solute, such as carbon, were to diffuse out of the matrix to more energetically favorable sites, such as grain boundaries or dislocations, this would cause a decrease in SSS. Additional work comparing solute segregation to grain boundaries and dislocations in both the as-received and thermally aged material would be necessary to test this hypothesis.

Through performing a multiple linear regression on time, temperature, and steel type it was determined that this decrease in hardness was due to the variable “time.” However, it was also determined that the variable “temperature” was not statistically significant. This result was unexpected as the diffusion of solute is temperature dependent.

5.2 Clustering within the Matrix

5.2.1 3D Distribution of Solute Association

Atom maps generated from the local chemistry method output were created in order to visualize and better interpret the detected solute association. These atom maps were created for each atom type pair (e.g. Ni and C) and ranged via number of nearest neighbors (NN). Selections of higher NN ranges are less likely to be random and therefore can lend insight into the 3D distribution of the non-random association. These distribution maps were used to determine if there existed any local enhancement of solute association near poles or carbides.

The 3D distributions of solute association for all of the as-received and thermally aged steels showed no clear structure and appeared to be randomly distributed by visual inspection, except for C-C association. This can be explained by the fact that carbon typically comes off in pairs in APT [91]. Thus, C-C association is expected and not considered a true effect. Carbon is also known to travel to the poles prior to ionization, a phenomenon which is visualized in the C-C association

atom map (Figure 46) [81].

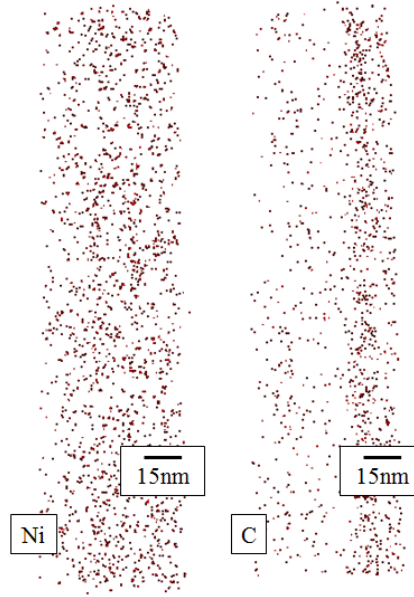


Figure 46: 3D distribution map of Ni-Ni association (for comparison) and C-C association in thermally aged sample H. It should be noted that the pole structure, which is a crystallographically induced aberration in APT data, is clearly visible in the C-C atom map whereas the Ni-Ni atom map appears to be randomly distributed.

5.2.2 Intra-sample Comparison

Prior to analyzing the association of solute elements within the matrix of the five model RPV steels, several atom probe runs of the same sample were analyzed. This was done in order to determine the significance of specimen-to-specimen variability. To this end, the local chemistry method was applied to the matrix of three sample K atom probe runs. The results, presented below, were subsequently compared.

Tables of p-values for the atom probe runs 17341, 19992, and 18463 are shown in Tables 18, 19, and 20, respectively. As before, statistically significant entries ($p\text{-value} < 0.02$) are shown in bold. Although there exists variability between the three samples, it should be noted that there exists considerable overlap of significant solute association. For example, Ni-Ni association was found to be statistically significant in all three of the atom probe runs.

It is important to note that the mere fact there are differences in statistically significant entries between atom probe runs does not mean that the runs are statistically different. Specifically,

although different solute association was found to be statistically significant, this does not mean that solute pairs with higher p-values were definitively not associated. In other words, failure to reject a hypothesis is not the same as accepting the null. Therefore, the observed differences in statistically significant entries for APT runs of sample K do not invalidate the subsequent inter-sample analysis.

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	13.79	1.19	16.85	39.74	15.39	26.11	38.97
Cu	12.51	40.52	0.6	24.83	12.71	31.56	16.6
Ni	18.14	19.49	<0.001	1.62	40.13	46.81	44.43
Mn	31.21	8.85	20.05	42.07	29.46	9.85	14.01
Mo	40.52	41.29	29.46	20.05	43.25	48.8	29.12
C	31.92	44.43	3.36	6.55	34.83	<0.001	42.86
Cr	34.46	21.77	50	1.39	36.69	20.05	12.3

Table 18: P-value table for association within the matrix of atom probe run 17341 (thermally aged sample K).

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	0.41	17.88	<0.001	20.9	31.56	15.39	46.02
Cu	48.01	N/A	0.023	18.67	42.86	N/A	N/A
Ni	<0.001	2.81	<0.001	5.26	13.57	32.28	34.46
Mn	9.01	N/A	1.1	23.27	37.83	46.81	27.43
Mo	50	44.04	19.49	36.32	41.68	21.77	36.32
C	17.11	N/A	45.22	44.43	26.76	<0.001	N/A
Cr	44.43	N/A	5.71	28.43	43.64	11.7	4.01

Table 19: P-value table for association within the matrix of atom probe run 19992 (thermally aged sample K).

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	18.41	2.87	<0.001	5.82	5.82	38.97	17.88
Cu	20.61	34.83	<0.001	3.75	21.19	31.56	29.81
Ni	0.023	0.069	<0.001	7.64	28.77	17.62	19.77
Mn	5.94	15.62	5.05	0.2	9.34	11.51	44.83
Mo	1.58	14.01	13.35	8.23	9.01	40.9	15.87
C	15.15	26.76	6.06	27.09	29.46	<0.001	9.85
Cr	18.94	18.67	37.83	31.92	5.59	5.82	10.2

Table 20: P-value table for association within the matrix of atom probe run 18463 (thermally aged sample K).

5.2.3 Inter-sample Comparison

The potential association of solute elements within the matrix was tested via the local chemistry method for both the as-received and thermally aged model RPV steels. A summary of the results is shown in Table 21. Statistically significant solute association was found in all but one of the as-received steels. Thus, solute was found not to be randomly distributed within the matrix of the as-received materials. This result was not entirely unexpected as clustering can occur during the cooling process after tempering.

In sample A, Ni-Ni association was found to be significant in both the as-received and thermally aged samples. In order to visualize any potential differences due to thermal aging the observed/expected ratios of Ni-Ni association at various nearest neighbor distances were plotted (Figure 47) for both the thermally aged and as-received material. This plot appears to show slightly more Ni-Ni association after thermal aging. The thermally aged ratio is greater than that of the as-received material at ten out of the thirteen NN distances⁷.

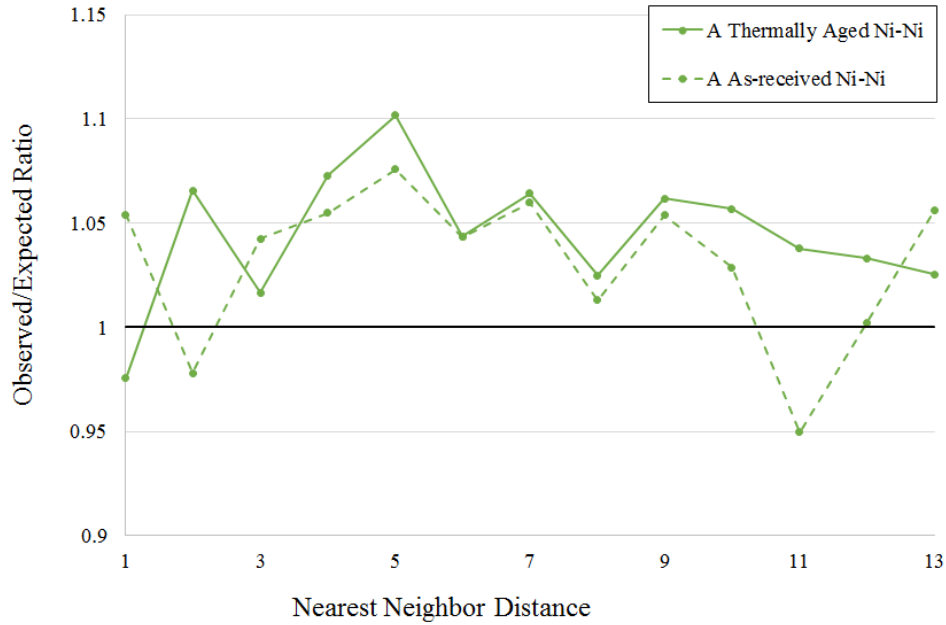


Figure 47: Results from the local chemistry method for sample A. The observed/expected ratio of Ni-Ni association at various nearest neighbor distances are shown for both the thermally aged and as-received RPV steels.

In the majority of samples, however, the distribution of different elements were found to be

⁷There is only a 3.5% chance that this would occur randomly.

statistically significant between the as-received and thermally aged material. For example, in the as-received sample C Si-Ni, Ni-Si, Ni-Ni, Ni-Mn, Mn-Ni, and Mn-Mn association was considered statistically significant. While in the thermally aged sample only Ni-Ni and Mn-Mn association was observed. In order to compare the levels of Ni-Ni and Mn-Mn association observed in the two samples the observed/expected ratios were plotted against nearest neighbor distances (Figure 48). From Figure 48 there is clearly a stronger Mn-Mn association within the thermally aged sample when compared to the as-received sample.

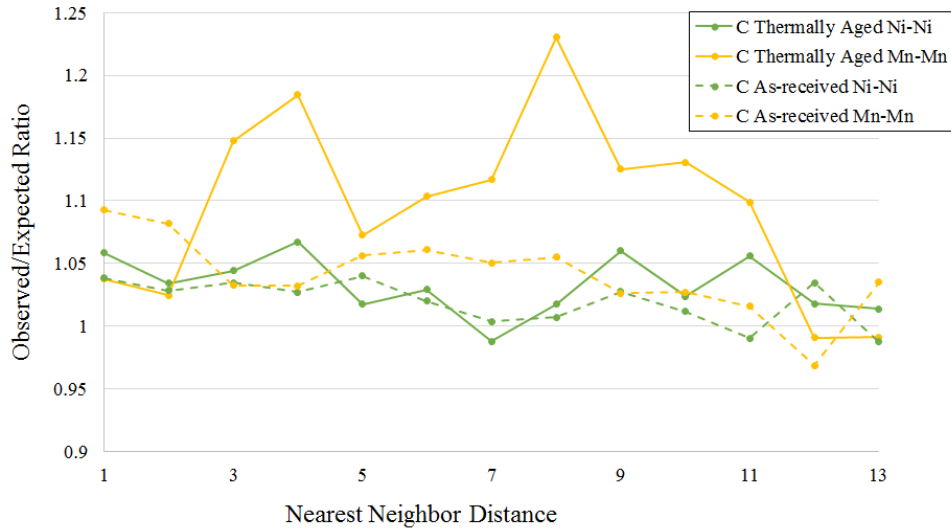


Figure 48: Results from the local chemistry method for sample C. The observed/expected ratio of Ni-Ni and Mn-Mn association at various nearest neighbor distances are shown for both the thermally aged and as-received RPV steels.

However, no definitive trends regarding the changes in solute association between the as-received and thermally aged samples were observed. This result, although null, is significant to nuclear industry RPV community as it illustrates the success of new generation RPV steels in withstanding long term thermal aging.

5.3 Clustering at Grain Boundaries and Carbide Interfaces

In this chapter the observation of clusters at both carbide interfaces and grain boundaries was presented. Often it is difficult to identify clusters within these regions due to solute segregation. These clusters were distinguished from solute segregation through the application of the maximum

Sample	Heat Treatment	Ni (at.%)	Mn (at.%)	Solute Association
C	As-received	3.3	2.0	Si-Ni, Ni-Si, Ni-Ni, Ni-Mn, Mn-Ni, Mn-Mn
	Thermally Aged	3.3	2.0	Ni-Ni, Mn-Mn
G	As-received	1.6	2.0	Si-Ni, Cu-Cu, Cu-Mn, Ni-Ni, Mn-Ni, Ni-Mn, Mn-Mn, Mo-Ni
	Thermally Aged	1.6	2.0	Ni-Si, Si-Ni, Ni-Ni, Mn-Ni, Ni-Mn, Mn-Mn, Cr-Cr
H	As-received	0.2	2.0	None
	Thermally Aged	0.2	2.0	Cu-Ni, Si-Mn, Mn-Mn
K	As-received	3.3	0.25	Ni-Si, Si-Ni, Ni-Ni
	Thermally Aged	3.3	0.25	Si-Ni, Cu-Ni, Ni-Ni
A	As-received	1.6	0.25	Ni-Ni
	Thermally Aged	1.6	0.25	Ni-Ni

Table 21: Summary chart of local chemistry method results. Statistically significant association is listed for each sample in both the as-received state and after thermal aging.

separation method. It is important to note that the clusters identified by the maximum separation method were classified as distinct clusters and not connected via solute segregation. This phenomenon would be expected if these regions were not in fact clusters but rather slight density fluctuations within the segregated solute.

The clusters found at various carbide/matrix interfaces within sample K were all high in Mn content, with an average of 41.4 at.%. Additionally, these clusters were low in Si content (3.1 at.%). Similarly, the clusters located along the low-angle grain boundary found in sample C contained low levels of Si (2.3 at.%). These clusters also contained relatively high levels of Ni, with an average of 23.7 at.%.

Investigating cluster formation at heterogeneous nucleation sites is of great interest to the RPV community. Although the formation of precipitates at grain boundaries do not contribute to hardening embrittlement, their presence can cause non-hardening embrittlement.

Furthermore, there exists controversy over the thermodynamic stability of MNPs – are these precipitates radiation induced or radiation enhanced? In the latter case, precipitation is thermodynamically driven, enhanced via segregation of solute to heterogeneous nucleation sites such as vacancy clusters. The presence of MNPs at heterogeneous nucleation sites within thermally aged steels would indicate that precipitation is thermodynamically driven, thus providing support to the hypothesis that MNPs are radiation enhanced instead of radiation induced. The presence of

small, non-random clusters, rich in Mn and Ni, lends support to this hypothesis. However, additional experimentation is necessary at longer aging times to determine if these clusters will grow into fully developed MNPs.

5.4 Secondary Precipitates within Cementite

Secondary CRPs and MNPs were observed within the cementite phase of a high copper and low copper RPV steel, respectively. Although the effects of solute clustering within cementite have already been implicitly included in estimates of RPV lifetime, this is the first time they have been explicitly recognized. The observation and characterization of these secondary precipitates has thus improved our understanding of where solute precipitates and consequently how different heat treatments may affect the available solute that is responsible for embrittlement.

6 Summary

Hardness measurements taken before and after thermal aging showed a statistically significant decrease in hardening in the five low copper RPV steels analyzed in this work. By regressing on time, temperature, and steel type it was possible to statistically determine that the decrease observed was due to thermal aging.

Consistent with hardness measurements, no precipitates were present within the matrix of the thermally aged steels. However, association was found to be statistically significant in both the thermally aged and as-received materials. However, there were no apparent trends regarding the changes in solute association between the as-received and thermally aged steels.

Clusters were, however, observed at heterogeneous nucleation sites within two of the thermally aged samples. The clusters in sample K were located at several carbide/matrix interfaces and extracted via the maximum separation method. These clusters were rich in Mn and approximately 100-300 atoms in size after detection efficiency was taken into account. The clusters in sample C were observed at a low-angle grain boundary. These clusters were significantly larger (350-650 atoms) and rich in Ni.

CRPs and MNPs were observed within the cementite phase of high and low copper RPV steels, respectively, using APT. This was the first study in which MNPs have been observed in cementite. This research has shown that a range of precipitation can take place within the

cementite phase of thermally aged RPV steels.

Chapter V

Ion Irradiated RPV Steels

This chapter presents APT results of the ion irradiated RPV steels conducted at UCSB. As stated previously, the steels were ion irradiated with 6.4 MeV Fe^{3+} ions at DUET in Kyoto, Japan. The irradiation was conducted at 290°C with a dose rate of 1.5×10^{-4} dpa/s. A total of 4dpa was obtained 500nm below the surface of the specimens. Additional details regarding the irradiation conditions can be found in Chapter 3. A table of successful atom probe runs for each sample is shown in Table 22.

	Run ID	Comments
Sample K (3.3 at.% Ni, 0.25 at.% Mn)	6285	
	6290	Short run
	6353	Short run
	6287	
	6352	Short run
Sample C (3.3 at.% Ni, 2.0 at.% Mn)	22359	Short run
	6364	Significant Ga and oxide present, discarded
	6363	Contains grain boundary
Sample G (1.6 at.% Ni, 2.0 at.% Mn)	6291	
	6293	Carbides present
	6295	
Sample A (1.6 at.% Ni, 0.25 at.% Mn)	6315	
	6317	Contains grain boundary
	6318	
	6321	Contains grain boundary
	6322	
Sample H (0.2 at.% Ni, 2.0 at.% Mn)	6359	
	6362	
	6293	Short run
	6354	Significant Ga present, discarded

Table 22: Log of ion irradiated atom probe runs.

It should be noted that for each material several successful atom probe runs were obtained. Therefore, weighted averages across multiple datasets were utilized where appropriate, including calculations of cluster composition, size, number density, and volume fraction.

All cluster size calculations presented in this chapter have been adjusted to account for detector efficiency using the methods described in detail in Chapter 3 and the Appendix. Additionally, Fe is not included in any of the cluster analyses as it is considered to be an artifact of APT. A discussion regarding Fe content in precipitates is presented in Section 3.2.3. Lastly, cluster size was calculated as the equivalent diameter of a sphere containing the appropriate number of atoms (corrected for Fe content and detection efficiency). In order to calculate this diameter it was assumed that all atoms occupy the volume of an Fe atom ($1.18 \times 10^{-29} \text{ m}^3$).

The goal of this work was to determine the effects of varying Ni and Mn concentrations in the parent steel on MNP composition and volume fraction. This chapter is divided into several sections: APT of each sample; analysis of dislocations and grain boundaries; analysis of precipitate composition; analysis of cluster composition vs. cluster size; and a statistical analysis of precipitate volume fraction.

1 Microstructural and Microchemical Analysis via APT

1.1 Sample K: High Ni, Low Mn

Five sample K specimens were successfully analyzed via APT (Table 22). A representative reconstruction is shown in Figure 49. Within this sample, MNPs nucleated both heterogeneously, along dislocations, and homogeneously within the matrix. Ni and Si segregation along the dislocations was also observed. The bulk sample contained 3.3 at.% Ni and 0.25 at.% Mn; however, the individual atom probe sample compositions varied depending on the local microstructure.

Ignoring Fe content, the average precipitate composition was 67.8 at.% Ni, 9.6 at.% Mn, and 20.1 at.% Si. The remaining 2.5 at.% consisted of other elements such as Cu, P, C, Mo, and Cr. The average precipitate number density for sample K was $2.9 \times 10^{23} \text{ m}^{-3}$. The precipitate volume fraction was 2.1%.

The precipitates observed in sample K contained the highest levels of Ni; the Ni content within the precipitates was strongly correlated to the total amount of Ni found within the individual APT reconstructions. The bulk composition for each APT reconstruction contained

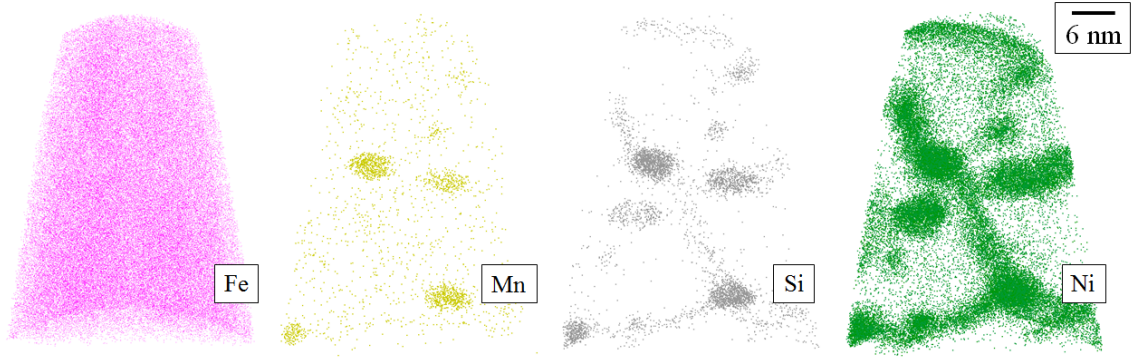


Figure 49: Atom maps of run 6287 (sample K). Precipitates have nucleated homogeneously within the matrix and heterogeneously along dislocations. Ni and Si segregation to dislocations can be observed.

between 2.4-4.0 at.% Ni. This local composition was strongly correlated to the amount of Ni found within the surrounding precipitates, which varied from 32.7-40.0 at.% (prior to removing Fe) between APT reconstructions. A summary of these compositions is shown in Table 23. Approximately 1.3 at.% of the solute remained in the matrix, the majority of which was Ni.

Run ID	Ni in APT Specimen (at.%)	Ni in Precipitates (at.%)
6285	3.4	34.0
6287	4.0	40.0
6290	2.4	32.7

Table 23: The Ni content within precipitates was strongly correlated to the amount of Ni found within the bulk of the individual APT tips.

Cluster composition versus cluster size is shown in Figure 50. Each bar represents a single cluster and illustrates the ratio between Ni (green), Mn (yellow), and Si (grey) content. Cluster size, after removing the iron and accounting for detection efficiency, increases along the x-axis. The high Ni content of the clusters is unsurprising as the bulk of sample K contains high levels of Ni (3.3 at.%). Similarly, the clusters' low Mn content can be attributed to the bulk sample's low Mn content (0.25 at.%).

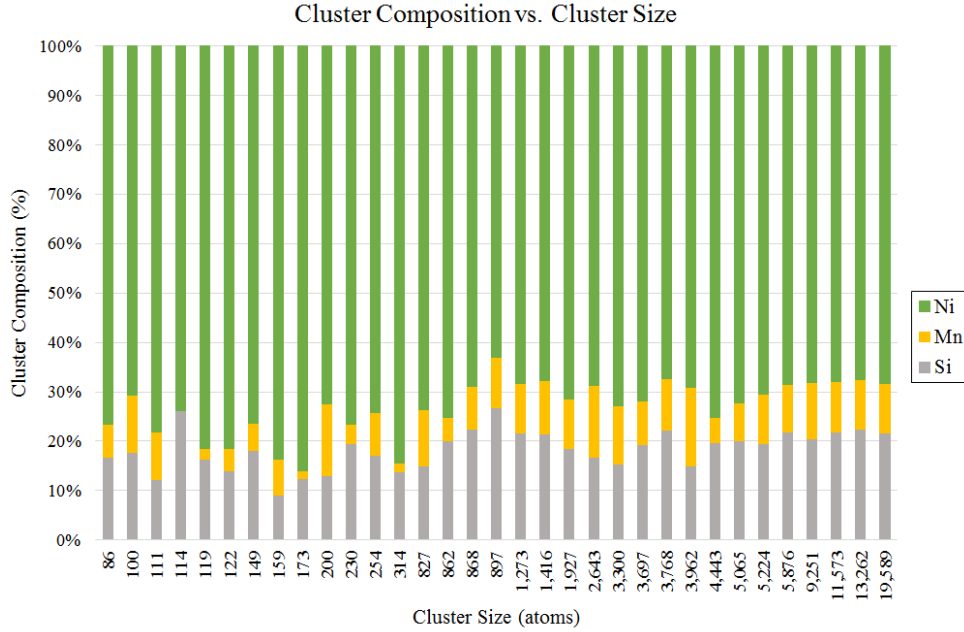


Figure 50: Cluster composition vs. cluster size for ion irradiated sample K. Each bar represents a single cluster and illustrates the ratio between Ni (green), Mn (yellow), and Si (grey) content.

