

Irradiation Effects on Fe-Cr Alloys



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A Thesis Submitted for the Degree of Doctor of
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Ferritic chromium steels are important structural materials for future nuclear fission and fusion reactors due to their advantages over traditional austenitic steels, including low swelling rates, better thermal fatigue resistance, and lower thermal expansion coefficients. Radiation-induced segregation or depletion (RIS/RID) of solute atoms at grain boundaries is considered to be a potentially significant phenomenon for structural materials because of its potentially detrimental role in affecting microstructure and furthermore mechanical properties. However, the behaviour of Cr at grain boundaries in ferritic steels is not well understood. Both segregation and depletion of Cr at grain boundary under irradiation have been previously observed and no clear dependency on irradiation condition or alloy type has been presented. Furthermore, ferritic alloys are known to undergo hardening and embrittlement after thermal aging in the temperature range of 300-550°C and this phenomenon is related with α and α' phase separation occurring in the solid solution. However the low temperature α - α' miscibility gap in the currently used phase diagram is extrapolated from high temperature results and conflicts with many experimental observations.

To understand the Cr behaviour at grain boundaries in ferritic steels under irradiation, a systematic approach combining SEM/EBSD, FIB specimen preparation and APT analysis has been developed and successfully applied to a Fe-15.2at%Cr to investigate the effect of pre-irradiation chemistry, grain boundary misorientation, impurities, irradiation damage, irradiation depth, and other possible factors to get a better understanding of RIS/RID phenomena. Both low sigma boundaries and randomly selected high angle boundaries have been investigated in detail. Systematic differences between the behaviour of different classes of boundaries had been observed, and the operating mechanisms are also discussed in this thesis.

The maximum separation method has been applied on APT data to study the C-enriched clusters and Cr-enriched clusters, which were not directly visible on the atom maps. The composition of the Cr-enriched clusters was consistent with α' phase and the irradiation was found to accelerate the nucleation rather than the growth of these clusters. Such results provided important information in re-determining the α - α' phase boundary.

Dedicated to My Dear Family

They would be Proud.

-

献给我挚爱的家人

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Preface

The research work presented in this doctoral thesis is conducted by the author in the Department of Materials, University of Oxford, from October 2008 to May 2012, under the supervision of Professor George D.W. Smith FRS, Dr. Emmanuelle A. Marquis and Dr. Jonathan M. Hyde. All of the thesis work is original, and the work of others cited has been clearly referenced and acknowledged. No part of this thesis has been submitted for any degree in this University or elsewhere. Some of the work in this thesis has been published in scientific journals and presented at conferences:

Journal Articles:

- R. Hu, G.D.W. Smith, and E.A. Marquis, *Atom Probe Study of Radiation Induced Grain Boundary Segregation/Depletion in a Fe-12%Cr Alloy*, Progress in Nuclear Energy, 2012. **57**: p. 14-19.
- E.A. Marquis, R. Hu, and T. Rousseau, *A systematic approach for the study of radiation-induced segregation/depletion at grain boundaries in steels*, Journal of Nuclear Materials, 2011. **413**: p. 1-4.
- R. Hu, G.D.W. Smith, and E.A. Marquis, *Effect of Grain Boundary Orientation on Radiation-Induced Segregation in a Fe-15.2 at%Cr Alloy* (submitted to Acta Materialia)

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- R. Hu and E.A. Marquis, ***Grain Boundary Chemistry in Irradiated Fe-Cr Alloys***, Poster Presentation, Materials Research Society 2010 Fall Meeting, 29/11/2010-03/12/2010, Boston, USA
- R. Hu, E.A. Marquis, and G.D.W. Smith, ***Quantitative Analysis of Fe-Cr Alloys by Atom-Probe Tomography***, Poster Presentation, 52nd International Field Emission Symposium, 05/07/2010-08/07/2010, Sydney, Australia

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Chapter 1

Introduction

The dramatic increase of energy demand world-wide and the gradual depletion of traditional energy sources have spurred international cooperative efforts for discovering new types of energy production. Nuclear power, with its enormous potential for meeting future energy needs while keeping the environment clean, is considered to be the most promising future energy source and is undergoing rapid development nowadays.

With the increasing need for developing nuclear power as a major energy source, iron-chromium alloys, which are often applied as structural materials for nuclear reactors, have attracted a huge amount of industrial interest due to their good properties under extreme conditions, such as high strength, low swelling rates, lower thermal expansion coefficients and resistance to radiation damage and corrosion at high temperature.[1] Currently, ferritic/martensitic steels are used mainly for in-core applications in fission reactors where they face an environment characterized by 320°C temperatures with neutron doses up to 10dpa and low He production. The same materials will be used as first wall and blanket structures of fusion reactors and will be required to withstand temperatures above 500°C, doses over 100dpa and high helium loading of plasma. [2] The next generation of fission reactors (Gen IV) is under development which will have operating conditions well beyond those of earlier designs, such as higher operating temperatures (500-1000°C), higher doses up to 30-100dpa, higher pressure than typical operating pressure (about 7MPa for boiling-water reactors and 15MPa for pressurized-water reactors [3]). Ferritic/martensitic steels are still considered to be the favorable candidate in the design of the next generation reactors, but the new design requires more advanced performance. Since all complex ferritic alloy systems are designed based on the binary Fe-Cr alloy, fundamental understanding of microstructure evolution of Fe-Cr

alloys under conditions of neutron irradiation is very important, since the mechanical properties and performance are strongly connected with the microstructure.

Irradiation can induce changes in both microstructure and microchemistry, and furthermore result in degradation of the mechanical properties of alloys. Point defects can be introduced in the alloys by ion or neutron irradiation. If not recombined, these point defects will diffuse to sinks such as grain boundaries. The interaction between point defect fluxes and solute atoms will cause coupled transport of solute atoms, giving rise to the non-equilibrium solute concentration gradients near the grain boundaries. This phenomenon is recognized as radiation-induced segregation/depletion (RIS/RID) [4]. RIS/RID of the solute atoms is believed to be one of the most important radiation-induced mechanisms and to have a strong link with the change of mechanical properties. The study of these phenomena in austenitic steels has been carried out for quite a long time and a consistent explanation has been found. The situation in ferritic/martensitic steel is not so clear and both radiation-induced segregation and depletion of Cr in grain boundaries have been reported as summarized by Lu et al.[5] and Was et al. [6]. The conclusions drawn from the literature on RIS/RID of Cr in grain boundary in ferritic steels are often based on incomplete data, for example authors often fail to take into account all the possible factors which could affect the RIS/RID phenomenon, such as pre-irradiation grain boundary chemistry, grain boundary misorientation, the presence of minor elements and precipitates and so on. Therefore it is necessary to develop a systematic approach to study the RIS/RID phenomenon in the Fe-Cr binary alloys while considering as many factors as possible. As the high Cr ferritic/martensitic steels are considered to be the leading candidates for advanced

nuclear applications, it is crucial to gain a better understanding of the radiation-induced segregation/depletion of Fe-Cr binary alloys.

Furthermore, it is well known that ferritic alloys undergo hardening and embrittlement after thermal aging in the temperature range of 300-550°C which is referred as ‘475°C embrittlement’, because there is a miscibility gap at low temperature in the Fe-rich corner of the phase diagram. This leads to α and α' phase separation occurring in the solid solution and the phenomenon is enhanced under irradiation conditions (details in Chapter 2) [7]. Currently the low temperature α and α' phase boundary on the phase diagram in the published handbook is extrapolated from high temperature results but not based on real data, and conflicts with many experimental observations. Many researches focus on re-determining the phase boundary by both experimental and theoretical methods as summarized by Bonny et al. [7], however there are still some discrepancies among them. The observations of α' phase separation made by TEM and other methods are also limited due to the nature of these techniques. On the other hand, atom probe tomography has proved to be a very efficient method in characterizing ultrafine scale microstructure evolution. Application of this technique will make it possible to observe α' phase, especially at the earliest stages of phase separation, and can provide vital information for re-determining the α - α' phase boundary in support the needs of the nuclear industry.

In this thesis, a systematic approach for studying RIS/RID has been developed and RIS/RID phenomena of Cr on grain boundaries with various misorientations as well as α' phase formation has been studied in Fe-Cr alloys under different irradiation conditions. The background information and literature review will be introduced in Chapter 2. The experimental methods will be discussed in Chapter 3. All results will be presented in Chapter 4, 5, 6 and 7, with conclusions in Chapter 8.

References

1. Takahashi, H., S. Ohnuki, and T. Takeyama, *Journal of Nuclear Materials*, 1982. **103**(1-3): p. 1415-1419.
2. Was, G.S., *Journal of Nuclear Materials*, 2007. **367**: p. 11-20.
3. Nanstad, R.K., ed. *Encyclopedia of Materials Science and Engineering*. ed. M.B. Bever 1986, Pergamon: New York.
4. Busby, J.T., G.S. Was, and E.A. Kenik, *Journal of Nuclear Materials*, 2002. **302**(1): p. 20-40.
5. Lu, Z., R.G. Faulkner, G. Was, and B.D. Wirth, *Scripta Materialia*, 2008. **58**(10): p. 878-881.
6. Was, G.S., J.P. Wharry, B. Frisbie, B.D. Wirth, D. Morgan, J.D. Tucker, and T.R. Allen, *Journal of Nuclear Materials*, 2011. **411**(1-3): p. 41-50.
7. Bonny, G., D. Terentyev, and L. Malerba, *Scripta Materialia*, 2008. **59**(11): p. 1193-1196.

Chapter 2

Literature Review

2.1 Review of the Iron-Chromium System

2.1.1 Technical importance and application in nuclear industry

Before the 1970s, austenitic stainless steels were the primary materials used in the field of fission reactors because they were corrosion resistant and had good mechanical properties, but there was some degradation due to exposure to fast neutrons. Components which were manufactured with austenitic stainless steels and used in water-cooled reactors included piping, pumps, core barrels and thermal shields. Stainless steel was also the preferred fuel cladding material in sodium-cooled fast breeder reactors, and creep was increased by neutron irradiation under this condition. Meanwhile, low-alloy carbon steels, such as A533B (consisting of 0.25%¹C, 1.5%Mn, 0.035%P, 0.04%S, 0.03%Si, 0.6%Mo, 0.7%Ni, in weight percent), was an important reactor material for use in pressure vessels and miscellaneous components [1]. Later on, 9-12%Cr-Mo steels were considered to be favored candidates for in-core (cladding, wrappers, and ducts) applications for fast reactors due to their higher thermal conductivities and lower expansion coefficients than those of austenitic steels. The in-core application of high-swelling austenitic steels has been limited by void swelling [2]. For example, Sandvik HT9 (consisting of 12%Cr, 0.2%C, 0.4%Si, 0.6%Mn, 0.5%Ni, 1%Mo, 0.5%W, 0.25%V, in weight percent) was the chosen candidate in the US fast reactor program. 2.25Cr-1Mo and modified 9Cr-1Mo steels were also studied as structural materials for the steam generator of the Clinch River Breeder Reactor (CRBR) [2].

¹ The compositions are given in weight percentage terms in this chapter (unless stated otherwise) because most industrial alloys are referred to in weight percentage terms in original references. Elsewhere in this thesis, the compositions are given in atomic percentage terms (unless stated otherwise).

In the field of fusion reactors, since large amounts of data had been collected on this steel during the 1970s, Sandvik HT9 was the first ferritic/martensitic steel used in the US Fusion Materials Program and it was used as the structural material for the first wall and blanket structures of experimental fusion reactors [3, 4]. In the mid-80s, the concept of low-activation materials was introduced into the international fusion program [5-7]. The object was to develop materials which would either not activate during neutron irradiation or only develop low-level radioactivity that would decay quickly, to improve safety of operation and allow hands-on maintenance of the reactors built using this kind of materials. Between the mid-1980s and early 1990s, reduced-activation ferritic/martensitic steels were developed in fusion reactor materials research programs in Japan, US and Europe. Based on nuclear calculations, the alloying elements Mo, Nb, Ni, Cr and N in a typical steel need to be minimized and the replacement of molybdenum by tungsten and/or vanadium, and niobium by tantalum in conventional Cr-Mo steels is necessary for the development of reduced-activation ferritic/martensitic steels [8, 9]. Since it was difficult to eliminate the formation of δ -ferrite, that would lower toughness and consequently cause embrittlement [10], in 12%Cr steel without increasing carbon or manganese for austenite stabilization, 7-9%Cr steels were favored. Eventually, EUROFER [11] (consisting of 8.5%Cr, 1%W, 0.05%Mn, 0.25%V, 0.08%Ta, 0.05%N, 0.005%B, 0.1%C) was selected by the European program while the Japanese program settled on F82H [12] (consisting of 7.5%Cr, 2%W, 0.2%V, 0.04%Ta, 0.1%C, in weight percent); and the alloy with best properties in the US was the ORNL 9Cr-2WVTa [8] (consisting of 9%Cr, 2%W, 0.25%V, 0.07%Ta, 0.1%C).

More recently, the 9-12%Cr elevated-temperature steels have been introduced into the nuclear industry since the creep properties have been improved vastly and these steels are far superior to HT9. Since the designs of generation IV fission reactors will require higher operating conditions as discussed in section 1, elevated-temperature ferritic/martensitic steels which contain high-chromium (9-12%Cr) are the first choice for in-core and out-of-core applications.

2.1.2 Phase diagram

The Fe-Cr binary phase diagram generally used and published in handbooks is shown in Fig.2.1 [13].

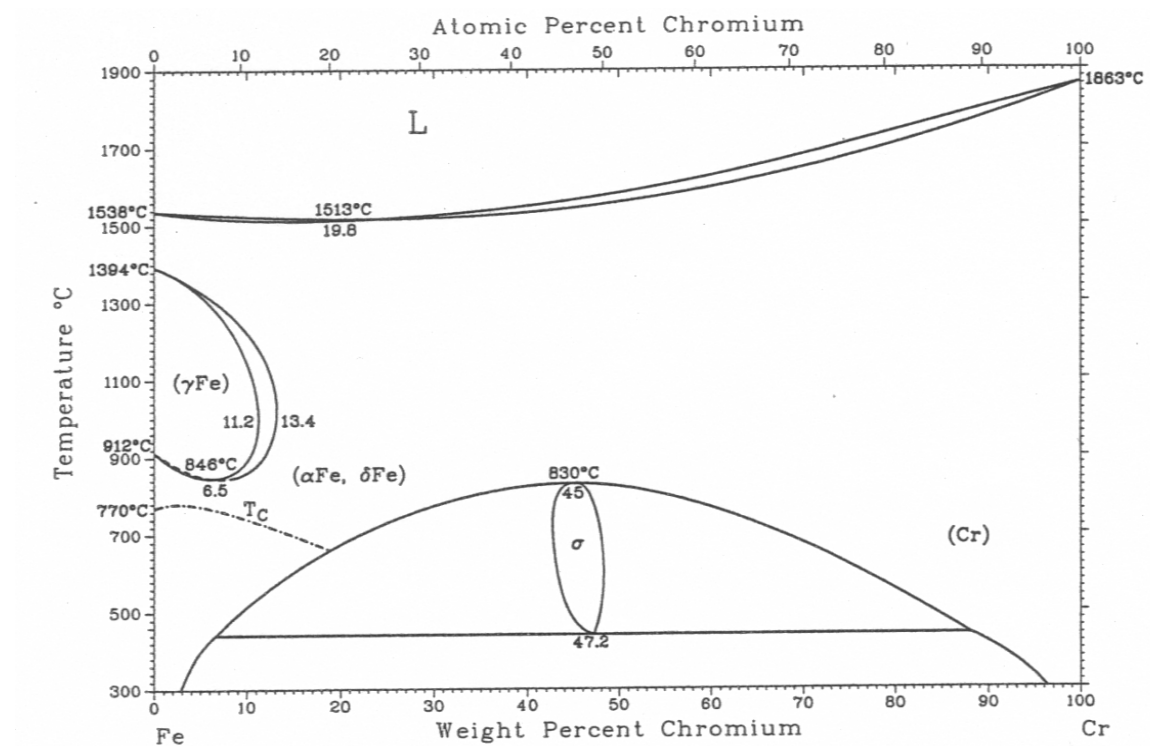


Fig.2.1 Fe-Cr binary phase diagram, from reference [13]

At low temperature, a large miscibility gap separates the Fe-rich α -phase and Cr-rich α' -phase which both have the body-centre cubic structure. The low temperature α - α' phase boundary is an extrapolation from the high temperature data but not based on actual experimental results. It is in conflict with many observations and is under re-determination by various researchers. Details will be discussed in section 2.3. A fairly complex σ -phase (containing 30 atoms in a unit cell) occurs at temperatures between 500°C and 830°C with a Cr concentration around 47.2%. However, Babakr et al. discovered that σ -phase was prone to form along grain boundaries in 18-

25%Cr alloy during prolonged exposures above 650°C [14]. A face-centre cubic γ -phase (γ -loop) forms at temperatures above 846°C for Cr concentrations below 13.4%. When the Cr concentration is beyond 13.4%, the microstructure of the alloy is α -phase (with α' -phase) from the freezing range to low temperature without forming γ -phase and the produces ferritic steel. The microstructure of the steady-state austenitic steel is mainly γ -phase with smaller amounts of α -phase and carbides. In order to produce the martensitic phase, the steel must have been in the form of austenite previously. Only steels with compositions which produce austenite at some stage during cooling will have the possibility of becoming martensite on further cooling.

2.2 Radiation Induced Segregation/Depletion

2.2.1 Introduction

Interactions between solute atoms and point defects (vacancies and interstitials) can cause coupled transport of solute atoms by point defect fluxes under irradiation conditions, which gives rise to the non-equilibrium phenomenon of radiation-induced segregation [15], that was first postulated by Anthony [16] and observed by Weidersich and Okamoto [17]. Since the 1970s, a great deal of experimental and theoretical research has been directed towards a basic understanding of this non-equilibrium phenomenon. The segregation of alloying elements towards or away from dislocations, grain boundaries and other types of defects has become a commonly observed effect in a wide range of alloys after irradiation. Solute segregation not only influences surface-composition-sensitive phenomena such as corrosion, and preferential sputtering, but also affects several bulk properties such as void swelling and phase instabilities [18]. This phenomenon is affected by temperature, irradiation dose rate, and pre-existing precipitation, as well as by grain boundary orientation and the presence of impurities. The importance of radiation-induced segregation is that the reduction of Cr concentration at grain boundaries is believed to increase the likelihood of cracking and to influence fracture of components by the mechanism of irradiation-assisted stress corrosion cracking [19, 20]. Since iron-chromium alloys are favoured as structural materials for fusion reactors, the technological impact of solute segregation effects and other radiation-induced properties should be of serious concern [21].

Anthony [16] has investigated the role played by the vacancy flux in producing solute depletion or solute enrichment in vacancy sinks or vacancy sources during heating, cooling, sintering or irradiation of a material. Whether the solute atoms deplete from, or segregate to, the vacancy sink is determined by the binding energy between a vacancy and a solute atom. In a binary system, for a dilute ($< \sim 1$ at% solute [15]) solution of B in A, when the binding energy between B and a vacancy is the order of the thermal energy,

$$|\Delta E/RT| < 1 \quad (2-1)$$

The steady-state can be achieved when:

$$\frac{\partial \ln C_B}{\partial x} = \frac{\partial \ln C_v}{\partial x} \frac{D_B - D_A}{D_B} \quad (2-2)$$

Where D_A and D_B are the diffusivities of A and B, C_B and C_v are the mole fraction concentrations of B and vacancies. Therefore in the case of a weak binding energy between a vacancy and a solute atom, the solute gradient in the steady-state is generated by the reverse atom flow caused by vacancy flow and the diffusivities of the solute and solvent atoms. When the diffusivity of solute B exceeds that of solvent A, a solute gradient will form in the same direction as the vacancy gradient and correspondingly lead to solute depletion of the vacancy sink. On the other hand, solute enrichment in the vacancy sink will form when the solute diffusivity is less than the solvent diffusivity [16].

In contrast to the case above, when the binding energy between a vacancy and a solute atom is much greater than the thermal energy kT , the solute atom and vacancy can form solute-vacancy pairs in which the solute atom is firmly bound to the vacancy and may be dragged to a vacancy sink. In the steady-state:

$$\nabla C_B = - \left(\frac{C_B - C_P}{C_V - C_P} \right) \nabla C_P \quad (2 - 3)$$

Where the C_B , C_P and C_V are the mole fraction concentrations of solute B, solute-vacancy pairs and vacancies. Since $C_B > C_P$ and $C_V > C_P$, the solute gradient is always the opposite to the solute-vacancy pair gradient and therefore produces solute enrichment at the vacancy sink.

Johnson and Lam [18] designed a kinetic model to investigate the conditions that may give rise to solute segregation to a sink under irradiation, including solute transport via free defect fluxes as well as via the migration of vacancy-solute and interstitial-solute complexes [21]. The calculation showed that if an appreciable binding between self-interstitials and solute atoms exists, solute segregation should be expected under appropriate irradiation conditions when the migration energies of the vacancy and interstitial-solute complex become comparable.

Okamoto and Rehn [21] summarized theoretical models which link solute segregation in irradiated alloys to the formation of mobile defect-solute complexes and/or the inverse Kirkendall effect resulting from differences in the diffusion rates of free solvent and solute atoms when migrating via an interstitial or vacancy mechanism.

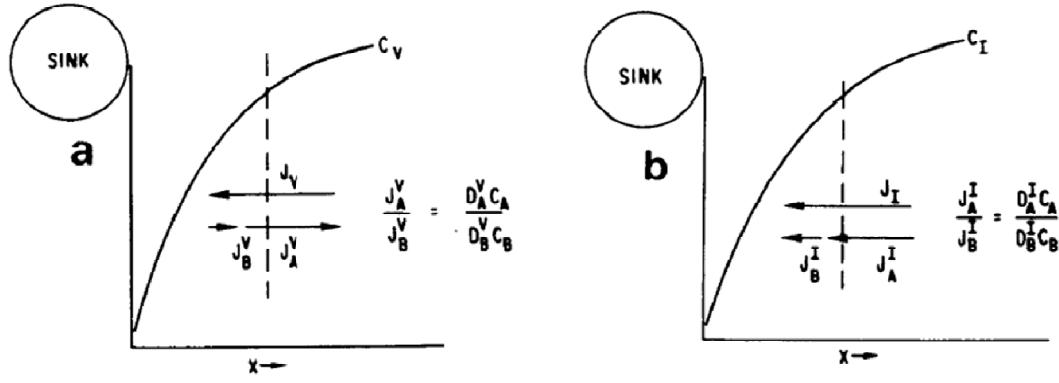


Fig.2.2 Schematic illustration of the inverse Kirkendall effect induced by (a) vacancy flux, (b) interstitial flux, from reference [21]

When the components of an alloy diffuse via vacancies at different rates, a net flux of vacancies can be induced by a composition gradient across a “marked” plane even though the distribution of vacancies is initially uniform. This phenomenon is well known as the Kirkendall effect. However, during irradiation, an inverse Kirkendall effect can happen near sinks where a gradient of vacancies or interstitials can induce a net flux of solute and solvent atoms across a “marked” plane in an initially homogeneous alloy, as illustrated in Fig.2.2 [21]. Fig. 2.2 (a) shows the case of a vacancy gradient near a sink in a binary alloy composed of elements A and B, where J_V , J_A^V and J_B^V are the fluxes of vacancies, element A and element B respectively. The vacancy flux towards the sink induces an atom flux of A and B ($J_A + J_B$) of equal magnitude in the opposite direction. The atom flux transports A and B atoms in amounts proportional to their local atomic fraction and diffusion coefficients, C_A , C_B , D_A^V and D_B^V respectively. If $D_A^V \neq D_B^V$, the atom flux of the faster diffusing component away from the sink will be proportionately greater than its concentration in alloy. Therefore, the vacancy flux will always cause the depletion of the faster diffusing component at the sink, as described earlier.

The inverse Kirkendall effect can also be induced by an interstitial gradient as illustrated in Fig.2.2 (b), where J_I , J_A^I , J_B^I , D_A^I and D_B^I are the fluxes of interstitials, element A and element B, and the diffusion coefficients of A and B by interstitial mechanisms respectively. Because the interstitial flux and the atom fluxes move in the same direction, when $D_A^I \neq D_B^I$, preferential transport of the faster diffusing component toward the sink will result from the different interstitial diffusion coefficients of the A and B. Therefore, the two inverse Kirkendall effects caused by vacancy and interstitial fluxes may aid or oppose each other in causing solute depletion or enrichment at a sink [21].