The average precipitate size was 6.1 nm in diameter. A cluster size distribution for sample K is shown in Figure 51. Cluster size in Figure 51 is given in atoms. As stated previously, cluster size does not include Fe and has been adjusted to account for detection efficiency. The cluster size distribution appears to contain a secondary mode at approximately 4,000 atoms. The presence of this secondary mode is discussed in Section 3.4. Several very large precipitates are also observed.

1.2 Sample C: High Ni, High Mn

Three atom probe specimens were successfully analyzed for sample C (Table 22). The bulk of sample C contained 3.3 at.% Ni and 2.0 at.% Mn. One of the APT datasets contained a grain boundary and is shown in Figure 52. The grain boundary, which runs the length of the sample, is highlighted by solute segregation and decorated with MNPs. Several dislocations and dislocation loops are also present within the atom probe tip.

Disregarding Fe, the precipitates contained an average of 61.1 at.% Ni, 22.0 at.% Mn, and 15.0 at.% Si. Approximately 1.4 at.% of the solute remained in the matrix. A plot of cluster composition versus cluster size is shown in Figure 53. The smaller clusters contain significantly more Mn as well as less Si. As the clusters grow, the Si content notably increases. Furthermore, the

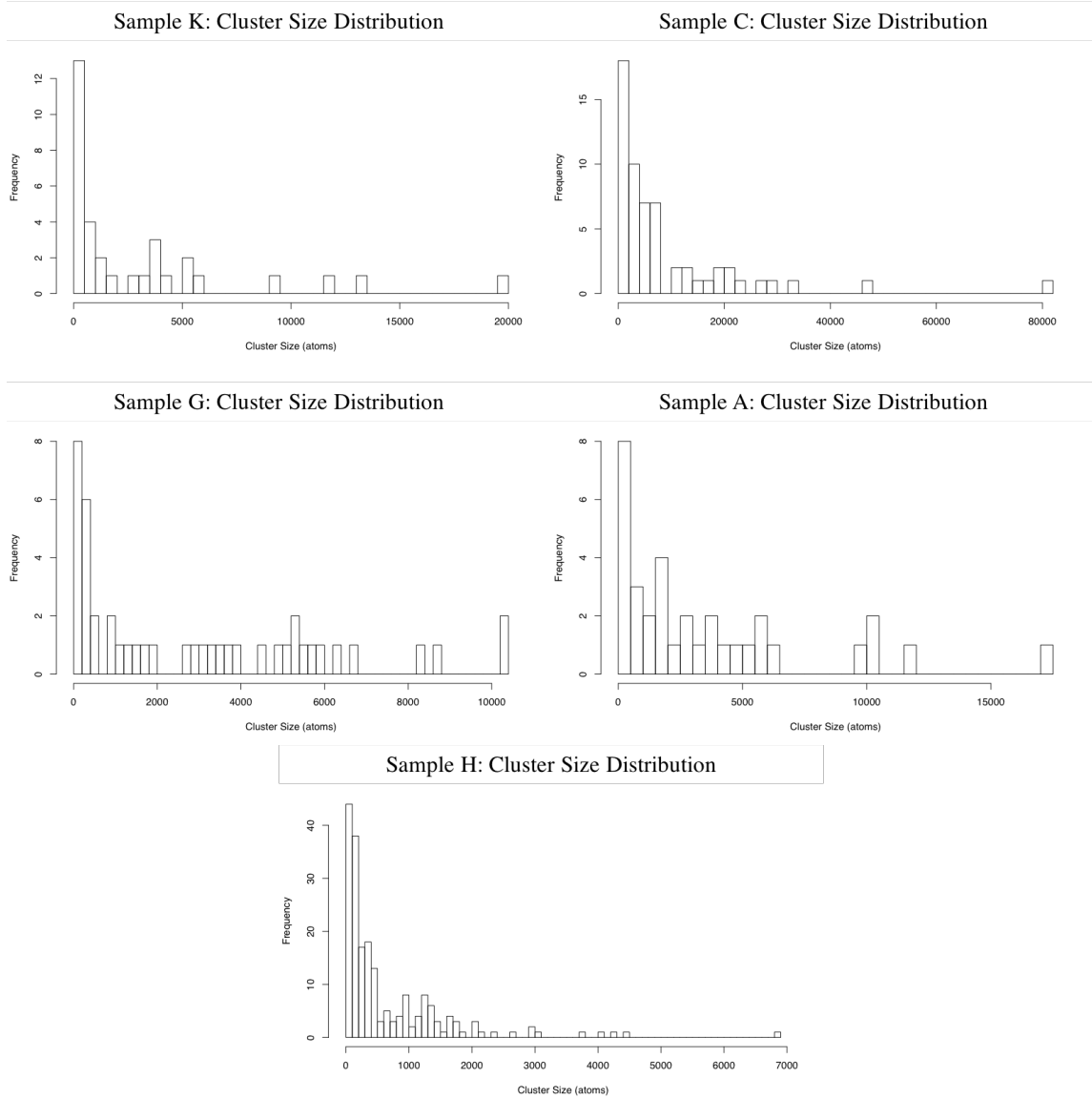


Figure 51: Cluster size distributions for each of the ion irradiated samples. Cluster size is shown on the x axis and given in atoms.

Ni, Mn, and Si content ratio appears to stabilize as the clusters become sufficiently large.

The clusters have a number density of $2.2 \times 10^{23} \text{ m}^{-3}$ with an average size of 8.1 nm in diameter. The precipitate volume fraction was 5.2%. A significant increase in average precipitate size and precipitate volume fraction was observed for sample C when compared to sample K. These trends are likely due to the presence of a grain boundary in one of the sample C datasets. MNPs which nucleate on grain boundaries are able to nucleate and grow relatively quickly, as solute segregates to and travels more freely along grain boundaries.

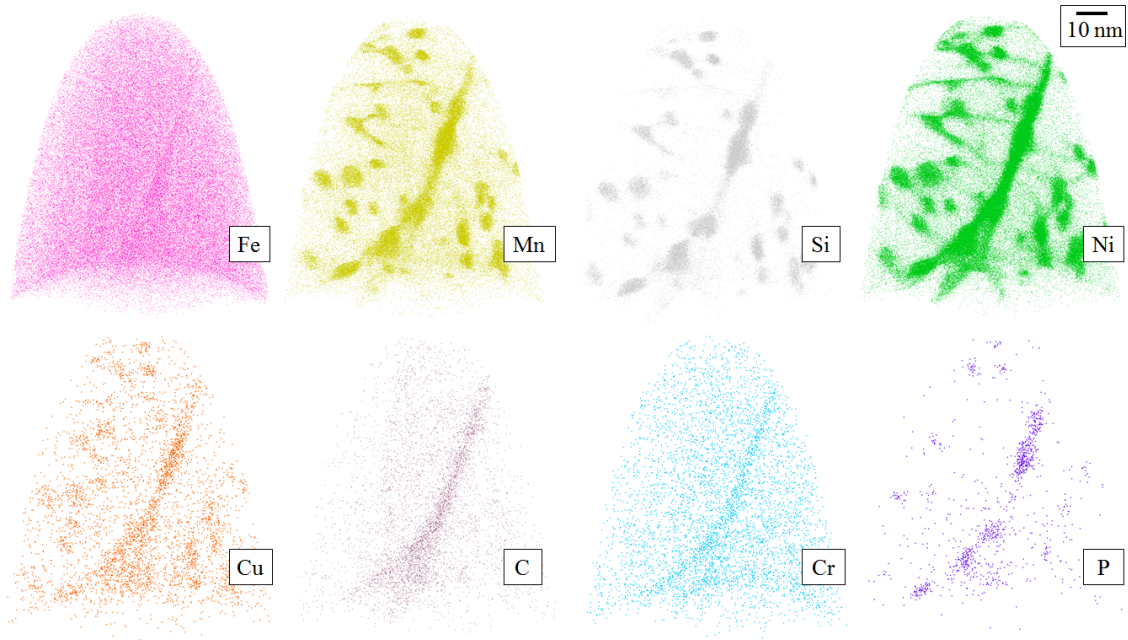


Figure 52: Atom maps of run 6363 (sample C). A grain boundary decorated with solute and several MNPs runs diagonally across the sample.

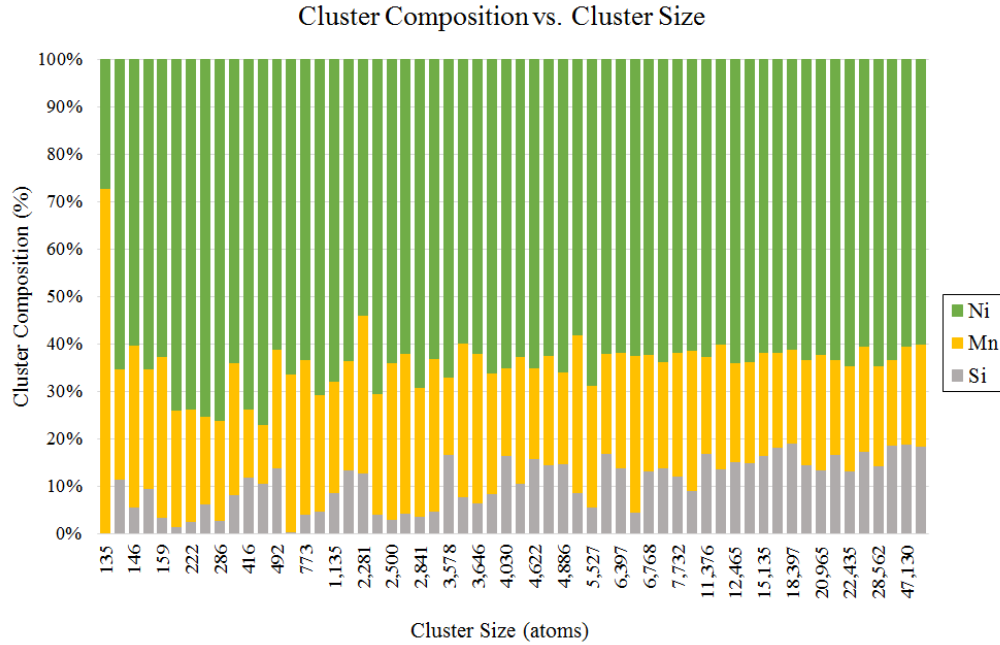


Figure 53: Cluster composition vs. cluster size for ion irradiated sample C. Each bar represents a single cluster and illustrates the ratio between Ni (green), Mn (yellow), and Si (grey) content.

A cluster size distribution is shown in Figure 51 for sample C. Again, cluster size in Figure 51 is given in atoms and has been adjusted to account for detection efficiency. Sample C's cluster size

distribution also appears to contain a second mode located at approximately 20,000 atoms. There exist two outliers in the distribution at approximately 47,000 and 80,000 atoms. These two clusters are located on the grain boundary observed in Figure 52 and thus are significantly larger than the other precipitates.

1.3 Sample G: Medium Ni, High Mn

Five atom probe specimens were successfully run for sample G, the bulk of which contained 1.6 at.% Ni and 2.0 at.% Mn (Table 22). One of the APT reconstructions is presented in Figure 54. This analysis contains several dozen MNPs but no visible (decorated) dislocations or grain boundaries.

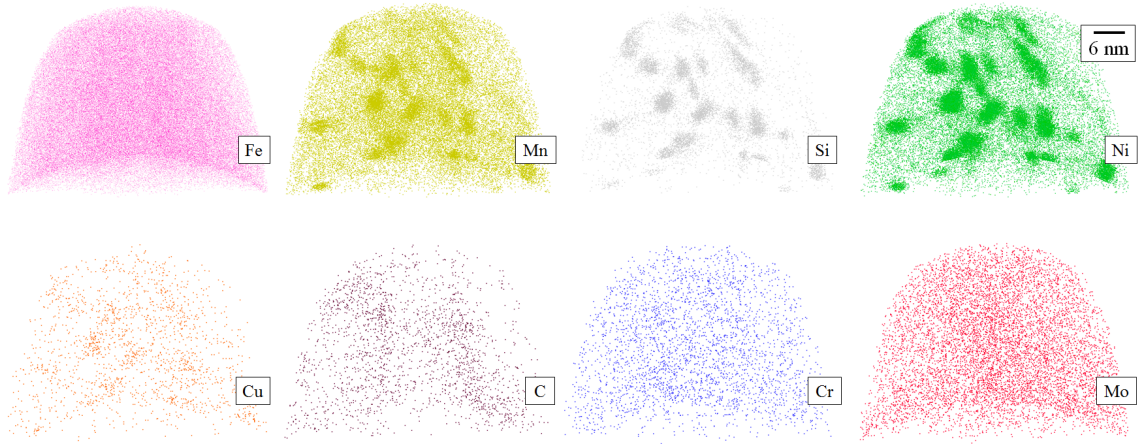


Figure 54: Atom maps of run 6291 (sample G).

Sample G had an average precipitate number density of $3.0 \times 10^{23} \text{ m}^{-3}$ and an average precipitate composition of 56.4 at.% Ni, 23.7 at.% Mn, and 17.5 at.% Si. On average, the precipitates were 7.1 nm in diameter. The precipitate volume fraction was 4.2%. Approximately 1.9 at.% of solute remained in the matrix.

Figure 51 contains a cluster size distribution for sample G. As with the other samples, a second mode was present at approximately 5,700 atoms. Several large clusters ($>10,000$ atoms) were also observed.

Figure 55 plots precipitate composition versus precipitate size. The plot shows Ni (green), Mn (yellow), and Si (grey) content ratios within each of the precipitates. As observed in sample C, there exists considerably more Mn and less Si in the smaller clusters. The potential implications of this observation are discussed in Section 3.3. It should be noted that the Ni, Mn, and Si

proportions level off as precipitate size increases. This effect appears to be present in each of the five model RPV steels. However, it is most prominent in sample G. Furthermore, the size at which this leveling off occurs varies significantly from sample to sample. For example, in sample G cluster composition becomes consistent after clusters reach approximately 3,000 atoms in size whereas in sample C this stability is obtained only after clusters reach sizes of greater than 10,000 atoms.

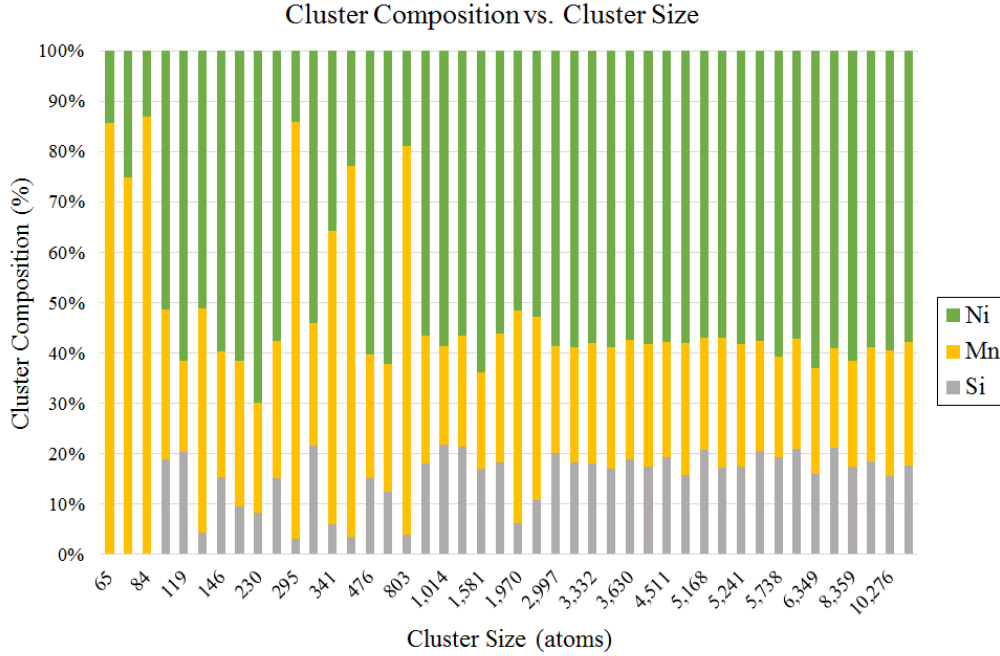


Figure 55: Cluster composition vs. cluster size for ion irradiated sample G. Each bar represents a single cluster and illustrates the ratio between Ni (green), Mn (yellow), and Si (grey) content.

1.4 Sample A: Medium Ni, Low Mn

A typical atom map of sample A is shown in Figure 56. Precipitates have nucleated on dislocations as well as within the matrix (or potentially on features within the matrix invisible to atom probe). Several dislocation loops are also present and discussed in Section 2.1. Sample A, which contains 1.6 at.% Ni and 0.25 at.% Mn, had a precipitate number density of $2.3 \times 10^{23} \text{ m}^{-3}$ and average precipitate size of 6.1 nm in diameter. A cluster size distribution for sample A is shown in Figure 51.

Ignoring iron content, the average precipitate composition was as follows: 63.8 at.% Ni, 8.7 at.% Mn, and 26.1 at.% Si. Approximately 1.2 at.% of solute remained in the matrix. Cluster composition versus cluster size is shown in Figure 57. Sample A's low Mn content (0.25 at.%) is

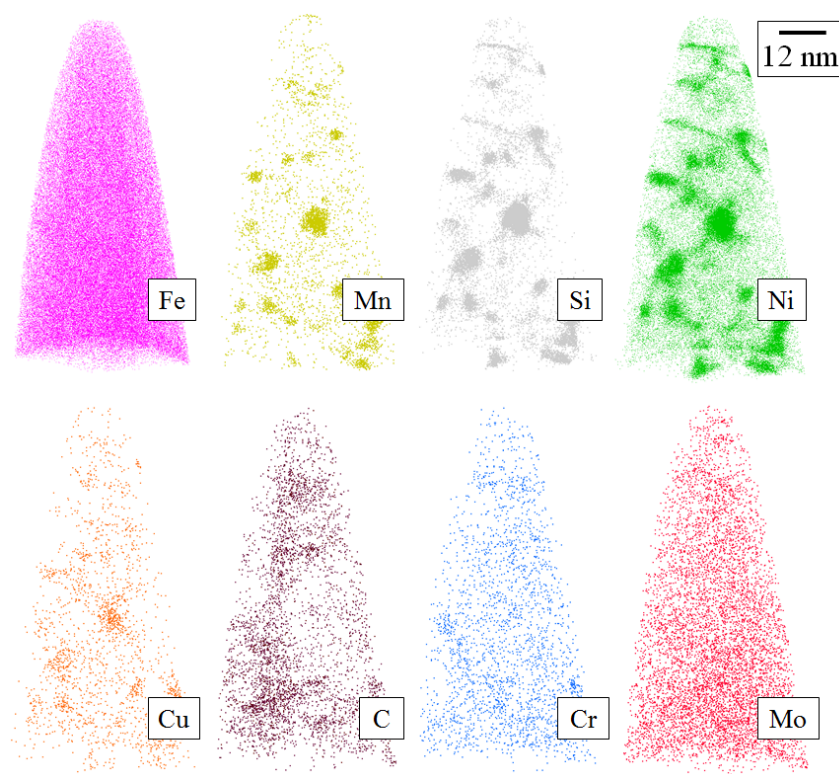


Figure 56: Atom probe maps of run 6315 (sample A).

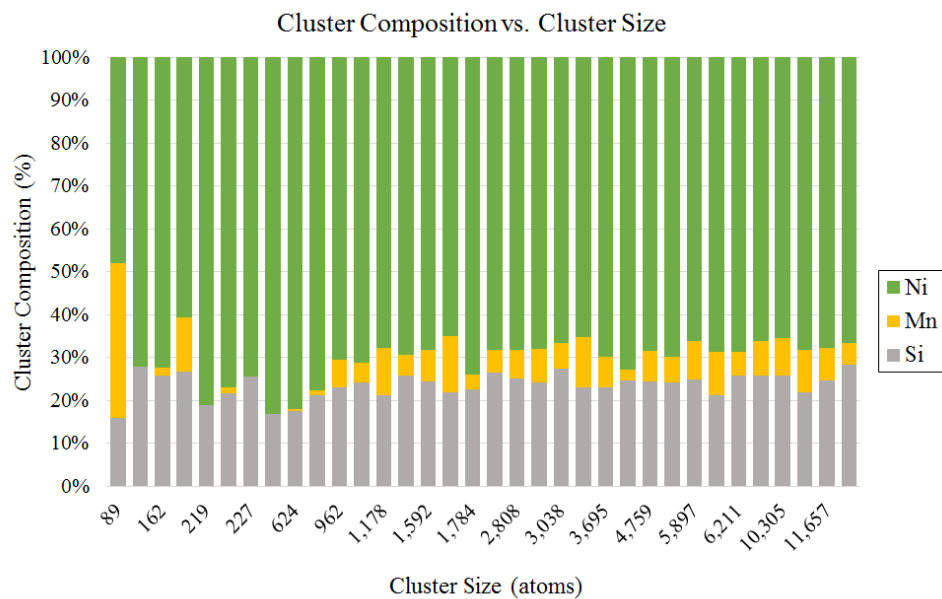


Figure 57: Cluster composition vs. cluster size for ion irradiated sample A. Each bar represents a single cluster and illustrates the ratio between Ni (green), Mn (yellow), and Si (grey) content.

reflected in the cluster composition as each of the clusters contain significantly less Mn than those found in the high Mn samples, C and H. Conversely, the Si content is significantly greater (26.1 at.%).

1.5 Sample H: Low Ni, High Mn

There were three successful atom probe reconstructions analyzed for sample H. The bulk material contained 0.2 at.% Ni and 2.0 at.% Mn. The clusters found in sample H were considerably smaller than those in the other four samples, with an average precipitate diameter of 4.9nm. Sample H was also noted for its high number density (5.1×10^{23}) of clusters and high levels of solute remaining in the matrix (2.0 at.%). An atom probe reconstruction is shown in Figure 58. Sample H contained clusters with an average composition of 27.4 at.% Ni, 44.6 at.% Mn, and 23.6 at.% Si.

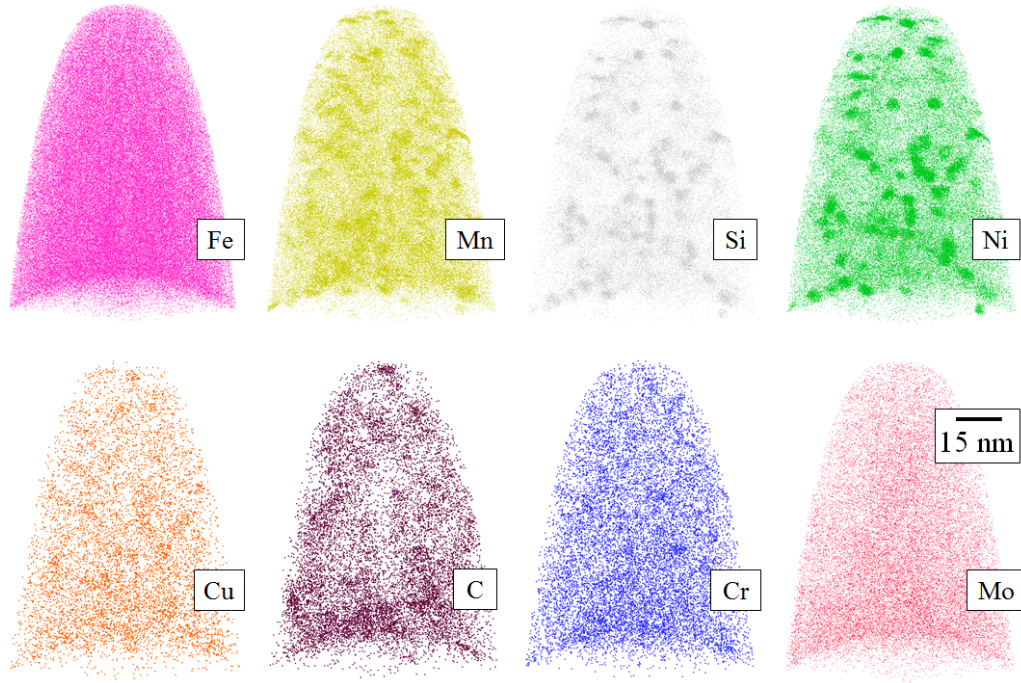


Figure 58: Atom maps of run 6359 (sample H).

A cluster size distribution for ion irradiated sample H is shown in Figure 51. This distribution contains two modes, the second of which is located at approximately 1,250 atoms. In general the clusters in sample H are significantly smaller than those found in the other samples, with the largest cluster being just under 7,000 atoms.

The cluster composition versus cluster size for sample H can be found in Figure 59. As

observed in several of the previous samples, the smaller precipitates contain significantly more Mn. This is exacerbated by the fact that sample H is high in Mn (2.0 at.%).

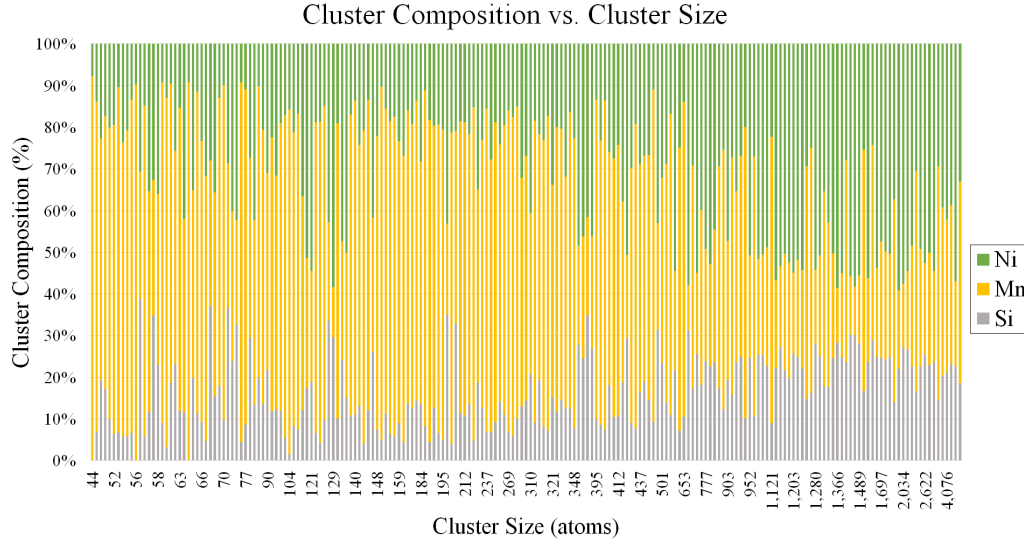


Figure 59: Cluster composition vs. cluster size for ion irradiated sample H. Each bar represents a single cluster and illustrates the ratio between Ni (green), Mn (yellow), and Si (grey) content.

2 Precipitation and Segregation to Grain Boundaries and Dislocations

2.1 Dislocations

The majority of atom probe runs from each of the five samples contained dislocations decorated by solute segregation. These dislocations were enriched in a variety of solute including Ni, Mn, Si, Cu, C, and Mo. The dislocations were also decorated with MNPs. The nucleation of MNPs on dislocations is facilitated by a reduction in surface energy, while their growth rate is facilitated by the fast diffusion of solute species along these defects. An example of a decorated dislocation is shown in Figure 60. In this example, there exists significant segregation of Ni, Mn, Si, and Cu to the dislocation as well as two small MNPs.

Full dislocation loops were observed in three atom probe runs, including run 6315 of sample A (Figure 56). One of the dislocation loops from this sample was isolated and further analyzed via a ROI (15 nm x 15 nm x 4 nm). After being extracted from the reconstruction an isodensity of 1.10

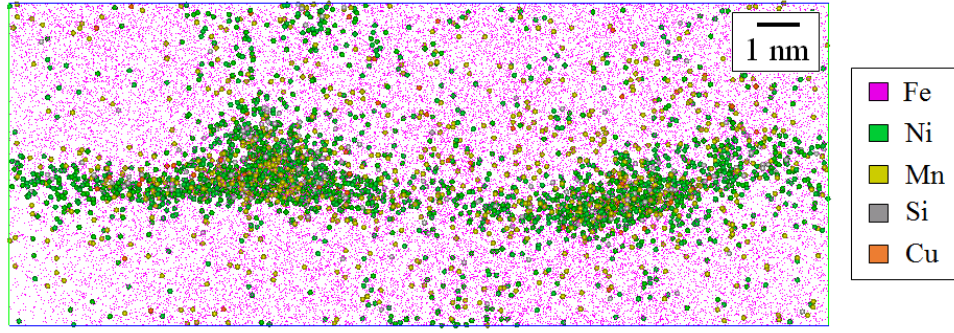


Figure 60: An example of a decorated dislocation from sample A enriched in Ni, Mn, Cu, and Si. Two precipitates are also visible.

Ni atoms/nm³ was applied to highlight the feature (Figure 61). This dislocation loop was decorated most prominently in Ni, but also Mn, Cu, and Si as shown in Figure 62. From the atom maps shown in Figure 62 it appears that Si and Mn tend to segregate to the inner part of the loop, while Ni and Cu are found to dominate the outer region.

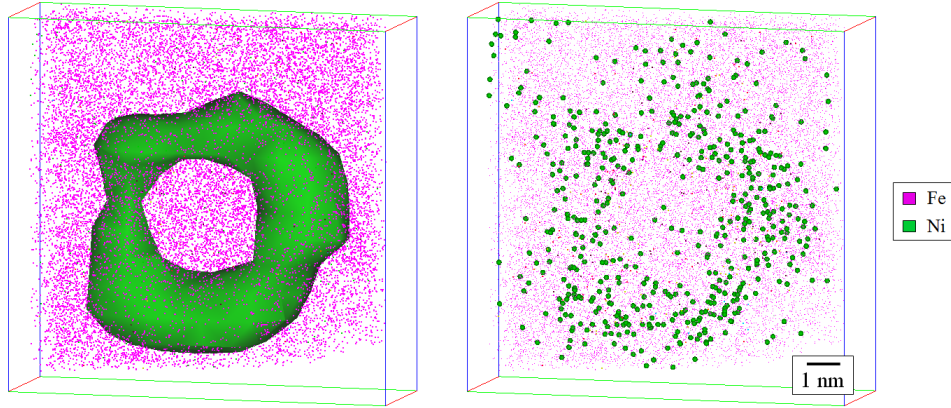


Figure 61: A dislocation loop from run 6315 of sample A. An isodensity of 1.10 Ni atoms/nm³ was applied to highlight the feature (left), which was primarily enriched in Ni (right).

2.2 Grain Boundaries

2.2.1 Grain Boundary in Sample A

A grain boundary was observed in ion irradiated sample A. The grain boundary, decorated by solute, is located along the right hand side of the reconstruction shown in Figure 63. Although decorated in solute, no precipitates were observed along this grain boundary.

A region of interest was placed across the grain boundary in order to obtain a 1D

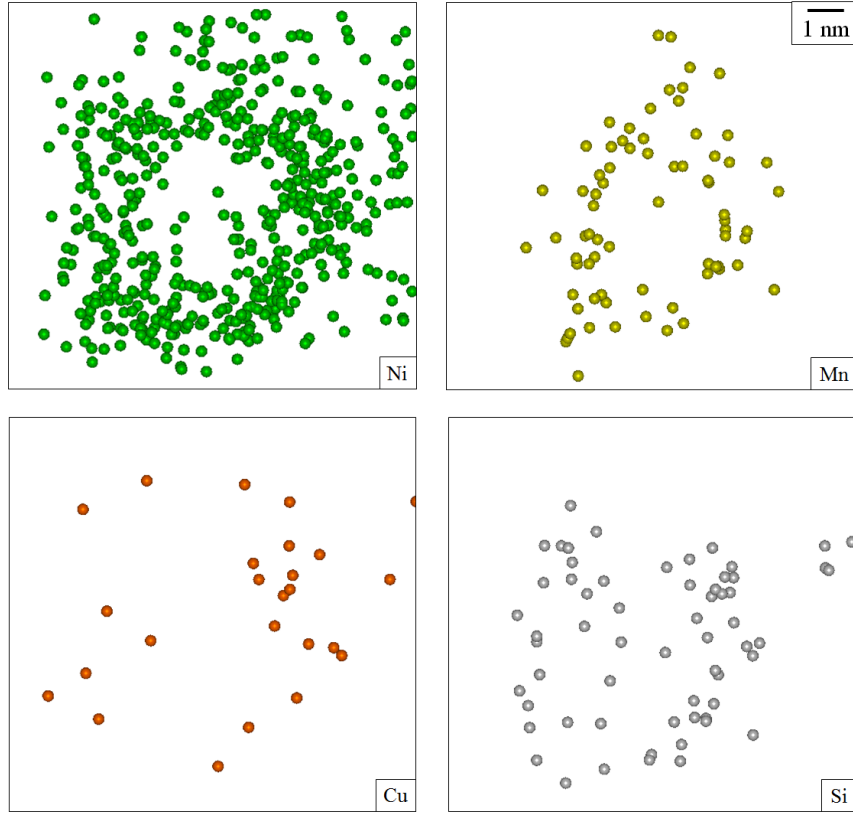


Figure 62: A dislocation loop from run 6315 of sample A enriched in Ni, Mn, Cu, and Si. Atom maps of Si and Mn show segregation to the inner part of the loop, while Ni and Cu segregation dominates the outer region.

concentration profile (Figure 64). From the 1D concentration profile the observed grain boundary is clearly enriched in Ni, Si, Mn, C, Cu, and Cr.

A ROI (10 nm x 10 nm x 11 nm) was placed across the grain boundary in order to quantify the amount of excess solute. This was done by calculating the Gibbs interfacial excess for each element. As shown in Chapter 5, the Gibbs interfacial excess was calculated via the equation:

$$\Gamma_i = \frac{N_{i(excess)}}{V} \quad (13)$$

where Γ_i is the Gibbs interfacial excess of element i , $N_{i(excess)}$ is the number of excess solute atoms at the interface, and V is the interfacial volume utilized to determine the interfacial excess [102, 103]. These calculations are summarized in Table 24.

Plots of the cumulative ion counts across the ROI are shown for the following elements: Ni, Si, Mn, Cr, C, and P (Figure 65). These plots enable the visualization of the Gibbs interfacial excess

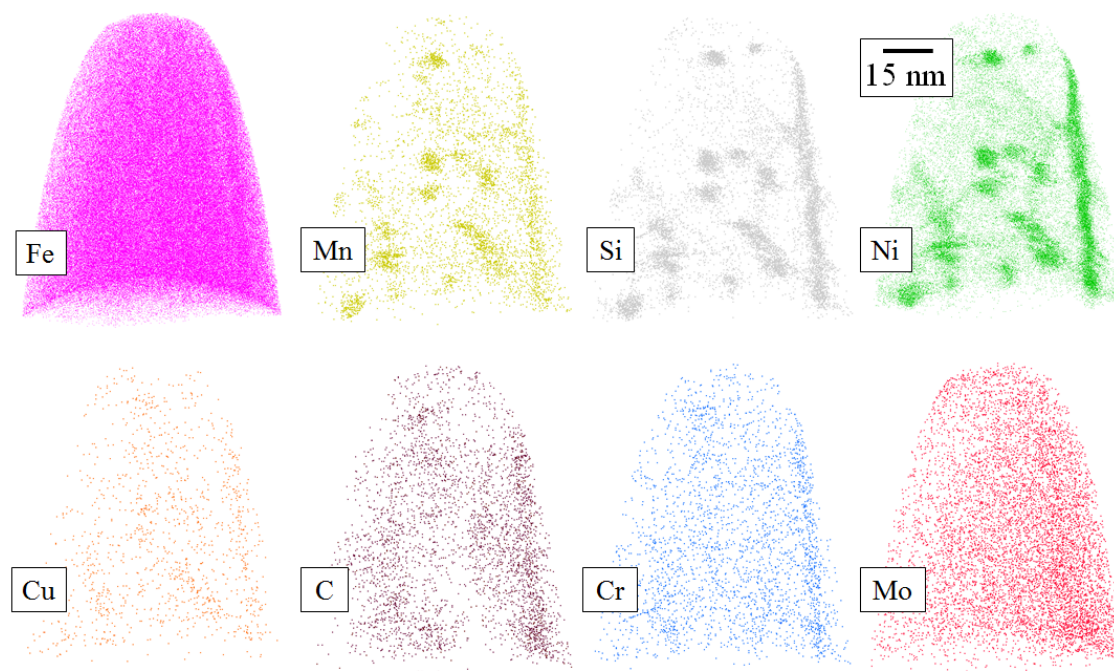


Figure 63: Atom maps of ion irradiated sample A. A decorated grain boundary is visible along the right hand side of the reconstruction.

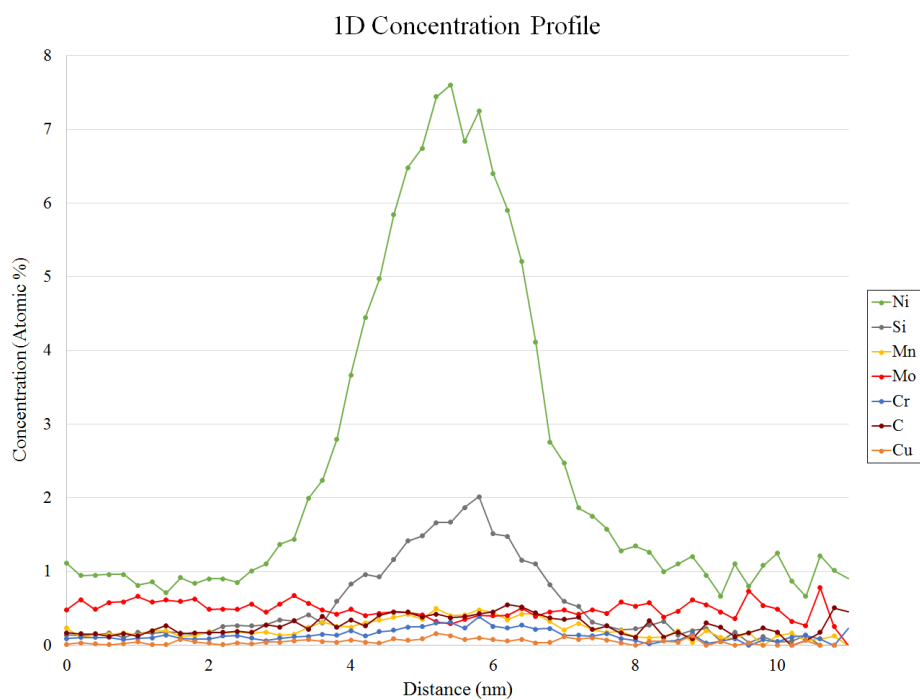


Figure 64: 1D concentration profile for grain boundary in ion irradiated Sample A.

Element	Gibbs interfacial excess (atoms/nm ³)
Ni	10.88
Si	2.70
Mn	0.53
C	0.47
Cr	0.38
Cu	0.15
P	0.01
Mo	-0.05

Table 24: Calculated Gibbs interfacial excess for various elements at the observed grain boundary in ion irradiated sample A.

for each element across the grain boundary. Ni had the highest Gibbs interfacial excess at 10.88 atoms/nm³, over four times that of Si, the element with the second highest excess. This high level of Ni segregation to the grain boundary is expected as the bulk of sample A contains 1.6 at.%Ni.

2.2.2 Grain Boundary in Sample C

A grain boundary was observed in run 6363 of ion irradiated sample C. This grain boundary ran diagonally across the sample and was highlighted via segregated solute (Figure 52). Additionally, several Mn- and Ni-rich precipitates were observed along this grain boundary.

As done previously, a 1D concentration profile was created using a ROI (10 nm x 10 nm x 25 nm) placed across the boundary (Figure 66). This 1D concentration profile showed elevated levels of Ni, Mn, C, and Si at the grain boundary. In order to quantify these levels of excess, the Gibbs interfacial excess was again calculated for each solute element (Table 25). These interfacial excesses are visualized via cumulative ion count plots shown in Figure 67. Plots of the cumulative ion count versus distance along the ROI are shown for Ni, Si, Mn, Cu, C, and P. These plots have been corrected for detection efficiency.

Six precipitates were observed along the grain boundary in sample C. However, only two of these precipitates were fully captured within the reconstruction. As a result only these two precipitates were utilized in the following analysis. Although the statistics are poor, several trends were identified.

First, in terms of size, the two precipitates located on the grain boundary were the largest observed. After the Fe was removed and the ion count was adjusted for detection efficiency, the two precipitates contained approximately 47,000 and 81,000 atoms, respectively. It is believed that

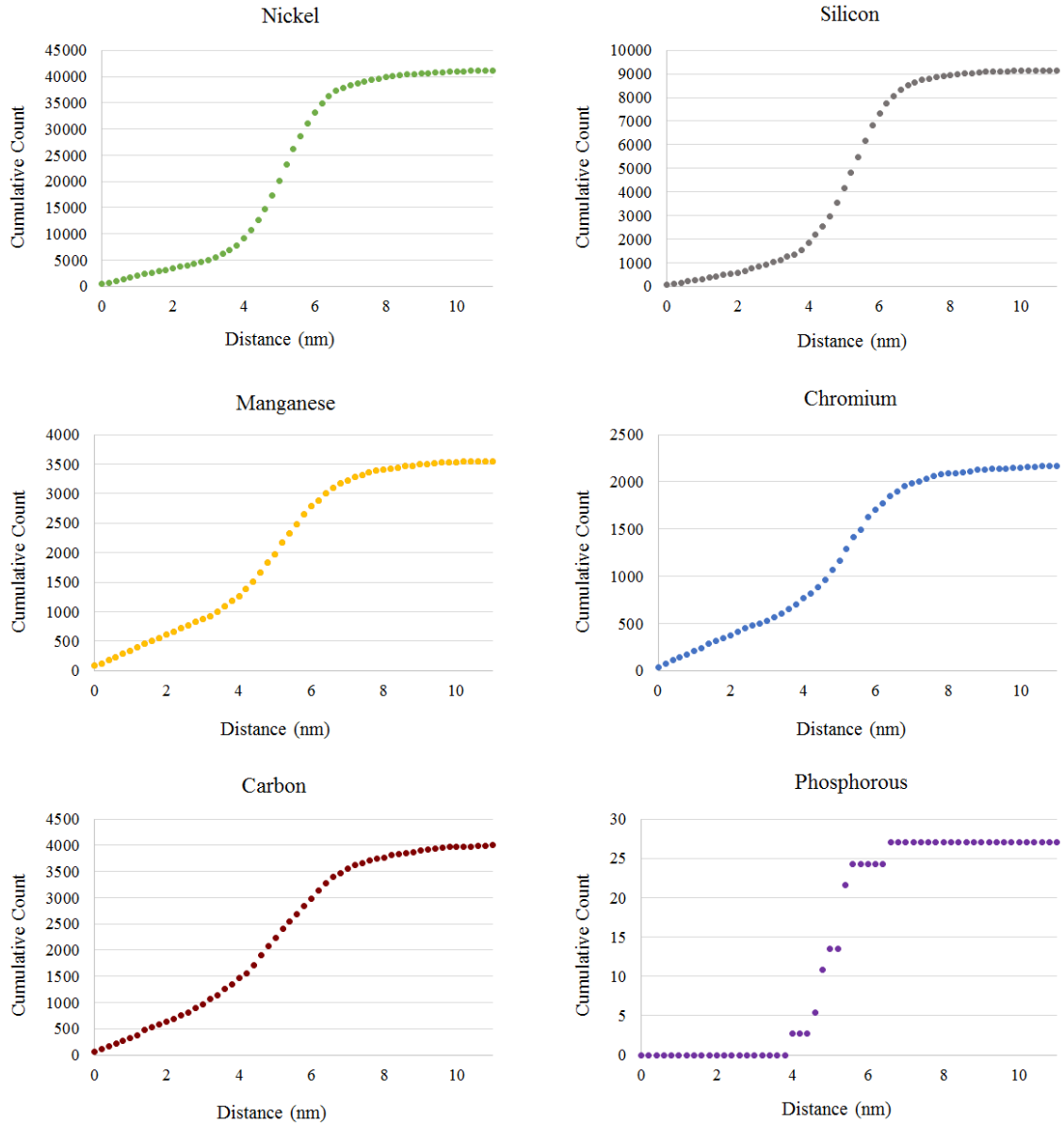


Figure 65: Plots of the cumulative ion count for Ni, Si, Mn, Cr, C, and P across the grain boundary in the ion irradiated sample A.

these precipitates were considerably larger than those found within the matrix because the grain boundary provided a fast solute diffusion pathway. For comparison, the next largest precipitate contained only 32,000 atoms. Additionally, the average precipitate size, discounting the two located on the grain boundary, was approximately 7,000 atoms, an order of magnitude lower than those found at the grain boundary.