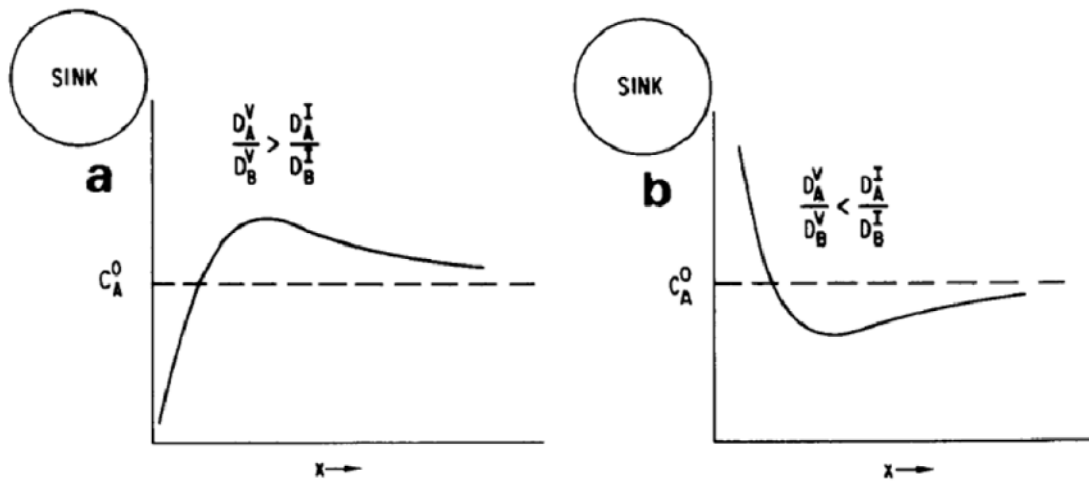


Fig.2.3 Effect of partial diffusion coefficients on the depth distribution of A atoms, from reference [21]

Wiedersich et al. [17] derived the following equation relating the concentration gradients of component A and vacancies in steady-state for a concentrated binary alloy:

$$\nabla C_A \propto \left(\frac{D_A^V}{D_B^V} - \frac{D_A^I}{D_B^I} \right) \nabla C_V \quad (2 - 4)$$

The two cases of interest predicted by equation 2-4 are illustrated in Fig.2.3. When $D_A^V/D_B^V > D_A^I/D_B^I$, component A depletes from the sink. Alternatively, enrichment of component A at the sink occurs when $D_A^V/D_B^V < D_A^I/D_B^I$. In addition, solute segregation to sinks can also occur when solute atoms interact with vacancies or interstitials to form mobile vacancy-solute or interstitial-solute complexes [21]. In general, the contribution of defect-solute complexes to the segregation depends on the magnitude of their binding energy and migration energy. This mechanism is considered to be especially important for undersize solutes (those which reduce the mean atomic volume of the alloy [22]) in dilute alloys since the undersize solutes bind interstitials much more strongly than oversize solutes in a mixed dumbbell configuration, leading to enrichment at the sink. In contrast, oversize solutes which exhibit weak binding with vacancies will drift away from the sink by a vacancy mechanism [15, 21].

Diffusion of defect-solute complexes can dominate at low temperature since the interactions between defects and solutes are less effective at high temperature. Meanwhile, inverse Kirkendall effects may dominate at high temperature [21]. In general, differences between the sizes of solute and solvent atoms are expected to result in enrichment of undersize solute atoms and depletion of oversize solute atoms near sinks during irradiation. However, accurate quantitative predictions of

the segregation behaviour of real alloys depends on precise knowledge of the defect-solute binding energies, and migration energies, migration mechanisms of defect-solute complexes, as well as the diffusivities of solutes via vacancy or interstitial mechanisms. In many cases, this information is not available [15].

In addition, the effect of irradiation on precipitation processes in alloys can generally be described in terms of two sets of phenomena: one is the modification of phases existing prior to irradiation, involving retardation or acceleration, changing spatial distribution and morphology [21]. The other is the formation of new non-equilibrium phases which are not expected after thermal treatment or appear out of the place on the known phase diagram. The second set of phenomena can be understood in terms of redistribution of alloying elements under irradiation caused by radiation-enhanced diffusion, displacement cascade mixing and radiation-induced segregation. It has been shown that the appearance of new phases can be simply explained as the result of radiation-induced segregation to sinks such as grain boundaries, dislocation and existing precipitation/matrix interfaces [15].

2.2.2 Research on austenitic steels

Many studies [20, 23-32] on radiation-induced segregation have been carried out on the austenitic Fe-Cr-Ni alloys and good correlation has been established with the theoretical models described above. STEM/TEM combined with energy-dispersive X-ray analysis (EDX) technique is a powerful method involving collecting spectra at discrete points across the grain boundary, which are used to build a 1D composition profile normal to the boundary plane. This technique provides information on the chemistry of the grain boundary and the width of segregation or depletion. The most accurate results can be obtained if (i) a field emission gun is used to provide enough intensity in small electron probes ($<1\text{nm}$), (ii) the sample is very thin and (iii) the grain boundary is positioned to be parallel to the beam. The width of the concentration profiles is often similar to the diameter of electron probe [33]. However, the radial distribution of current in the electron probe is complex. 80% of current is confined within a diameter of 1-2nm [31]. High-angle scattering of the electrons occurring in the specimen will further broaden the effective probe and complicate deconvolution of the real concentration profile. Furthermore, low-atomic-number elements such as B and C which are not easily detected by EDX, could form complexes with elements such as Cr and consequently affect segregation/depletion as well as the concentration profile obtained by EDX. Titchmarsh et al. [31] developed a Monte Carlo code to predict the dependence of STEM-EDX measurement of Cr concentration profile in irradiated stainless steel when RIS/RID are both present. Later, these authors [20, 34] applied a multivariate statistical analysis method to improve the quantification of EDX concentration measurement of alloying elements. This method was particularly useful due to the

possibility of separation of the information components when trying to detect small signals which may be obscured by artefacts or random noise. It could become a powerful tool for analysis of complex concentration profiles and lead to an improved understanding of RIS/RID mechanism. Auger spectroscopy is an alternative method, but it is difficult to detect and avoid the influence of grain-boundary precipitates in the analysis [20].

Nakata et al. [23] conducted EDS analysis of solute distributions in the vicinity of grain boundaries in Type 316L austenitic steel after irradiation, and discovered that undersized alloying elements such as nickel, silicon and phosphorus segregated toward the grain boundary while oversized chromium and molybdenum depleted from the grain boundary after electron beam irradiation up to about 30dpa at temperatures from 623 to 873K. One of the irradiation results is shown in Fig.2.4.

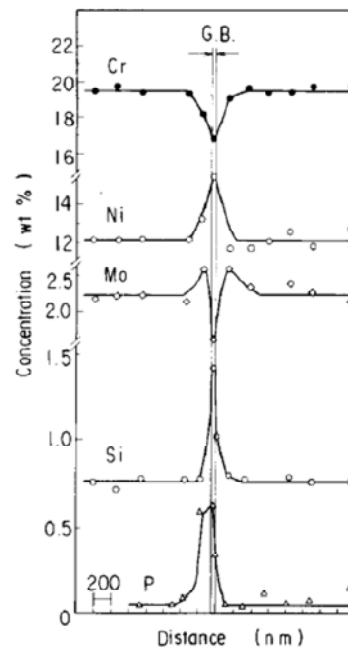


Fig.2.4 The solute distribution in the vicinity of a grain boundary in Type 316L austenitic steel irradiated to 30dpa at 723K, from reference [23]

Allen et al. [24] compared the grain boundary compositions measured by EDS in seven different austenitic Fe-Cr-Ni alloys (irradiated with 3.2MeV protons at temperatures from 200°C to 600°C and to doses from 0.1 to 3dpa) with the calculation results predicted by the inverse Kirkendall mechanism. They concluded that radiation-induced segregation in this alloy is mainly driven by the interaction of solute atoms with the vacancy flux and can be explained by the inverse Kirkendall mechanism.

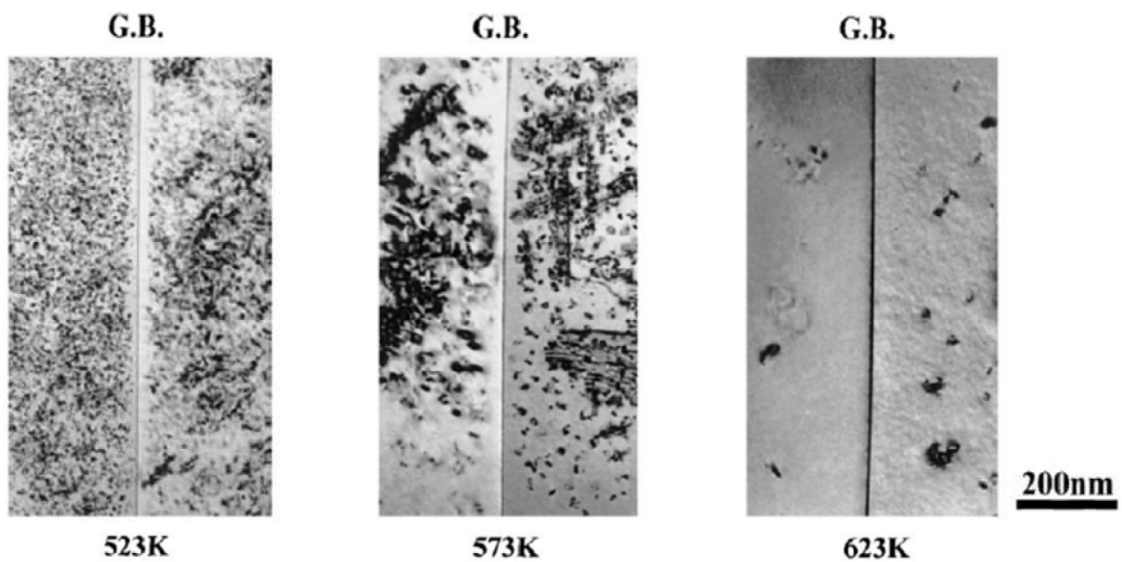


Fig.2.5 Dislocation free zone formation at a grain boundary in Fe-15Cr-20Ni alloy at different temperature with 0.6dpa, from reference [27]

Watanabe et al. [27] discovered radiation-induced segregation and heterogeneous microstructures which involved dislocation free zone formation in the vicinity of grain boundaries under irradiation in a typical austenitic Fe-15Cr-20Ni (irradiated with 1MeV electrons at 523-623K with 1.0-10dpa), as shown in Fig.2.5. The authors explained that the supersaturated point defects introduced during irradiation, such as vacancies and interstitials, diffuse to grain boundary sinks and dislocation free zones

form near the grain boundaries where there is no secondary defect formation. After the radiation-induced segregation reaches a steady state, secondary defects start to form inside the dislocation free zone and reduce its width. These authors also applied computer simulation to compare with the experimental results on austenitic steel in their other work [25, 28, 35] and found that the temperature dependence of radiation-induced segregation is quite weak, and the grain boundary misorientation should be considered as an important factor in affecting radiation-induced segregation.

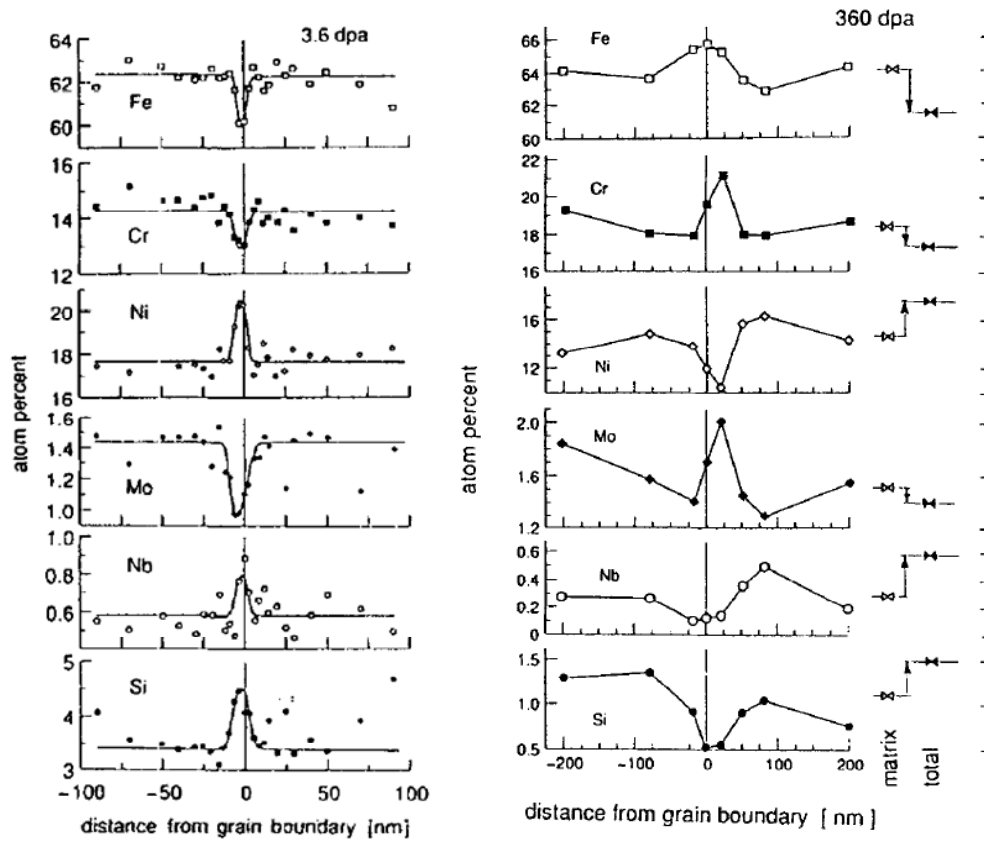


Fig.2.6 Concentration profile at grain boundaries irradiated at 600°C (a) 3.6dpa, (b) 360dpa, from reference [30]

However, some other researches show that the depletion of Cr from the grain boundary does not definitely happen in all cases. Kesternich et al. [30] reported the dose of irradiation has an effect on solute atoms depletion or segregation in the grain boundaries of austenitic steel (Nb-stabilized steel of type DIN 1.4981 irradiated by Ni^{++} ion at 600°C for 3.6 and 360dpa) and for the first time discovered the effective inversion of radiation-induced segregation. At low doses the commonly observed radiation-induced segregation behaviour was confirmed while at high doses the segregation behaviour at grain boundaries completely inverted as shown in Fig.2.6. It was proposed that the radiation-induced segregation inversion is due to formation and growth of radiation-induced precipitates which are rich in Ni, Si and poor in Cr content and therefore lead to Cr enrichment in the grain boundary.

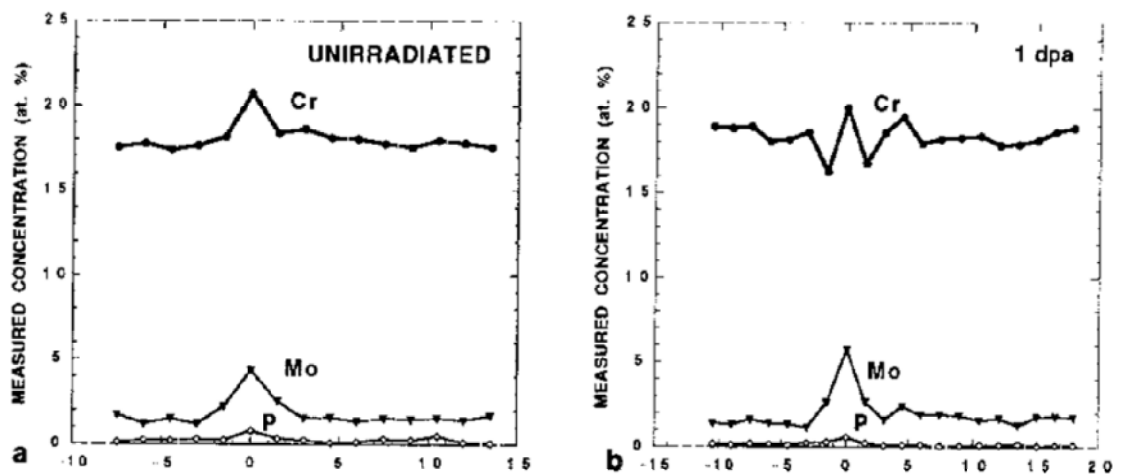


Fig.2.7 Composition profiles of Cr and Mo at grain boundaries in 304CP and 316CP steel (a) un-irradiated, (b) 1dpa, from reference [29]

Meanwhile, Kenik et al. [29] observed a “W-shape” Cr profile across grain boundaries in austenitic stainless steels (304CP and 316CP irradiated by 1dpa with protons at 360°C) by analytical electron microscopy as shown in Fig.2.7. The

authors believed this could be explained by the depletion resistance effect of other impurity elements such as B, C and P. Such pre-existing co-segregation of impurities may have a positive interaction with Cr and Mo and therefore provide a resistance to subsequent depletion of Cr and Mo from the grain boundary by radiation-induced segregation.

2.2.3 Research on ferritic/martensitic steels

In austenitic steels, radiation-induced depletion of Cr at grain boundaries seems to be the dominant process [20, 23-32], though there are some exceptions [29, 30]. However in ferritic/martensitic steels, both radiation-induced segregation and depletion of Cr in grain boundaries have been reported [36-47], which mechanism Cr is undergoing still needs to be clarified.

Lu et al. [36] compiled literature data [37-44, 46] showing both radiation-induced segregation and depletion of Cr in ferritic/martensitic steel irrespective of Cr content or means of irradiation. Neklyudov et al. [37] showed that Cr depleted at neutral sinks (mainly grain boundaries) in ferritic steel after irradiation, while the preferential sinks (dislocation loops) were enriched in Cr. The second result was in good agreement with the data in reference [45]. Little [15] also showed a “W-shape” concentration gradient for Cr on either side of a martensite lath boundary in FV448 steel irradiated to 46dpa at 465°C as shown in Fig.2.8.

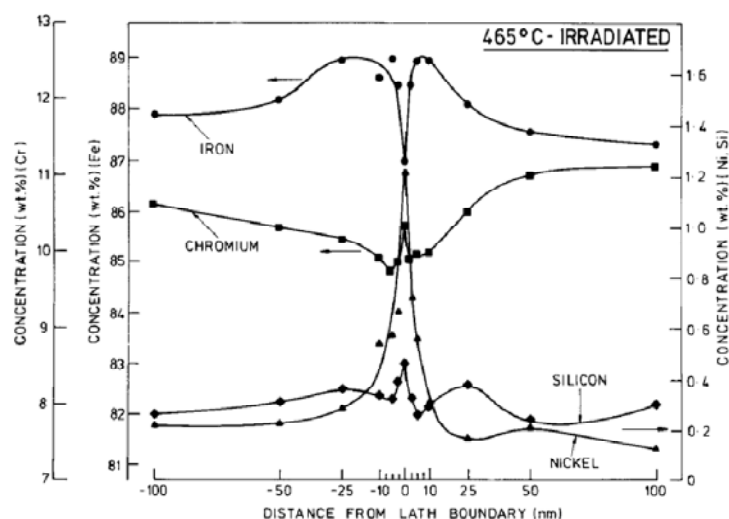


Fig.2.8 Concentration gradients on either side of a martensite lath boundary in FV448 steel irradiated to 46dpa at 465°C, from reference [15]

However, Kato et al. [41] investigated the solute distribution in the vicinity of grain boundaries in ferritic Fe-10Cr-xMn-3Al (x=5, 10 or 15) irradiated by electron to 10dpa at 723K, and discovered the concentration of Cr rose sharply at the boundary. They suggested that the enrichment of Cr at the grain boundary seemed to relate primarily to the formation of Cr-rich precipitates at the boundary. Allen et al. [47] conducted research on 12%Cr ferritic-martensitic steel and found that Cr was enriched at grain boundaries prior to irradiation, possibly due to grain boundary Cr carbides. This increased further during irradiation which the authors believed was at least partially caused by radiation-induced segregation.

Lu et al. [36] suggested an explanation for the discrepancies among these results. In austenitic steels for nuclear applications, the major elements are Cr and Ni. Since the atomic radius of Ni is smaller than Fe while that of Cr is slightly larger than Fe, generally, Cr is considered to be the oversized atom and radiation-induced depletion is observed in austenitic steels. But in the ferritic steels, the major elements are Cr and W, Nb, Mo, Ta, V and Ti which are all larger elements than Fe and Cr and may increase the average lattice constant. Furthermore, recent MD simulation [48] reveals that in the body-centred cubic Fe-Cr system, nearest neighbours may relax towards Cr atoms. All of these could result in changing Cr from an oversized atom to an undersized atom and alter the segregation/depletion behaviour under irradiation. Therefore whether Cr should to be regarded as an undersized or oversized atom depends on concentration and electronic/magnetic effects. Meanwhile, the coarsening or dissolving of pre-existing precipitation such as $M_{23}C_6$ and the formation of new phases clearly have an effect on the grain boundary microchemistry. The presence of these precipitates is believed to have an influence

on the radiation-induced segregation/depletion behaviour, however no coherent explanation can be deduced from current data.

Was et al. [49] conducted a series of experiments on three ferritic-martensitic alloys, T91 (Cr concentration 8.26%), HT9 (Cr concentration 12%) and HCM12A (Cr concentration 12%), which are all candidate cladding and structural alloys for generation IV fast reactors and future fusion reactors. These alloys were irradiated from 3 to 10dpa at both 400°C and 500°C with 2.0MeV protons. Both Cr segregation and depletion were observed as shown in Fig.2.9. A general tendency was that Cr enrichment occurred in the alloys with lower Cr content (T91) and at lower temperature whilst depletion occurred in higher Cr alloys (HT9 and HCM12A) and at higher irradiation temperature. The authors also applied a Kinetic Lattice Monte Carlo (KLMC) model to simulate the RIS behavior of Cr in BCC Fe-Cr alloy by a vacancy-mediated mechanism, and explained that though the experimental results were more complicated, the KLMC simulation showed that the modeling results were fully consistent with an inverse Kirkendall mechanism determined by the ratio of Cr to Fe diffusion.

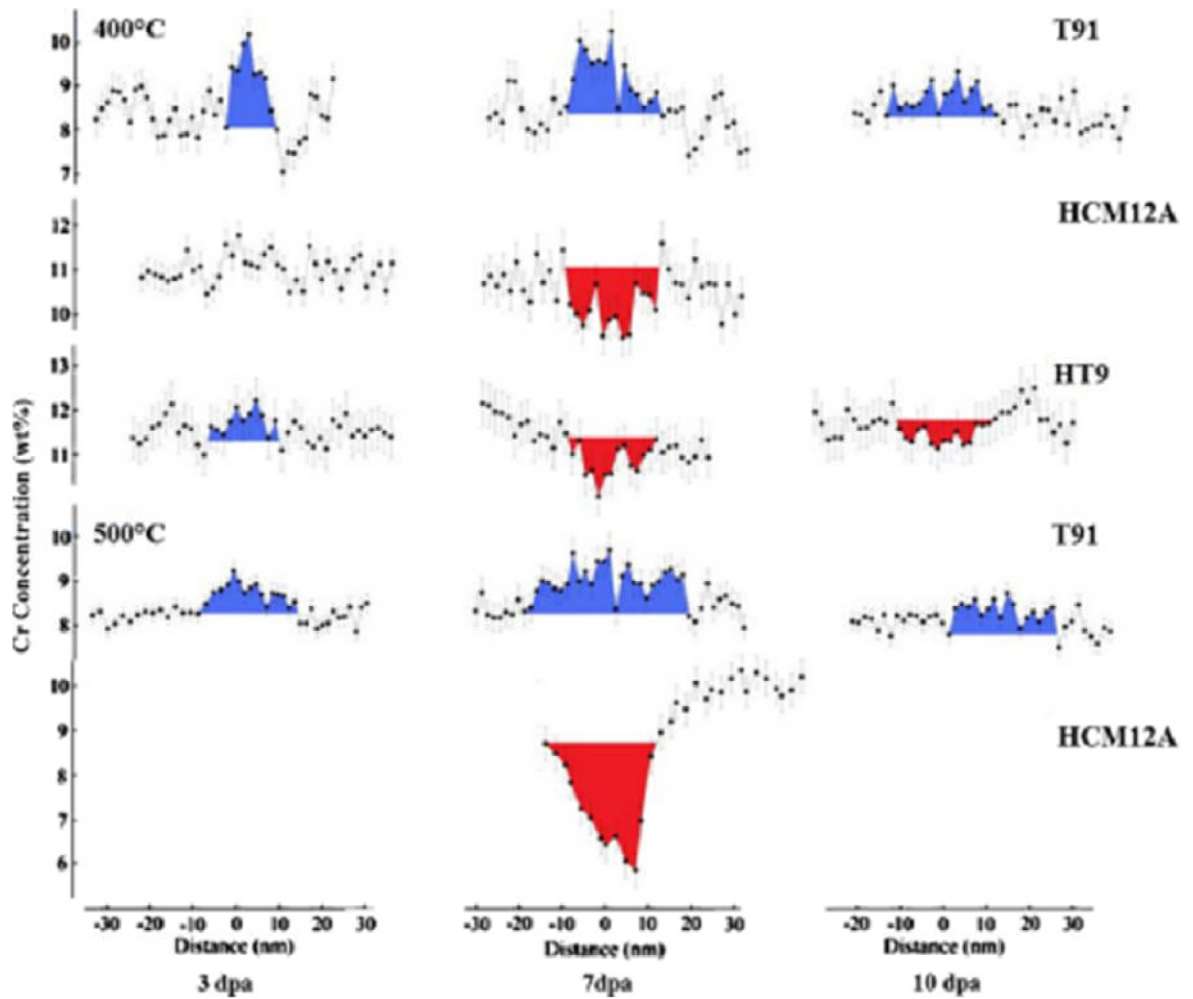


Fig.2.9 Dose, temperature and alloy dependence of grain boundary segregation of Cr following irradiation with 2MeV protons for T91, HCM12A and HT9 at 400°C and T91 and HCM12A at 500°C, from reference [49]

Jiao et al. [50] applied the atom probe technique to study the RIS at grain boundaries, precipitate/matrix interfaces and dislocations in these three ferritic-martensitic alloys, HCM12A, T91 and HT9. While Ni, Si and P were found to enrich at all grain boundaries in HCM12A irradiated by either proton irradiation to 7dpa at 400°C or Fe^{2+} irradiation to 100dpa at 500°C, both Cr segregation and depletion were observed at different grain boundaries. The enrichment of Cr was generally less than 1at% and the depletion was as high as 4at% in the Fe^{2+} irradiated alloy. The authors explained that the large variation of Cr concentration at grain

boundaries was not solely dependent on grain boundary type, but also on the inhomogeneous distribution of Cr carbides in the grain boundary and the formation of Cr-rich precipitates in the matrix. Cr enrichment at grain boundaries in proton-irradiated T91 was also observed. Furthermore, Cr was observed to enrich at dislocation lines in T91 but deplete at dislocation lines/loops in HCM12A. This was similar to the segregation/depletion behavior at grain boundaries in these two alloys. Cr enrichment at precipitate (Cr carbide)/matrix interfaces was also observed in both HCM12A and HT9 following irradiation to 7dpa at 400 °C. The authors suggested that all three types of sinks, dislocations, grain boundaries and precipitate/matrix interfaces should be taken into account when discussing RIS in ferritic-martensitic alloys.