The MNPs located on the grain boundary contained significantly more Si than precipitates

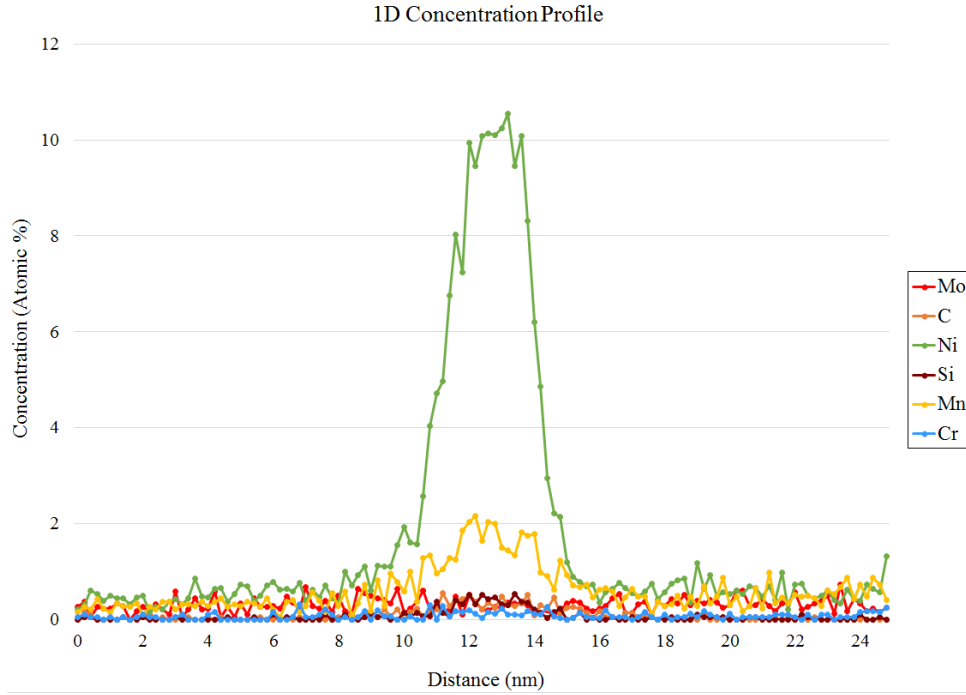


Figure 66: 1D concentration profile for grain boundary in Sample C.

Element	Gibbs interfacial excess (atoms/nm ³)
Ni	18.47
Mn	2.88
Si	0.73
C	0.57
Mo	0.34
Cr	0.21
Cu	0.13
P	0.08

Table 25: Calculated Gibbs interfacial excess for various elements at the observed grain boundary in ion irradiated sample C.

that had nucleated within the matrix. This trend was not due to a correlation with size, as the larger precipitates ($> 20,000$ atoms) located within the matrix did not contain similar elevated levels of Si. The Mn and Ni content within the two grain boundary precipitates were similar to that of the other precipitates. A summary of this data is presented in Table 26.

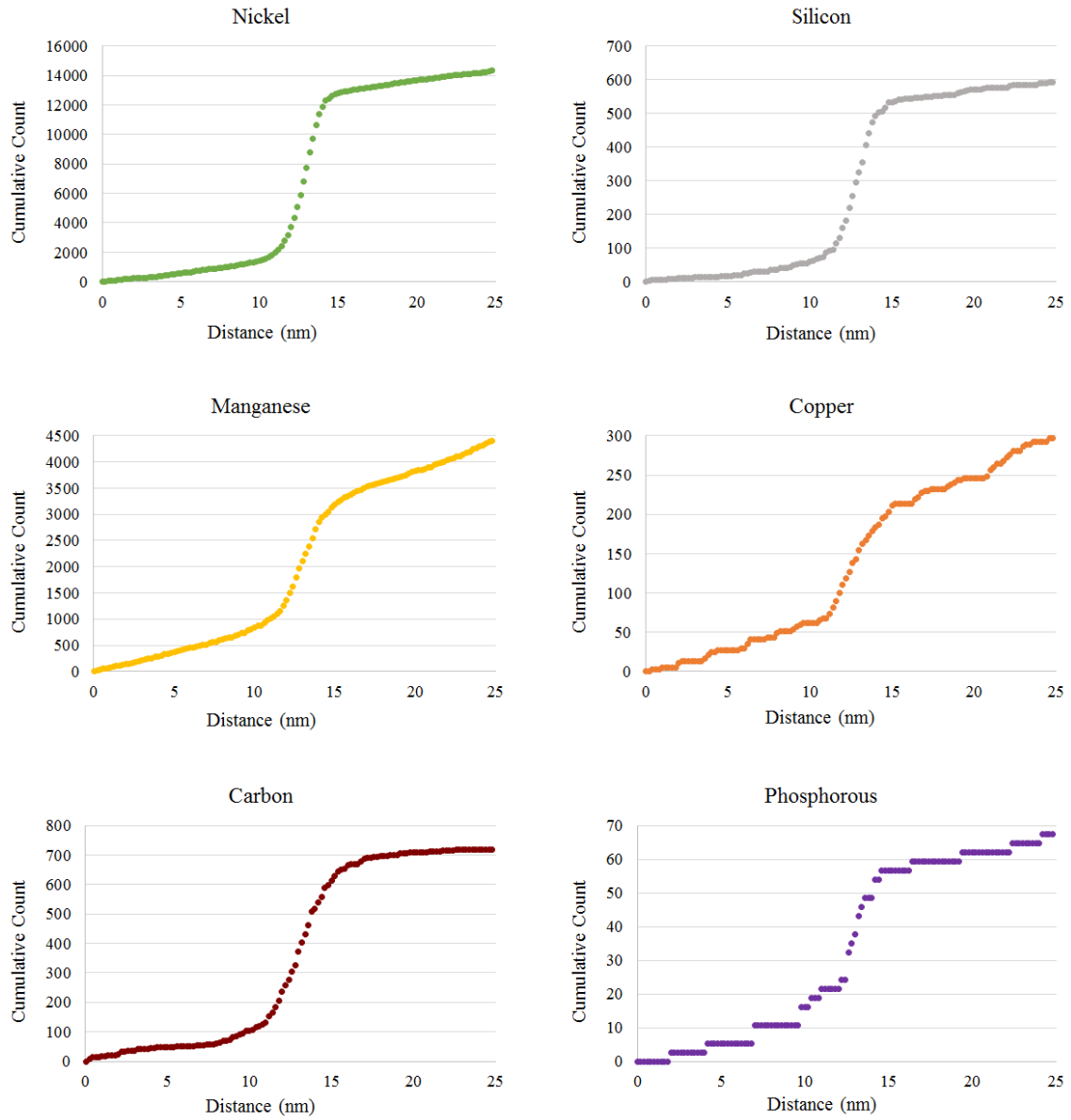


Figure 67: Plots of the cumulative ion count for Ni, Si, Mn, Cu, C, and P across the grain boundary in the ion irradiated sample C.

	Location	Corrected Size (atoms)	Si (at.%)	Ni (at.%)	Mn (at.%)
Cluster 57	grain boundary	47130	12.1	39.2	13.4
Cluster 58	grain boundary	81154	10.3	33.8	12.1
Average	-	8963	8.7	34.2	12.1

Table 26: Table of precipitate size and composition for grain boundary precipitates.

3 Discussion

3.1 Atom Probe Statistics

Although atom probe only samples a small region of the material, these regions are randomly drawn and thus in expectation will be representative of the material; such subsamples are ubiquitously used to draw inferences about entire populations in all areas of statistics.

However, the argument can be made that the process of selecting a region for atom probe analysis is not in fact random. For example, preferential etching during electropolishing or specimen fracture at certain features such as precipitates, carbides, and grain boundaries could have an affect on which regions are analyzed via APT. Regardless, it is generally assumed that atom probe analyses are randomly drawn.

Despite this assumption, it is important to perform multiple atom probe analyses of a particular sample. The more atom probe analyses performed, the more accurately one can determine quantities such as precipitate size, composition, etc.

3.2 Precipitate Composition

3.2.1 Intra-sample Precipitate Composition

Mean precipitate compositions between atom probe analyses of the same sample were generally in close agreement. Mean precipitate compositions for two sample K atom probe analyses are shown in Figure 68. Each of the main solutes, Ni, Mn, and Si, were within a 12% error.

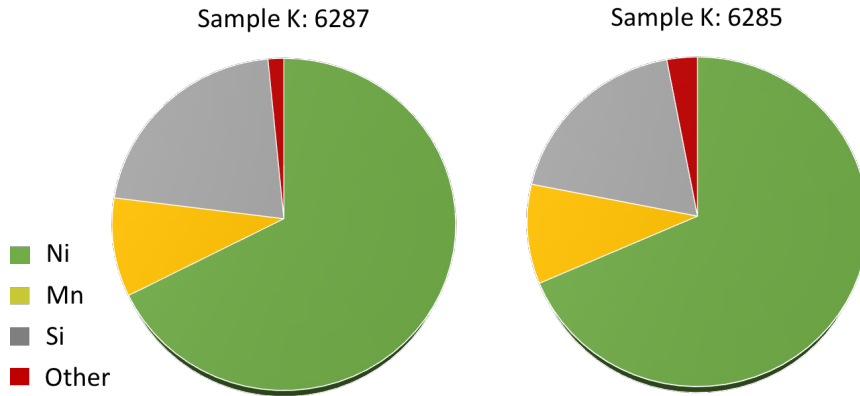


Figure 68: Intra-sample precipitate composition analysis for sample K.

3.2.2 Inter-sample Precipitate Composition

A bar chart illustrating average precipitate composition for each of the five steels is shown in Figure 69. Sample H was low in Ni (0.2 at.%) and high in Mn (2.0 at.%) and therefore approximately half the amount of Ni was observed within these precipitates as those found within the other four samples. Additionally, significantly higher levels of Mn were found within these precipitates.

Precipitates within samples K, C, G, and A all contained similar amounts of Ni, but varying amounts of Si and Mn. It was observed that the bulk Mn content directly effects the amount of Mn found in the precipitates; samples K and A as well as samples C and G have very similar bulk Mn and, consequently, Si contents.

From these observations we see several emerging trends: Ni content within the MNPs did not vary significantly within the medium and high Ni steels; bulk Mn content appeared to dictate Si content (and Mn content) within the MNPs; and low Ni content was correlated with a higher number density of smaller precipitates rich in Mn. However, atom probe analyses of additional steels are necessary to quantify and confirm these trends.

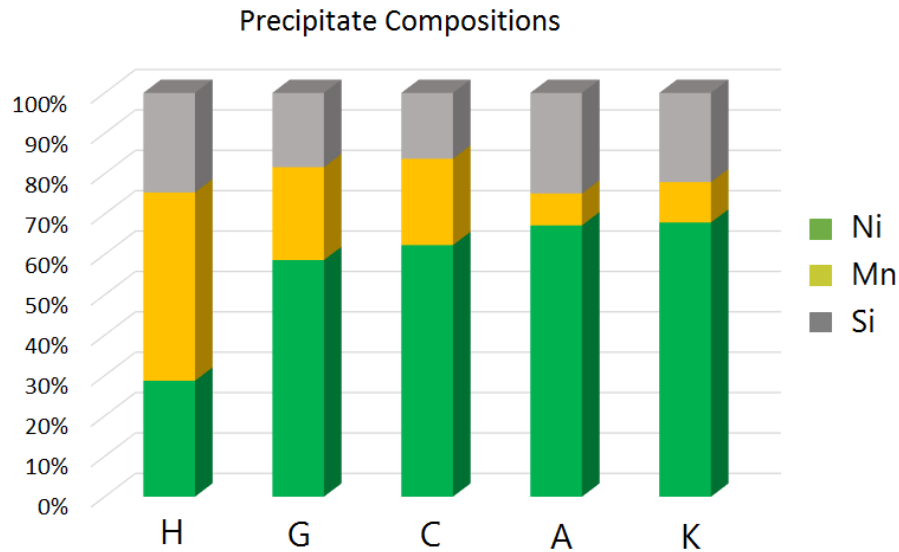


Figure 69: Plot illustrating precipitate compositions.

3.2.3 Iron Content in Precipitates

Iron content within MNPs and CRPs has been the subject of ongoing debate for over a decade. Much of this conflict derives from conflicting results between atom probe tomography and small angle neutron scattering (SANS) experiments. SANS experiments indicate that there exists little or no Fe within these precipitates. Conversely, APT results indicate high levels of Fe. This discrepancy is likely due to atom probe artefacts.

As discussed in Chapter 3, differences in field evaporation between the solute and matrix can cause preferential evaporation. Eventually this can cause protrusions (in the case of high-field precipitates) or divots (in the case of low-field precipitates). These surface imperfections are deviations from the assumed hemispherical cap and thus results in regions of erroneous atomic density in the reconstructed data. For high-field precipitates the ions are directed outward, away from their original positions. In low-field precipitates, ions are directed inward, thus increasing the perceived atom density of the precipitate. Fe requires an evaporation field of approximately 35 V/nm, while solute elements Ni, Mn, and Si have evaporation fields of approximately 35 V/nm, 30 V/nm, and 33 V/nm, respectively [70]. Therefore, MNPs are considered to be low-field precipitates, which can cause artificially increased amounts of Fe to be detected within the precipitates. It should be noted, however, that these values are calculated for pure metals (e.g. Fe atom evaporated from a pure Fe sample), and therefore not encountered experimentally.

The presence of these trajectory aberrations is confirmed via APT density maps containing MNPs. These regions are routinely 2-3 times more dense than the matrix. For example, the density of a precipitate from sample C was determined to be 50 atoms/nm³, while the matrix had an average density of 23 atoms/nm³ (Figure 70). As densities of this magnitude are simply not physical, atom probe trajectory aberrations are certainly present. In addition, Wells et. al. point out that the presence of Fe is at odds with thermodynamic considerations, which suggest MNPs are iron free [65, 110, 111].

The ion irradiation studies presented in this chapter are a part of a collaboration with UCSB, where they do not include Fe in their analyses. In order to remain consistent within this collaboration Fe is not included in the analyses of MNPs in this work.

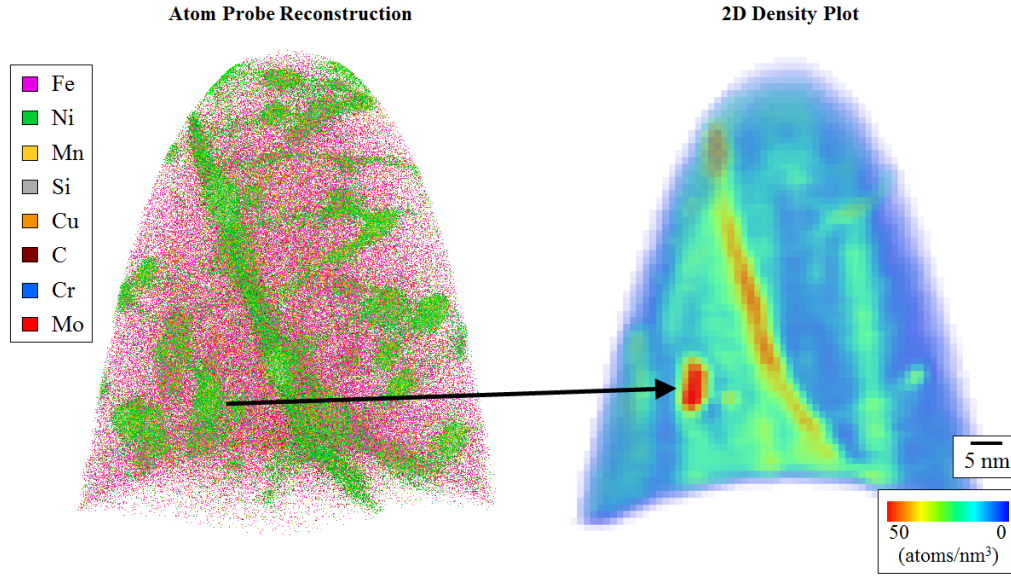


Figure 70: Atom probe reconstruction and 2D density slice are shown for sample C. The density of the highlighted precipitate was determined to be 50 atoms/nm³, while the matrix had an average density of 23 atoms/nm³.

3.3 Cluster Composition vs. Cluster Size

The cluster composition versus cluster size plots presented in Sections 1.1-1.5 provide valuable insight regarding the changes in cluster composition as clusters nucleate, grow, and coarsen. In the absence of any changes, the composition would be expected to fluctuate around an average composition. Additionally, greater fluctuations would be expected for smaller clusters as they have fewer counts. However, this was only observed for samples A and K.

For the other three samples (C, G, and H), the average composition was observed to change systematically with precipitate size. These samples were all high in Mn (2.0 at.%). It was observed that the smaller clusters contained larger amounts of Mn. Additionally, higher levels of Mn were often associated with lower levels of Si content within the clusters. This was particularly prominent in sample G (Figure 55). Clusters smaller than 100 atoms contained between 70-90% Mn, with the balance being Ni. As the precipitates grew in size an average composition ratio was reached: 18% Si, 22% Mn, and 60% Ni.

Cluster composition in samples low in Mn (K and A) did not follow this trend. Although cluster composition stabilized as the clusters grew in size, the average cluster composition did not significantly change. However, a larger sample of clusters would be needed in order to confirm this observation.

Lastly, cluster composition was observed to stabilize after cluster size became sufficiently large. This trend was most prominent in sample G (Figure 55). It should be noted that the stabilizing of cluster composition occurred at different sizes for the various samples.

3.4 Cluster Size Distribution

Despite low counting statistics, several trends were observed within the cluster size distributions of the five ion irradiated model RPV steels. Most notably, secondary modes were observed in each of the five cluster size distributions presented. These modes occurred at different cluster sizes for each of the steels, and ranged from 1,250 to 20,000 atoms.

This bimodal distribution is hypothesized to be a result of clusters dissolving due to bombardment during irradiation and subsequently reprecipitating to form new, smaller clusters. Thus, these new clusters are believed to produce the first peak in the cluster size distribution. This mechanism of radiation-induced dissolution of precipitates and subsequent reprecipitation has been previously suggested in the literature [112, 113, 114]. Experimentally, these bimodal cluster size distributions have been observed in several irradiation studies [113, 114, 115].

It is interesting to speculate that this may be connected to the observed differences in composition between the larger and smaller precipitates within the high Mn steels (C, G, and H). For these steels, the cluster composition versus cluster size plots exhibited a clear change in composition as cluster size increased. For each steel, this shift in composition was correlated with the beginning of the second peak within the cluster size distribution as shown in Table 27. It is hypothesized that these differences in cluster composition observed between the small and large precipitates are due to radiation-induced dissolution and the subsequent reprecipitation. As solute atoms are displaced from precipitates the matrix becomes supersaturated, thus providing a driving force for new precipitates to form.

Furthermore, it should be noted that the smaller precipitates in all three high Mn steels were characterized by a larger percentage of Mn. If these smaller precipitates are indeed newly formed precipitates, this observation could lend insight into the mechanism behind MNP nucleation. Specifically, increased proportions of Mn within the smaller precipitates could be interpreted as support for the mechanism put forth by Ngayam-Happy et al. discussed in Chapter 2. Ngayam-Happy et al. suggested Mn dumbbells form and cluster via diffusion [46]. These dumbbell clusters then act as sinks for additional Mn dumbbells as well as Ni solute atoms, eventually leading

to the formation of Mn- and Ni-rich precipitates.

Sample	Start of Second Mode (Cluster Size Distribution)	Peak of Second Mode (Cluster Size Distribution)	Composition Change (Cluster Composition vs. Size)
C	10,000	20,000	10,375
G	3,000	5,700	2,997
H	600	1,200	653

Table 27: Table illustrating the correlation between the shift in cluster composition and the beginning of the second mode within the cluster size distribution.

3.5 Volume Fraction

The precipitate volume fraction, calculated as solute atoms within precipitates over the total number of solute atoms, was determined to be statistically dependent on the interaction between Ni and Mn content present within the atom probe analysis. After regressing on bulk levels of Ni, Mn, Si, Cu, and their interactions, only the Ni/Mn interaction was statistically significant. Interactions occur when the effect of one variable is dependent on the level or value of another variable. The coefficients, error, t-values, and p-values are shown in Table 28.

	Coefficients	Error	t-value	p-value
Intercept	2.7	0.5	6.0	0.001
Ni:Mn	0.3	0.2	2.2	0.07

Table 28: Table showing results of precipitate volume fraction statistical analysis.

The statistical significance of the Ni/Mn interaction can lend insight into the mechanism behind MNP formation. A positive coefficient for the Ni/Mn interaction indicates that when the value Ni x Mn is increased by one unit, the volume fraction is expected to increase by 0.3. Numerous studies have suggested precipitate volume fraction is dependent on Mn [116, 117], an observation which is consistent with the interaction relationship determined above. In one study, Almirall et. al. observed that below a certain Mn content, precipitate volume fraction decreased considerably. This mechanism is referred to as Mn starvation [117].

4 Summary

MNPs were observed in all five of the low copper RPV steels analysed. These clusters precipitated at homogeneous nucleation sites within the matrix, as well as at heterogeneous nucleation sites, such as dislocations and grain boundaries.

Due to its very low Ni content, sample H was characterized by a very high number density and significantly smaller precipitates. These precipitates contained approximately twice as much Mn as precipitates found within other samples. Similar precipitate compositions were found between samples G and C as well as A and K; these pairs contained similar amounts of Mn within the bulk. Figure 69 shows the average precipitate composition for each of the steels, allowing easy comparison.

Precipitate composition within the high Mn samples (C, G, and H) was correlated with precipitate size. For all three of the samples, the smaller precipitates contained larger proportions of Mn, while the larger precipitates contained greater proportions of Ni and Si.

The cluster size distributions for each of the samples were characterized by a double peak. It is believed that the first peak within this bimodal distribution is due to the radiation-induced dissolution of precipitates and subsequent reprecipitation.

Lastly, by regressing precipitate volume fraction against the interaction of Ni and Mn, a linear relationship was determined to be statistically significant. This statistical analysis supports the Mn starvation mechanism.