The discrepancies among the results discussed above demonstrate that further research is needed to quantify the RIS/RID behavior of Cr and its controlling mechanism in ferritic-martensitic steels.

2.3 α - α' Phase Boundary at Low Temperature

2.3.1 Introduction

The ferritic/martensitic Fe-Cr alloys have the disadvantage of a phase separation which causes loss of ductility and corrosion resistance due to the precipitation of a Cr-rich phase (α' -phase). The phase separation happens at the nanometer scale and induces hardening of the binary solid solution [51]. For example, above 12% Cr, the alloys undergo hardening and embrittlement after thermal aging, which has been known for decades as “475°C embrittlement” and is related to the α - α' phase separation [52]. At present, Fe-9%Cr has been selected as optimum for nuclear applications due to its observed minimum ductile-to-brittle transition temperature shift after neutron irradiation [53]. However, in principle the optimum concentration choice should be determined by whether or not phase separation will occur at the operating temperature, which requires a precise knowledge of the α - α' phase boundary.

The Fe-rich part of the Fe-Cr phase diagram has been discussed in section 2.1.2. It essentially coincides with the CALPHAD formula proposed in 1987 [54]. The low temperature (<700K) solubility limit is an extrapolation but not based on actual experiment data made in this temperature range. However, theoretical calculations at 0K made in 1983 [55] have suggested that the interaction potential in the Fe-Cr system can change its sign when the Cr concentration varies. Also, Mirebeau et al. [56] using diffuse-neutron-scattering and resistivity measurements observed that partial short-range order of Cr (negative Cowley-Warren short-range order [57])

formed in alloys with <10% Cr at 700K. These findings obviously conflict with the low solubility limit in the standard phase diagram, suggesting much more detailed research is necessary to establish a new α - α' phase boundary at low temperature.

2.3.2 Current research on re-determination of the phase boundary

The current experimental data [51, 58-77] regarding ordering and α' precipitation formation have mainly been obtained by MR (Mössbauer spectroscopy), TEM (transmission electron microscopy) with EDS (energy dispersive spectroscopy), SANS (small angle neutron scattering) and APT (atom probe tomography). In addition to the obtained experimental results, various DFT-parameterized (density functional theory) cohesive models [78-81] have been used to predict the corresponding phase diagram, as discussed below.

Kuwano et al. [59] applied the MR technique to several different ferritic Fe-Cr alloys irradiated by 16MV protons, with Cr concentrations ranging from 4.7%-16.9%. Compositional changes were measured at room temperature after specimens were aged for 1h at various temperatures sequentially. Depletion of Cr in the matrix occurred in the alloys containing more than 7.4% Cr and was interpreted as α' phase precipitation formation, which was enhanced by the proton irradiation. The authors concluded that a Cr concentration of 7.4% Cr alloy was outside the miscibility gap at 748K while a Cr concentration of 9.3% Cr was inside the miscibility gap at 673K and 748K. It was obvious that the precipitation of α' phase was accelerated during the annealing of the irradiated alloys and irradiation enhanced precipitation at temperatures where phase separation would not be expected in the absence of irradiation. Meanwhile, enrichment of Cr was found in the 4.7% Cr alloy and might be explained by the mechanism of radiation induced segregation which is discussed in section 2.2.

Konobeev et al. [60] used TEM to observe various Fe-Cr binary alloys in both annealed and heavily cold worked conditions after irradiation to 25.8dpa at 400°C.

Formation of α' phase was discovered in the Fe-12%Cr and Fe-18%Cr alloys as well as a precipitation-free zone of less than 150nm in width along grain boundaries. The mean precipitate diameter in annealed samples was approximately identical at ~14nm while slightly smaller precipitates (~10nm) were found in cold-worked alloys. This result indicated that the Cr concentrations of the 12% and 18% Cr alloys were inside the miscibility gap at 673K. However, it is difficult to use TEM to detect and study α - α' phase separation because the electron scattering contrast between Fe and Cr is quite weak [62]. For example, the total volume fraction of α' phase deduced from TEM in F17 steel (containing 17% Cr and thermally aged at 450°C [61]) was probably underestimated to be of the order of 0.5%. A value between 5%-10% is expected from the phase diagram and confirmed by recent SANS experiments [63]. Furthermore, the ferromagnetic character of the matrix and the high density of interfaces also limit the possibility of fine structural analysis by TEM [62].

The SANS technique is a much more powerful tools than TEM in some specific cases for the study of nanoscale precipitation in ferritic/martensitic steels, for example to detect very small particles (<5nm) or to characterize the mean size, shape and number density of particles, due to a more favorable contrast between matrix and precipitates. In addition, SANS can examine a much larger volume of materials than TEM. Mathon et al. [62] studied α - α' phase separation in several martensitic steels with Cr contents ranging from 7 to 12% after neutron irradiation (0.7-2.9dpa between 250 and 400°C) employing the SANS technique. Precipitation of α' phase was found on the nanometer scale under irradiation at temperatures as low as 250°C when the Cr concentration was $\geq 8\text{at}\%$. The Cr threshold concentration for α - α' phase un-mixing was estimated to be 7.2at%Cr at 325°C and 8.3at% Cr at

400°C. The volume fraction of α' phase increased with Cr concentration and the irradiation dose, and as the irradiation temperature was lowered. The authors also investigated the influence of impurities on α - α' phase separation and discovered that Mo (and perhaps Ni) could induce an unidentified secondary precipitation and/or play a role in the phase separation while the effect of Ta and W was negligible. It was found that the precipitation of α' phase in the Cr-rich steel contributed significantly to the irradiation-induced hardening.

Compiling the data discussed above [56, 59-62] and more results from Ref. [65-77], Bonny et al. [64] drew a new phase boundary, comparing it with the conventional Fe-Cr phase diagram as shown in Fig.2.10. The data selection was restricted to the region of 5-15% Cr and 300-900K so that the issue regarding sigma phase and spinodal decomposition could be excluded, as well as the body-centre cubic to face-centre cubic transformation.

The determined steep phase boundary at low temperature is mainly supported by experiments involving irradiation, which may produce non-equilibrium states. Therefore, it is possible that α' phase precipitates could have been induced by irradiation and preferentially nucleate at irradiation-induced defects. However, TEM observations [60, 61, 65, 69, 73, 75, 77] confirmed that the fine α' phase precipitates were dispersed in the bulk and did not attach to radiation defects such as dislocation loops or voids; furthermore, precipitation was equally detected under electron, proton and neutron irradiation, showing insensitivity to the source or damage dose. Thus, α' phase precipitation under irradiation is probably simply due to radiation-enhanced diffusion and phase separation is accelerated by irradiation [64]. In these

conditions, the position of the phase boundary is therefore not expected to be affected by irradiation.

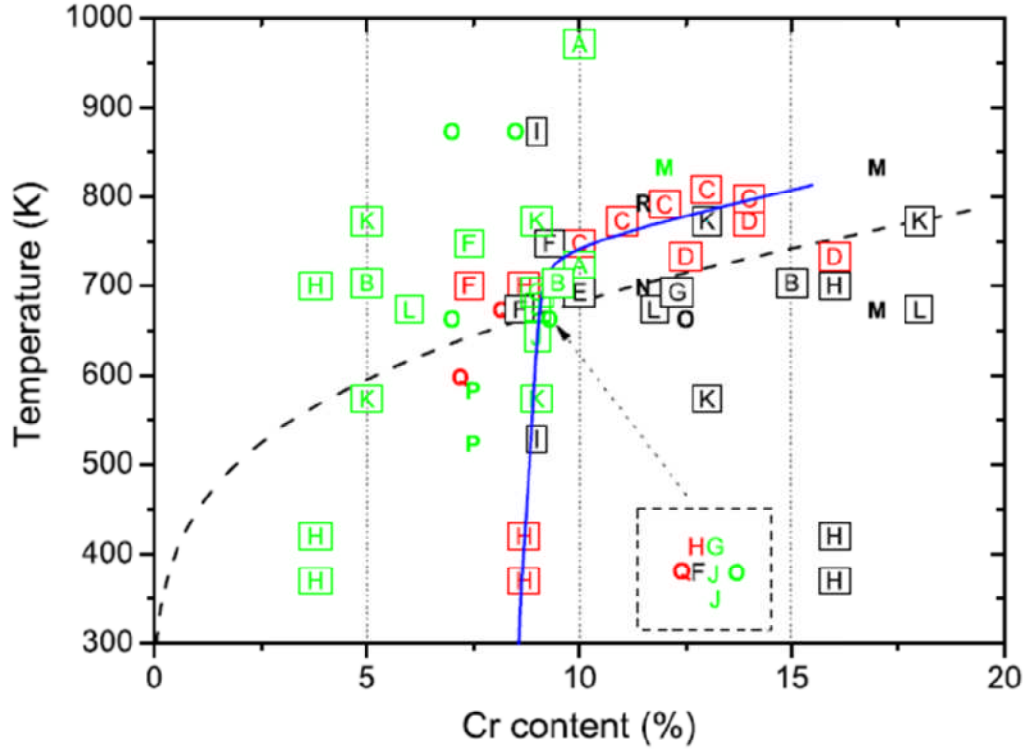


Fig.2.10 Conventional Fe-Cr phase diagram (dashed line) and experimental points related to Cr ordering (in green), precipitation (in black) and suggested phase boundary (in red). The solid line represents the phase boundary based on the given experimental data. Symbols and related reference: A [65], B [56], C [66], D [67], E [68], F [59], G [69], H [70], I [71], J [72], K [73], L [60], M [61], N [74], O [75], P [76], Q [62], R [77], from reference [64].

Density functional theory provides a physical explanation for the observed ordering and precipitation phenomena, in terms of the electron-band and magnetic properties of Fe and Cr [82, 83]. When an isolated Cr atom is present in Fe, it lowers the density of states at the Fermi level, providing a negative heat of formation [83]. On the other hand, BCC Fe is ferromagnetic while BCC Cr can be considered as anti-ferromagnetic in its ground state [84, 85]. Therefore, a Cr atom in Fe has an anti-

parallel magnetic moment to those of the surrounding Fe atoms [82, 85]. If a second Cr atom is introduced nearby, the most energetically favorable situation occurs when Cr atoms distribute as far as possible from each other. By increasing the Cr concentration, Cr-Cr interaction cannot be avoided, leading to a positive heat of mixing and α' phase precipitation becomes favorable.

The recent development of DFT has made it possible to perform calculations of the energy of clusters containing several hundreds of atoms and enables the accurate comparison of enthalpies of formation of disordered atomic configurations [78]. Although there are some quantitative differences between different DFT approximations, the results are qualitatively similar and in agreement with current experimental data as discussed above. For example, Caro et al. [86] carried out *ab initio* calculations of formation energies for the Fe-Cr systems by making an approximation that consisted of creating a classic potential which was developed by the same authors [79] based on the reported Fe and Cr potential [87, 88], that reproduced the energetic and several other quantities, and with it the author calculated free energies with no further approximation. The authors calculated the phase diagram at low temperature of the Fe-rich corner by this approximation combining with thermodynamic integration techniques. These authors propose a solubility limit above $\sim 700\text{K}$ which is much less than the value in SSOL (Scientific Group Thermodata Europe Solution Database) [89] and below $\sim 700\text{K}$ a value which is much higher.

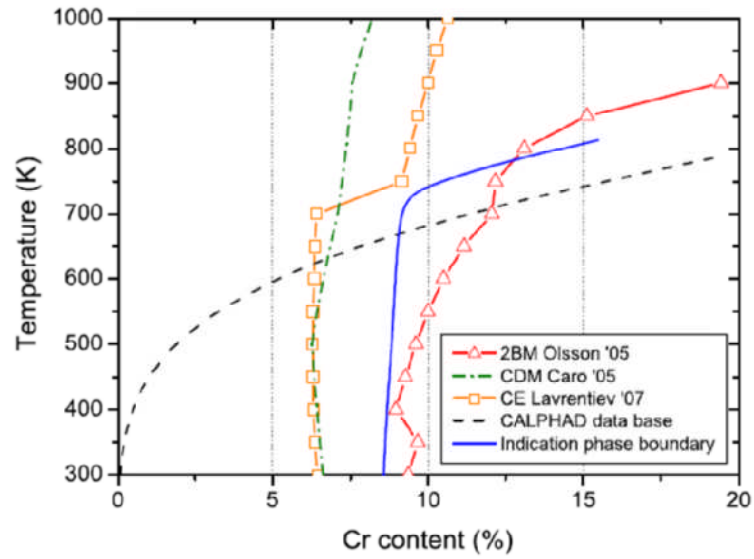


Fig.2.11 Phase boundary according to cohesive models for Fe-Cr, compared with the CALPHAD [54] phase boundary and the phase boundary deduced in Fig.2.10. Symbols: 2BM [80, 81], CDM [79], CE [78], from reference [64].

Bonny et al. [64] compiled three cohesive DFT models to re-determine the phase boundary at low temperature. These are: the interatomic potential model which is an extension of the embedded atom method, developed by Caro et al. [79, 86] and Olsson et al. [80, 81] separately; and the cluster expansion developed by Lavrentiev et al. [78]. The phase boundary predicted by each model is shown in Fig.2.11. The steep behavior of the Fe-rich solubility limit obtained from these cohesive models is considered to be the direct consequence of the negative heat of mixing. Although the actual position of the phase boundary depends on the model used, all of the models predict a similar steepness of the solubility limit at low temperature (<700K).

To conclude, the steepness of the phase boundary has been predicted by all the models and has also been observed experimentally. It is believed that the experiments involving irradiation only accelerate α - α' phase separation or partial ordering of Cr. The combination of DFT model calculation and experimental results

clearly suggests a much larger solubility limit of Cr in the Fe-rich corner than predicted by the conventional Fe-Cr phase diagram found in handbooks [13]. Therefore, the introduction of an appropriate correction to the currently accepted Fe-Cr phase diagram is necessary.

2.3.3 APT Study of α' phase

There have been many studies of microstructure evolution during α - α' phase separation using SANS and MS, but it was not until the 1980s that real space images were obtained using Atom Probe Field-Ion Microscopy (APFIM). Initial work by Brenner et al. [90] was carried out on Fe-32%Cr aged at 470°C up to 11,000h, and the aim was to show evidence of the early stage of the phase separation occurring within the miscibility gap. The FIM images in Fig.2.12 show that the dark regions increased in size as aging time proceeded and had an unusual morphology: they consisted of thin, irregularly shaped veins threading across the bulk of the material. These veins formed a continuous network on the imaging surface and within the depth of the material. APT analysis showed that these dark regions were Cr-rich, containing up to 80-90%Cr. The phase separation began after aging for 50h and the veined structure still persisted in the longest aged samples (11,000h). This was the first work to report APT experimental evidence of spinodal decomposition within the miscibility gap in Fe-Cr binary alloys [91].

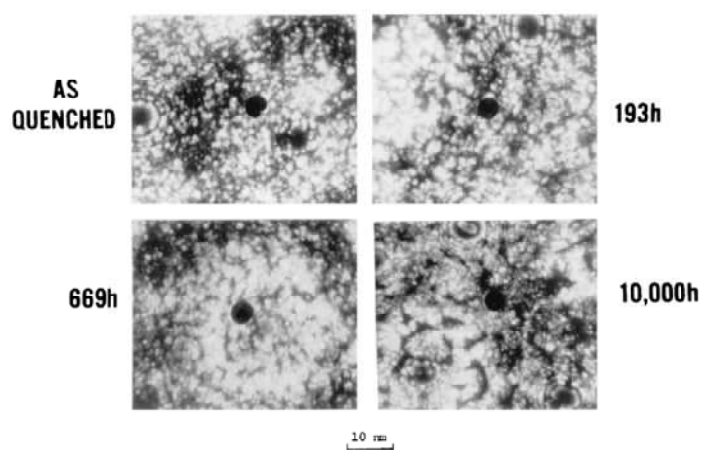


Fig.2.12 FIM images of decomposition in Fe-32%Cr aged at 470°C, from reference [90]

Later on, the most important studies were made by Miller et al. and Hyde et al [92-94] within the framework of a large project combining Monte Carlo simulation and 3DAP reconstruction results for direct comparison. These authors studied alloys containing 17%-45%Cr during aging at 500°C. FIM observation revealed that the decomposition scale increased as a function of aging time in the Fe-45%Cr alloy. Furthermore, the volume fraction of α' phase increased as the content of Cr increased and the morphology transformed from approximately spherical particles to a fully interconnected structure. Isosurface reconstruction using PoSAP (Position Sensitive Atom Probe) analysis showed that while α' phase formed some interconnected regions and some isolated particles in Fe-24%Cr alloy, it only formed percolation structures in the Fe-32%Cr and Fe-45%Cr alloys, as shown in Fig.2.13. Such results indicated that the spinodal mechanism was achieved in these cases and whether or not the structures were connected depended on the relative volume fractions of the two phases. Moreover, this work focused on the determination of evolution of α and α' domain size, composition and their interface. Monte Carlo simulation accurately matched the 3DAP experimental data and gave predictions of the observed kinetics of phase separation. This work is a good example of the advantage of APT in examining the 3D composition variation on a sub-nano scale.

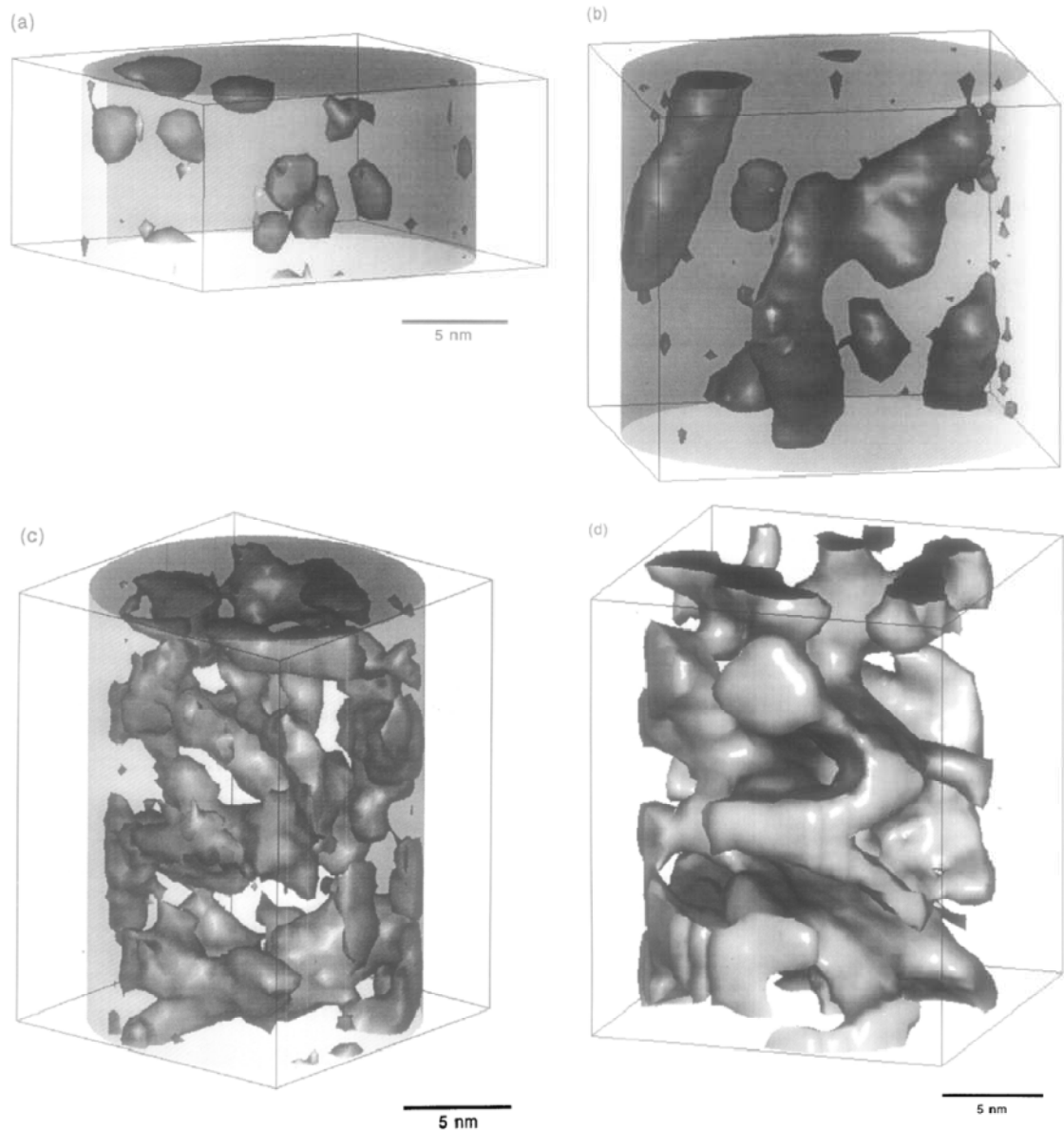


Fig.2.13 Isosurface reconstructions from PoSAP analyses showing the morphology evolution of the Cr-rich regions as a function of Cr content after aging for 500h at 500 °C, (a) Fe-17%Cr (isosurface at 20%Cr), (b) Fe-24%Cr (isosurface at 30%Cr), (c) Fe-32%Cr (isosurface at 30%Cr) and (d) Fe-45%Cr (isosurface at 40%Cr), from reference [92]

As the development of APT technology has proceeded, it has become possible to observe the very early stage of the phase separation or just the formation of clusters even before the nucleation of a discrete second phase takes place. Novy et al. [95]

studied the phase separation in a Fe-20at%Cr alloy thermally aged at 500°C. The mean radius of α' precipitates increased as a function of aging time, from $0.95\pm0.31\text{nm}$ (aged after 50h) to $2.53\pm0.51\text{nm}$ (aged after 1067h), which represented a non-classical nucleation mechanism. The composition of precipitates evolved temporally from $60.6\pm0.9\text{at}\%\text{Cr}$ after 50h up to $83\pm1\text{at}\%\text{Cr}$ after 1067h and in good agreement with the α' phase concentration determined by Kuwano et al. [66] (85at%) and Dubiel et al. [67] ($88\pm1\text{at}\%$). A transient coarsening region of α' phase was also observed due to the overlap of the nucleation, growth and coarsening regimes.

α' phase is also expected to form under the condition of irradiation due to radiation-enhanced diffusion and phase separation accelerated by irradiation [64], which is confirmed by TEM observation [60, 61, 65, 69, 73, 75, 77]. Kuksenko et al. [96] studied a Fe-12at%Cr alloy which was neutron irradiated at 300°C up to a dpa level of 0.6, and used a threshold of $X_{\text{Cr}} > 28\text{at}\%$ in order to detect α' clusters and to avoid artificial segregation appearing in a random Fe-12%Cr alloy. The authors discovered two different types of clusters, Cr-rich clusters and Ni-Si-P-Cr-rich clusters as shown in Fig.2.14, and concluded that the formation of these two types of clusters were driven by different mechanisms, enhanced precipitation and induced precipitation respectively. As driven by enhanced precipitation, the Cr-rich clusters were found to be distributed uniformly inside grains and had no correlation with dislocation loops. The mean radius of Cr-rich clusters was determined to be $1.1\pm0.2\text{nm}$ while the average concentration in the core reached $58.5\pm1.1\text{at}\%\text{Cr}$. Meanwhile, the Ni-Si-P-Cr-rich clusters were found to be distributed homogeneously in the matrix and to be independent of Cr-rich clusters.

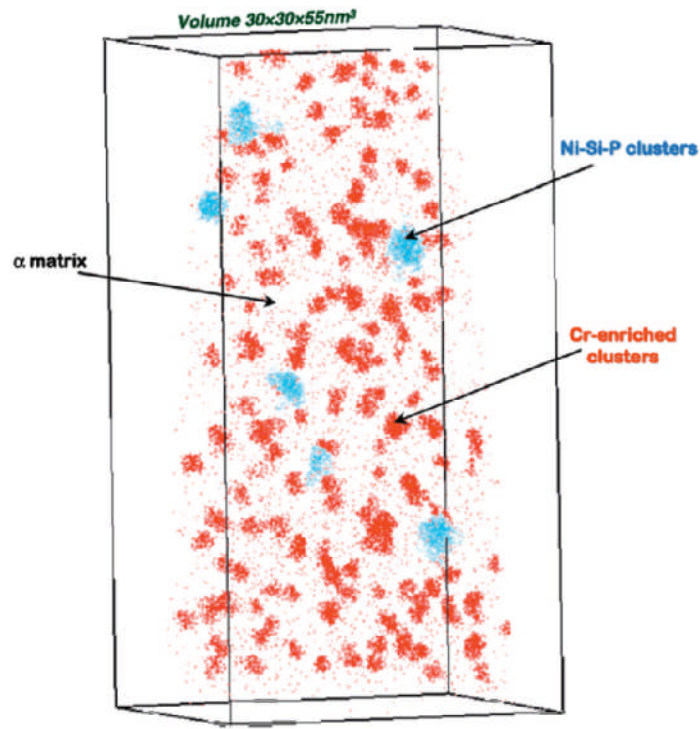


Fig.2.14 3D reconstruction of Cr, Ni, P and Si atoms in Fe-12at%Cr after neutron irradiation at 300 °C up to 0.6dpa. Red areas represent Cr-rich clusters, in which the local Cr concentration is higher than 28at%, from reference [96].

Previous research shows that APT is very efficient in the study of ultrafine scale microstructure evolution. While the TEM technique is limited in characterizing the fine scale of α and α' phase due to the high coherency of these two phases [91] and the weak electron scattering contrast between Fe and Cr [62], APT has proved to be a very well-suited technique to study phase separation in Fe-Cr binary alloy. With its lateral resolution smaller than the extent of the individual phase regions, it can provide high quality information on microstructure and chemical composition analysis of α' phase in three dimensional form.

2.4 Conclusion

The iron-chromium alloy system has attracted a huge amount of attention for its great potential in the nuclear industry. The 9-12%Cr steels are considered to be especially important for the design of the next generation of fission and fusion reactors. Fundamental research is necessary to obtain precise knowledge for actual application in industry. The understanding of the basic Fe-Cr binary system is the first step before considering any more complex systems. The phenomena discussed in this chapter are very important and affect both the microstructure and properties of the alloy system under irradiation conditions in nuclear reactors, and more work is necessary to clarify these crucial topics.

References

1. Glasstone, S. and A. Sesonske, *Nuclear Reactor Engineering*. Third ed 1981, New York: Van Nostrand Reinhold Company.
2. Klueh, R.L. and A.T. Nelson, *Journal of Nuclear Materials*, 2007. **371**: p. 37-52.
3. Klueh, R.L. and D.R. Harries, *High-chromium Ferritic and Martensitic Steels for Nuclear Applications* 2001, West Conshohocken, PA: American Society for Testing and Materials.
4. Rosenwasser, S.N., P. Miller, J.A. Dalessandro, J.M. Rawls, W.E. Toffolo, and W. Chen, *Journal of Nuclear Materials*, 1979. **85-6**: p. 177-182.
5. Butterworth, G.J. and O.N. Jarvis, *Journal of Nuclear Materials*, 1984. **123**: p. 982-988.
6. Tamura, M., H. Hayakawa, M. Tanimura, A. Hishinuma, and T. Kondo, *Journal of Nuclear Materials*, 1986. **141**: p. 1067-1073.
7. Klueh, R.L., D.S. Gelles, and T.A. Lechtenberg, *Journal of Nuclear Materials*, 1986. **141**: p. 1081-1087.
8. Klueh, R.L. and E.E. Bloom, *Nuclear Engineering and Design-Fusion*, 1985. **2**: p. 383-389.
9. Dulieu, D., K.W. Tupholme, and G.J. Butterworth, *Journal of Nuclear Materials*, 1986. **141**: p. 1097-1101.
10. Gelles, D.S., *Reduced Activation Materials for Fusion Reactors*, in *ASTM STP 1047*, R.L. Klueh, et al., Editors. 1990, American Society for Testing and Materials: Philadelphia.

11. Ehrlich, K., S. Kelzenberg, H.D. Rohrig, L. Schafer, and M. Schirra, *Journal of Nuclear Materials*, 1994. **212**: p. 678-683.
12. Tamura, M., H. Hayakawa, A. Yoshitake, A. Hishinuma, and T. Kondo, *Journal of Nuclear Materials*, 1988. **155**: p. 620-625.
13. Okamoto, H., P.R. Subramanian, and L. Kacprzak, eds. *Binary Alloy Phase Diagrams (Second Edition)*. ed. T.B. Massalski. Vol. 2. 1990, ASM International, Materials Park: Ohio.
14. Babakr, A.M., A. Al-Ahmari, K. Al-Jumayiah, and F. Habiby, *Journal of Minerals & Materials Characterization & Engineering*, 2008. **7**: p. 127-145.
15. Little, E.A., *Journal of Nuclear Materials*, 1993. **206**: p. 324-334.
16. Anthony, T.R., *Acta Metallurgica*, 1969. **17**: p. 603-&.
17. Wiedersich, H., P.R. Okamoto, and N.Q. Lam, *Journal of Nuclear Materials*, 1979. **83**: p. 98-108.
18. Johnson, R.A. and N.Q. Lam, *Journal of Nuclear Materials*, 1978. **69-7**: p. 424-433.
19. Andreson, P.L., F.P. Ford, S.M. Murphy, and J.M. Perks, in *Proceeding of 4th International Conference on Environmental Degradation of Materials in Nuclear Power Systems-Water Reactors* D. Cubicciotti, Editor 1990, NACE: Jekyll Island, GA
20. Titchmarsh, J.M. and S. Dumbill, *Journal of Microscopy-Oxford*, 1997. **188**: p. 224-236.
21. Okamoto, P.R. and L.E. Rehn, *Journal of Nuclear Materials*, 1979. **83**: p. 2-23.
22. King, H.W., *Journal of Materials Science*, 1966. **1**: p. 79-90.

23. Nakata, K. and I. Masaoka, *Journal of Nuclear Materials*, 1987. **150**: p. 186-193.
24. Allen, T.R., J.T. Busby, G.S. Was, and E.A. Kenik, *Journal of Nuclear Materials*, 1998. **255**: p. 44-58.
25. Watanabe, S., N. Sakaguchi, N. Hashimoto, and H. Takahashi, *Journal of Nuclear Materials*, 1995. **224**: p. 158-168.
26. Watanabe, S., N. Sakaguchi, N. Hashimoto, M. Nakamura, H. Takahashi, C. Namba, and N.Q. Lam, *Journal of Nuclear Materials*, 1996. **232**: p. 113-118.
27. Watanabe, S., N. Sakaguchi, S. Mochizuki, and H. Takahashi, *Journal of Nuclear Materials*, 1999. **271**: p. 184-188.
28. Watanabe, S., Y. Takamatsu, N. Sakaguchi, and H. Takahashi, *Journal of Nuclear Materials*, 2000. **283**: p. 152-156.
29. Kenik, E.A., J.T. Busby, M.K. Miller, A.M. Thuvander, and G. Was, *Origin and influence of pre-existing segregation on radiation-induced segregation in austenitic stainless steels*, in *Microstructural Processes in Irradiated Materials*, S.J. Zinkle, et al., Editors. 1999, Materials Research Society: Warrendale. **540**. p. 445-450.
30. Kesternich, W. and A. GarciaBorquez, *Scripta Materialia*, 1997. **36**: p. 1127-1132.
31. Titchmarsh, J.M. and S. Dumbill, *Journal of Nuclear Materials*, 1996. **227**: p. 203-219.
32. Sakaguchi, N., S. Watanabe, and H. Takahashi, *Journal of Materials Science*, 2005. **40**: p. 889-893.
33. Vatter, I.A. and J.M. Titchmarsh, *Ultramicroscopy*, 1989. **28**: p. 236-239.
34. Titchmarsh, J.M., *Micron*, 1999. **30**: p. 159-171.

35. Watanabe, S., J. Satou, N. Sakaguchi, H. Takahashi, and C. Namba, *Journal of Nuclear Materials*, 1996. **239**: p. 200-204.
36. Lu, Z., R.G. Faulkner, G. Was, and B.D. Wirth, *Scripta Materialia*, 2008. **58**: p. 878-881.
37. Neklyudov, I.M. and V.N. Voyevodin, *Journal of Nuclear Materials*, 1994. **212**: p. 39-44.
38. Ohnuki, S., H. Takahashi, and T. Takeyama, *Journal of Nuclear Materials*, 1982. **103**: p. 1121-1125.
39. Schaublin, R., P. Spatig, and M. Victoria, *Journal of Nuclear Materials*, 1998. **258**: p. 1350-1355.
40. Lu, Z., R.G. Faulkner, N. Sakaguchi, H. Kinoshita, H. Takahashi, and P.E.J. Flewitt, *Journal of Nuclear Materials*, 2006. **351**: p. 155-161.
41. Kato, T., H. Takahashi, S. Ohnuki, K. Nakata, and J. Kuniya, *Journal of Nuclear Materials*, 1991. **179**: p. 623-625.
42. Clausing, R.E., L. Heatherly, R.G. Faulkner, A.F. Rowcliffe, and K. Farrell, *Journal of Nuclear Materials*, 1986. **141**: p. 978-981.
43. Little, E.A., T.S. Morgan, and R.G. Faulkner, *Physics of Irradiation Effects in Metals*, 1992. **97**: p. 323-328.
44. Gupta, G., Z. Jiao, A.N. Ham, J.T. Busby, and G.S. Was, *Journal of Nuclear Materials*, 2006. **351**: p. 162-173.
45. Yoshida, N., A. Yamaguchi, T. Muroga, Y. Miyamoto, and K. Kitajima, *Journal of Nuclear Materials*, 1988. **155**: p. 1232-1236.
46. Allen, T.R., L. Tan, J.D. Tucker, J. Gan, G. Gupta, G.S. Was, S. Shutthanandan, and S. Thevuthasan, *Radiation resistance of advanced ferritic-martensitic steel HCM12A*, in *Effects of Radiation on Materials*:

- 22nd Symposium, T.R. Allen, et al., Editors. 2006, American Society Testing and Materials: W Conshohocken. **1475**. p. 135-147.
47. Allen, T.R., L. Tan, J. Gan, G. Gupta, G.S. Was, E.A. Kenik, S. Shutthanandan, and S. Thevuthasan, *Journal of Nuclear Materials*, 2006. **351**: p. 174-186.
 48. Wirth, B.D., *Wechsler Symposium on Radiation Effects* 2006: TMS Meeting.
 49. Was, G.S., J.P. Wharry, B. Frisbie, B.D. Wirth, D. Morgan, J.D. Tucker, and T.R. Allen, *Journal of Nuclear Materials*, 2011. **411**: p. 41-50.
 50. Jiao, Z. and G.S. Was, *Acta Materialia*, 2011. **59**: p. 4467-4481.
 51. Miller, M.K., J.M. Hyde, A. Cerezo, and G.D.W. Smith, *Applied Surface Science*, 1995. **87-8**: p. 323-328.
 52. Grobner, P.J., *Metallurgical Transactions*, 1973. **4**: p. 251-260.
 53. Kohyama, A., H. Matsui, K. Abe, K. Hamada, and K. Asano, *Journal of Nuclear Materials*, 1988. **155**: p. 1354-1358.
 54. Anderson, J.O. and B. Sundman, *Calphad-Computer Coupling of Phase Diagrams and Thermochemistry*, 1987. **11**: p. 83.
 55. Hennion, M., *Journal of Physics F-Metal Physics*, 1983. **13**: p. 2351-2358.
 56. Mirebeau, I., M. Hennion, and G. Parette, *Physical Review Letters*, 1984. **53**: p. 687-690.
 57. Cowley, J.M., *Physical Review*, 1950. **77**: p. 669-675.
 58. Yamauchi, H., J.M. Sanchez, D.d. Fontaine, and R. Kikuchi, *Proceeding of the International Conference on Irradiation Behavior of Metallic Materials for Fast Reactor Core Components*, ed. J. Poirier and J.M. Dupouy 1979, Gif-sur-Yvette, France: CEA-DMECN.

59. Kuwano, H. and Y. Hamaguchi, *Journal of Nuclear Materials*, 1988. **155**: p. 1071-1074.
60. Konobeev, Y.V., A.M. Dvoriashin, S.I. Porollo, and F.A. Garner, *Journal of Nuclear Materials*, 2006. **355**: p. 124-130.
61. Dubuisson, P., D. Gilbon, and J.L. Seran, *Journal of Nuclear Materials*, 1993. **205**: p. 178-189.
62. Mathon, M.H., Y. de Carlan, G. Geoffroy, X. Averty, A. Alamo, and C.H. de Novion, *Journal of Nuclear Materials*, 2003. **312**: p. 236-248.
63. Mathon, M.H., C.d. Novion, Y.d. Carlan, G. Geoffroy, and A. Alamo, *SAS 2002, XII International Conference on Small-Angle Scattering 2002*, Venice, Italy: Not published, cited by reference 62.
64. Bonny, G., D. Terentyev, and L. Malerba, *Scripta Materialia*, 2008. **59**: p. 1193-1196.
65. Horton, L.L., J. Bentley, and W.A. Jesser, *Journal of Nuclear Materials*, 1981. **103-104**: p. 1085.
66. Kuwano, H., *Transactions of the Japan Institute of Metals*, 1985. **26**: p. 473-481.
67. Dubiel, S.M. and G. Inden, *Zeitschrift Fur Metallkunde*, 1987. **78**: p. 544-549.
68. Little, E.A. and D.A. Stow, *Journal of Nuclear Materials*, 1979. **87**: p. 25-39.
69. Gelles, D.S., *Journal of Nuclear Materials*, 1995. **225**: p. 163-174.
70. Filippova, N.P., V.A. Shabashov, and A.L. Nikolaev, *Physics of Metals and Metallography*, 2000. **90**: p. 145-152.
71. Wakai, E., A. Hishinuma, K. Usami, Y. Kato, S. Takaki, and K. Abiko, *Materials Transactions Jim*, 2000. **41**: p. 1180-1183.

72. Gelles, D.S. and R.E. Schaublin, *Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing*, 2001. **309**: p. 82-86.
73. Sagaradze, V.V., Kositsyna, II, V.L. Arbuzov, V.A. Shabashov, and Y.I. Filippov, *Physics of Metals and Metallography*, 2001. **92**: p. 508-517.
74. Kimura, A. and H. Matsui, *Journal of Nuclear Materials*, 1994. **212**: p. 701-706.
75. Kohno, Y., A. Kohyama, T. Hirose, M.L. Hamilton, and M. Narui, *Journal of Nuclear Materials*, 1999. **271**: p. 145-150.
76. Schaeublin, R., D. Gelles, and M. Victoria, *Journal of Nuclear Materials*, 2002. **307**: p. 197-202.
77. Dvoriashin, A.M., S.I. Porollo, Y.V. Konobeev, and F.A. Garner, *Journal of Nuclear Materials*, 2004. **329**: p. 319-323.
78. Lavrentiev, M.Y., R. Drautz, D. Nguyen-Manh, T.P.C. Klaver, and S.L. Dudarev, *Physical Review B*, 2007. **75**: p. 014208
79. Caro, A., D.A. Crowson, and M. Caro, *Physical Review Letters*, 2005. **95**: p. 075702
80. Olsson, P., J. Wallenius, C. Domain, K. Nordlund, and L. Malerba, *Physical Review B*, 2006. **74**: p. 229906(E).
81. Olsson, P., J. Wallenius, C. Domain, K. Nordlund, and L. Malerba, *Physical Review B*, 2005. **72**: p. 214119.
82. Klaver, T.P.C., R. Drautz, and M.W. Finnis, *Physical Review B*, 2006. **74**: p. 094435.
83. Olsson, P., I.A. Abrikosov, and J. Wallenius, *Physical Review B*, 2006. **73**: p. 104416

84. Cottenier, S., B. De Vries, J. Meersschaut, and M. Rots, *Journal of Physics-Condensed Matter*, 2002. **14**: p. 3275-3283.
85. Hafner, R., D. Spisak, R. Lorenz, and J. Hafner, *Journal of Physics-Condensed Matter*, 2001. **13**: p. L239-L247.
86. Caro, A., M. Caro, E.M. Lopasso, and D.A. Crowson, *Applied Physics Letters*, 2006. **89**: p. 121902
87. Mendelev, M.I., S. Han, D.J. Srolovitz, G.J. Ackland, D.Y. Sun, and M. Asta, *Philosophical Magazine*, 2003. **83**: p. 3977-3994.
88. Wallenius, J., P. Olsson, C. Lagerstedt, N. Sandberg, R. Chakarova, and V. Pontikis, *Physical Review B*, 2004. **69**.
89. Saunders, N. and A.P. Miodownik, *CALPHAD: A Comprehensive Guide*, R.W. Cahn, Editor 1998, Pergamon: Oxford.
90. Brenner, S.S., M.K. Miller, and W.A. Soffa, *Scripta Metallurgica*, 1982. **16**: p. 831-836.
91. Danoix, F. and P. Auger, *Materials Characterization*, 2000. **44**: p. 177-201.
92. Miller, M.K., J.M. Hyde, M.G. Hetherington, A. Cerezo, G.D.W. Smith, and C.M. Elliott, *Acta Metallurgica et Materialia*, 1995. **43**: p. 3385-3401.
93. Hyde, J.M., M.K. Miller, M.G. Hetherington, A. Cerezo, G.D.W. Smith, and C.M. Elliott, *Acta Metallurgica et Materialia*, 1995. **43**: p. 3403-3413.
94. Hyde, J.M., M.K. Miller, M.G. Hetherington, A. Cerezo, G.D.W. Smith, and C.M. Elliott, *Acta Metallurgica et Materialia*, 1995. **43**: p. 3415-3426.
95. Novy, S., P. Pareige, and C. Pareige, *Journal of Nuclear Materials*, 2009. **384**: p. 96-102.
96. Kuksenko, V., C. Pareige, C. Genevois, F. Cuvilly, M. Roussel, and P. Pareige, *Journal of Nuclear Materials*, 2011. **415**: p. 61-66.

Chapter 3

Experimental Methods

3.1 Materials

3.1.1 As-received alloys

Two different batches of Fe-Cr ferritic alloys have been used in this study. The first batch was made by Metals Crystals and Oxides Ltd., Cambridgeshire, UK, and consisted of four different materials: Fe-10.6at%Cr (10wt%Cr), Fe-11.7at% (11wt%Cr), Fe-12.8at%Cr (12wt%Cr) and Fe-13.9at%Cr (13wt%Cr). The microstructure of the as-received Fe-12.8%Cr is shown in Fig.3.1 (a). Detailed bulk concentration analysis for minor elements and impurities was not performed due to insufficient materials.

The second batch was a ferritic Fe-15.2at%Cr (14.25wt%Cr) alloy of high purity supplied by EFDA (European Fusion Development Agreement). The report from the manufacturer indicates that the alloy contained 4-5 wt ppm of C, with other impurities such as S, O, N and P of less than 10 wt ppm. The alloy was produced by induction melting in a cold crucible, under high purity hydrogen and argon. After cold reduction of 70%, the ingot was then heat treated at 850°C for 1h under pure argon flow followed by air cooling. The microstructure of the as-received material is shown in Fig.3.1 (b).

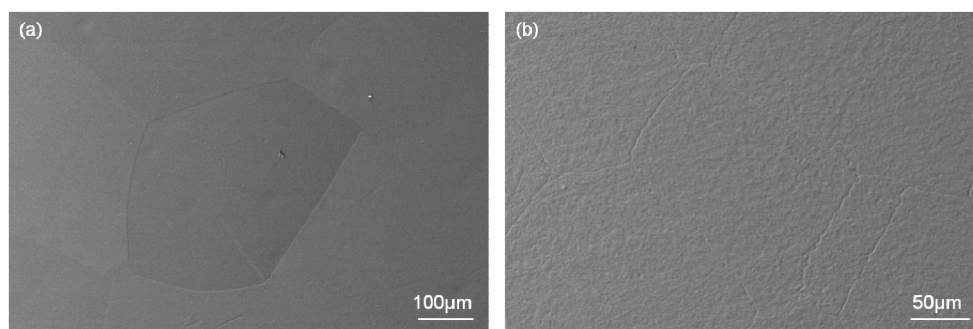


Fig.3.1 SEM image of microstructure of the (a) as-received Fe-12.8%Cr in the first batch, and (b) as-received Fe-15.2%Cr in the second batch.

3.1.2 Cutting, heat treatment and polishing

For the first batch, thin rectangular-shaped samples (10x5mm with 2mm in thickness) were cut using a low speed diamond saw. The annealing temperature and time were carefully chosen to result in recrystallisation of the grain structure while the alloy was still kept in the single α phase region. According to the binary Fe-Cr phase diagram [1], at 800°C when the Cr concentration is between 10%-14%, the alloys are in the α phase region and have a BCC structure. Therefore pre-annealing was carried out at 800°C for 1h in vacuum followed by a water quench. The recrystallisation produced large grains (~100 μm across) with long straight grain boundaries which would be useful for the following FIB specimen preparation.

A similar specimen preparation route was chosen for the second batch of materials. Thin, circular samples (12mm in diameter and 2mm in thickness) were cut from the ingot using a low speed diamond saw. However, for these samples, a longer heat treatment at 800°C for 6 hours in vacuum followed by a water quench was then applied. On some occasions, a similar heat treatment was applied in argon atmosphere or argon-filled tubes. Note that it was not possible to eliminate the possibility of C contamination during the heat treatment. The time of heat treatment was extended for grain growth to obtain even longer grain boundaries.

After heat treatment, the samples were then polished using 600grit, 800grit, 2500grit and 4000grit sand paper consecutively. Final polishing was performed using a diamond suspension and finished by electro-polishing for 15 seconds in a solution of 5% perchloric acid in methanol at -40°C to obtain a flat surface and reveal grain boundaries. The SEM images of Fe-12.8%Cr from the first batch and Fe-15.2%Cr from the second batch are shown in Fig.3.2.