Chapter VI

GEMA: A Novel APT Cluster Identification Algorithm

As the need to characterize clusters extends across many materials and users, a versatile and reliable cluster search algorithm is essential. Numerous algorithms have been developed to identify individual clusters within APT data including the maximum separation method [118], local concentration-based metrics [93], the core-linkage algorithm [88], and Voronoi partitioning [94]. Currently, the most prevalent approach used to detect clusters is the maximum separation method. This heuristic relies heavily upon four parameters, each manually chosen by the user: Dmax, the maximum distance separating two solute atoms within the same cluster; Nmin, the minimum number of atoms a cluster must contain to be considered a cluster; and L and E, which are metrics related to the incorporation of solvent atoms within clusters. Although there have been commendable efforts to provide guidelines for parameter selection and sensitivity analyses, the process still remains largely arbitrary and inconsistent [5-7].

This raises the fundamental issue of scientific objectivity. Experiments should be reproducible, and results should be independent of the researcher. The application of current APT data analysis algorithms requires selection of numerous user-defined parameters that unavoidably introduce subjective variation into the analysis. The outcome is a chronic lack of comparability between quantitative data obtained by different users. This represents a significant issue for APT-based research and becomes ever more apparent as the number of researchers in the field increases. Therefore, a more objective method for cluster analysis is essential.

In this chapter, a new cluster search algorithm, which uses a Gaussian mixture model (GMM) to probabilistically distinguish clusters from the matrix, has been developed. This unsupervised machine learning algorithm maximizes the data likelihood via

expectation-maximization (EM). Specifically, using APT data, the algorithm learns the position and size of each cluster. This new clustering algorithm is called the Gaussian mixture model Expectation Maximization Algorithm (GEMA). Arguably, the most important feature of GEMA is that it eliminates the need for external parameter selection while simultaneously improving power, thus providing a key step towards routine reproducibility of quantitative measurements.

k -means, one of the simplest machine learning algorithms used to cluster data, is first introduced to illustrate the key ideas underlying iterative clustering algorithms. Next the development of GEMA is described in detail, focusing on the interpretation of GMMs and how they are estimated using expectation maximization. The chapter is concluded by illustrating the successful application of GEMA to both simulated and real APT data, respectively showing that GEMA is often superior to the state-of-the-art and that GEMA provides useful cluster representations of real APT data. Overall, this novel approach provides a powerful, statistically principled, and immensely extensible baseline for cluster detection in APT.

1 A first approach: k -means

k -means is one of simplest and most common clustering algorithms utilized in statistics and machine learning [121]. After a random initialization of the cluster centers, k -means jointly learns cluster locations and assigns atoms to clusters by iterating two steps:

1. Given a set of initial cluster locations, each atom is assigned to the nearest cluster.
2. Given atom assignments to clusters, each cluster center (or cluster mean) is placed at the average location of all atoms assigned to that cluster (Figure 71).

The value of this approach is that it breaks down a complex problem, i.e. jointly determining cluster parameters and assigning atoms, into two simple sub-problems, which are iteratively solved. GEMA uses a similar iterative approach, as do, more generally, all EM algorithms.

However, there are several disadvantages to using k -means on APT data. Primarily, all atoms must belong to a cluster in k -means, and thus atom assignments to the matrix are not possible (Figure 72). Additionally, atoms must deterministically belong to a single cluster, ignoring matrix/cluster and cluster/cluster uncertainty. The uncertainty associated with precipitate interfaces, in particular, matrix/cluster interfaces, has real scientific significance, which should be

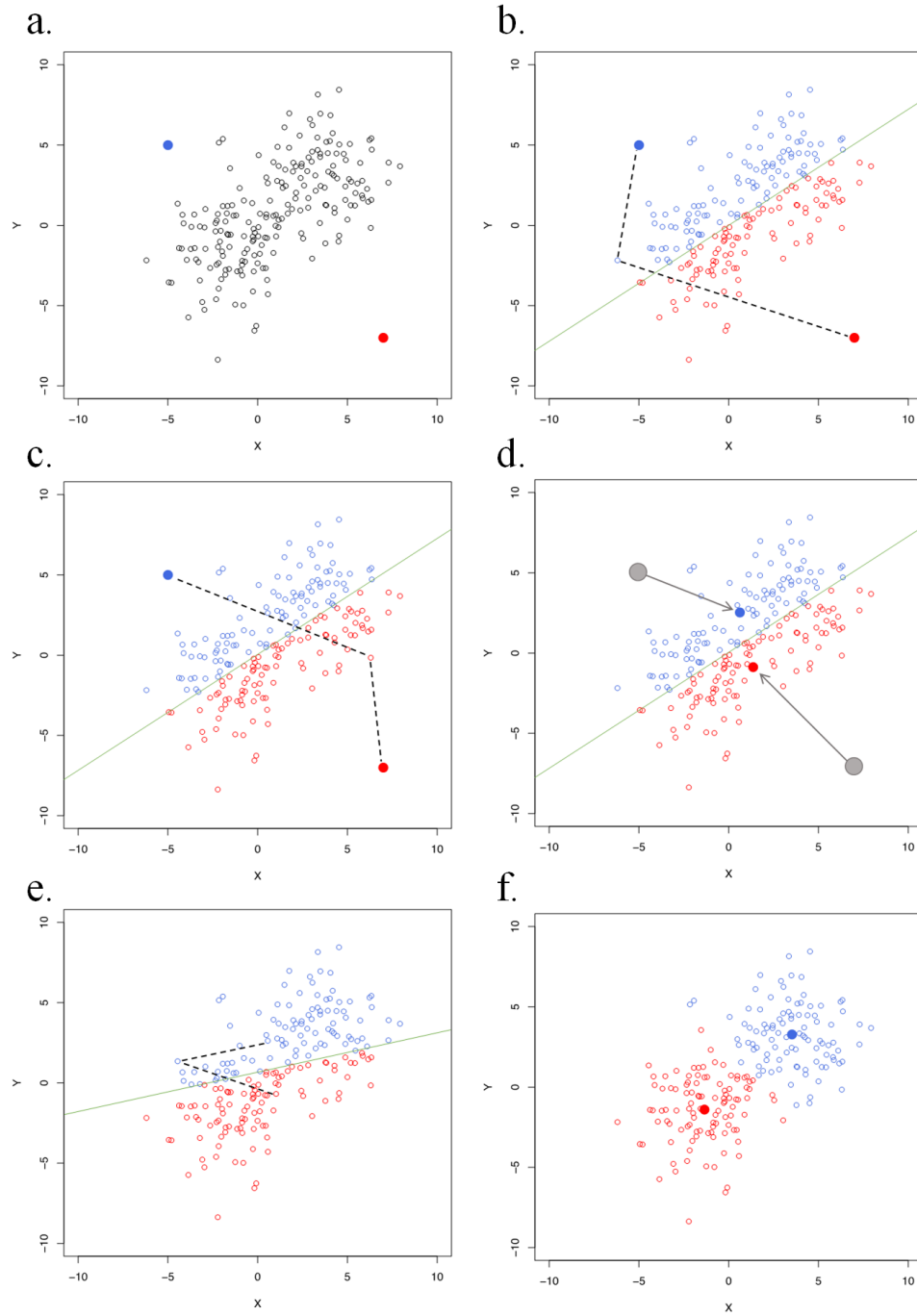


Figure 71: Illustration of how k-means assigns atoms to clusters. In (a) the two cluster mean locations are randomly initialized. (b) and (c) show how atoms are assigned to the nearest cluster mean (E-step). In panel (d), the cluster means are updated (M-step). The grey circles represent the original cluster means, while the arrows indicate the new, updated cluster means. In panels (e) and (f), respectively, the E-step and M-step are repeated until convergence.

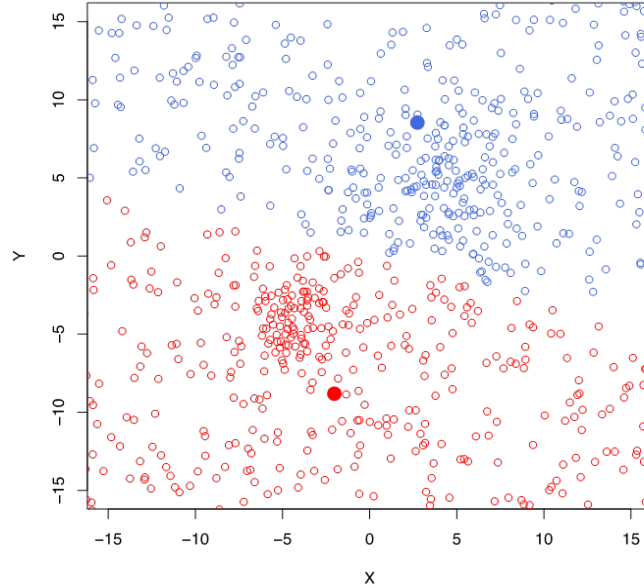


Figure 72: k-means’ implicit requirement that all atoms must belong to a cluster lead to its failure in modeling solute atoms within the matrix.

reflected in the modeling assumptions. Currently, all APT clustering algorithms share this undesirable property with *k*-means.

2 GEMA

2.1 Gaussian Mixture Models

GEMA utilizes a Gaussian mixture model [121] to probabilistically learn cluster locations and assign atoms to clusters and the matrix. As its name suggests, a Gaussian mixture model is a distribution defined by a weighted sum, or mixture, of Gaussians:

$$p(X) = \sum_{k=1}^K w_k N(X|\mu_k, \sigma_k^2) \quad (14)$$

where K is the number of Gaussian components and w_k , μ_k , and σ_k^2 are the weight, mean, and variance of the k -th Gaussian component, respectively. Weight, in the context of mixture models, refers to the summed probability of each solute atom belonging to a particular Gaussian, k . The mean is the expectation of each Gaussian component, k , while the variance describes the spread of the Gaussian. The goal of GEMA is to find a set of parameters, w_k , μ_k , and σ_k^2 for each k , such

that this analytic distribution optimally matches the empirical distribution.

In the current stage of development, GEMA assumes that the covariance matrix is spherical, or a multiple of the identity matrix. This is equivalent to the assumption that all clusters are spherical.

2.2 Expectation-Maximization

An expectation-maximization (EM) algorithm [121] was implemented to determine the most likely GMM for the given APT data. Similar to k -means, GEMA's EM algorithm alternates between an expectation (E) step and maximization (M) step until convergence.

First, the Gaussian parameters μ_k , σ_k , and w_k for each k are initialized. This is non-trivial and described in Section 2.3. Next, each atom, n , is assigned a probability for being in each cluster, $p(k|x_n)$, based on its location, x_n . This is referred to as the E-step and can be described mathematically by the equation:

$$p(k|n) = \frac{w_k g(x_n; \mu_k, \sigma_k)}{\sum_{k=1}^K w_k g(x_n; \mu_k, \sigma_k)} \quad (15)$$

where $g(x_n; \mu_k, \sigma_k)$ is a D -dimensional Gaussian function. In this equation the numerator is essentially a weighted probability of finding an atom, n , in cluster, k . The denominator normalizes this probability across all clusters.

The Gaussian parameters are then optimized given the newly updated atomic probabilities of being in each cluster. This step, which maximizes the parameter likelihood, is called the M-step:

$$\mu_k = \frac{\sum_{n=1}^N p(k|n) x_n}{\sum_{n=1}^N p(k|n)} \quad (16)$$

$$\sigma_k = \sqrt{\frac{1}{D} \frac{\sum_{n=1}^N p(k|n) \|x_n - \mu_k\|^2}{\sum_{n=1}^N p(k|n)}} \quad (17)$$

$$w_k = \frac{1}{N} \sum_{n=1}^N p(k|n) \quad (18)$$

where N is the total number of atoms and D is the Gaussian dimension. Equations 3 and 4 determine the mean and standard deviation of cluster k , respectively. The contribution of each atom to these values are weighted by the probability of that atom being in the cluster, which was

calculated in the previous E-step. Similar to Equation 2, the denominators of Equations 3 and 4 perform normalizations. Equation 5 computes the weight of a given cluster, k . This is calculated by taking the probability of an atom belonging to cluster k , summing over all atoms, and dividing by the total number of atoms, N .

The E-step and M-step are repeated until convergence⁸, resulting in an estimate of μ_k , σ_k , and w_k for each cluster, k .

An illustration of an expectation-maximization algorithm being utilized to determine the best GMM to fit 2D data is shown in Figure 73. In the first panel, (a), the data points are shown in green and the two randomly initialized Gaussians are shown in blue and red. The atoms are probabilistically assigned to the two clusters as shown in panel (b). Atoms are colored based on their probability of belonging to each cluster. Atoms that are equally likely to belong to either the blue and red cluster have been colored purple. This is referred to as the E-step. In panel (c), the Gaussian/cluster parameters (mean, weight, and variance) are updated (M-step) based on the cluster assignments from the previous step. In panels (d), (e), and (f) the E- and M-steps are repeated until convergence. A similar process is executed in GEMA, except for a few key differences: GEMA fits an additional background cluster; GEMA assumes the clusters are spherical; and GEMA’s initialization utilizes a kernel density estimate, which is described in the next section.

In summary, the solute clusters within the APT data are modelled using 3D Gaussian distributions, one for each cluster. GEMA learns the parameters of these Gaussians/clusters and which atoms belong to each one via an iterative process. In each iteration GEMA slightly improves its estimate as to which atoms belong to each Gaussian/cluster and the parameters of each Gaussian/cluster. These parameters include the location of the cluster (μ_k), the width of the cluster (σ_k), and the density of the cluster (w_k).

2.3 Initialization using Kernel Density Estimates

EM is highly sensitive to the initialization of the Gaussian parameters μ_k , σ_k , and w_k , for each cluster k . Local maxima, specifically in this case random solute density fluctuations within the matrix, often prevent the algorithm from finding the global maximum, as convergence can occur at any local maximum. However, this problem can be solved with careful initialization.

Although initialization sensitivity is a thoroughly studied problem for general mixture models,

⁸EM is guaranteed to converge to a local maximum of the likelihood.

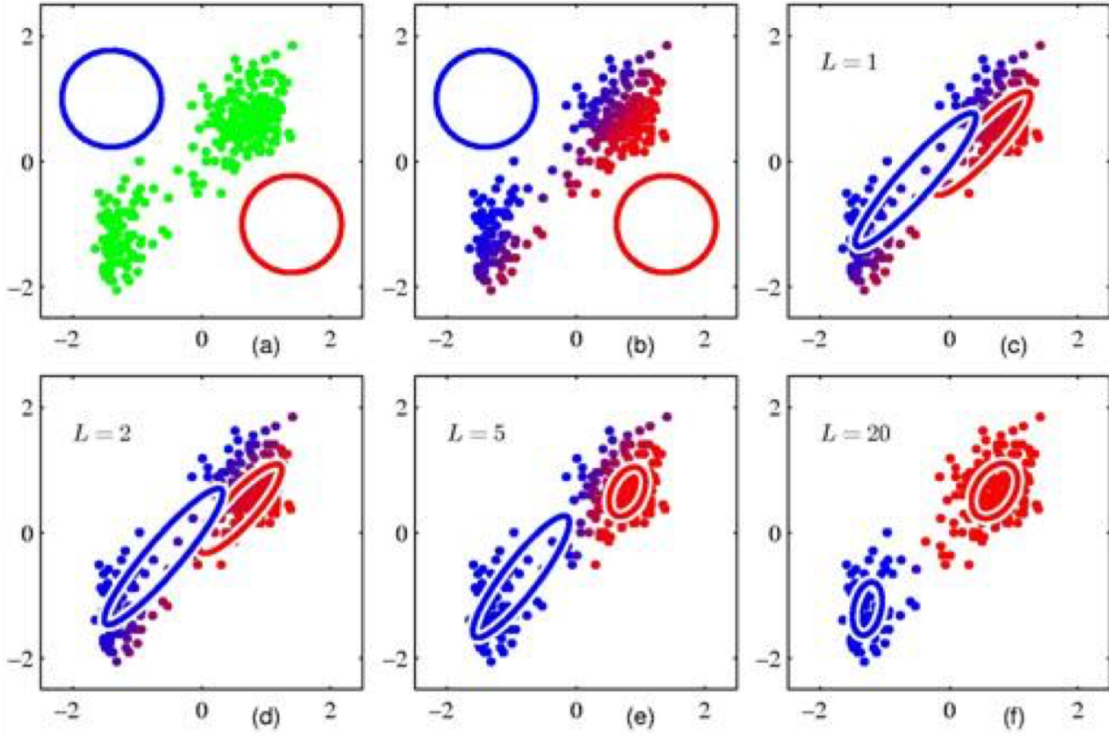


Figure 73: Illustration of an expectation-maximization algorithm being utilized to determine the best GMM to fit 2D data. In (a) two Gaussian means are randomly initialized. The atoms are then assigned to the nearest cluster mean (b). This is referred to as the E-step. In panel (c), the cluster means are updated (M-step). In panels (d), (e), and (f) the E- and M-steps are repeated until convergence. [121]

typical initializations, such as k -means or repeated random restarts, were not viable for APT data. This is due to solute density fluctuations within the matrix. As a result, initializations get stuck in these local maxima, which is not a problem for typically encountered datasets. Therefore a novel initialization approach was developed and specifically adapted to the peculiarities of APT data.

First, a kernel density estimate (KDE) [121] was fit to the empirical solute distribution. KDEs are smoothed estimates of density, i.e. atoms from high solute density regions, notably from clusters, have high KDE values. An example for 1D data is shown in Figure 74. In Figure 74, each of the blue lines along the x-axis represent atoms and the black line is the KDE. It should be noted that regions of higher atomic density correspond to larger KDE values.

The location of the cluster centers within GEMA were initialized using a KDE. In particular, the solute atom with the highest KDE value was identified and defined as the first initialization point. Using this point to initialize the cluster center, GEMA was run with K set equal to 1.

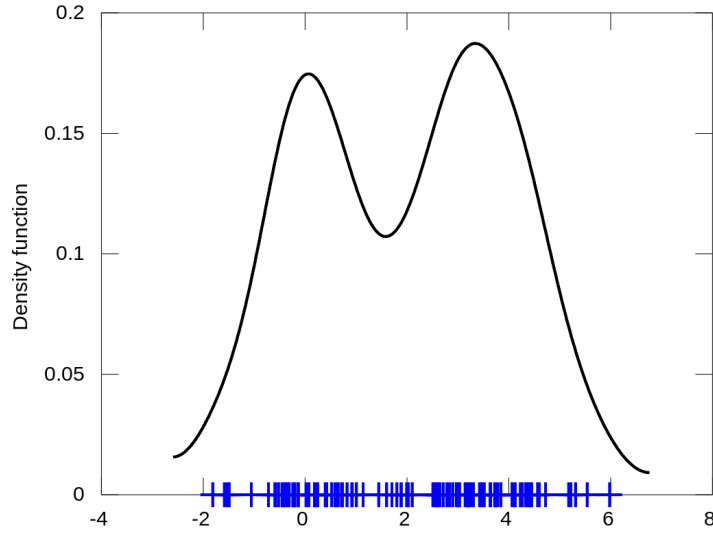


Figure 74: A diagram illustrating a kernel density estimate of 1D data. The blue lines along the x-axis represent atoms and the black line represents the KDE. It should be noted that regions of higher atomic density correspond to larger KDE values. [122].

GEMA's output was then used to produce a parametric estimate of atomic density, which was subsequently compared to the non-parametric density estimate given by the initial KDE. Successive initialization points were determined by subtracting the parametric density from the KDE and choosing the highest point, or, in other words, the point on the KDE which was not yet described by the model. This was done to ensure multiple initialization points did not come from the same cluster. This process was repeated until a specified number of initialization points were identified, and then stopped.

In other words, clusters were added one-by-one to the model in order to avoid fitting a single cluster with two Gaussians. As each cluster was modeled with a Gaussian distribution, the model was subtracted from the data, leaving the residuals from that cluster fit, as well as the remaining clusters. This new dataset was then fit with an additional Gaussian, and the process was repeated until all the clusters were identified.

The number of initialization points, or number of clusters, can be chosen via numerous model selection tools. One standard approach is to minimize the Bayesian information criterion (BIC) [121]. BIC is a model selection tool in statistics based on a compromise between the likelihood function and parsimony. The BIC is formally defined as:

$$\text{BIC} = -2\ln\hat{L} + k\ln(N), \quad (19)$$

where $\hat{L}$ is the maximum of the likelihood function, k is the number of parameters being estimated, and N is the number of data points, in this case solute atoms. GEMA uses the BIC to automatically and objectively determine the optimal number of clusters (Figure 75).

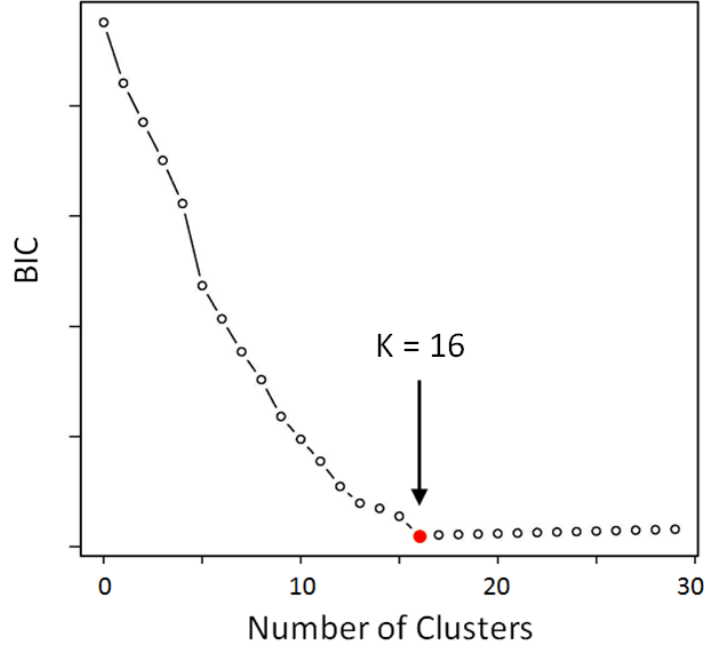


Figure 75: The number of clusters is determined by minimizing the BIC. The selected number of clusters (K) is highlighted red. Specifically, this BIC plot corresponds to the simulation in Figure 78.

In summary, GEMA is run for a range of K , or number of clusters. The BIC is utilized to determine which K is optimal. Naturally, a GMM will improve as additional Gaussians are added to the model, even after all of the clusters are accounted for. For example, if there are 16 clusters within a dataset, and K is set equal to 20, the remaining 4 Gaussians will end up fitting solute fluctuations within the matrix. The BIC determines the optimal number of clusters by taking into account how much of the data is explained by the model as well as penalizing larger K s.