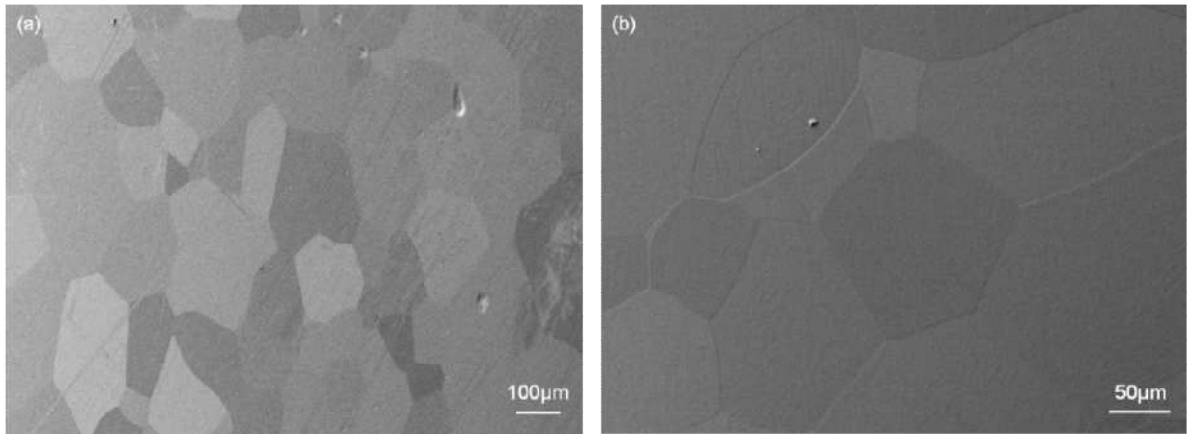


Fig.3.2 SEM image of microstructure of the (a) heat treated Fe-12.8%Cr in the first batch, and (b) heat treated Fe-15.2%Cr in the second batch

3.1.3 Irradiation and SRIM calculation

Ion implantation using Fe^+ was performed in the Ion Beam Facility at the University of Surrey, UK. Three different sets of irradiation conditions were chosen to allow the specimen to be damaged at different levels and different rates, as detailed in Table 3.1 (implantation 1 was the high dose, 2 and 3 were the same low dose). Each set of irradiations was performed by applying several implantations with different energy, dose and dose rates sequentially to obtain a flat damage profile at maximum damage range. A schematic illustration of the implantation chamber is shown in Fig.3.3.

Table 3.1 Implantation sequence and details of three implantations.

	Implantation 1		Implantation 2			Implantation 3		
Sequence	1	2	1	2	3	1	2	3
Energy (MeV)	2	0.5	2	1	0.5	2	1	0.5
Dose (ions/cm ²)	3×10^{15}	1.5×10^{15}	2.5×10^{14}	7.5×10^{13}	5×10^{13}	2.5×10^{14}	7.5×10^{13}	5×10^{13}
Dose rate (ion/cm ² /s)	2.5×10^{11}	2.5×10^{11}	2.28×10^{11}	2.16×10^{11}	1.87×10^{11}	1.14×10^{10}	1.08×10^{10}	9.35×10^9
Temperature (°C)	350±50		350±50			350±50		

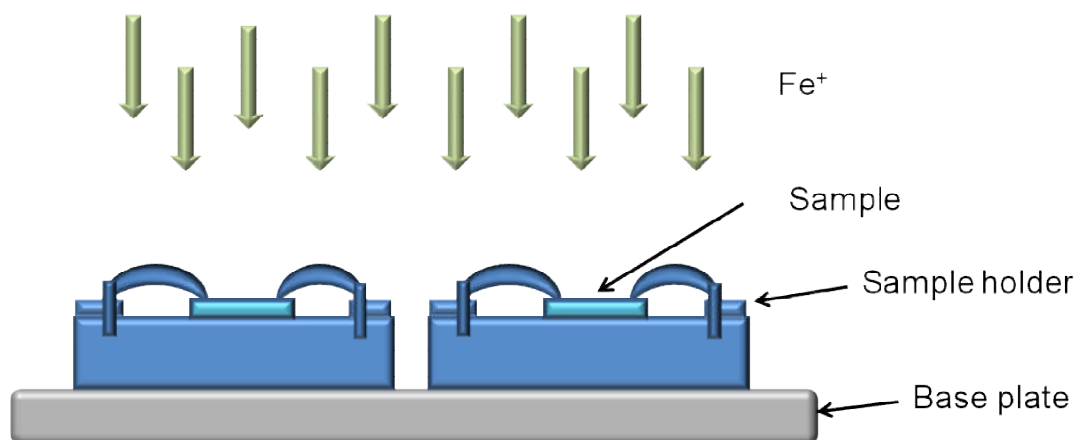


Fig.3.3 Illustration of the implantation chamber

The software "Transport of Ions in Matter" (TRIM) was used to estimate the irradiation damage. TRIM is a Monte Carlo computer program that calculates the interaction of energetic ions with a target. TRIM is contained in the Stopping and Range of Ions in Matter (SRIM) software package [2]. The calculation type was set to be the 'Detailed Calculation with Full Damage Cascades' in order to calculate all the collisional damage to the target. This methodology follows every recoiling atom until the recoiling atom energy drops below the lowest displacement energy of any target atom [3]. This is the formalism adopted by Norgett, Robinson and Torrens who developed the NRT standard [4]. The displacement energy of Fe, which is the minimum energy required to knock a target atom far enough away from its lattice site to not return immediately, was set to be 40eV according to ref [5]. To balance the time required for the calculation and the accuracy of simulated results, the total number of ions calculated was set to be several thousands. The calculation took several hours. The value of displacement per atom (dpa) can be calculated using equation 3-1, where ϕ is the number of displacements calculated from SRIM for a specific energy, in the unit of displacement/Å/ion, D is the dose applied at each energy (ions/cm²), and N_w is the number of atoms per unit volume:

$$dpa = \sum \frac{D \times \phi}{N_w} \quad (3 - 1)$$

The dpa values of three irradiations are plotted as a function of irradiation depth in Fig.3.4. Since implantation 2 and 3 used the same energies, the SRIM calculation would also be the same as shown in Fig. 3.4(b). The plot for the high dose irradiation indicates a maximum implantation depth of ~1000nm and a maximum

damage of 8dpa. The average damage level between 100-700nm depth is about 6dpa. For the low dose irradiations, the maximum implantation depth is also ~1000nm and the average damage level is ~0.6dpa between 100-700nm.

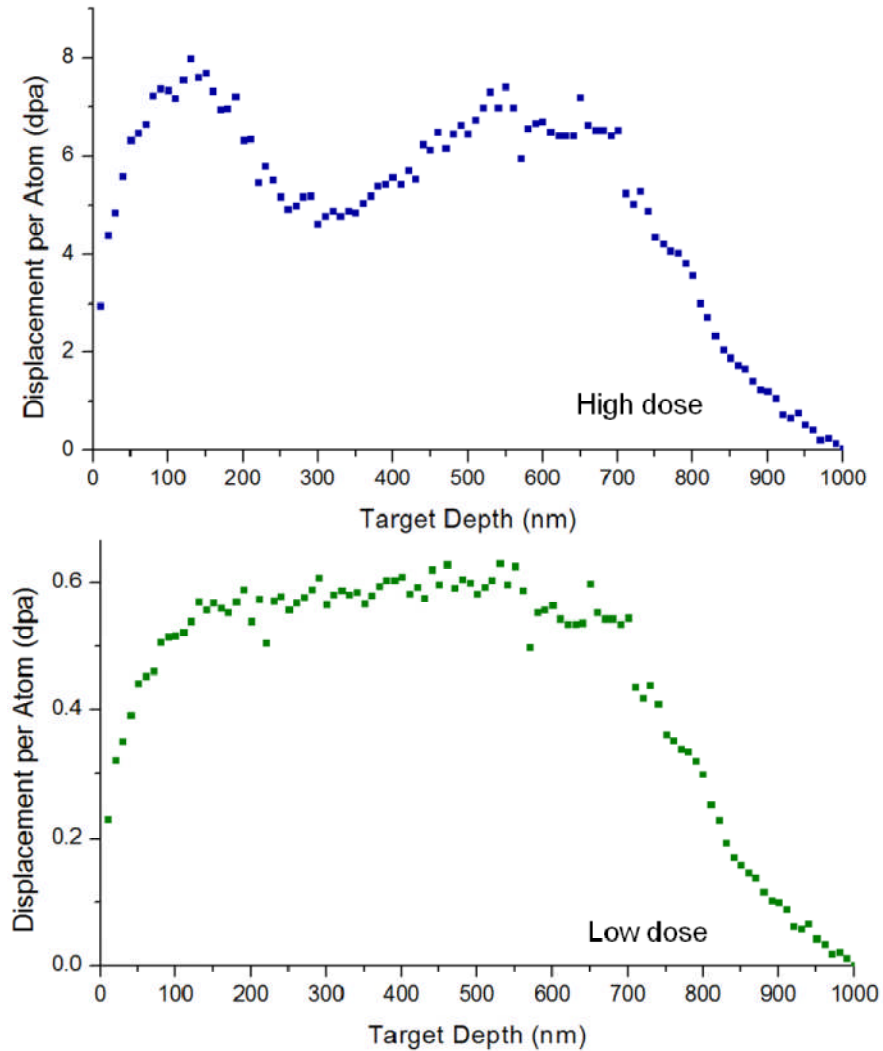


Fig.3.4 SRIM calculation for three implantations, displacement per atom (dpa) plotted as a function of target depth.

3.2 Specimen Preparation

3.2.1 Focused Ion Beam

Focused ion beam (FIB) machining can provide a site-specific specimen preparation method. The Zeiss NVision 40 is a FIB instrument equipped with dual beams (electron beam and Ga^+ ion beam) and can operate in both Scanning Electron Microscopy (SEM) and FIB mode. At high extraction field, the Ga^+ beam can be focused to form a very fine probe (less than 10nm in diameter). By controlling the electrostatic lenses and effective aperture size, the probe current density can be altered from tens of pA to several nA corresponding to beam diameters ranging from 5nm to 0.5 μm . With a built-in micromanipulator, a small beam size and simultaneous imaging capability in SEM view, this FIB is an ideal instrument for preparing Transmission Electron Microscopy (TEM) and Atom Probe Tomography (APT) specimens.

3.2.1.1 TEM specimen preparation

With FIB, TEM specimens can be directly prepared from a bulk sample (square or circular shape, pre-cut by low speed saw) in a couple of hours [6, 7]. The FIB methods can be described as *ex situ* lift-out and *in situ* lift-out.

Fig.3.5 shows the procedure of the *in situ* lift-out. As illustrated in Fig.3.5 (a), a protective layer (Pt or W) which is several microns thick is usually deposited over the area of interest. Two large, stair-step, FIB trenches are cut on both sides of the area of interest separated by a distance of 1 μm between the trenches and the protective layer. Line-milling is then applied to gradually enlarge the trenches, to

attach the edges of the protective layer and to remove any re-deposited materials. Prior to final thinning, the sample is tilted to 45° and then the bottom, right side and a portion of left side of the specimen is cut free as shown in Fig.3.5(b), and the built-in micromanipulator is welded onto the right side of the specimen using Pt/W deposition. Fig.3.5 (c) shows a cut is made to remove the remaining left side of the specimen. The sample stage is lowered to move the specimen away from the bulk material. A similar welding process is also performed to attach the specimen to the centre pillar of a TEM half grid shown in Fig.3.5 (d). A final FIB cut is performed at an angle of $1-2^\circ$ with respect to the plane of the specimen surface until the specimen is electron transparent in the SEM view, normally with electron energy of 15kV.

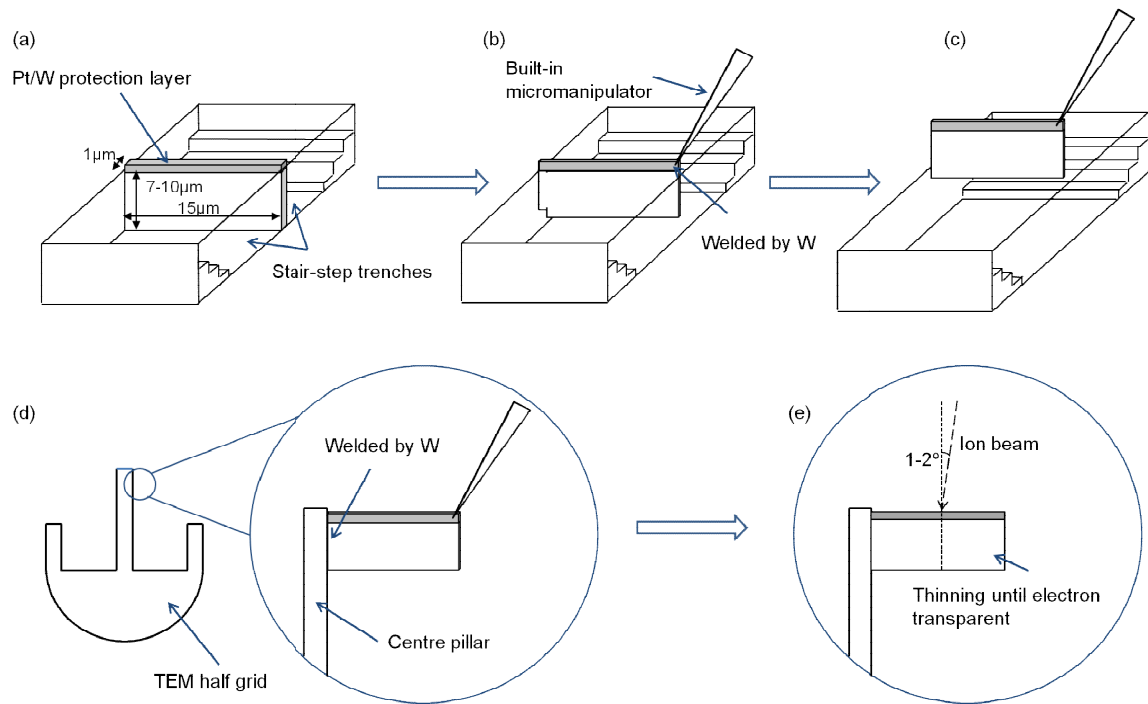


Fig.3.5 Illustration of FIB *in situ* lift-out method of preparing TEM specimen

In the *ex situ* lift-out method, the trenches are still cut as shown in Fig.3.5 (a). Instead of attaching a built-in micromanipulator as in Fig.3.5 (b), the specimen is

totally cut free from the bulk sample, and then lifted out and moved onto the a TEM grid using a glass needle. The process is observed using an optical microscope outside of the FIB chamber. This procedure is not reliable and has a low chance of success, simply because the electrostatic forces between the glass needle and the specimen are too unpredictable and consequently the specimen could either be repelled and lost, or attached too tightly in which case it could not be moved onto the TEM grid. On the other hand, with a built-in micromanipulator, the entire lift-out procedure can be finished inside the vacuum chamber under SEM view with precise control. The *in situ* lift-out method has been proved to be a much more reliable and easily-controlled way for TEM specimen preparation.

For high resolution TEM or Electron Energy Loss Spectroscopy (EELS) analysis, which requires even thinner specimens than conventional TEM, the specimen should be electron transparent in the SEM view with a 5KV beam current. Furthermore, during the preparation, Ga^+ ions are implanted and mix into the specimen due to the sputtering mechanism and therefore induce damage artifacts. To remove the Ga^+ contamination and ion-damaged layer, a 2KV low energy milling can be applied at an angle of $10\text{-}12^\circ$ with respect to the plane of the specimen surface for several minutes. The procedure is similar to Fig.3.5 (e).

3.2.1.2 APT specimen preparation

An APT specimen is needle-shaped with an apex diameter of less than 100nm. Traditionally APT specimens are prepared using a two-stage electropolishing method (see section 3.2.2). However it is also possible to manufacture them using FIB techniques. The approach is similar to the *in situ* method used for TEM

specimen preparation. This procedure has been described by Miller et al. [8] and also Thompson et al. [9].

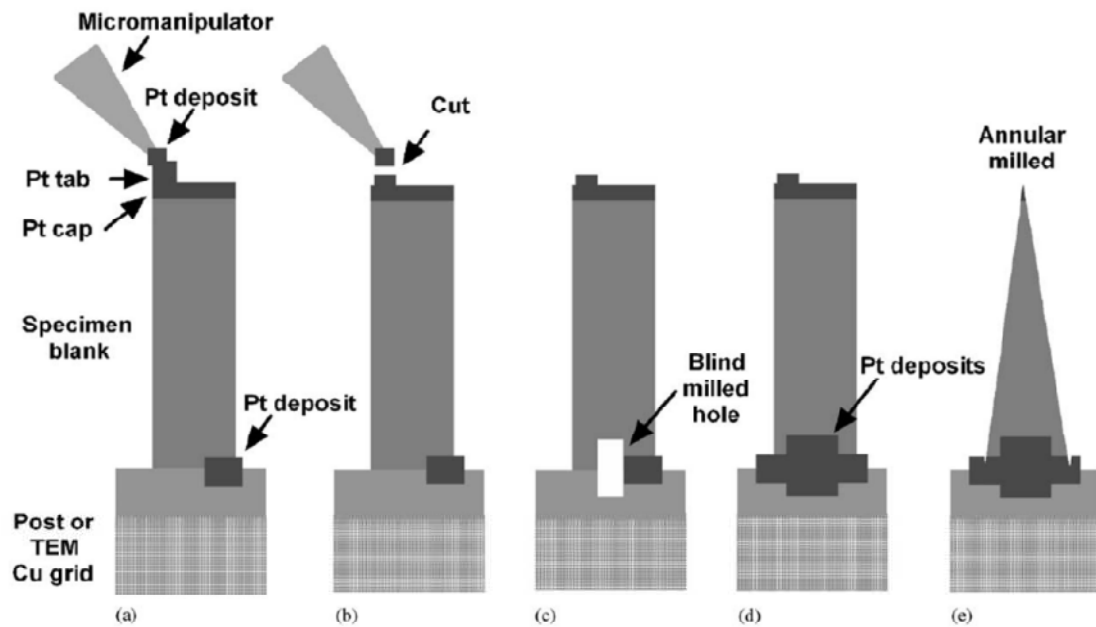


Fig.3.6 Illustration of final steps of FIB *in situ* lift-out method of preparing atom probe specimen, from reference [8]

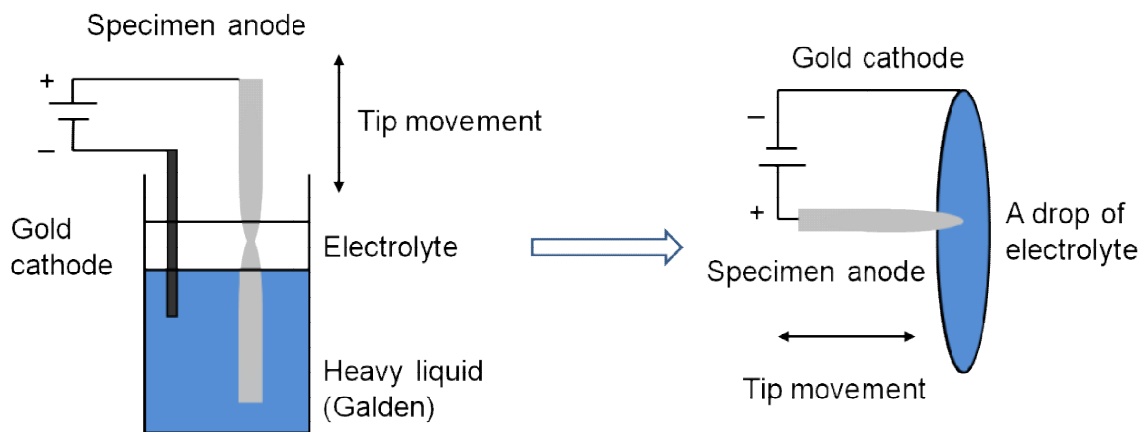
First, similarly as in Fig.3.5 (a), two trenches are cut on the both sides of the region of interest to form a thin lamella. The rest of the APT specimen manufacture procedure is illustrated in Fig.3.6. The tip of the micromanipulator is welded by Pt/W deposition to the edge of lamella. Instead of lifting out the entire lamella as in TEM specimen preparation, only one small pillar with a cross section area of $2\mu\text{m} \times 2\mu\text{m}$ is cut free and lifted out. As shown in Fig.3.6 (a), the pillar is then attached to a post or TEM Cu grid. A Pt/W deposit is introduced to fill the gap between the pillar base and the post to make sure the pillar is firmly attached on the post and the area of interest is coated with a protective layer as shown in Fig.3.6 (d). A sequence of rectangular and annular patterns is milled to form a sharp tip having a

sufficiently small radius of curvature (smaller than 100nm) and shank angle, as shown in Fig.3.6 (e). Though some criteria about the shape of specimen have been taken into account during the final stage sharpening, the diameter and shank angle still vary from one specimen to another after finishing. However the APT specimens prepared by FIB are much more self-consistent in shape than the ones prepared by the traditional electropolishing method.

During the sharpening of the specimen, special care should be taken to avoid accidentally forming secondary needles near the specimen apex. These additional needles could reduce the region of specimen which can be analyzed by APT and may also influence the trajectories of the evaporated ions.

3.2.2 Electropolishing method of APT specimen preparation

Traditionally, a two-stage electropolishing method is used to prepare atom probe specimens from conductive materials. The procedure is shown in Fig.3.7, and the chemical solutions listed are used for Fe-Cr alloys.



	Active Ingredient	Base
Stage 1	25% perchloric acid (60%)	75% acetic acid (100%)
Stage 2	2% perchloric acid (60%)	98% 2-butoxyethanol

Fig.3.7 Two-stage electropolishing method for preparing APT specimens, with solution ingredients listed.

To use this two-stage method, the sample should be first cut and polished into thin pieces (2mm×2mm×20~30mm) and generally two specimens can be made from one piece. This method requires less time and effort comparing with the FIB technique introduced in section 3.2.1.2. However, the FIB is capable of providing a much more precise site-specific specimen preparation which allows APT analysis on a designated small region of interest. Furthermore, the FIB method can provide some

control over the shape of the specimens, such as limiting the diameter below a certain level while the electropolishing method is unable to make any precise adjustment to the shape of the specimen.

3.3 Electron Energy Loss Spectroscopy in Scanning Transmission Electron Microscopy

Modern TEM or Scanning Transmission Electron Microscopy (STEM) instruments are often equipped with advanced techniques for providing structural and chemical information from the samples being examined. Electron Energy Loss Spectroscopy (EELS) is one of them. It involves measuring the change in kinetic energy of incident electrons as a result of interactions with a specimen.

When a beam of electrons with a known and narrow range of kinetic energies passes through a specimen, they are scattered by the interaction with the atoms in the specimen. The scattering can be divided into elastic scattering and inelastic scattering. If the incident electron interacts with an atom nucleus, the energy exchange due to elastic scattering is extremely small due to the massive difference between the mass of an atom nucleus and the mass of an electron. Consequently the resultant energy loss is often unmeasurable in the EELS system. These electrons will form a peak at 0eV on the EELS spectrum and be referred as the zero-loss peak. The width of the zero-loss peak mainly reflects the energy distribution of the electron source. Meanwhile, inelastic scattering can result from different mechanisms including inner shell ionization which is particularly useful for EELS. When an incident electron interacts with an inner shell atom electron, the similarity between their masses allows the energy exchange to be measurable, typically several eV to hundreds of eV. The incident electrons keep moving with lower energies and are detected by EELS to form ionization edges on the spectrum. Each edge corresponds to an inner shell electron energy and is characteristic of a particular element, and therefore the physical and chemical information of the specimen can be obtained

from these features of the spectrum [10]. Fig.3.8 shows Fe and Cr low loss edges and core loss edges from an EELS atlas [11].

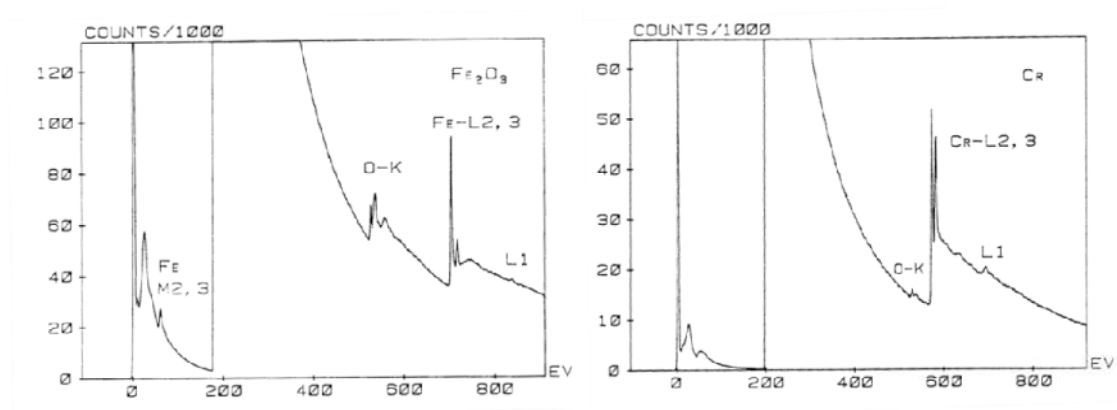


Fig.3.8 Fe and Cr low loss edges (M2, 3) and core loss edges (L2, 3) obtained from Fe_2O_3 thin film and slightly oxidized Cr thin film.

EELS is capable of analyzing all kinds of elements due to the fact that the energy threshold for the ionization edge occurs at the specific binding energy of each electron shell and these are known for all elements. Furthermore, EELS has been proved to be useful in identifying nano-scale second phases where other techniques such as diffraction or EDX (Energy Dispersive X-ray Spectroscopy) are difficult due to resolution limits and difficulties of detecting light elements such as C [12].