3 Application of GEMA

3.1 2D Simulated Data

In this section, the capabilities of GEMA are visualized by considering several 2D simulated datasets. In Figure 76, GEMA has been applied to a 2D APT-like simulation containing two clusters, which are easily recovered. Atoms identified as belonging to the matrix are drawn as hollow points, while the atoms belonging to the clusters are color coded. The shading indicates the likelihood of an atom belonging to the cluster, with lighter shades indicating a lower probability.

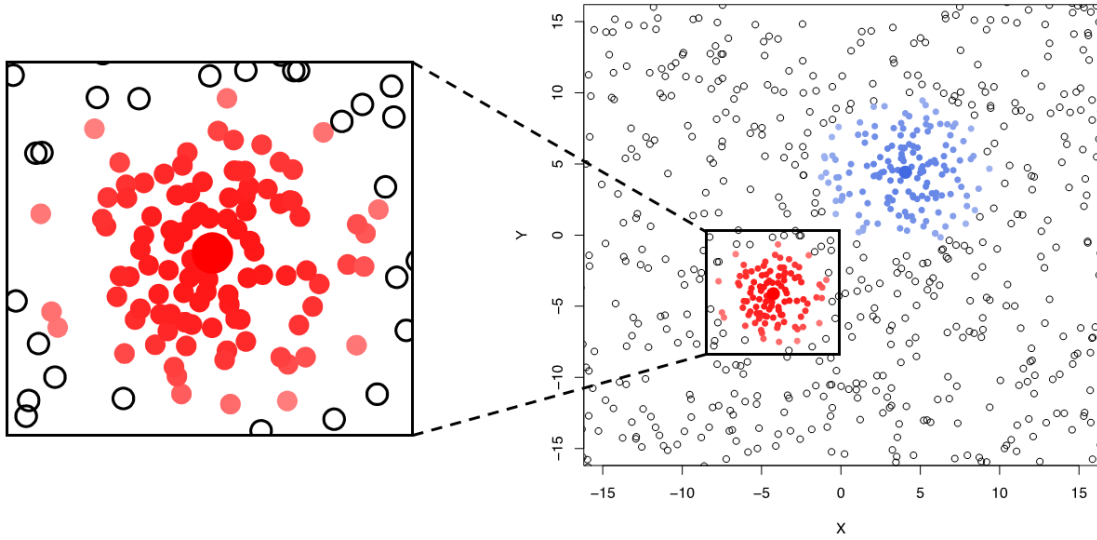


Figure 76: 2D atom probe simulation containing two solute clusters. Matrix and clustered atoms are indicated by hollow and solid dots, respectively. Shading indicates the probability that an atom is associated with a specific cluster.

Figure 77 illustrates GEMA's ability to recover a true cluster model given a noisy 2D simulated dataset. Each panel in Figure 77 represents a kernel density estimate with height indicating solute density at each point in 2D space. The true model, unknown to GEMA, is characterized by a uniform background with added Gaussian modes (left panel). Atoms are drawn from this true model distribution to produce a simulated two-dimensional APT-like dataset (center). GEMA is applied to the generated APT-like data, almost perfectly recovering the true cluster model (right).

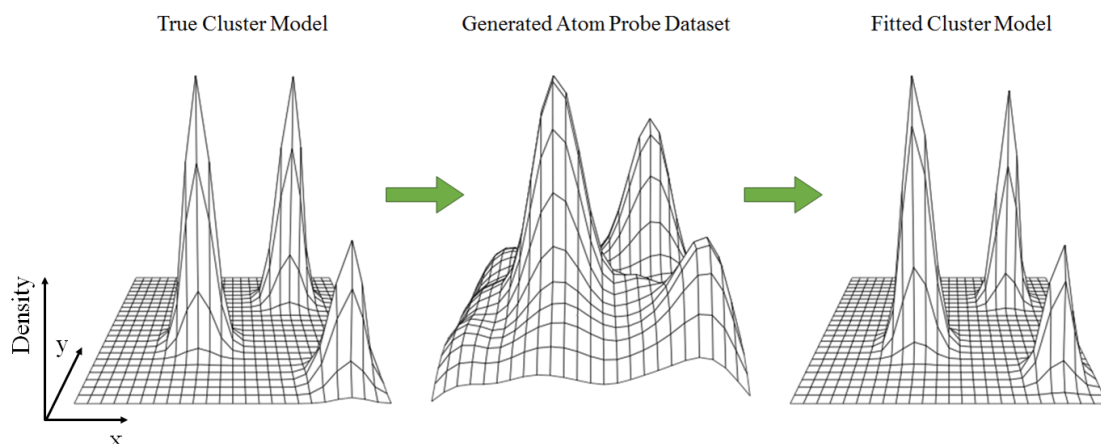


Figure 77: The true cluster model (left) was used to randomly generate a 2D atom probe dataset (center) containing three distinct clusters (these three clusters correspond to the three peaks seen in each panel). The fitted cluster model (right) shows the GEMA reconstruction. Each panel is shown as a kernel density estimate with height representing solute density.

3.2 3D Simulated Data

3.2.1 GEMA vs. Maximum Separation Method

Several simulations were used in order to test the accuracy of GEMA and compare its performance to the maximum separation method. The clustering performance of GEMA and the maximum separation method were quantitatively compared with receiver operating characteristic (ROC) curves. ROCs plot the power, or true positive rate, against the false positive rate to illustrate the trade-off between sensitivity and specificity presented by a method. The true positive rate is defined as the fraction of atoms correctly assigned to a cluster, while the false positive rate is defined as the fraction of atoms erroneously assigned to a cluster. Methods with a higher power are deemed to outperform those with a lower power for a given percentage of false positives. As the choice of false positive level is subjective, a method is only considered superior if it has higher sensitivity for all levels of specificity. Simply stated, curves located near the upper left hand corner of the plot are desirable as this indicates a high level of power with very few false positives.

The model estimates the probability of each atom belonging to a cluster, which is then thresholded at some level τ . If an atom has less than τ probability of being in a cluster, it is deemed to be in the matrix. This is the standard approach for ROCs. The maximum separation method, however, deterministically assigns atoms to clusters or the matrix; in other words, the choice of $D_{\max}$ implicitly defines τ .

For GEMA, the ROC curves are created by smoothly varying the threshold τ from 0 to 1. For the maximum separation method, Dmax is varied, thus enabling an unbiased comparison between GEMA and the maximum separation method without the author subjectively choosing Dmax. Thus, for the maximum separation method, each point on the ROC curve represents a different Dmax. The remaining three parameters for the maximum separation method were chosen in a consistent, standard manner: Nmin was set equal to the point at which the random cluster size distribution dropped to zero; L and E were set equal to Dmax. The red line connects points of adjacent Dmax values in order to illustrate how changes in Dmax can have a drastic effect on power.

The first simulation, previously detailed and utilized in [123], was characterized by a face-centered cubic structure in which sixteen precipitates were distributed uniformly at random. To model imperfect detection efficiency of a reflectron fitted LEAP 3000, 63% of the atoms were stochastically removed. Additionally, Gaussian noise was added to all atomic positions offsetting them from the lattice to reflect the imperfect spatial resolution of APT.

GEMA was applied to the simulated dataset and accurately identified each of the sixteen clusters (Figure 78). GEMA achieved a power, or percent of true positives, of 99.99% given a false positive rate of approximately 6%.

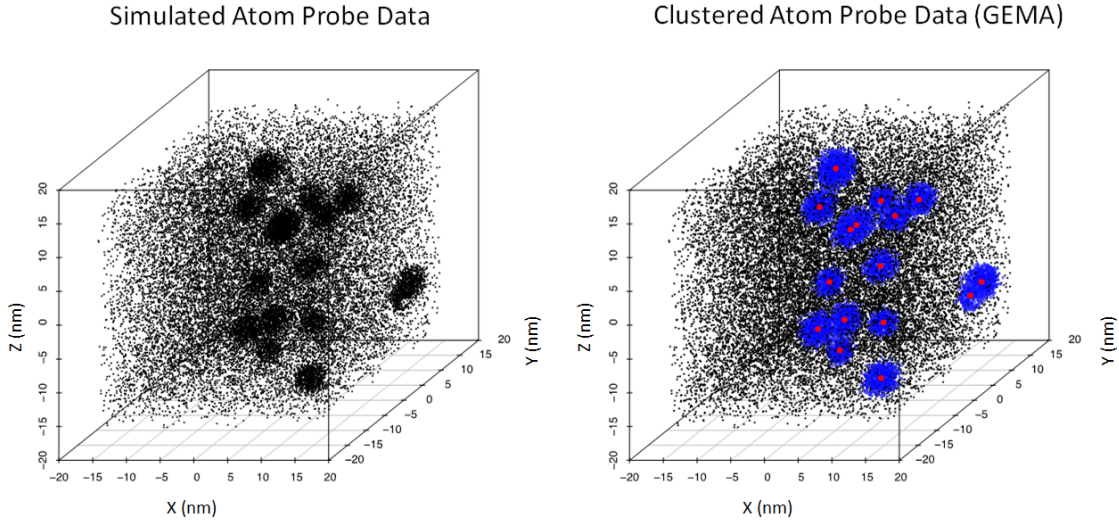


Figure 78: A simulated dataset (left) was used to test the accuracy of GEMA. The clustered dataset (right) highlights the clusters (blue) identified by GEMA. The learned cluster centers are shown in red.

Due to the relatively simplistic nature of the precipitates in this simulation, both GEMA and the maximum separation method performed near-perfectly. The power of each method was

comparable, with GEMA outperforming the maximum separation method by 0.2% at a 6% false positive rate. However, the clusters in Figure 78 all have similar cluster weights and widths. Both of these properties, which are generally not realistic when dealing with actual APT data, favor the maximum separation method, which implicitly anticipates homogeneity between clusters. Typically the same set of parameters are used to identify all clusters within a given dataset.

In order to investigate the full capabilities of GEMA, two additional simulations were created: the first varied the weight (w) of each cluster (Figure 79) and the second contains relatively small clusters with an average variance of approximately 3 nm (Figure 80). For these

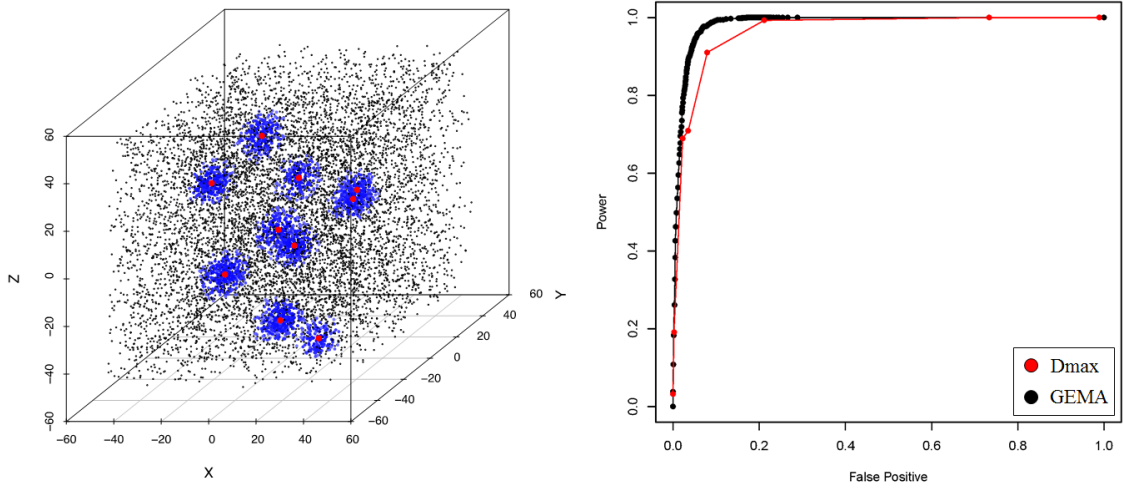


Figure 79: The application of GEMA to a simulation containing clusters varied in weight. GEMA probabilistically assigned atoms to clusters (blue) and the matrix (black). The learned cluster centers are shown in red. On the right, the ROC plot for this simulation is shown. GEMA results are plotted for systematically varied levels of τ (black). The maximum separation method results are plotted for systematically varied $D_{\max}$ (red).

more complex precipitate distributions GEMA outperformed the maximum separation method by 18% and 66%, respectively, at a fixed false positive rate of approximately 3%.

It should be noted that in the third simulation, the ROC plot for the maximum separation method jumps sporadically as $D_{\max}$ is varied. This illustrates that slight changes in $D_{\max}$ can have drastic effects on the power when using the maximum separation method. This undesirable property is a product of having very sensitive parameters.

A fourth simulation was created in which cluster size was varied. In this simulation half of the clusters were only approximately 25% denser than the matrix. GEMA's success in identifying these clusters shows promise in its ability to identify clusters within high solute concentration alloys.

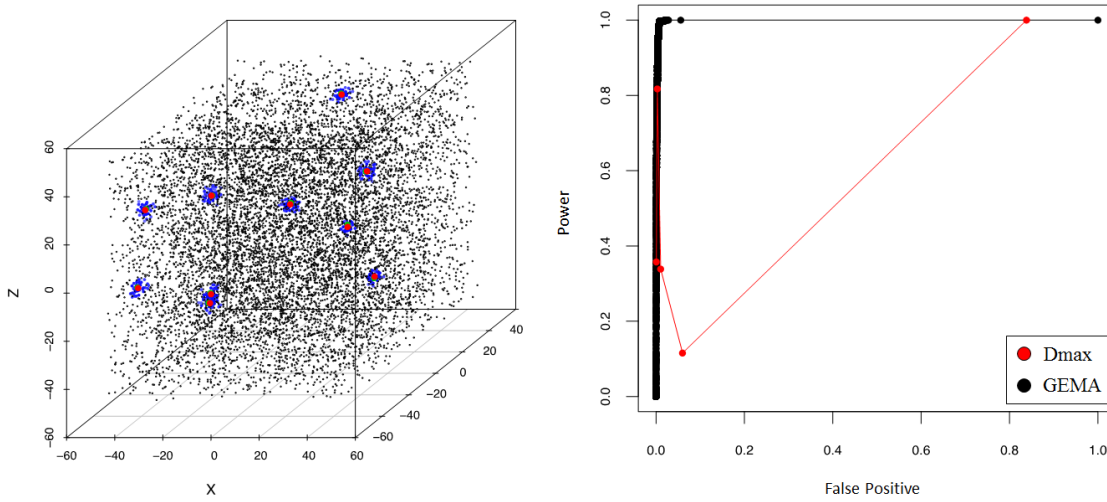


Figure 80: GEMA was run on the third simulation, which contained clusters with an average variance of approximately 3 nm. GEMA probabilistically assigned atoms to clusters (blue) and the matrix (black). The learned cluster centers are shown in red. On the right, the ROC plot for this simulation is shown. Again, GEMA is shown in black and the maximum separation method is shown in red.

The results are presented in Figure 81.

In order visually compare GEMA and the maximum separation method, each algorithm was applied to the fourth simulation (Figures 81 and 82, respectively). GEMA accurately identified all ten of the clusters, including the larger, less dense clusters. However, despite choosing Dmax such that the power to false positive rate ratio was maximized, the maximum separation method failed to identify all of the clusters. Furthermore, some of the clusters identified by the maximum separation method were incorrectly split into two separate clusters as indicated by the yellow circle in Figure 82.

3.3 Application of GEMA to Actual Atom Probe Data

Next GEMA was used to characterize clustering in the APT reconstruction of a model reactor pressure vessel (RPV) steel, provided by Rolls-Royce Plc. Needle-shaped specimens of the steel were created from matchsticks via a standard two-stage electropolishing process [70]. The samples were then analysed via APT on a LEAP 3000X HR. The sample was run at 50K with a pulse fraction of 20%. The data reconstruction was performed using IVAS 3.6.8. For additional details pertaining to the material or methodology please refer to Chapter 3.

Due to imperfect detector efficiency, it is impossible to quantitatively determine the success

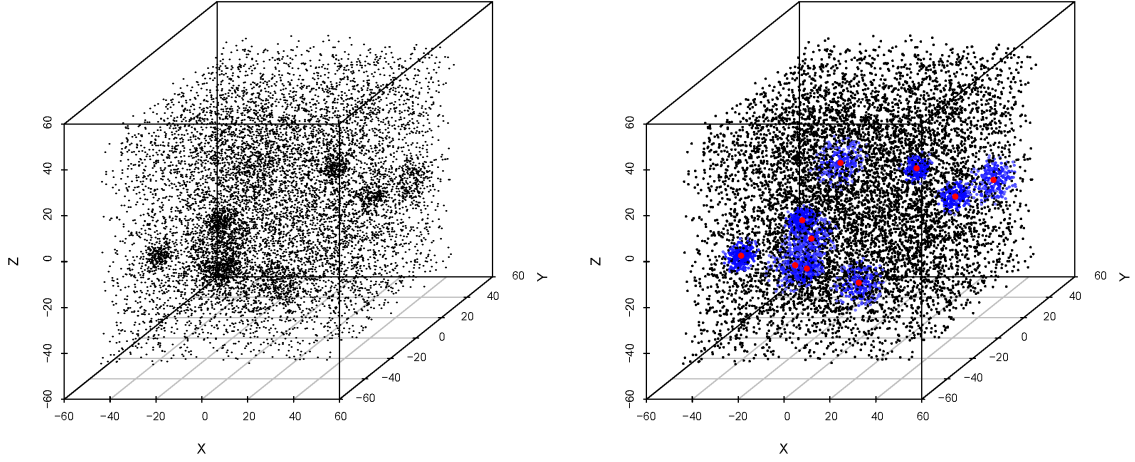


Figure 81: GEMA applied to simulation in which cluster size was varied. GEMA probabilistically assigns atoms to clusters (blue) and the matrix (black). The learned cluster centers are shown in red.

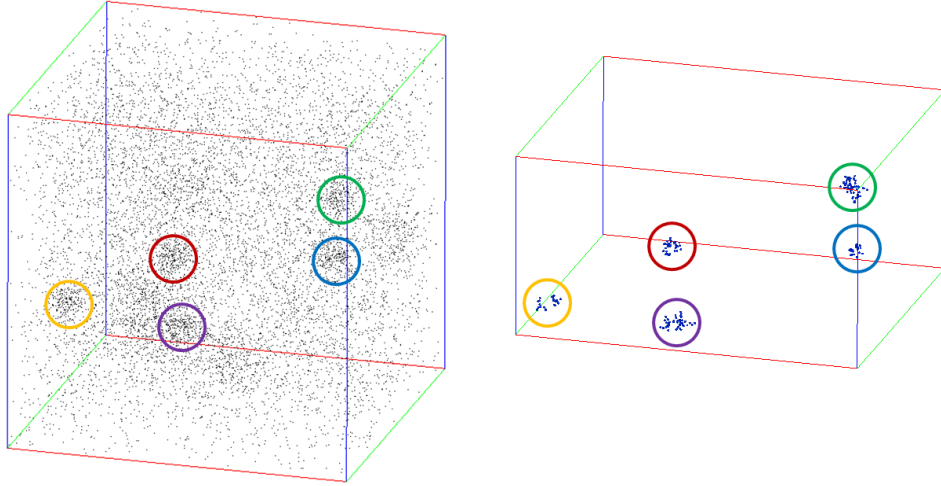


Figure 82: Maximum separation method results for the simulation in which cluster size was varied. Dmax was chosen to maximize power to false positive rate. It should be noted that the five larger, less dense clusters are not identified (left). Extracted clusters are highlighted by colored circles within the raw data (right)

of GEMA when applied to real APT datasets. However, by visual inspection, GEMA appears to successfully identify each of the clusters as presented in Figure 83.

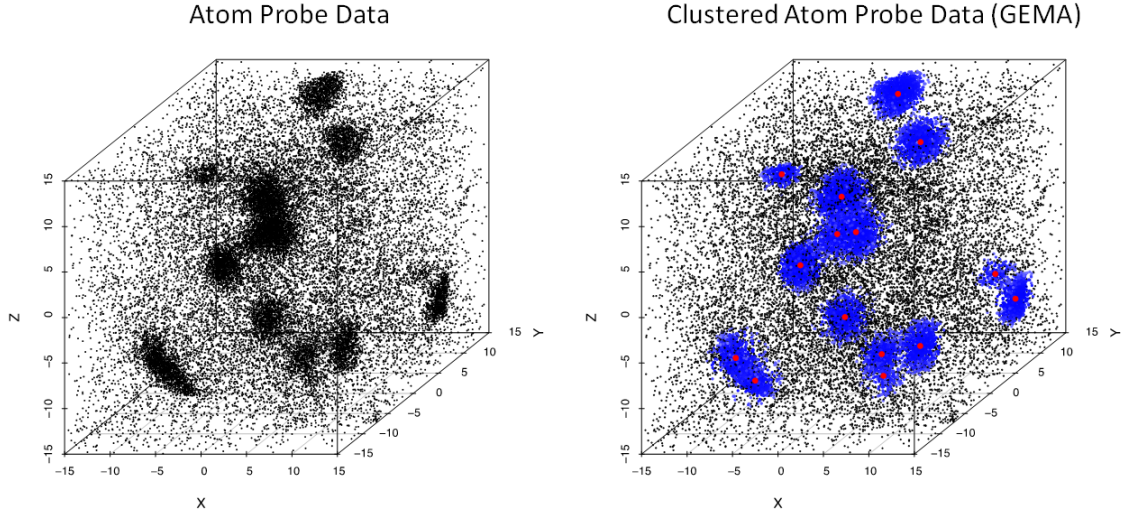


Figure 83: GEMA applied to actual APT data (left), giving the clustered output shown (right). GEMA probabilistically assigns atoms to clusters (blue) and the matrix (black). The learned cluster centers are shown in red.

4 Discussion

GEMA has several key advantages over the maximum separation method. GEMA probabilistically assigns atoms to clusters and the matrix, eliminating hard cluster assignments. This is advantageous when considering atoms located at precipitate/matrix interfaces as it reflects genuine uncertainty regarding their classification. By contrast, the maximum separation method simply provides an “in” or “out” verdict. Another key advantage of GEMA is that it does not require user input; all parameters are learned by the algorithm itself, thus eliminating the problem of reproducibility between users.

Accurately identifying and extracting clusters within atom probe datasets is critical to the field of APT. In order for the field to continue to grow as a reliable technique within the greater scientific community, cluster analysis results cannot vary from user to user. An approach that produces reliable and reproducible results is essential. GEMA can provide this reliability and reproducibility.