To obtain accurate results, the specimen examined by EELS must be very thin in the analyzed region (50-100nm for 100keV incident beam energy [13]), and the requirement is more stringent than for conventional TEM studies. The reason arises from the potential for plural inelastic scattering of the incident electrons. It is possible that an electron which suffers from high energy loss will also go through one or more low energy losses and this possibility increases rapidly with specimen

thickness and will cause a dramatic increase in the background noise near the ionisation edges. However, the intensity of initial rise of the ionization edge only increases linearly with the specimen thickness. As a result, an ionization edge will become more and more difficult to identify as the specimen thickness increases [13]. Therefore the thickness of specimen must be carefully controlled.

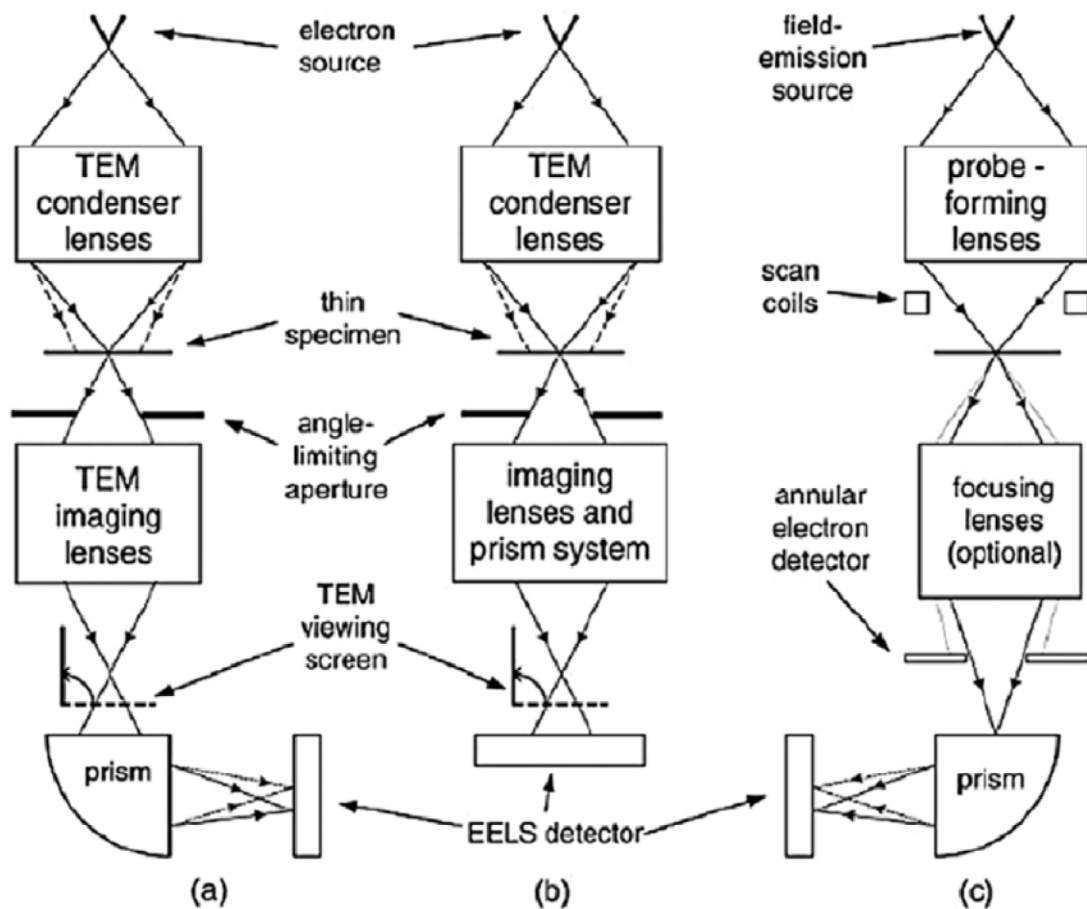


Fig.3.9 Illustration of TEM-based EELS systems, (a) conventional TEM with a magnetic-prism spectrometer below the viewing screen, (b) TEM incorporating an in-column imaging filter and (c) STEM system [10]

The JEOL 3000F is equipped with a field emission gun (FEG) and EELS can be operated under both TEM and STEM modes at 300KV. Illustrations of TEM-based

EELS systems are shown in Fig.3.9, (a) is the conventional TEM with a magnetic-prism spectrometer below the viewing screen, (b) is the TEM incorporating an in-column imaging filter and (c) is the STEM system. STEM has proved to be useful in analyzing grain boundary structure at atomic level [14]. The JEOL 3000F working in STEM mode is able to form a very fine probe (0.3-0.4nm). When combined with EELS in conjunction with a spatial drift correction function, it has the ability to analyze chemical information variation across the grain boundary with a lateral spatial resolution of 0.14 nm and energy resolution of 1eV in the EELS spectrum.

3.4 Atom Probe Tomography

3.4.1 Instrument development

The field ion microscope (FIM) was first designed by Muller in the 1950s. In the FIM, a sharp tip specimen is placed inside the vacuum chamber, orientated along the centre axis and about 50mm from the screen. The tip is held at a cryogenic temperature, and a low pressure imaging gas is admitted into the chamber. After a high positive potential is applied on the specimen, the imaging gas atoms in the neighbouring region of the tip apex are polarized by the strong field. These polarised atoms are attracted towards the specimen surface and are then ionized. These positively charged ions are then repelled from the specimen towards the phosphor screen to create a highly magnified (about a million times), projected image of the surface [15].

The first generation of atom probe field ion microscopes (APFIM), designed by Muller, Panitz and McLane in the late 1960s [16], are now referred as 1D atom probes. The second generation of atom probe is the three dimensional atom probe (3DAP) which was introduced in the mid to late 1980s and used a variety of position-sensitive single atom detectors. These allow the reconstruction of a three dimension atom map with chemical composition information. Instead of using the imaging gas to create projected images, the analysis chamber was kept at high vacuum. If a series of high-voltage pulses with nanosecond rise-time is applied on the tip specimen, atoms on the surface will field-evaporate and, being charged, are accelerated towards the detector. The times of flight of ions from the tip to the detector and the positions where the ions hit the detector are recorded. This information is necessary in the reconstruction of the 3D atom map and the mass

spectrum according to equation 3-2 [17], where e is the elementary charge, t is the time of flight, V_0 is total voltage and d is the total distance the ion travels from the specimen to detector:

$$\frac{m}{n} = \frac{2eV_0t^2}{d^2} \quad (3 - 2)$$

The first use of laser pulses instead of voltage pulses in 1D atom probe was reported in the early 1980s [18], and the first use of laser pulses in 3D atom probe was developed by Cerezo et al. [19]. Experiments performed during the 1980s had identified the fact that field evaporation is assisted by heating of the specimen tip [20], which led to the development of the pulsed-laser evaporation mode. After many years of development, the latest generation of Local Electrode Atom Probe (LEAP) was commercially introduced by Kelly et al. in 2003 [21]. The LEAP 3000HR is equipped with a laser which has spot size (4σ) less than $10\mu\text{m}$, a wavelength of 532nm and repetition rate of 200 kHz . This atom probe can be operated in either pulsed-laser mode or pulsed-voltage mode. In a LEAP, the specimen is positioned nearly one aperture diameter in front of a $\sim 10\text{-}50\mu\text{m}$ diameter aperture. The relative position of the specimen and the local electrode is aligned while viewing from a pair of video cameras. A positive voltage is applied to the specimen while high repetition rate negative voltage pulses are applied to the local electrode. Once the specimen starts to field evaporate, the specimen position can be fine-tuned to ensure that the specimen is correctly aligned with the aperture and at the optimal distance. After the specimen is aligned, the evaporation rate can be controlled by the computer to maintain continuous and steady evaporation of atoms. Since the electric field strength depends on the difference in potential and the distance between specimen apex and the electrode, the potential required at the

specimen apex for field evaporation can be minimised by reducing the distance between specimen and the extraction electrode. The local electrode configuration can lower by nearly 50% the standing and pulse voltages required to generate field evaporation [22]. A large-angle spherical reflectron is implemented to enhance the mass resolution. The high-speed laser pulse generator [23] combined with multiple channel plate (MCP), crossed delay line detector (DLD) [24] and fast timing system can provide data acquisition rates of $\sim 500,000$ ions/s in maximum (normally a much lower rate of $\sim 5,000$ ions/s is in use), and detect ions from a significantly larger field of view (~ 100 nm) than was possible using the second generation instruments [25]. An illustration of LEAP configuration is shown in Fig.3.10.

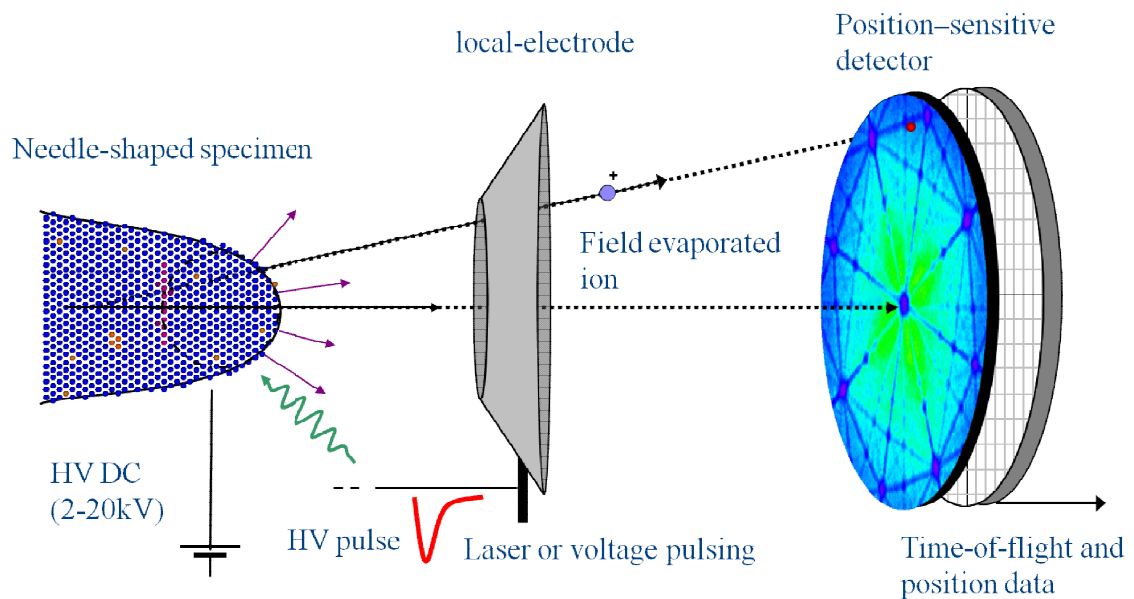


Fig.3.10 Illustration of the configuration of Local Electron Atom Probe (LEAP), based on reference [26]

3.4.2 Atom probe principles

Successful application of this analysis technique requires a deep understanding of the principles of field evaporation, and material response to voltage or laser pulses as well as certain limitations.

3.4.2.1 Pulsed-voltage mode

Under the pulsed-voltage mode, surface ion evaporation is achieved by applying voltage pulses lasting a few nanoseconds to the tip in addition to a significantly larger DC standing voltage, while the specimen is kept at cryogenic temperatures (several tens of degree Kelvin). Typical DC voltages often range from 3000V to 10000V. The voltage pulses are usually chosen to be a certain fraction of the DC voltage and the value is defined as pulse fraction which typically ranges from 5%-30% [27].

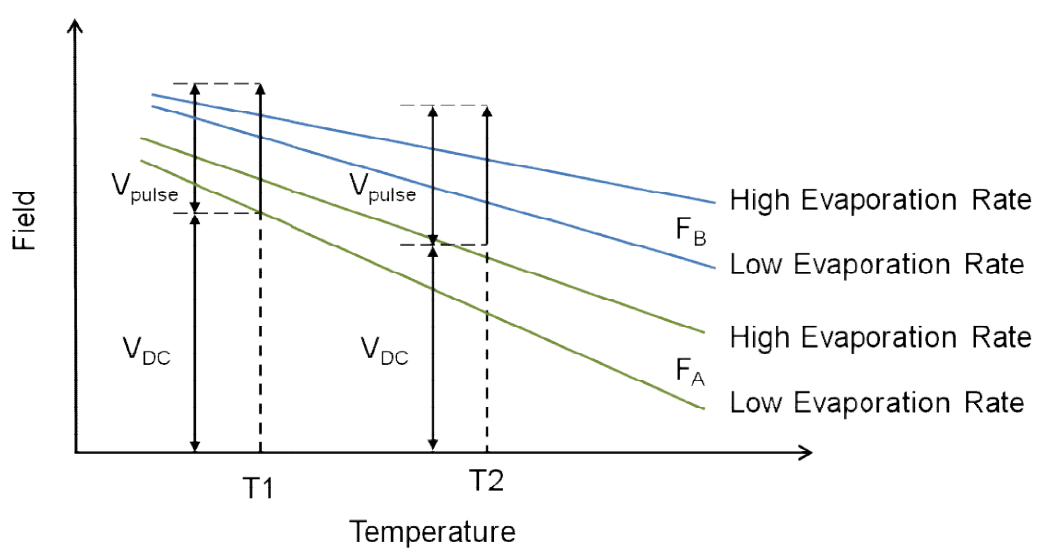


Fig.3.11 Schematic diagram of the variation in the evaporation field of an A-B binary alloy as a function of temperature, based on reference [17]

Based on the image hump model provided by Tsong et al. [28], the evaporation fields and charge states for each element can be calculated [15]. If we study a simple case such as an A-B binary alloy, B has higher evaporation field than A and then is referred to as the more refractory element. From Fig.3.11, at different evaporation rates, the evaporation fields of B decrease more slowly than A as temperature increases [17]. Element A with a lower evaporation field is more easily removed by the standing voltage between pulses and this can result in preferential evaporation of A. The field evaporation of atoms during the period of voltage pulses and removal of atoms by standing DC voltage between pulses can both occur. Only atoms evaporated during individual voltage pulses can be correctly recorded. Atoms that evaporate between pulses are either be filtered out by the mass spectrometer or contribute to the overall background noise in the spectrum. The V_{dc} and V_{pulse} show that temperature T_1 is a suitable base temperature for analysis, since the evaporation of element A caused by V_{dc} is negligible compared with the total evaporation caused by V_{pulse} . If V_{pulse} is not large enough, then the preferential removal of element A becomes more pronounced. At temperature T_2 , preferential evaporation of element A between pulses will occur resulting in a reduction in the estimated concentration of element A from the results. Therefore higher pulse fractions are required at higher temperatures for accurate analysis [29].

A variation of ion charge state with varying field evaporation conditions is often observed. To explain this phenomenon, Kingham [30] developed the theory of post-ionization. It is believed that when an atom is first evaporated from the matrix, it will lose one or more electrons. If the electron field is strong enough, when the ion reaches the critical distance, it is possible that the ion will be post-ionized one or more times before reaching its final charge state. The author computed the

possibility of post ionization for most elements as a function of field strength. The plots for Fe and Cr are shown in Fig.3.12. Generally, the relative abundance of highly charged ions increases with increasing field strength. Therefore the field evaporation can be explained as a two-stage model with initial evaporation caused by a charge exchange [31] or image hump model [32] and followed by a subsequent probability of post ionization.

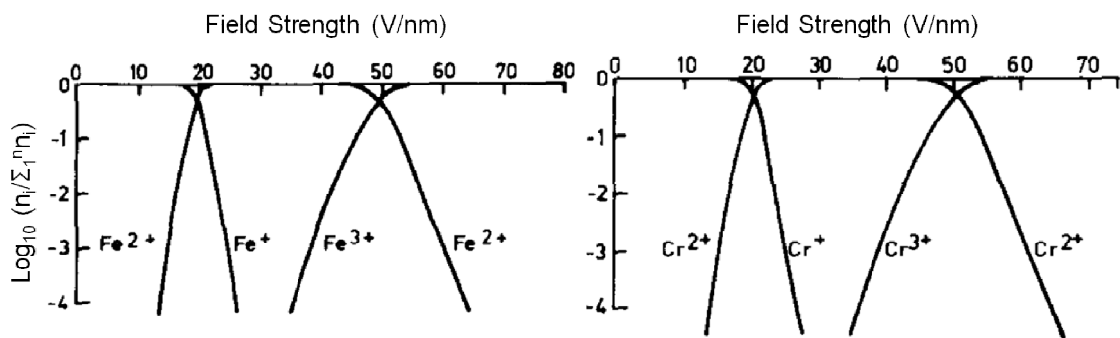


Fig.3.12 Calculation of the probability of post-ionization of Fe and Cr. The relative abundance of ions with different charge states is plotted logarithmically against field strength [30]

3.4.2.2 Pulsed-laser mode

Under the pulsed-laser mode, evaporation of surface ions is achieved by applying a thermal pulse lasting less than 100ps (even shorter than a voltage pulse) on top of a standing DC potential [27]. The specimen apex is heated and the temperature increases by up to several hundred degrees Kelvin. The field evaporation is promoted by the thermal energy introduced by the laser [33]. Since this process is associated with significant specimen heating, the cooling rate of the specimen should be taken into account to minimize degradation of the mass resolution and spatial resolution [34]. If the cooling rate is slow, continued field evaporation after

laser pulses will give rise to long tails in the peaks in the mass spectrum and degrade the mass resolution. Meanwhile the surface diffusion caused by thermal effects will also lead to the degradation of spatial resolution. However the actual cooling rate of each specimen depends on the thermal diffusivity and also the shape of the tip which will vary from one sample to another and is difficult to predict. The laser conditions such as spot size and repetition rate also need to be taken into account.

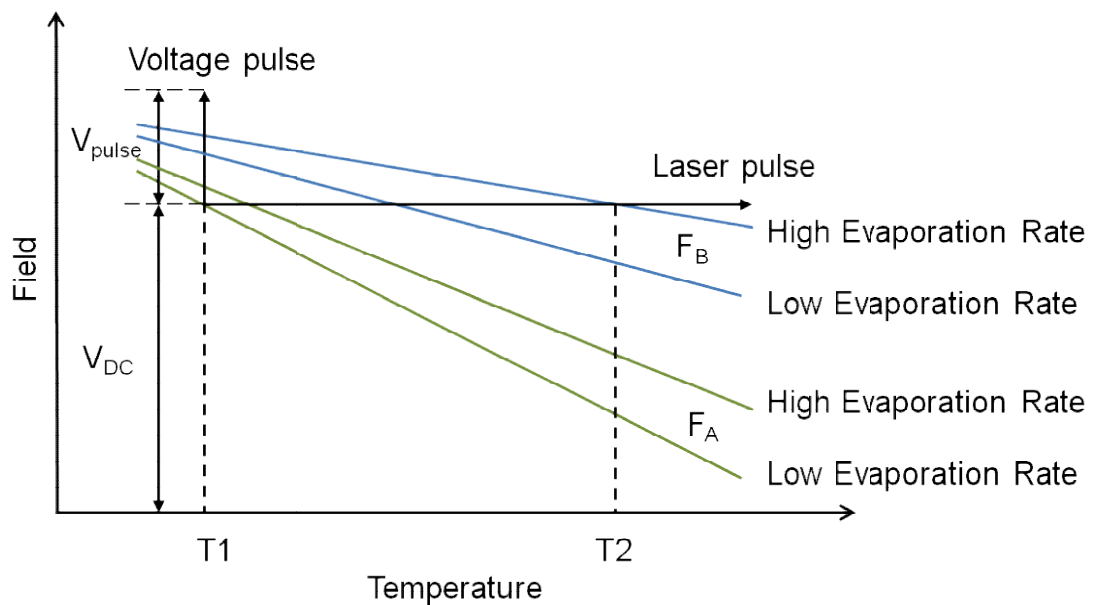


Fig.3.13 Illustration of the concept of voltage pulse and laser pulse evaporation mode for an A-B binary alloy, T1 is the base temperature and T2 is the peak temperature caused by laser heating, based on the reference [17].

Fig.3.13 shows how both pulsed-voltage and pulsed-laser methods achieve field evaporation. The pulsed-voltage method triggers field evaporation by applying a short voltage pulse to increase field, and the pulsed-laser method reduces the field required for field evaporation by increasing the temperature at the specimen apex. Bunton et al. [23] introduced the concept of effective pulse fraction PF_{eff} , which is probably the most important instrumentation parameter in a pulsed-laser atom probe

experiment. This enables reasonable comparison between different atom probe instruments. PF_{eff} is defined by the ratio of the specimen voltage V during the laser evaporation process and the standing DC voltage V_{ef} needed to evaporate ions from the surface of the specimen at a certain rate, as shown in equation 3-3:

$$PF_{eff} = 1 - \frac{V}{V_{ef}} \quad (3 - 3)$$

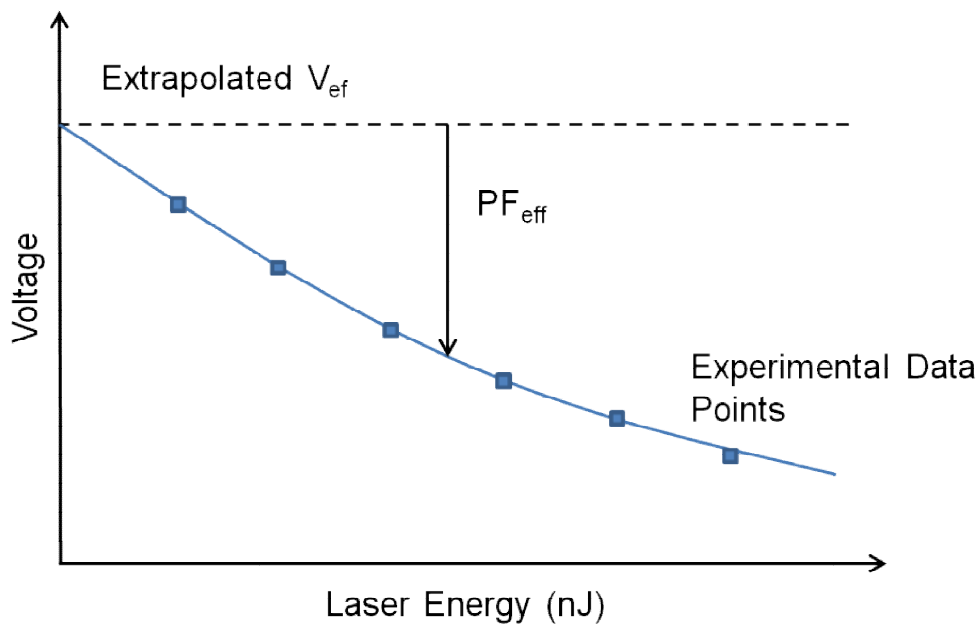


Fig.3.14 Illustration of the concept of effective pulse fraction in pulsed-laser mode, as modified by Gault et al, based on reference [35]

Bunton and co-workers obtained the standing DC voltage V_{ef} at zero laser energy. This method has been modified by Gault et al. [35] to become a more practical approach, since determining the V_{ef} at zero laser energy may cause the specimen to fracture during calibration. Gault et al. measured the voltage necessary to field evaporate atoms from a single specimen at a constant evaporation rate (in terms of atoms per pulse) as a function of applied laser energy. The voltage was taken as an

average applied potential during the evaporation of more than 500,000 detected ions after the shape of the specimen had adopted a steady shape as revealed by the detector histogram. The voltage was plotted as a function of applied laser energy and a second order polynomial fitted as shown in Fig.3.14. V_{ef} at zero laser energy is extrapolated from the plot and PF_{eff} described the drop in DC voltage with respect to this extrapolated V_{ef} as shown in equation 3-3.

3.4.2.3 Correlated evaporation and multiple hits

When a pulse (voltage or thermal) is triggered, atoms close to each other on the tip surface often tend to evaporate on the same pulse. This phenomenon has been referred as correlated evaporation and has been studied by both field ion microscopy [17] and atom probe tomography [36]. Geuser et al. [36] observed that the evaporation of neighbouring atoms is strongly correlated in both space and time, and explained this phenomenon by two facts. One is that when one atom evaporates, it will increase the electrical field applied on its neighbours; another is that there are definite zones where all the atoms are likely to evaporate at a given time. The correlated evaporation is especially drastic at the centre of a low index pole mainly due to the fact that the electrical field increases as the pole terrace diameter decreases.

For a position sensitive detector (PSD), difficulties arise when more than one atom evaporates from the probed area on the same triggering pulse within a certain period of time. This phenomenon is referred to as "multiple hits" whatever the correlation in the arrival time of these ions. Because of the statistical nature of the field evaporation process, a triggering pulse could give rise to the removal of several

atoms. These ions could either reach the detector within a very short period of time or almost simultaneously depending on their chemical nature. Strasser et al. [37] introduced the term of multiplicity and De Costa et al. [24] further refined the concept by defining serial multiplicities and simultaneous multiplicities to describe the ability of the PSD detector to separate serial events and simultaneous events. Furthermore, ions are also likely to hit the detector at places very close together if they evaporate within a very small region and close to each other, resulting in multiple events which are correlated in both time and space. Therefore, in addition to high serial and simultaneous multiplicities, a high performance PSD should also have a high spatial resolving power as well as a good special resolution and timing accuracy, otherwise the occurrence of multiple hits can severely limit the accuracy of the reconstructed data.

A large amount of work has been dedicated to instrument development to overcome these drawbacks. Equipped with a MCP and a DLD, the LEAP 3000X HR has a lateral resolution of 0.2nm and a depth resolution of 0.1nm with high multiplicities. Due to some innate design limitations, the detector efficiency is still only 37%. This loss is mainly due to the fact that the open area of the channel plates is ~60% and the transmission efficiency of the grids at the entrance and exit of the reflectron is much less than 100%. The single hits and multiple hits which can be distinguished are all included in the data reconstruction. It is also possible to extract important information just from multiple hits as discussed in Chapter 4 .

3.4.3 Mass spectrum and data reconstruction

The time-of-flight spectrum is a histogram in which the numbers of ions detected are plotted as a function of their time of flight from the surface of the specimen to the detector. Using equation 3-2, the mass spectrum can be derived from the time-of-flight spectrum, and the numbers of ions are plotted as a function of their mass-to-charge ratios. The exact positions of the observed mass peaks may not perfectly align with their theoretical positions because of the slight inconsistencies in relative position of specimen apex and electrode and also electronic time-delays which arise from the fact that electric signals take time to generate and travel through. This can be simply corrected in the reconstruction process by reassigning two major peaks in the spectrum to their expected positions and this scaling factor then applied to shift the entire spectrum to the theoretical position. Each peak on the spectrum can then be assigned to a specific isotope of an element according to the periodic table and mass-to-charge ratio whilst taking into consideration the possibility that some peaks may correspond to molecular ions. The width of each peak also needs to be defined, which determines which events are treated as specific ions and which are treated as noise. However to date, no standard protocol of how to range the mass peaks has been established and accepted by the atom probe research community, which perhaps is one reason for the discrepancies in concentration measurements between different researchers. In this work, the width of peaks was defined as the full width at 10% maximum for each peak in the mass spectrum. An example of defining Fe^{2+} and Cr^{2+} peaks can be found in Fig.3.15, with the counts axis is shown in log scale.

The concept of mass resolution has been introduced to describe the ability to separate two mass peaks, and is defined as $M/\Delta M$, where M is the value of the mass

peak and ΔM is the peak width which is necessary to separate peak M. It can be calculated as the full width at half maximum (FWHM) or full width at 10% maximum (FWTM). This will be discussed further in Chapter 4.

In theory, the atom probe is able to detect all kinds of elements with equal sensitivity. However this may not be straightforward if the mass-to-charge ratios of different elements overlap. In some severe cases, accurate composition measurement becomes impossible due to the overlap of mass peaks of major isotopes of different elements, such as $^{14}\text{N}^+ / ^{28}\text{Si}^{2+}$ or $^{16}\text{O}^+ / ^{32}\text{S}^{2+}$. In less severe case, the elements may share identical weights for minor isotopes or have an overlap because of different charge states. A method for peak deconvolution has been discussed in reference [17]. A typical mass spectrum of doubly charged ions for Fe-Cr binary alloy is shown in Fig.3.15, with the periodic table of Fe and Cr showing the relative abundance of their isotopes. The peaks of $^{54}\text{Fe}^{2+}$ and $^{54}\text{Cr}^{2+}$ overlap on the mass spectrum. According to the relative abundance, for a Fe-15.2%Cr, only 0.3% of Cr atoms evaporate as $^{54}\text{Cr}^{2+}$ and 5% of Fe atoms evaporate as $^{54}\text{Fe}^{2+}$, which means that only 5.7% ions in the total numbers counted in this minor peak are Cr. The presence of $^{54}\text{Cr}^{2+}$ ions in this peak can be taken in account, though generally this peak at 27 is marked as $^{54}\text{Fe}^{2+}$. Similarly, for singly charged ions the peak at 54 is usually marked as $^{54}\text{Fe}^+$.

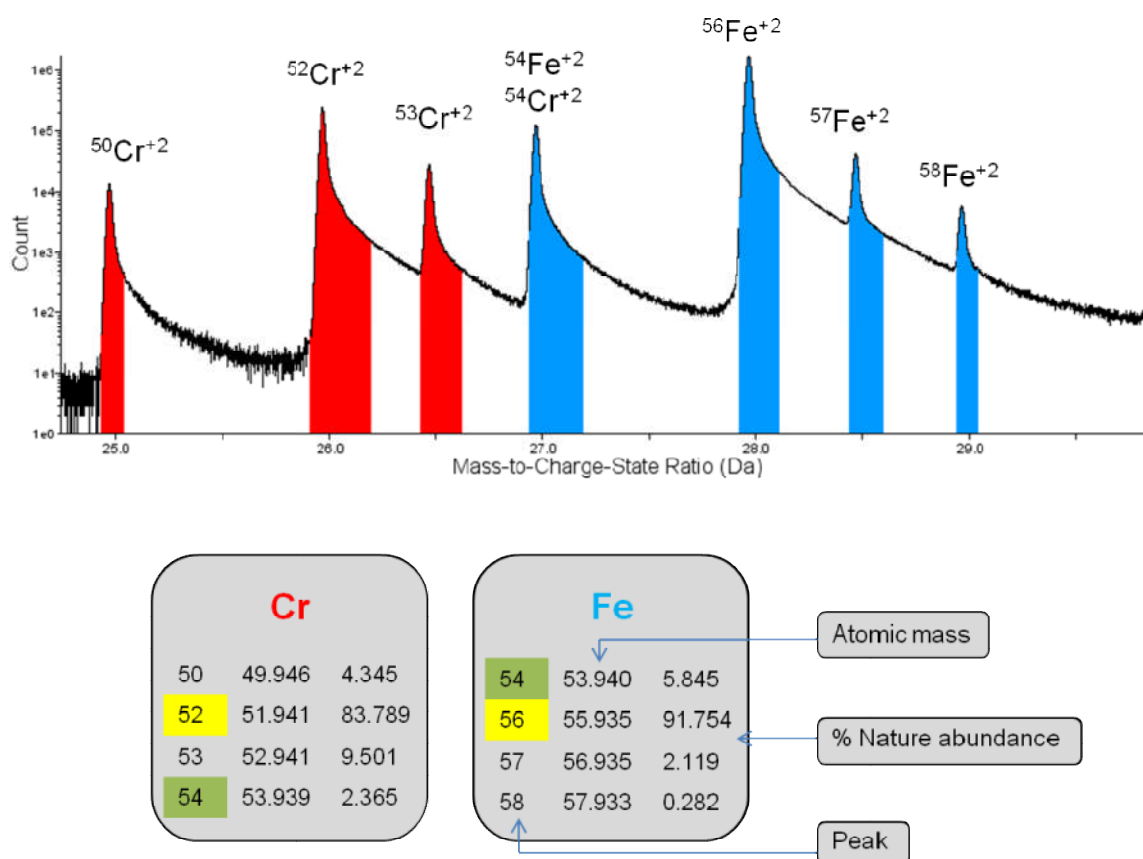


Fig.3.15 A typical mass spectrum for Fe-Cr binary alloy with tables showing the relative abundance of isotopes

After the ranges on the mass spectrum have been defined, the data is ready to be reconstructed to generate a three dimensional atom map. The other necessary information such as the positions of the ion impacts on the detector and ion hit sequences are directly recorded by the LEAP software during the data acquisition. Data reconstruction has been studied extensively to optimize the accuracy of the reconstructed data [38]. It can be carried out using IVASTM 3.4.3 or 3.6.0 software packages. The reconstruction parameters can be divided into material parameters, specimen parameters and instrument parameters. For material parameters, it is necessary to indicate the primary element contained in the specimen with its evaporation field. For a binary Fe-Cr alloy, Fe is identified as the primary element

with its evaporation field set to be 33V/nm [17]. The specimen parameters such as initial tip radius and shank half angle can be directly estimated by the software itself or can be input manually if such information is available from preceding experiments, for example TEM observation. Most of the instrument parameters are fixed, including detector efficiency (set at 0.37), specimen to detector distance (382mm as default), K factor (determining the relationship between specimen radius and evaporation field, often set to be 3.3), and the image compression factor (1.2 as default). The reconstructed three dimensional atom maps, along with mass spectra, contain all the chemical and physical information useful for the subsequent analysis. The quantitative chemical analysis methods will be discussed in Chapter 5 and cluster searching methods, such as the maximum separation method, will be discussed in Chapter 7. Note that despite advances in reconstruction methodologies there are still uncertainties resulting from effects such as local magnification, trajectory aberrations, surface migration of atoms and evaporation of multiple species. These issues are discussed in chapters 4 and 6.

References

1. Baker, H., H. Okamoto, S.D. Henry, G.M. Davidson, M.A. Fleming, L. Kacprzak, and H.F. Lampman, eds. *Alloy Phase Diagrams*. ASM Handbook. Vol. 3. 1992, Materials Park: ASM International: Ohio
2. Ziegler, J.F., M.D. Ziegler, and J.P. Biersack, *Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms*, 2010. **268**: p. 1818-1823.
3. Ziegler, J.F., J.P. Biersack, and M.D. Ziegler, *The Stopping and Range of Ions in Matter* 2008, Chester, Maryland: SRIM Co.
4. Norgett, M.J., M.T. Robinson, and I.M. Torrens, *Nuclear Engineering and Design*, 1975. **33**: p. 50-54.
5. *ASTM E521-96, Standard Practices for Neutron Radiation Damage Simulation by Charged-Particle Irradiation* 2003, Philadelphia, PA: American Society of Testing and Materials.
6. Lekstrom, M., M.A. McLachlan, S. Husain, D.W. McComb, and B.A. Shollock, *Using the in situ lift-out technique to prepare TEM specimens on a single-beam FIB instrument*, in *EMAG: Electron Microscopy and Analysis Group Conference 2007*, R.T. Baker, G. Mobus, and P.D. Brown, Editors. 2008, Iop Publishing Ltd: Bristol. **126**.
7. Giannuzzi, L.A. and F.A. Stevie, *Micron*, 1999. **30**: p. 197-204.
8. Miller, M.K., K.F. Russell, and G.B. Thompson, *Ultramicroscopy*, 2005. **102**: p. 287-298.
9. Thompson, K., D. Lawrence, D.J. Larson, J.D. Olson, T.F. Kelly, and B. Gorman, *Ultramicroscopy*, 2007. **107**: p. 131-139.
10. Egerton, R.F., *Reports on Progress in Physics*, 2009. **72**.

11. Ahn, C.C., O.L. Krivanek, R.P. Burgner, M.M. Disko, and P.R. Swann, *EELS atlas : a reference guide of electron energy loss spectra covering all stable elements* 1983, Warrendale, PA: Gatan, Inc.
12. Egerton, R.F. and M. Malac, *Journal of Electron Spectroscopy and Related Phenomena*, 2005. **143**: p. 43-50.
13. Egerton, R.F., Y.Y. Yang, and F.Y.Y. Chen, *Ultramicroscopy*, 1991. **38**: p. 349-352.
14. Browning, N.D. and S.J. Pennycook, *Journal of Physics D-Applied Physics*, 1996. **29**: p. 1779-1798.
15. Miller, M.K. and G.D.W. Smith, *Atom Probe Microanalysis: Principles and Applications to Materials Problems* 1989, Pittsburgh, Pennsylvania: Materials Research Society.
16. Muller, E.W., J.A. Panitz, and S.B. McLane, *Review of Scientific Instruments*, 1968. **39**: p. 83-&.
17. Miller, M.K., A. Cerezo, M.G. Hetherington, and G.D.W. Smith, *Atom Probe Field Ion Microscopy* 1996, Oxford, UK: Oxford University Press.
18. Kellogg, G.L. and T.T. Tsong, *Journal of Applied Physics*, 1980. **51**: p. 1184-1193.
19. Cerezo, A., T.J. Godfrey, C.R.M. Grovenor, M.G. Hetherington, R.M. Hoyle, J.P. Jakubovics, J.A. Liddle, G.D.W. Smith, and G.M. Worrall, *Journal of Microscopy-Oxford*, 1989. **154**: p. 215-225.
20. Kellogg, G.L., *Journal of Applied Physics*, 1981. **52**: p. 5320-5328.
21. Kelly, T.E., T.T. Gribb, J.D. Olson, R.L. Martens, J.D. Shepard, S.A. Wiener, T.C. Kunicki, R.M. Ulfing, D.R. Lenz, E.M. Strennen, E. Oltman, J.H.

- Bunton, and D.R. Strait, *Microscopy and Microanalysis*, 2004. **10**: p. 373-383.
22. Kelly, T.F., P.P. Camus, D.J. Larson, L.M. Holzman, and S.S. Bajikar, *Ultramicroscopy*, 1996. **62**: p. 29-42.
 23. Bunton, J.H., J.D. Olson, D.R. Lenz, and T.E. Kelly, *Microscopy and Microanalysis*, 2007. **13**: p. 418-427.
 24. Da Costa, G., F. Vurpillot, A. Bostel, M. Bouet, and B. Deconihout, *Review of Scientific Instruments*, 2005. **76**.
 25. Kelly, T.F. and M.K. Miller, *Review of Scientific Instruments*, 2007. **78**.
 26. Gault, B., M.P. Moody, F. De Geuser, A. La Fontaine, L.T. Stephenson, D. Haley, and S.P. Ringer, *Microscopy and Microanalysis*, 2010. **16**: p. 99-110.
 27. Thompson, K., J. Sebastian, and S. Gerstl, *Ultramicroscopy*, 2007. **107**: p. 124-130.
 28. Tsong, T.T., *Surface Science*, 1978. **70**: p. 211-233.
 29. Miller, M.K. and G.D.W. Smith, *Journal of Vacuum Science & Technology*, 1981. **19**: p. 57-62.
 30. Kingham, D.R., *Surface Science*, 1982. **116**: p. 273-301.
 31. Gomer, R. and L.W. Swanson, *Journal of Chemical Physics*, 1963. **38**: p. 1613-&.
 32. Muller, E.W., *Physical Review*, 1956. **102**: p. 618-624.
 33. Vurpillot, F., J. Houard, A. Vella, and B. Deconihout, *Journal of Physics D-Applied Physics*, 2009. **42**.
 34. Cerezo, A., P.H. Clifton, A. Gombert, and G.D.W. Smith, *Ultramicroscopy*, 2007. **107**: p. 720-725.

35. Gault, B., M. Muller, A. La Fontaine, M.P. Moody, A. Shariq, A. Cerezo, S.P. Ringer, and G.D.W. Smith, *Journal of Applied Physics*, 2010. **108**.
36. De Geuser, F., B. Gault, A. Bostel, and F. Vurpillot, *Surface Science*, 2007. **601**: p. 536-543.
37. Strasser, D., X. Urbain, H.B. Pedersen, N. Altstein, O. Heber, R. Wester, K.G. Bhushan, and D. Zajfman, *Review of Scientific Instruments*, 2000. **71**: p. 3092-3098.
38. Bas, P., A. Bostel, B. Deconihout, and D. Blavette, *Applied Surface Science*, 1995. **87-8**: p. 298-304.

Chapter 4

Optimizing Atom Probe Analysis Parameters for Fe-Cr Alloys

4.1 Introduction

The discussion in Chapter 3 argued that to accurately perform atom probe tomography requires a thorough understanding of the field evaporation process and the response of materials to both voltage and laser pulsing. The experimental conditions which include instrument parameters, specimen parameters and analysis parameters could significantly affect the behaviour of materials in terms of field evaporation as well as in the accuracy of the analysed results. For example, APT has been used to measure composition variation during spinodal decomposition on the nano scale in Fe-Cr alloys [1] and it was found that the experimental conditions affected the observations. In particular, setting appropriate experimental conditions including the standing voltage on the specimen, the pulse fraction and a suitable sample temperature has proved vital for avoiding preferential evaporation and/or retention of alloy atoms and hence obtaining reliable composition measurements [2].

The development of the pulsed-laser atom probe has brought certain advantages, including an increased data acquisition rate and the ability to analyse less conductive materials [3]. For pulsed-laser APT, it is also necessary to understand how the field evaporation is triggered by laser pulses. Sha et al. [4] found that the laser pulse energy and base temperature both have large effects on the composition measurement of an Al-Mg-Si-Cu alloy, and that the mass resolution is sensitive to the local taper angle near the apex of the specimen.

In the pulsed-laser mode, the instrument parameters include laser beam spot size, wavelength and laser pulse duration. Bunton and co-workers [5] have studied the optimum performance in a pulsed-laser atom probe and found that the mass resolving power generally improves as the laser spot size and wavelength are

decreased, though some discrepancies still existed when different materials were used in the calibration. However in the LEAP, the instrument parameters are often fixed and unchangeable, for example the LEAP 3000X HR is equipped with a laser which has a spot size (4σ) less than $10\mu\text{m}$ and wavelength of 532nm .

The specimen parameters include specimen shank angle, tip radius and thermal diffusivity. Bunton et al. [5] found that the mass resolving power increases as the specimen shank angle, tip radius and thermal diffusivity increase in a pulsed-laser atom probe. Cerezo et al. [6] also confirmed that a large specimen shank angle can improve the mass resolution and reduce the noise level and degradation in the compositional accuracy caused by the base temperature increasing. Furthermore, low thermal diffusivity of the specimen was found to have a negative effect on mass resolution due to the slow cooling-down of the specimen after a laser pulse was applied. The shape of the specimen cannot be controlled if it is manufactured using the traditional two-stage electropolishing specimen preparing method. When the FIB *in situ* lift-out method is applied, there is some control over the specimen shank angle and tip radius, however precise control still proves to be difficult.

The analysis parameters, on the other hand, such as pulse fraction in pulsed-voltage mode, pulse energy in pulsed-laser mode, target evaporation rate and base cryostat temperature in the analysis chamber are adjustable and play important roles in the quantitative accuracy of measured results. Various optimum instrument parameter settings for analyzing different materials are presented by many researchers. Sometimes discrepancies exist between the commonly used parameters and the newly obtained results. Yao et al. discovered the lowest specimen temperature (20K) and high pulse fraction (up to 30%) are most suitable for the tiny NbN clusters in microalloyed steels under pulsed-voltage mode, which was in contrast with the usual

temperature setting ($\sim 60\text{K}$) used in previous experiments [7]. The authors suggested that the commonly used settings were presumably due to reducing the chance of specimen rupture, however they believe that the conditions they investigated can provide superior data in terms of several criteria such as signal-to-noise ratio (SNR) and the accuracy of chemical composition measurements. Such cases remind scientists of the importance of optimizing the analysis parameters for each material before carrying out any actual atom probe experiment. Another essential point is to consider other parameters while determining and calibrating the optimum analysis parameters. For example, thermal diffusivity needs to be taken into account because it is very important in determining the actual temperature of the specimen during field evaporation. Cerezo et al. [6] suggested using a lower laser energy to minimize tip temperature increases when analyzing a material with low thermal diffusivity.

A series of systematic calibration tests was designed and carried out on binary Fe-Cr alloys to examine the effect of each variable analysis parameter separately under both pulsed-voltage mode and pulsed-laser mode in a LEAP 3000X HR. The goal of this work was to determine the optimum analysis parameters for both evaporation modes to maximize the mass resolution and accuracy of chemical analysis, and to obtain relative uniformity of Cr content within the field of view, while minimizing the background noise and multiple events.

4.2 Design of the Calibration Tests

The test materials were reference Fe-Cr alloys with Cr concentrations between 10-13%. These were taken from the first batch of materials. Due to the limited amount of as-received materials, it was difficult to carry out the entire calibration test on a single specific material condition. All the specimens were prepared using the two-stage electropolishing method as described in section 3.4.3.

Under the pulsed-voltage mode, the three analysis variables for optimization are pulse fraction, target evaporation rate and cryostat temperature which is measured on the specimen stage. Reference data and instrument specification were used to identify suitable ranges for the testing of each parameter. To examine the effect of one parameter independently, the other two need to be fixed at certain values. The pulse fraction can be set in the range 5% to 30% (the maximum possible) [8]. The previous discussion in section 3.4.2.3 has shown that the existence of multiple hits could limit the quantitative accuracy of the measured results. To avoid significant loss of data, one solution is to decrease the target evaporation rate to reduce the statistic occurrence of multiple hits. Therefore the target evaporation rate was set at 0.002ions/pulse (which is close the minimum possible in the instrument). Analyses were performed using three cryostat temperatures, 30K, 50K and 70K. 50K and 70K were the most commonly used temperature setting for analyzing Fe-Cr alloys [1, 9], and 30K was to examine the evaporation behaviour at low temperature. The calibration tests to determine the best range of pulse fraction are summarized in the first row of Table 4.1 as Test No.1. Experiments covering all 23 of the combinations listed in test No. 1 were performed.

Table 4.1 Design of calibration tests under pulsed-voltage mode

Test No.	Material	Pulse Fraction (%)	Base temperature (k)	Target Evaporation Rate (ions/pulse)
1	Fe-11.7/13.9%Cr	10, 15, 17, 20, 22, 25, 30	30, 50, 70	0.002
3	Fe-12.8%Cr	Optimum range	30, 50, 70, 90, 110	0.002
5	Fe-13.9%Cr	Optimum range	Optimum range	0.002, 0.004, 0.006, 0.008, 0.01

After an optimum range of pulse fractions had been determined for the designated temperatures (as the relationship shown in Fig.3.11), the calibration of determining the optimum cryostat temperature setting could be carried out as shown in the second row of Table 4.1 as Test No.3. Later, having identified optimum pulse fraction and cryostat temperature, experiments were performed to determine a suitable evaporation rate (Table 4.1 - Test No.5).

Under the pulsed-laser mode, there are also three parameters that need optimizing: pulse energy, target evaporation rate and cryostat temperature. To examine the effect of pulse energy first, the target evaporation was set at 0.002ions/pulse (to minimize the effect of multiple hits), and the cryostat temperature was set at 50K. During the calibration, the pulse energy was varied from 0.2nJ to 1nJ as shown in the first row of Table 4.2 as Test No. 2.

Using the same method, determination of the optimum cryostat temperature setting was carried out after the optimum range of pulse energy been decided. The target evaporation rate was the last parameter to be tested, as shown in Table 4.2 as Test No. 4 and No. 6.

Table 4.2 Design of calibration tests under pulsed-laser mode

Test No.	Material	Pulse Energy (nJ)	Base temperature (K)	Target Evaporation Rate (ions/pulse)
2	Fe-12.8%Cr	0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1	50	0.002
4	Fe-10.6%Cr	Optimum range	30, 50, 70, 90, 110	0.002
6	Fe-10.6%Cr	Optimum range	Optimum range	0.002, 0.004, 0.006, 0.008, 0.01

4.3 Pulse Fraction in Pulsed-voltage Mode

In Test No.1, the target evaporation rate was fixed at 0.002ions/pulse. The cryostat temperature was set to 50K and independent data were collected at each of the seven pulse fractions detailed in the first row of Table 4.1 between 10% and 30%. The temperature was then increased to 70K and the experiments were repeated. About 0.6 million ions were collected after the tip had adopted a steady shape as revealed by detector histogram for each experiment and each dataset was then reconstructed using the same parameters. In IVAS version 3.4.3, the single hits and multiple hits which can be distinguished are all included in the data reconstruction and it is these data that are used to determine the chemical concentration measurement. The multiple hits can be retrieved from the original data as well, and the reconstruction of multiple hits can also provide some important information. The background information was directly provided by IVAS using the time-of-flight (TOF) spectrum rather than the mass spectrum, and in units of ppm/ns, which means the number of ions that contribute to the background noise compared with the total number of ions detected per nano second. The comparison of the measured Cr concentrations, fraction of events that are multiple hits and also the observed background count rate is shown in Fig.4.1. The statistical errors of measured concentrations are very small, therefore not shown on the figure. There were other errors introduced due to imperfect detector efficiency and other reasons, however it was very difficult to quantify these errors.

It is clearly shown that when the pulse fraction is set at 10%, with a cryostat temperature of either 50K or 70K, the measured Cr concentrations are significantly lower than the known bulk concentration, and the levels of background noise are

higher than in the experiments performed using a higher pulse fraction. When the pulse fraction is set larger than 15%, all experiments exhibit similar levels of background noise and measured Cr concentrations are close to the bulk concentration. The levels of multiple hits are also quite similar despite the variation of pulse fraction at a given temperature. All experiments used the same evaporation rate which approximately equated to the rate of data acquisition, therefore comparing the background noise rate is a reasonable approach.