Additionally, the generality of GEMA enables the algorithm to be applied to a wide range of APT datasets without requiring user input. This is illustrated in the first simulation (Figure 78) where the maximum separation method performs very well for simple, homogeneous clusters, but then fails to accurately model more complex simulations (Figures 80 and 82). Conversely, GEMA

has excelled in all studied simulations.

Lastly, the modular nature of this approach facilitates modifications to the model. Potential extensions of GEMA are detailed in the Chapter 8.

5 Summary

In this chapter, a new clustering algorithm, GEMA, was presented, which utilizes a Gaussian mixture model to probabilistically distinguish clusters from random fluctuations in the matrix. This machine learning approach maximizes the data likelihood via expectation-maximization: given atomic positions, the algorithm learns the position, size, and width of each cluster. A key advantage of GEMA is that atoms are probabilistically assigned to clusters, thus reflecting scientifically meaningful uncertainty regarding atoms located near precipitate/matrix interfaces. It was demonstrated that GEMA can outperform the maximum separation method in cluster detection accuracy when applied to realistically simulated data. Lastly, GEMA was successfully applied to real APT data.

Chapter VII

Conclusions

This thesis was part of an ongoing collaboration with Rolls-Royce. In this work, the microstructure and mechanical properties of low copper, model RPV steels were analyzed after 11,690 hours of thermal aging. This was accomplished through the parallel use of hardness measurements and atom probe tomography. The goal of this research was to determine if MNPs form under thermal aging conditions in low copper RPV steels. By systematically varying the amount of Ni and Mn in the model RPV steels analyzed, this research aimed to determine the specific roles of these solutes in cluster formation. Subsequently, an identical set of model RPV steels were analyzed after ion irradiation. The goal of this work was to determine the effects of bulk Ni and Mn content on the composition, size, and volume fraction of MNPs. The main conclusions of this thesis are summarized below:

Decrease in Hardness in Thermally Aged, Low Copper RPV Steels

A statistically significant decrease in hardness was observed in the low copper model RPV steels after 11,690 hours of thermal aging. A multiple linear regression indicated that this decrease in hardness was due to the variable ‘time.’ After removing the effects of steel type and temperature, hardness was expected to decrease by approximately 11 Hv after 11,690 hours of thermal ageing. Additionally, predictor variables such as ‘temperature’ were determined not to be statistically significant.

Non-random Solute Distribution in As-received and Thermally Aged, Low Copper RPV Steels

The association of solute elements within the matrix of as-received and thermally aged, low copper model RPV steels was determined via the local chemistry method. A summary of the

results is shown in Table 29. Statistically significant solute association was found in both the as-received and thermally aged RPV steels. This result indicated that the solute within the as-received model RPV steels was not randomly distributed. It was hypothesized that the observed solute association within the as-received RPV steels was due to solute movement during cooling after tempering. The finite time over which quenching occurs allows solute to diffuse within the material, and thus the probable cause of the observed, statistically significant cluster association.

Ultimately, no trends were observed regarding changes in solute association between the as-received and thermally aged material. This null result exhibits the ability of new generation, low copper RPV steels to withstand the effects of long-term thermal aging.

Sample	Heat Treatment	Ni (at.%)	Mn (at.%)	Solute Association
C	As-received	3.3	2.0	Si-Ni, Ni-Si, Ni-Ni, Ni-Mn, Mn-Ni, Mn-Mn
	Thermally Aged	3.3	2.0	Ni-Ni, Mn-Mn
G	As-received	1.6	2.0	Si-Ni, Cu-Cu, Cu-Mn, Ni-Ni, Mn-Ni, Ni-Mn, Mn-Mn, Mo-Ni
	Thermally Aged	1.6	2.0	Ni-Si, Si-Ni, Ni-Ni, Mn-Ni, Ni-Mn, Mn-Mn, Cr-Cr
H	As-received	0.2	2.0	None
	Thermally Aged	0.2	2.0	Cu-Ni, Si-Mn, Mn-Mn
K	As-received	3.3	0.25	Ni-Si, Si-Ni, Ni-Ni
	Thermally Aged	3.3	0.25	Si-Ni, Cu-Ni, Ni-Ni
A	As-received	1.6	0.25	Ni-Ni
	Thermally Aged	1.6	0.25	Ni-Ni

Table 29: Summary of local chemistry method results. Statistically significant association is listed for each sample in both the as-received state and after thermal aging.

Clustering at Grain Boundaries and Carbide Interfaces within Low Copper, Thermally Aged RPV Steels

Solute clusters were observed at several heterogeneous nucleations sites within the thermally aged model RPV steels. Five clusters, rich in Mn, were observed within sample K at various carbide/matrix interfaces. Additionally, six clusters, high in Ni, were observed at the low-angle grain boundary within thermally aged sample C. All eleven clusters were characterized by low levels of Si (less than 5.5 at.%). Although the formation of precipitates at grain boundaries does not contribute to hardening embrittlement (the focus of this work), it is of great interest to the RPV

community. The presence of clusters, rich in Mn and Ni, at heterogeneous nucleation sites provides support to the hypothesis that MNPs are simply radiation enhanced, not radiation induced. However, as stated previously, analysis at longer aging times is essential in order to determine if these clusters develop into MNPs.

Secondary Precipitates within Cementite of Thermally Aged RPV Steels

Previously unobserved manganese-, nickel-, and silicon-rich precipitates (MNPs) were observed in the cementite phase of a thermally aged, low copper model RPV steel. Additionally, copper-rich precipitates (CRPs) were observed in a thermally aged, high copper RPV steel. APT was utilized to characterize these precipitates and obtain detailed chemical information. The secondary precipitates observed in the high copper steel were rich in Cu, Ni, Mn, and Si, while those in the low copper steel were rich in Ni and Si. It was hypothesized that the precipitates were depleted in Mn due to their location within cementite, as Mn is a strong carbide former.

Although the effects of solute clustering within cementite was already implicitly included in estimates of RPV lifetime, this was the first time they were explicitly recognized. The observation and characterization of these secondary precipitates has thus improved the community's understanding of where solute precipitates and consequently how thermal ageing can affect the available solute that is responsible for embrittlement.

MNP Composition in Low Copper, Ion Irradiated RPV Steels

MNPs were observed at homogeneous and heterogeneous nucleation sites within the low copper, ion irradiated RPV steels. Although only five steels were analyzed, several trends were observed. First, the bulk Mn content was positively correlated to the amount of Mn found within the precipitates. Similarly, bulk Mn content was negatively correlated with Si content. Low Ni content within the bulk was correlated with a higher number density of smaller precipitates. These precipitates were found to be high in Mn content. Lastly, MNPs within steels with greater than 1.6 at.% bulk Ni, contained similar proportions of Ni.

Additionally, for samples high in Mn (2.0 at.%), the average composition was observed to change systematically with precipitate size. Smaller clusters contained larger proportions of Mn, while larger clusters contained greater proportions of Si and Ni.

MNP Size Distribution in Low Copper, Ion Irradiated RPV Steels

Despite low counting statistics, several trends were observed within the cluster size distributions of the five ion irradiated model RPV steels. Most notably, secondary modes were observed in each of the five cluster size distributions presented. These modes occurred at different cluster sizes for each of the steels, and ranged from 1,250 to 20,000 atoms.

This bimodal distribution is hypothesized to be a result of clusters dissolving due to bombardment during irradiation and subsequently reprecipitating to form new, smaller clusters. Thus, these new clusters are believed to produce the first peak in the cluster size distribution.

MNP Volume Fraction in Low Copper, Ion Irradiated RPV Steels

The precipitate volume fraction, calculated as solute atoms within precipitates over the total number of solute atoms, was determined to be statistically dependent on the interaction between Ni and Mn content present within the atom probe analysis. After regressing on bulk levels of Ni, Mn, Si, Cu, and their interactions, only the Ni/Mn interaction was found to be statistically significant. Interactions occur when the effect of one variable is dependent on the level or value of another variable. A positive coefficient for the Ni/Mn interaction indicates that when the value Ni x Mn is increased by one unit, the volume fraction is expected to increase by 0.3.

GEMA: A New Clustering Algorithm

GEMA, a new cluster search algorithm, which uses a Gaussian mixture model to probabilistically distinguish clusters from the matrix, was developed. This unsupervised machine learning algorithm maximizes the data likelihood via expectation-maximization (EM). Specifically, using APT data, the algorithm learns the position, size, and weight of each cluster. Arguably, the most important feature of GEMA is that it eliminates the need for external parameter selection while simultaneously improving power, thus providing a key step towards routine reproducibility of quantitative measurements.

Chapter VIII

Future Work

During the course of completing this thesis, new questions arose which merit further investigation. Unfortunately, these areas of research could not be investigated within the time frame of this thesis and are therefore outlined below:

Grain Boundaries in Low Copper, Thermally Aged RPV Steels

This work has uncovered solute clustering at grain boundaries as well as other heterogeneous nucleation sites, such as carbide/matrix interfaces. The presence of clustering at these sites raises concern regarding non-hardening embrittlement, which should be fully investigated. Micro-cantilever testing should be carried out in order to test for changes in non-hardening embrittlement. These tests could then be paired with site-specific APT analysis in order to link changes in the microstructure to changes in the mechanical properties.

Additionally, an in depth analysis of clustering at heterogeneous nucleation sites could lend insight into the thermodynamic stability of MNPs. Atom probe analysis of a wide range of heterogeneously nucleated clusters within these thermally aged steels would enable an informed compositional comparison to the MNPs found within ion and neutron irradiated RPV steels.

Work Hardened, Thermally Aged RPV Steels

One of the long-term aims of this research is to determine if MNPs form within thermally aged RPV steels. It is hypothesized that even if these precipitates do form under thermal aging conditions, they would be very difficult to nucleate. Therefore, it would be of interest to perform a parallel thermal aging study on an identical set of model RPV steels that have been work hardened. Work hardening would generate numerous dislocations within the matrix of the steels. This would ensure the presence of many heterogeneous nucleation sites within the matrix at which precipitates

could readily nucleate. Such an experiment would shed light upon the long standing debate regarding whether MNPs are radiation induced or simply radiation enhanced.

Additionally, in order to observe clustering within the current set of steels, one must use site-specific FIB lift-out in order to encapsulate grain boundaries, dislocations, or carbide interfaces within an APT specimen. FIB preparation of atom probe specimens is a very time consuming process, which would not be necessary if analyzing material that had been work hardened.

GEMA Extensions

In its current form, GEMA models clusters as spherical Gaussians. Although this assumption does not noticeably hinder GEMA’s performance, generalizing the covariance matrix to allow ellipsoidal clusters would be advantageous. Additionally, GEMA currently only considers solute atoms. If GEMA is to be used widely within the APT community it would be necessary to incorporate a function which addresses non-solute atoms. The simplest extension would presumably automate the L and E step of the maximum separation method. Although seemingly straightforward, an intelligent automation of these parameters is non-trivial.

Another potential extension, and perhaps the most interesting, is updating GEMA so that it learns not only the location, size, and width of each precipitate, but also information regarding composition. Through unsupervised learning the algorithm could simultaneously characterize different phases present in the dataset and determine the most probable phase of each precipitate. Furthermore, by adapting GEMA into a Bayesian approach the user could incorporate prior knowledge regarding phases commonly found within the material, as well as their level of certainty.

Finally, the algorithm could be extended to learn across APT datasets. One could, in principle, have a hierarchical model that learns the differences between materials at the top-level; differences between regions of the same material at the mid-level; and then, finally, run GEMA within each APT dataset while leveraging this information. Such hierarchical models are ubiquitous in the world of “big data” and extremely useful. As such GEMA provides a small but crucial first step toward integrating the trillions of data points generated from thousands of APT analyses to make broad claims about the structure of materials.

Chapter IX

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Chapter X

Appendix

1 Derivation of Equation for Shear Stress

The Russell-Brown model is derived using the following equation for shear stress:

$$\tau = \frac{0.8Gb}{L} \cos(\phi/2), \quad (20)$$

where G is the shear modulus, b is the Burgers vector, L is the distance between obstacles, and ϕ is the angle between the arms of the bent dislocation. This equation can be derived from materials science principles and geometric considerations [31].

For a screw dislocation the shear strain, γ , is equal to the deformation over the original length, or

$$\gamma = \frac{b}{2\pi r}, \quad (21)$$

where b is the Burgers vector and r is the radius of the dislocation.

Therefore, shear stress is given by,

$$\tau = G\gamma = \frac{Gb}{2\pi r}, \quad (22)$$

where G is the shear modulus.

The line tension (energy per unit length), T , of a dislocation can be determined using the shear stress, shear strain, and the definition of dE ($dE = 1/2(\text{stress} \times \text{strain} \times \text{volume})$).

$$dE = \frac{Gb}{2\pi r} \frac{b}{2\pi r} 2\pi r dr \quad (23)$$

$$\Rightarrow dE = \frac{Gb^2}{4\pi r} dr \quad (24)$$

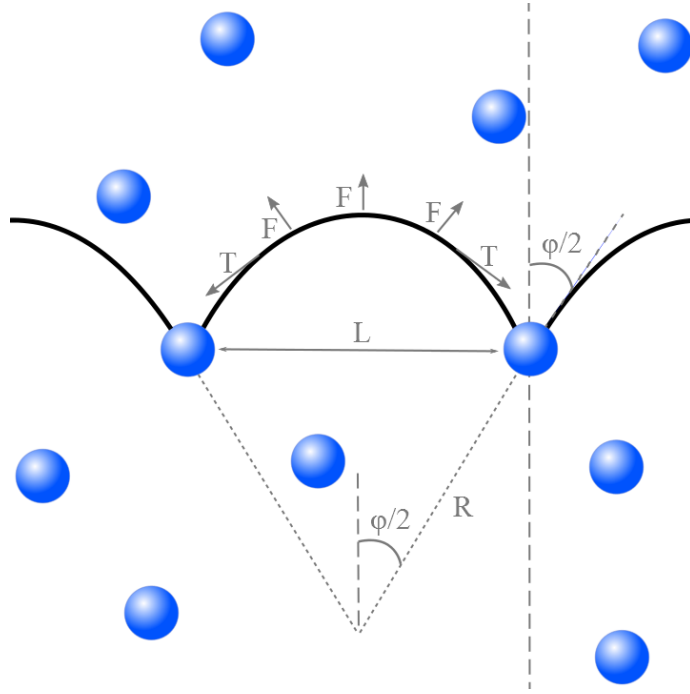


Figure 84: Schematic of the forces present when precipitates pin a dislocation.

$$\Rightarrow E = \int_{r_0} \frac{Gb^2}{4\pi r} dr = \frac{Gb^2}{4\pi} \ln \left(\frac{R}{r_0} \right) \approx \frac{Gb^2}{2} \quad (25)$$

$$\Rightarrow T = \frac{Gb^2}{2}. \quad (26)$$

The force of the crystal, F , is determined using the work done by the crystal, $W_{crystal} = \tau w l b$, and the work done by the dislocation, $W_{dislocation} = F w l$.

$$W_{crystal} = W_{dislocation} \quad (27)$$

$$\Rightarrow \tau w l b = F w l \quad (28)$$

$$\Rightarrow F = \tau b \quad (29)$$

In order to minimize the line length of a dislocation, and therefore energy of the system, a curved dislocation will tend to straighten. The forces present on a dislocation, which are ultimately responsible for this straightening, are illustrated in Figure 4.

Using the equations for line tension and the force of the crystal one can determine the radius

of curvature of the dislocation, R . The x component of the total line tension is given by,

$$T_x = Gb^2 \sin(\delta\phi) \quad (30)$$

$$\Rightarrow T_x \approx Gb^2 \delta(1/2\phi) \quad (31)$$

$$\Rightarrow T_x \approx \frac{Gb^2}{2} \delta\phi \quad (32)$$

The force of the crystal,

$$F = \tau b \delta l = \tau b R \delta\phi, \quad (33)$$

is then set equal to T_x ,

$$F = T_x \quad (34)$$

$$\Rightarrow \tau b R \delta\phi = \frac{Gb^2}{2} \delta\phi \quad (35)$$

$$\Rightarrow R = \frac{Gb}{2\tau}. \quad (36)$$

Rearranging Equation 16 and substituting Equation 6 an equation for shear stress in terms of the radius of curvature and tension is obtained,

$$\tau = \frac{T}{bR}. \quad (37)$$

Letting F be the force on an obstacle (precipitate) by line tension, T , of a dislocation, the equation

$$F = 2T \cos(1/2\phi) \quad (38)$$

is obtained, where ϕ is the angle between the arms of the bent dislocation. The assumption that the line tension of the dislocation is constant is inherent in this equation.

The distance between obstacles, L , is determined via geometry, $L = 2R \cos(\phi/2)$. Using the equations, $\tau = \frac{T}{bR}$ and $L = 2R \cos(\phi/2)$ the equation for shear stress from Russell and Brown's paper is obtained:

$$\tau = \frac{Gb}{L} \left[\cos \frac{\phi}{2} \right] \approx 0.8 \frac{Gb}{L} \left[\cos \frac{\phi}{2} \right]. \quad (39)$$

2 Estimating Physical Cluster Size Distributions

2.1 An Analytical Solution: *A priori* Known θ

The cluster size distribution for a given atom probe dataset can be perfectly described by a function with an infinite parameter vector, $\vec{\theta}$. However, determining this exact function and finding the maximum likelihood estimate is an intractable problem. Thus a low-dimensional approximation of this function is needed.

For a single cluster x atoms (detected cluster size) are drawn from of a y -atom cluster (physical cluster size) with probability θ , the detection efficiency. The binomial distribution is a discrete probability distribution that determines the probability of obtaining x “successes” (in this case, detected atoms) in y Bernoulli trials. The binomial distribution is a good approximation of the problem and fulfills the requirement of being discrete. Thus, the binomial distribution is utilized as a low-dimensional estimate of the cluster size distribution.

Since x is a binomial random variable, the size probability function of a single cluster, i , can be written as follows,

$$f(x_i|\theta, y_i) = \text{Binom}(y_i, \theta). \quad (40)$$

Extending to the multiple cluster case, assuming independence of clusters, the joint distribution is simply the product of the marginal distributions,

$$f(\vec{x}|\theta, \vec{y}) = \prod_{i=1}^k f(x_i, \theta|y_i) \quad (41)$$

$$= \prod_{i=1}^k \left[\binom{y_i}{x_i} \theta^{x_i} (1 - \theta)^{y_i - x_i} \right], \quad (42)$$

where k is the number of clusters. This means the log-likelihood is,

$$\begin{aligned}
\ell(\vec{y}|\vec{x}, \theta) &= \log \left[\prod_{i=1}^k \left[\binom{y_i}{x_i} \theta^{x_i} (1-\theta)^{y_i-x_i} \right] \right] \\
&= \sum_{i=1}^k \left[\log \left(\binom{y_i}{x_i} \theta^{x_i} (1-\theta)^{y_i-x_i} \right) \right] \\
&= \sum_{i=1}^k \left[\log \left(\frac{y_i!}{x_i!(y_i-x_i)!} \theta^{x_i} (1-\theta)^{y_i-x_i} \right) \right] \\
&= \sum_{i=1}^k [\log y_i! - \log x_i! - \log(y_i-x_i)! + x_i \log \theta + (y_i-x_i) \log(1-\theta)].
\end{aligned}$$

Using Stirling's approximation, the log-likelihood becomes,

$$\begin{aligned}
\ell(\vec{y}|\vec{x}, \theta) &= \sum_{i=1}^k [y_i \log y_i - y_i - x_i \log x_i + x_i - (y_i-x_i) \log(y_i-x_i) \\
&\quad + (y_i-x_i) + x_i \log \theta + (y_i-x_i) \log(1-\theta)].
\end{aligned}$$

Next, the derivative of the log-likelihood with respect to a particular y_i , denoted y_j , is taken,

$$\frac{\partial \ell(\vec{y}|\vec{x}, \theta)}{\partial y_j} = \log y_j - \log(y_j - x_j) + \log(1-\theta).$$

Maximizing the above equation with respect to y_j leads to an analytical solution :

$$\begin{aligned}
0 &= \log y_j - \log(y_j - x_j) + \log(1-\theta) \\
&\Rightarrow \log y_j - \log(y_j - x_j) = -\log(1-\theta) \\
&\Rightarrow \log \frac{y_j}{y_j - x_j} = -\log(1-\theta) \\
&\Rightarrow \frac{y_j}{y_j - x_j} = \frac{1}{(1-\theta)} \\
&\Rightarrow y_j = x_j \theta^{-1}.
\end{aligned}$$

Hence, the estimated physical cluster size of a particular cluster, y_j , is as follows,

$$y_j = x_j \theta^{-1}. \tag{43}$$

Thus, there exists an analytical solution to the maximum likelihood estimate for the case in which there is a known θ and y is unconstrained. The result is intuitive: the observed cluster size, x_j divided by the efficiency, θ , equals the physical cluster size, y_j . Therefore, in order to determine the physical cluster size distribution one simply divides the observed cluster size distribution by the detector efficiency.

2.2 Simulation Verification

In order to evaluate the analytical solution presented above, an artificial non-degraded dataset was created using Posgen (Figure 85) [124]. The lattice generated had a cubic structure with lattice constant $a = 0.286$. The 50 x 50 x 50nm lattice was composed of 90 at.% Fe and 10 at.% Cu. A Gaussian noise was added to each atomic position in x , y , and z .

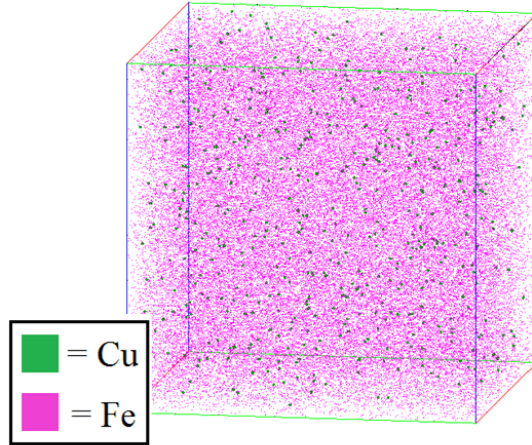


Figure 85: Artificial non-degraded dataset created using Posgen [124].

Once the lattice was constructed, a cluster search was carried out using the maximum separation method. D_{max} was chosen by maximizing the number of clusters via visual inspection of the cluster count distribution. The physical cluster size distribution was then acquired. In order to obtain a degraded dataset, 63% of the atoms were randomly removed. Once again a cluster search was conducted using the maximum separation method. D_{max} was chosen independent of the previous D_{max} by maximizing the number of clusters using the cluster count distribution and the degraded cluster size distribution was obtained. The analytical solution was then successfully used to estimate the physical distribution from the degraded distribution (Figure 86).

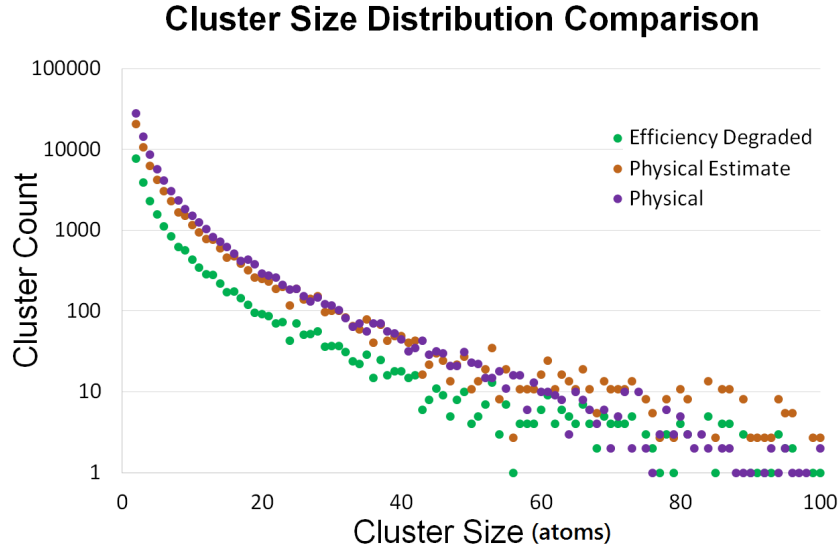


Figure 86: Cluster size distribution comparison where the efficiency degraded cluster size is shown in green, the physical cluster size is shown in purple, and the physical cluster size estimate is shown in orange.

It should be noted that the model only breaks down when the cluster count is small (less than 10 clusters). This is shown in the normalized error plot which becomes heteroscedastic in this region (Figure 87). Normalized error is defined as,

$$\frac{||y_i - \hat{y}_i||}{y_i}. \quad (44)$$

This is reasonable because there exists fewer clusters on which to base an estimate.

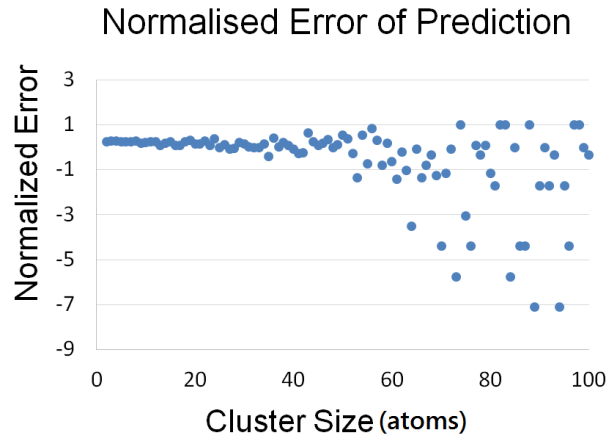


Figure 87: Normalized error plot.

3 Hardness Measurements

Material	Temp. (°C)	Avg. Hardness (Hv)	Standard Dev.
A	330	230.38	7.38
	365	230.13	5.01
	405	229.63	5.41
B	330	156.13	5.18
	365	156.63	6.40
	405	158.75	4.58
C	330	301.00	3.81
	365	304.50	7.57
	405	310.38	5.17
D	330	311.50	4.21
	365	315.88	8.43
	405	314.63	5.81
E	330	251.50	6.02
	365	254.50	6.32
	405	257.38	6.48
F	330	286.63	7.97
	365	284.88	6.99
	405	287.13	7.30
G	330	264.00	6.78
	365	261.63	9.80
	405	261.13	11.87
H	330	227.38	8.17
	365	224.13	9.84
	405	225.50	9.67
I	330	307.63	10.62
	365	309.63	4.61
	405	307.13	6.81
J	330	250.13	5.80
	365	249.75	6.24
	405	254.00	5.15
K	330	261.88	12.08
	365	261.13	5.84
	405	255.75	5.54
L	330	242.13	7.04
	365	235.25	5.09
	405	243.13	9.29

Table 30: Hardness measurements for as-received RPV steels. The average hardness was based on eight indents.

Material	Temp. (°C)	Avg. Hardness (Hv)	Standard Dev.
M	330	275.50	7.14
	365	277.25	7.45
	405	279.88	4.08
N	330	156.75	4.35
	365	155.63	5.02
	405	158.13	7.03
O	330	319.00	5.85
	365	317.25	3.63
	405	319.00	9.50
P	330	165.38	7.14
	365	157.88	6.97
	405	158.75	6.94
Q	330	230.25	3.99
	365	237.75	6.68
	405	238.75	4.60
R	330	173.13	5.97
	365	173.13	2.89
	405	175.38	4.58
S	330	268.50	9.87
	365	264.63	8.80
	405	265.38	6.95

Table 31: Hardness measurements for as-received RPV steels. The average hardness was based on eight indents.

Material	Temp. (°C)	Avg. Hardness (Hv)	Standard Dev.
A	330	215.25	7.84
	365	215.50	4.38
	405	220.69	5.38
B	330	145.13	4.05
	365	148.19	4.16
	405	148.50	4.89
C	330	292.75	3.96
	365	286.50	3.75
	405	290.06	2.24
D	330	299.69	3.80
	365	303.38	4.12
	405	299.38	2.64
E	330	241.69	5.34
	365	242.44	4.63
	405	241.19	3.84
F	330	298.69	8.18
	365	322.56	10.02
	405	277.13	6.11
G	330	256.00	3.72
	365	250.63	4.88
	405	254.44	2.82
H	330	218.56	6.10
	365	212.25	7.97
	405	216.88	7.50
I	330	297.00	5.75
	365	301.00	3.80
	405	293.81	7.68
J	330	242.63	3.44
	365	245.44	5.74
	405	243.00	6.83
K	330	251.75	3.23
	365	245.38	5.15
	405	245.44	6.59
L	330	224.06	6.27
	365	223.31	5.44
	405	228.69	6.98
M	330	264.13	5.88
	365	261.44	8.44
	405	258.56	5.56
N	330	147.56	5.99
	365	150.25	4.47
	405	148.69	4.22

Table 32: Hardness measurements for RPV steels thermally aged for 11,688 hours. The average hardness was based on eight indents.

Material	Temp. (°C)	Avg. Hardness (Hv)	Standard Dev.
O	330	300.75	2.73
	365	301.13	4.20
	405	297.25	4.65
P	330	151.75	5.05
	365	147.31	3.92
	405	151.56	3.10
Q	330	222.25	4.19
	365	223.75	4.15
	405	229.50	3.05
E	330	158.19	4.11
	365	160.25	3.00
	405	161.94	5.23
S	330	258.56	5.36
	365	257.31	4.44
	405	256.31	5.72

Table 33: Hardness measurements for RPV steels thermally aged for 11,688 hours. The average hardness was based on eight indents.

4 Local Chemistry Method Analyses

4.1 As-Received RPV Steels

4.1.1 Sample G: Medium Ni, High Mn

The local chemistry method was first applied to the as-received sample G atom probe reconstruction (Figure 88). Sample G, which contains 1.6 at.% Ni and 2.0 at.% Mn, had no visually apparent microstructure or APT artifacts. Association of Cu-Cu, Si-Ni, Cu-Mn, Ni-Ni, Ni-Mn, Mn-Ni, Mn-Mn, Mo-Ni, and C-C was found to be statistically significant ($p\text{-value} < 0.02$). A table of p -values is shown in Table 34; statistically significant entries are shown in bold. As discussed in Chapter 3, C-C association is regarded as an atom probe artifact.

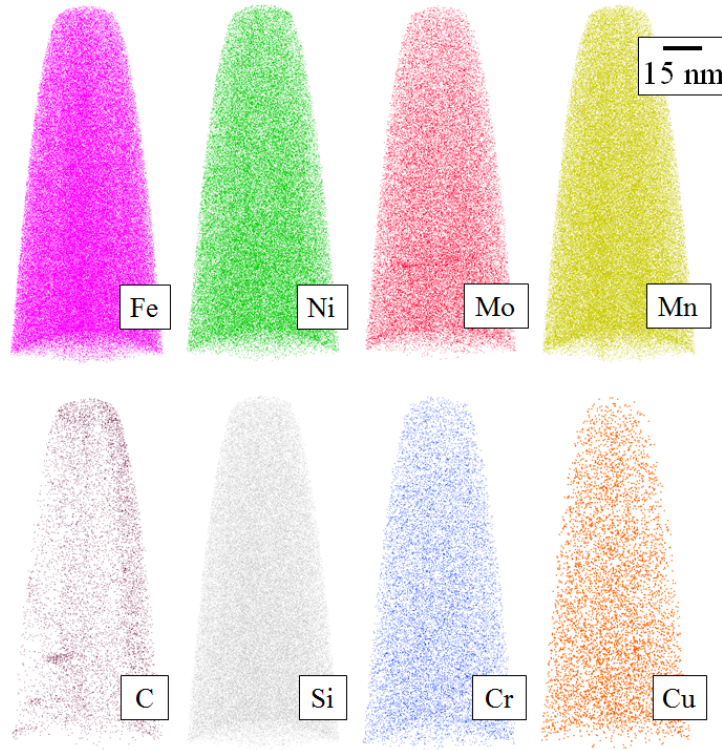


Figure 88: Atom maps of as-received sample G.

4.1.2 Sample A: Medium Ni, Low Mn

Solute association was also found in as-received sample A (Figure 89), which contains 1.6 at.% Ni and 0.25 at.% Mn. Ni-Ni and C-C association was found to be statistically significant (Table 35).

Elements	Si	Cu	Ni	Mn	Mo	Cr	C
Si	2.94	16.11	<0.001	0.15	33.72	46.81	48.01
Cu	32.64	0.011	0.18	0.016	27.09	30.85	23.89
Ni	0.048	1.13	<0.001	<0.001	0.005	1.25	9.34
Mn	0.097	0.55	<0.001	<0.001	8.23	0.84	19.22
Mo	43.64	38.21	0.005	7.93	0.73	9.85	29.46
Cr	41.29	43.25	0.54	0.4	13.79	10.2	1.54
C	43.25	16.85	1.54	35.57	46.81	9.68	<0.001

Table 34: P-value table for association within the matrix of sample G in the as-received state. Bold entries are considered statistically significant.

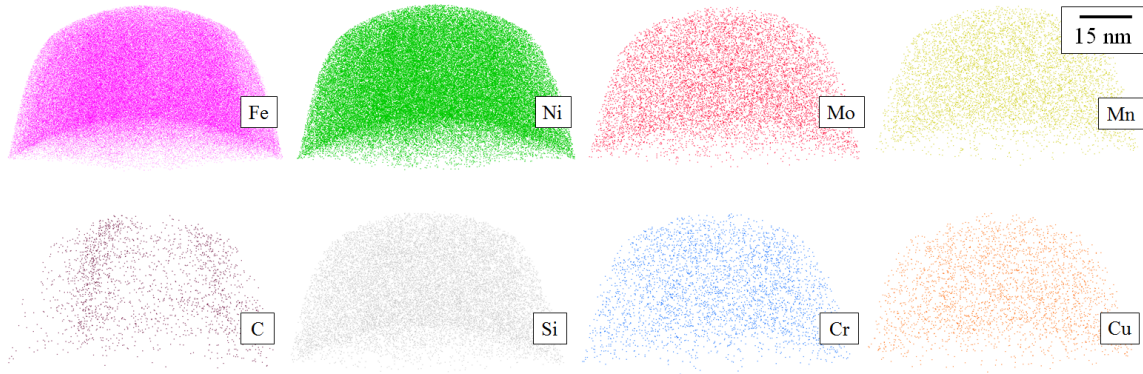


Figure 89: Atom maps of as-received sample A.

Elements	Si	Cu	Ni	Mn	Mo	Cr	C
Si	6.3	43.64	0.12	25.78	33	5.94	35.94
Cu	37.83	4.27	46.41	2.68	24.2	35.2	23.27
Ni	4.75	16.11	0.005	2.68	29.81	16.11	12.1
Mn	7.21	10.93	0.39	30.85	0.87	28.43	43.64
Mo	38.97	17.36	12.51	1.66	0.51	29.81	11.31
Cr	10.2	34.83	5.16	47.21	36.69	36.32	31.92
C	46.41	27.76	39.36	21.77	14.46	13.35	<0.001

Table 35: P-value table for association within the matrix of sample A in the as-received state. Bold entries are considered statistically significant.

4.1.3 Sample H: Low Ni, High Mn

There were two successful atom probe runs of the as-received sample H. The reconstruction presented here contained a layer of redeposited Si on the surface due to improper cleaning after electropolishing. This layer was removed prior to applying the local chemistry method. No association was found in sample H in the as-received state (Table 36). It should be noted that out

of the five as-received samples tested this was the only sample with no statistically significant association. Sample H was also the only sample low in bulk Ni content (0.2 at.%).

Elements	Si	Cu	Ni	Mn	Mo	Cr	C
Si	0.8	4.01	47.61	29.81	2.5	37.83	16.11
Cu	11.7	27.43	22.36	26.11	26.76	7.21	N/A
Ni	48.8	32.64	0.048	7.93	40.52	0.75	35.57
Mn	26.11	23.89	5.48	0.034	18.41	4.27	27.43
Mo	15.62	35.2	22.96	40.13	43.64	48.8	24.83
Cr	40.13	18.14	8.08	6.68	41.68	23.27	3.29
C	32.64	50	30.5	35.94	16.35	6.3	N/A

Table 36: P-value table for association within the matrix of sample H in the as-received state. No association was found to be statistically significant.

4.2 Thermally Aged RPV Steels

4.2.1 Sample G: Medium Ni, High Mn

Sample G contained two large carbides, enriched in manganese and molybdenum, respectively (Figure 90). The manganese carbide was also enriched in nickel; both carbides contained chromium and were depleted of iron. After removing these carbides, the local chemistry method was used to detect potential solute association within the matrix. Association of Si-Ni, Ni-Si, Ni-Ni, Mn-Ni, Ni-Mn, Mn-Mn, Cr-Cr, and C-C was found to be statistically significant (Table 37).

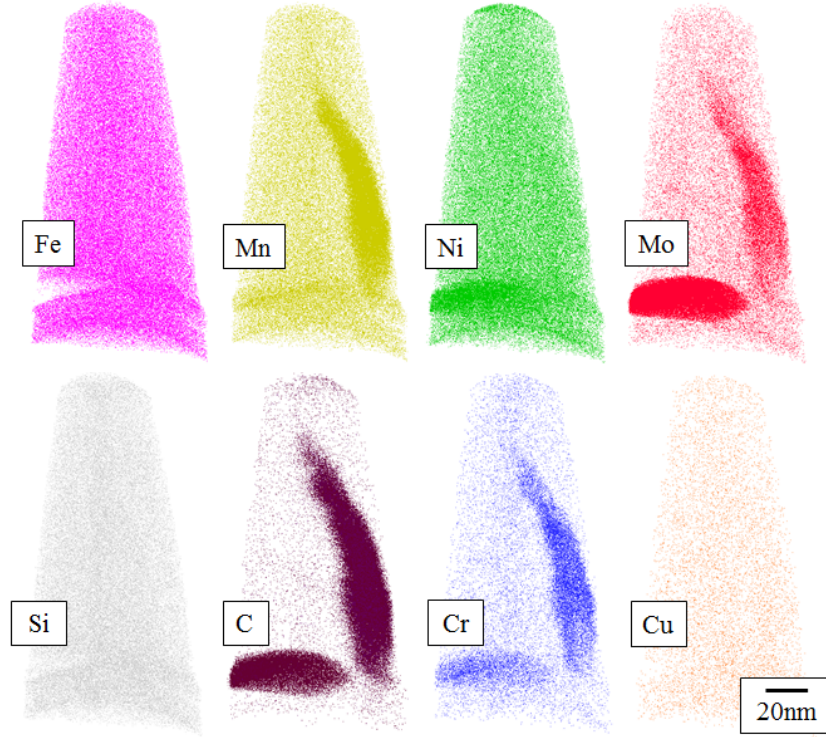


Figure 90: Atom maps of sample G. The sample was aged for 11,690 hours at 405°C.

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	0.28	29.81	0.002	1.54	46.81	10.75	1.70
Cu	29.81	27.43	6.81	8.23	21.48	46.02	23.58
Ni	0.01	1.13	<0.001	0.01	16.11	7.08	5.05
Mn	1.62	3.59	<0.001	<0.001	22.66	1.02	0.26
Mo	27.43	21.77	3.14	37.83	4.46	48.80	5.94
C	22.36	40.52	26.43	0.19	8.69	<0.001	29.46
Cr	6.30	20.61	36.69	0.41	15.15	12.30	0.02

Table 37: P-value table for association within the matrix of thermally aged sample G. Bold entries are considered statistically significant.

4.2.2 Sample A: Medium Ni, Low Mn

Sample A contained several small molybdenum carbides (Figure 91), which were removed prior to the analysis of the sample via the local chemistry method. Association of Ni-Ni and C-C was found to be statistically significant in sample A (Table 38).

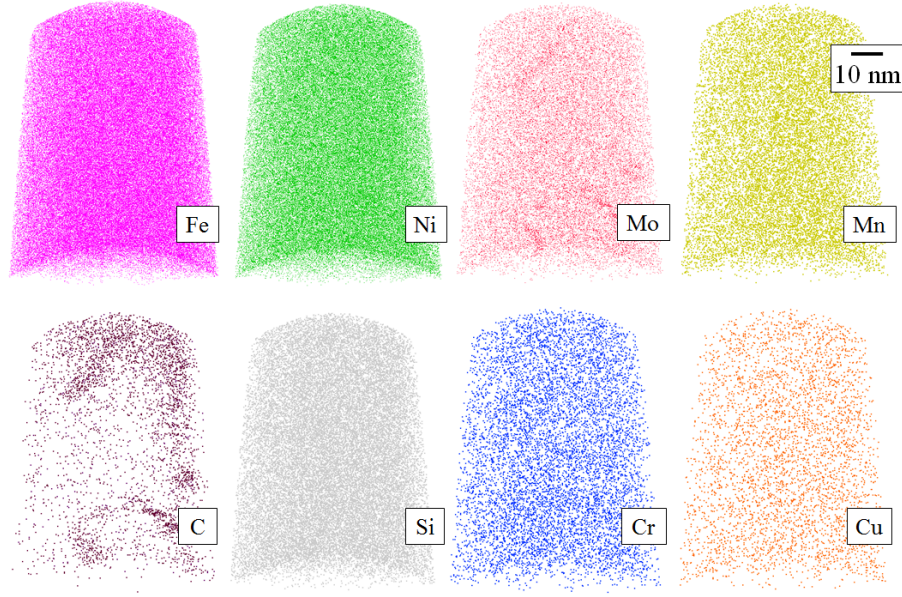


Figure 91: Atom maps of sample A after thermal aging at 405°C for 11,690 hours.

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	0.10	48.80	0.51	0.05	2.02	30.15	26.76
Cu	26.76	2.87	41.68	33.72	37.83	35.94	48.40
Ni	1.07	48.80	<0.001	4.85	32.64	19.22	49.60
Mn	0.71	29.12	3.92	0.71	12.92	30.85	15.87
Mo	2.87	40.52	5.16	6.43	0.48	36.32	44.43
C	14.23	48.80	19.22	46.81	27.76	<0.001	24.20
Cr	11.70	47.61	20.61	15.87	45.62	5.94	12.51

Table 38: P-value table for association within the matrix of thermally aged sample A. Bold entries are considered statistically significant.

4.2.3 Sample H: Low Ni, High Mn

Thermally aged sample H (Figure 92) contained one decorated dislocation, which was removed prior to the analysis of the sample via the local chemistry method. Association of Cu-Ni, Si-Mn, Mn-Mn, and C-C was found to be statistically significant (Table 39).

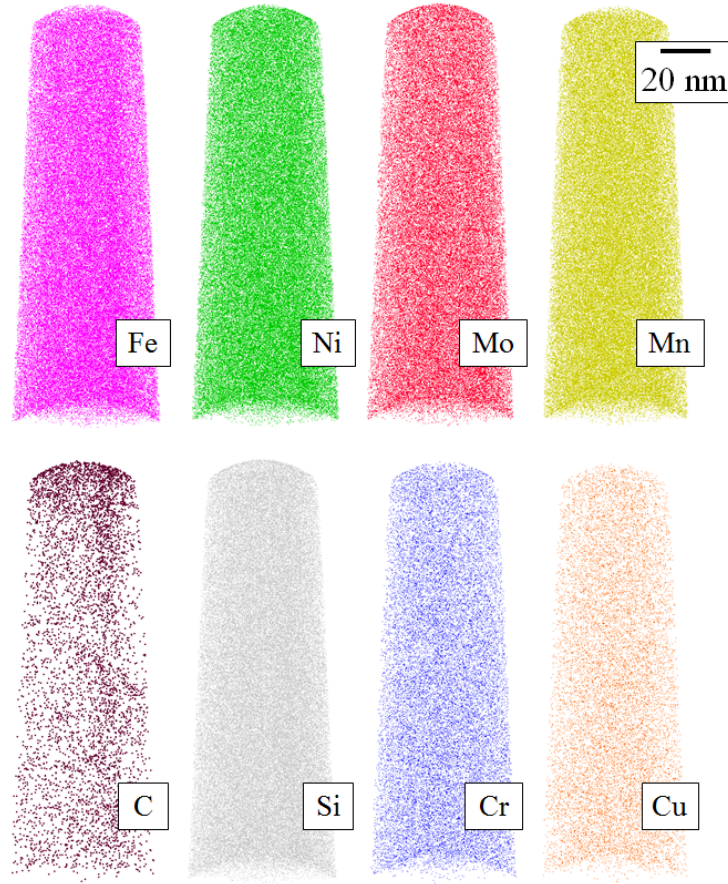


Figure 92: Atom maps of sample H after thermal aging at 405°C for 11,690 hours.

Elements	Si	Cu	Ni	Mn	Mo	C	Cr
Si	12.3	0.3	0.32	<0.001	8.23	6.81	40.13
Cu	1.13	8.85	0.016	0.96	1.54	7.64	43.25
Ni	0.048	0.22	1.54	0.097	45.62	24.83	33.36
Mn	0.023	7.49	3.92	<0.001	14.69	33.72	5.48
Mo	2.12	13.14	17.11	0.069	29.81	11.51	48.8
C	25.14	18.41	37.83	17.11	24.83	<0.001	36.69
Cr	41.68	34.46	32.28	1.7	24.2	33	45.62

Table 39: P-value table for association within the matrix of thermally aged sample H. Bold entries are considered statistically significant.