Analysing the data presented in Fig.4.1, it seems unlikely that multiple hits are the reason for the underestimate of the Cr concentration at low pulse fractions since the multiple hits fractions are similar for all the experiments irrespective of pulse fractions. Considering the differences in the evaporation field of Fe^{2+} (33V/nm) and Cr^{2+} (29V/nm), it appears that the most probable explanation is that there is preferential removal of Cr atoms during the time intervals between the voltage pulses. As discussed in section 3.4.2.1, Cr atoms have a lower evaporation field and are therefore more easily removed by a high standing DC voltage which results in the evaporation of Cr by the standing voltage. These atoms are detected as noise rather than Cr atoms and hence lead to an underestimate of the Cr concentration. The unusually high background noise when the pulse fraction was is at 10% at both 50K and 70K as shown in Fig.4-1 is consistent with this explanation. A similar phenomenon has been observed by Miller et al. [10] and was found to be especially pronounced at low pulse fractions ($\leq 10\%$ in this case). Therefore, a minimum pulse fraction of about 15% is required for analysis of Fe-Cr samples at a temperature of 50K or 70K.

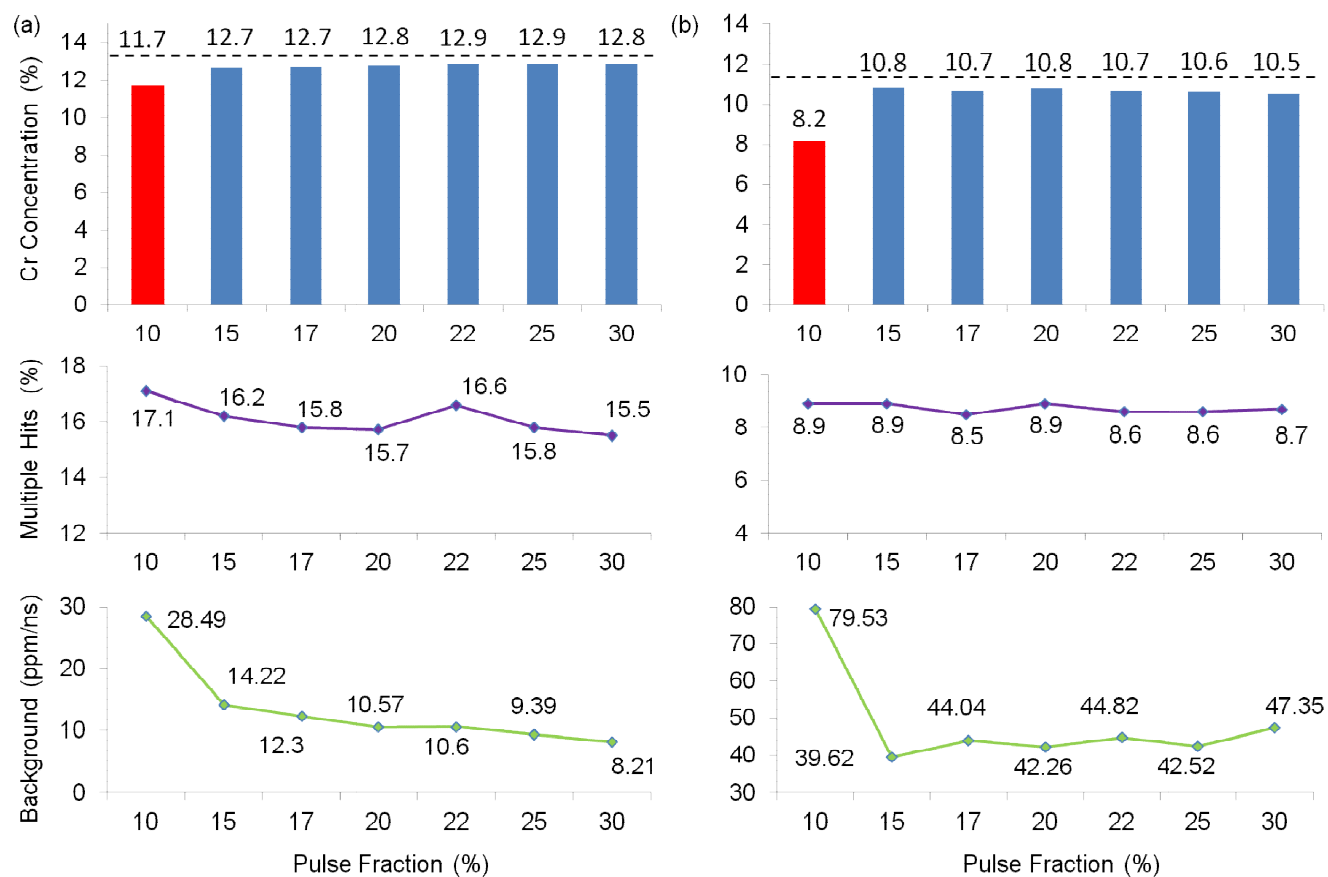


Fig.4.1 The comparison of Cr concentration, multiple hits and background count rate when pulse fraction is varied from 10%-30% with target evaporation rate set at 0.002ions/pulse in pulsed-voltage mode, (a) Fe-13.9%Cr at 50K, (b) Fe-11.7%Cr at 70K, bulk concentrations are indicated as black dashed lines.

From Fig.3.11 shown in section 3.4.2.1, to compensate for the increase in the relative difference of evaporation rate between two elements at higher temperature, one solution is to increase the pulse fraction. Such a solution ensures that the field evaporation by the standing DC voltage is still negligible compared to the amount of atoms evaporated during the pulses. Therefore it is reasonable to predict that the threshold of pulse fraction will be larger than 15% at even higher temperatures ($>70\text{K}$). For the commonly used temperature setting of 50K and 70K, to optimize the accuracy of chemical measurement in pulsed-voltage mode, it is best to keep the pulse fraction between 15%-25%.

Once the optimum suitable range of voltage pulse fraction had been determined, an additional set of 9 calibration experiments was performed using three different temperatures 30K, 50K and 70K, and three different pulse fractions at 15%, 20% and 25%. For each the target evaporation rate was still fixed at 0.002ion/pulse. For a designated temperature, the calibration was started after the tip shape of the specimen reached a stable state, and about 2.5 millions ions were collected on the same specimen for each pulse fraction value. Even though the tip shape of the specimens evolved during the field evaporation, the removal of 7.5 millions ions did not cause a large alternation on the tip shape, which was confirmed using the grain orientation on the reconstructed atom map. The detailed comparisons between Cr concentrations, multiple hits and background count rates are shown in Fig.4.2.

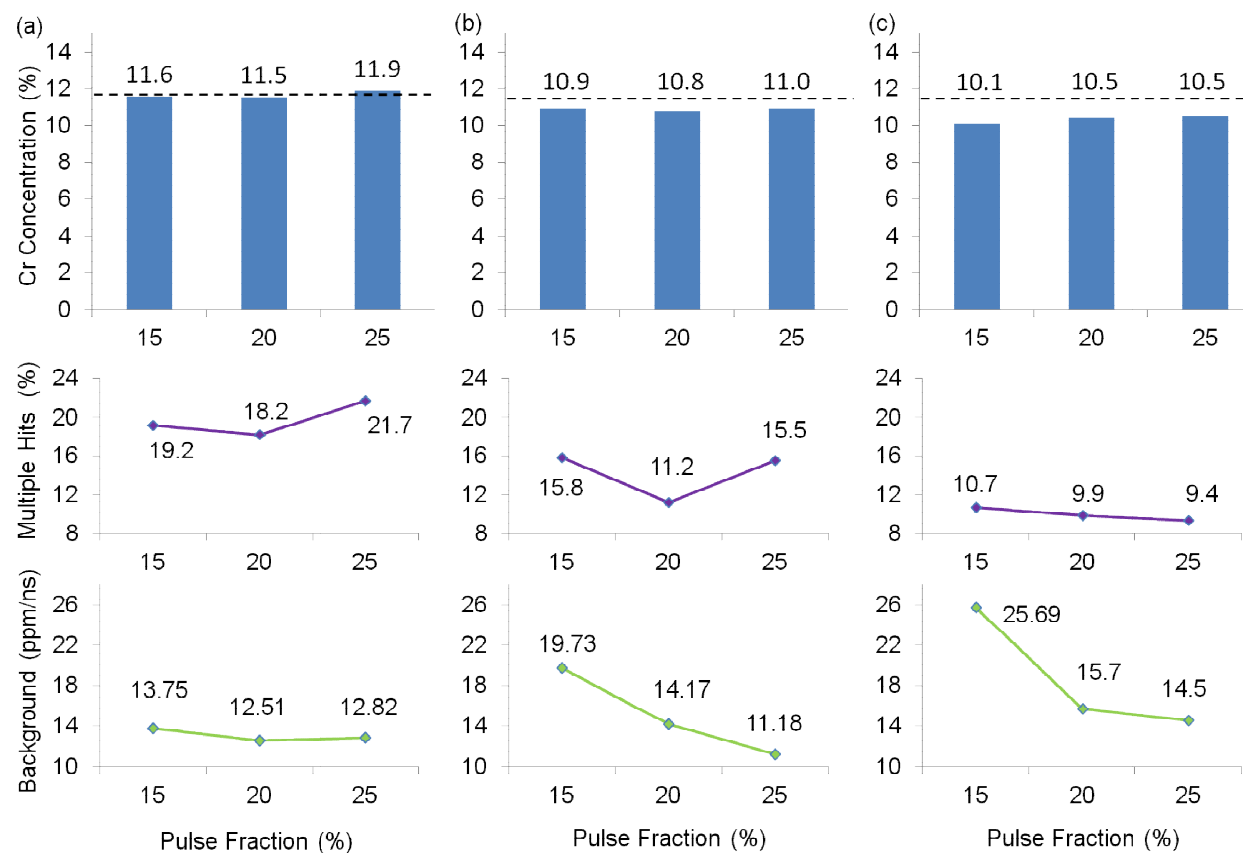


Fig.4.2 The comparison of Cr concentration, multiple hits and background when pulse fraction is varied from 15%-25% with target evaporation rate set at 0.002ions/pulse in pulsed-voltage mode, (a) Fe-11.7%Cr at 30K, (b) Fe-11.7%Cr at 50K, (b) Fe-11.7%Cr at 70K, bulk concentrations are indicated as black dashed lines.

At the same temperature, each experiment demonstrated similar levels of multiple hits and measured Cr concentration, $11.7 \pm 0.2\%$ (at 30K), $10.9 \pm 0.1\%$ (at 50K) and $10.4 \pm 0.2\%$ (at 70K) respectively, showing invariance to the pulse fraction in the range of 15% to 25%. At 30K, the background levels were similar at different pulse fractions. Meanwhile at 50K and 70K, the highest background level appeared when the pulse fraction was set at 15%, and it showed a tendency to decrease as the pulse fraction is increased, which implies that preferential evaporation of Cr contributes to the high background levels at lowest pulse fraction. As the cryostat temperature was increased from 30K to 70K, the average level of multiple hits gradually reduced, while the average level of background noise rose significantly. The measured Cr concentration obtained at 50K is closest to the bulk concentration.

The lowest temperature selected ($\leq 30\text{K}$) gave rise to the highest level of multiple hits. If the correlated evaporation happens on a pair of Fe-Cr atoms, they can easily be distinguished by the detector due to differences in the time of flight. Statistically, there are more Fe atoms than Cr atoms in the alloy, so correlated evaporation is more likely to happen for a Fe-Fe pair rather than for a Cr-Cr pair. Multiple hits of Fe would reduce the measured Fe concentration and increase the measured Cr concentration. When the temperature is too high, the measured Cr concentrations decrease. The detailed effect of temperature will be discussed in section 4.5.

Four two-dimensional density maps plotted with the z-axis as the analysis direction are shown in Fig.4.3. The 2D density maps include single hits and multiple hits of Cr and Fe with the indexes of the major poles. These were obtained from the experiment carried out at 50K, with a pulse fraction of 20% and a target evaporation rate of 0.002ions/pulse.

The poles and crystallographic zone lines are shown most clearly on the maps of multiple hits rather than single hits, indicating that most multiple hits are detected from these regions. As discussed in section 3.4.2.3, the electrical field increases as the pole terrace diameter decreases. Consequently the correlated evaporation is especially drastic at the centre of low index poles, which explains the high density of multiple hits of Fe observed in the centre of low index poles such as (110) and (200). Since a large fraction of Fe atoms from the centre of the low index poles are evaporated as multiple events, the high density of Cr and low density of Fe in the same region are also observed on the single hits maps.

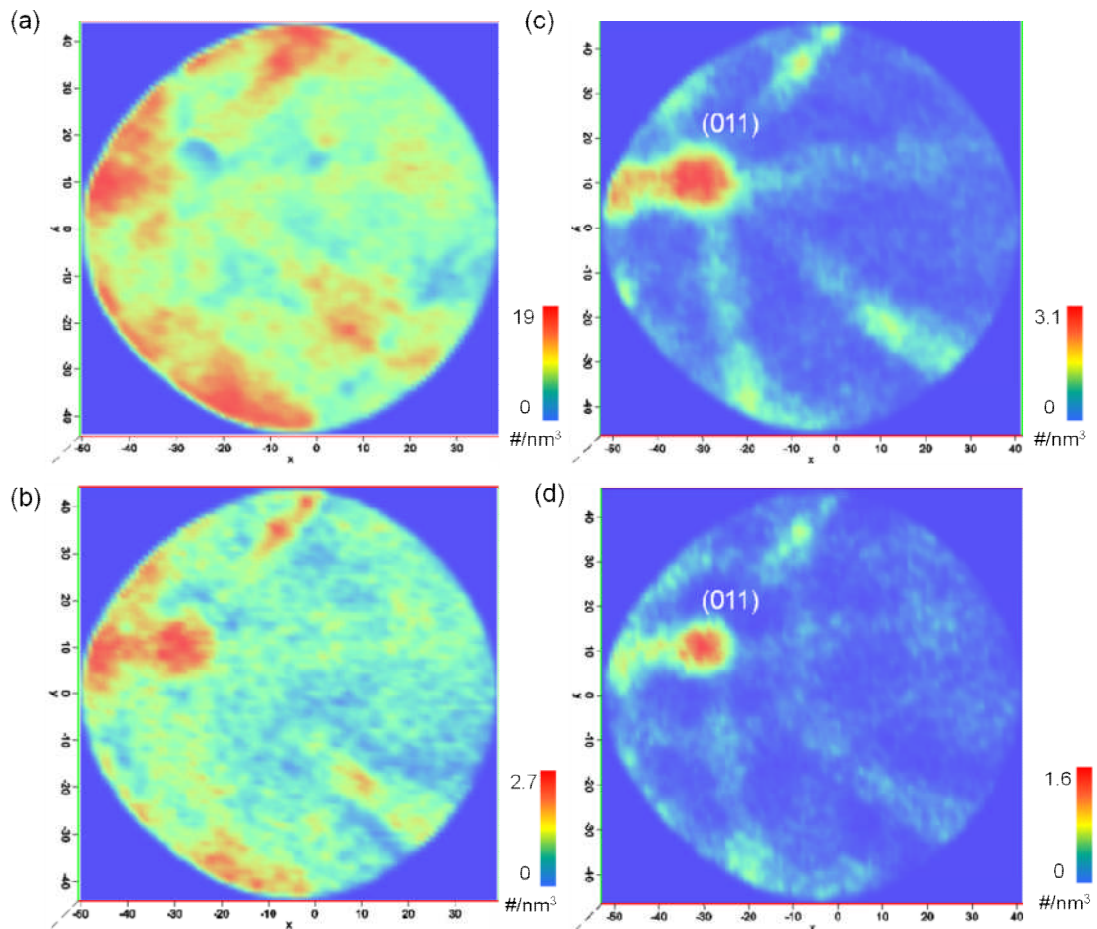


Fig.4.3 2D Density maps of Fe-11.7%Cr obtained under pulsed-voltage mode at 50K, with pulse fraction at 20% and target evaporation rate at 0.002ions/pulse, (a) Fe^{2+} single hits, (b) Cr^{2+} single hits, (c) Fe multiple hits, (d) Cr multiple hits

4.4 Pulse Energy in Pulsed-laser Mode

In test No.2 shown in the second row of Table 4.1, the target evaporation rate was fixed at 0.002ion/pulse. 9 calibration experiments were carried out on one specimen using a pulse energy between 0.2nJ and 1nJ at 50K. About 0.8 million ions were collected after the tip reached a stable evaporation state for each experiment and the same parameters were used for each in the reconstruction process using IVAS 3.6.0. The comparisons in terms of Cr concentration, multiple hits and background count rate are shown in Fig.4.4.

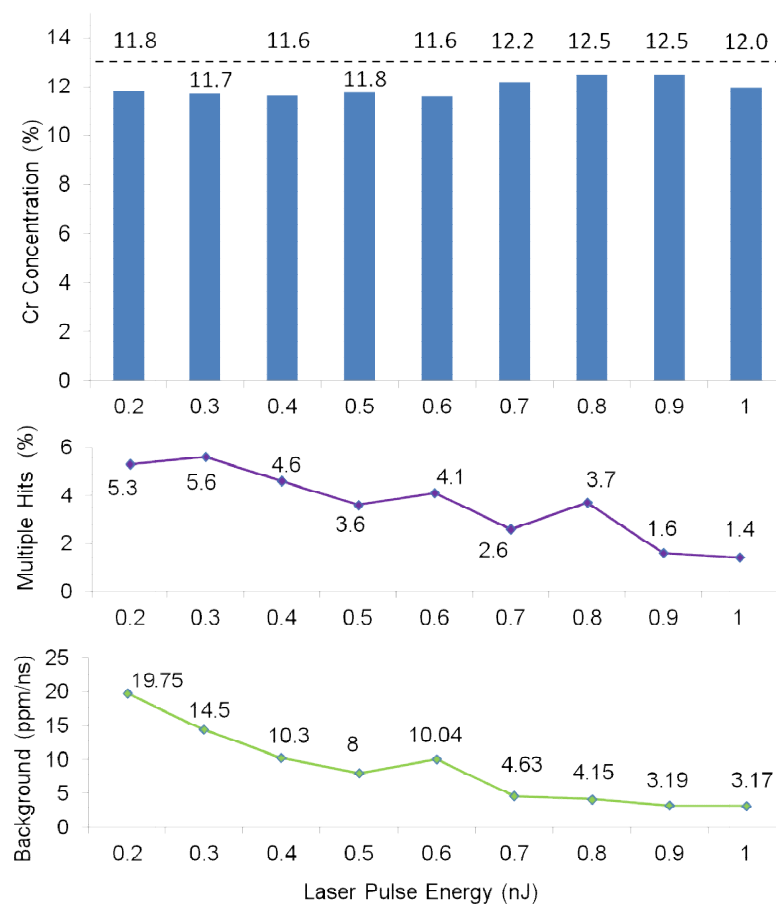


Fig.4.4 The comparison of Cr concentration, multiple hits and background of Fe-12.8%Cr when the laser pulse energy was varied from 0.2nJ to 1nJ with target evaporation rate set at 0.002ions/pulse in pulsed-laser mode, bulk concentration is indicated as black dashed line.

It is clear that when the pulse energy was varied from 0.2nJ to 1nJ, the multiple hits were always maintained at a quite low level which is below 6%. The multiple hits level was generally lower in comparison with all the data obtained in pulsed-voltage mode under different conditions. The measured Cr concentrations were also self-consistent, indicating approximately 12%Cr in each case. The laser energy did not have a large effect on the overall measured Cr concentration. The background level changed from 19.75ppm/ns to 3.17ppm/ns, demonstrating a tendency to decrease as pulse energy was increased.

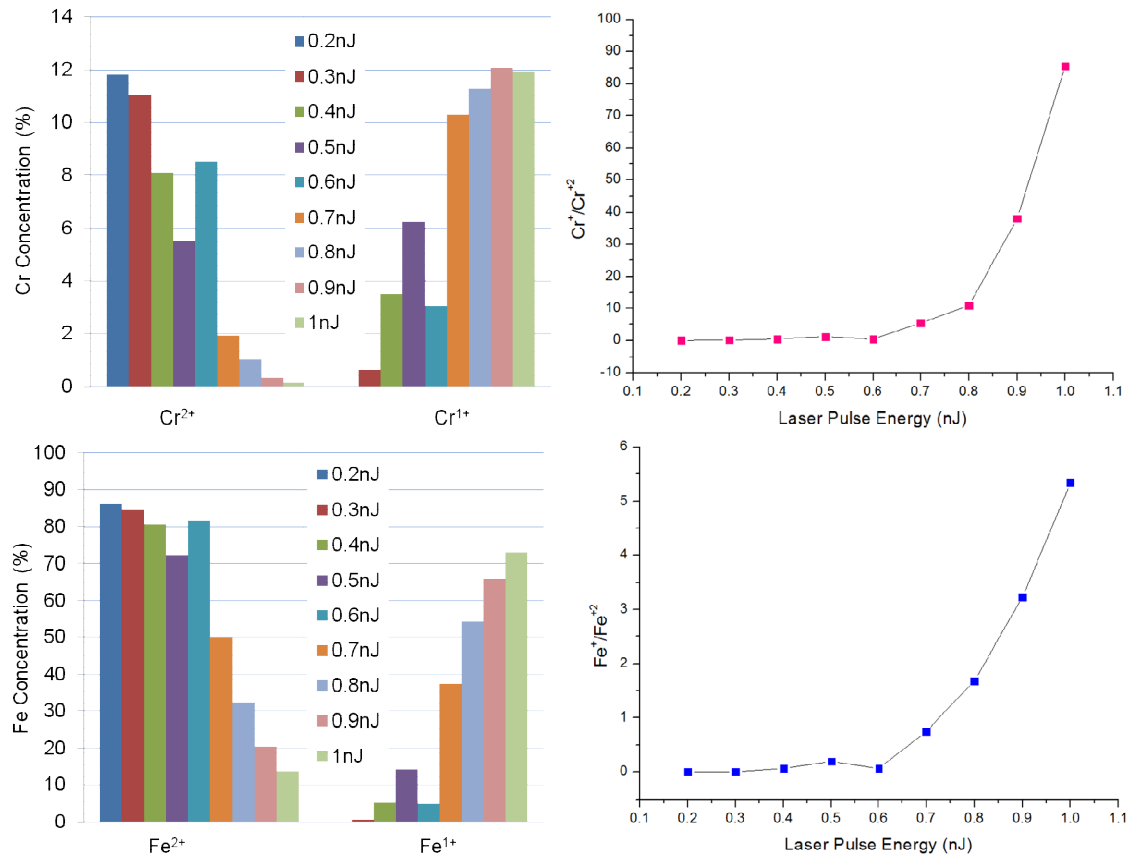


Fig.4.5 The concentrations and the relative abundance of Fe and Cr ions in singly and doubly charged states of Fe-12.8%Cr when the pulse energy was varied from 0.2nJ to 1nJ with target evaporation rate set at 0.002ions/pulse in laser mode, 50K

Note that even though the measured Cr concentrations were quite similar when the specimen was run using different laser pulse energies, the ratios between ions with different charge states can vary a lot. Fig.4.5 shows a detailed analysis of the concentrations and relative abundance for singly charged and doubly charged Fe and Cr ions.

As discussed in Fig.3.13, the increasing laser energy can cause an increase in specimen temperature as well as a decrease in the evaporation field. According to Kingham's theory [11], an increasing fraction of Fe and Cr atoms evaporate as singly charged ions as the field decreases. When the pulse energy was set at 0.7nJ, over 90% of the Cr atoms and almost half of the Fe atoms were observed to evaporate in a singly charged state. Since thermal heating of the specimen is enhanced by increasing the laser energy, the abundant evaporation of singly charged ions is an indication that the specimen was overly heated when the laser pulse energy was high. This phenomenon is even worse in the region directly heated by the laser. As shown in Fig.4-6, when the laser energy is 0.2nJ, most of atoms evaporate as doubly charged ions. However when laser energy was 0.7nJ, the reconstructed atom maps showed marked non-uniform distributions of Fe^{2+} , Fe^+ and Cr^+ . This phenomenon became even worse as the laser energy was further increased. A significant fraction of singly charged ions was observed in the areas directly heated by the laser or the regions between crystallographic lines. This may be caused by surface thermal diffusion due to the overheating of the specimen. The map of Cr^{2+} does not provide much information due to very limited fraction of Cr atoms evaporated in the doubly charged state at such high laser energy. High laser power, in our case larger than 0.7nJ, and hence high specimen temperatures must be avoided to ensure minimal surface diffusion.

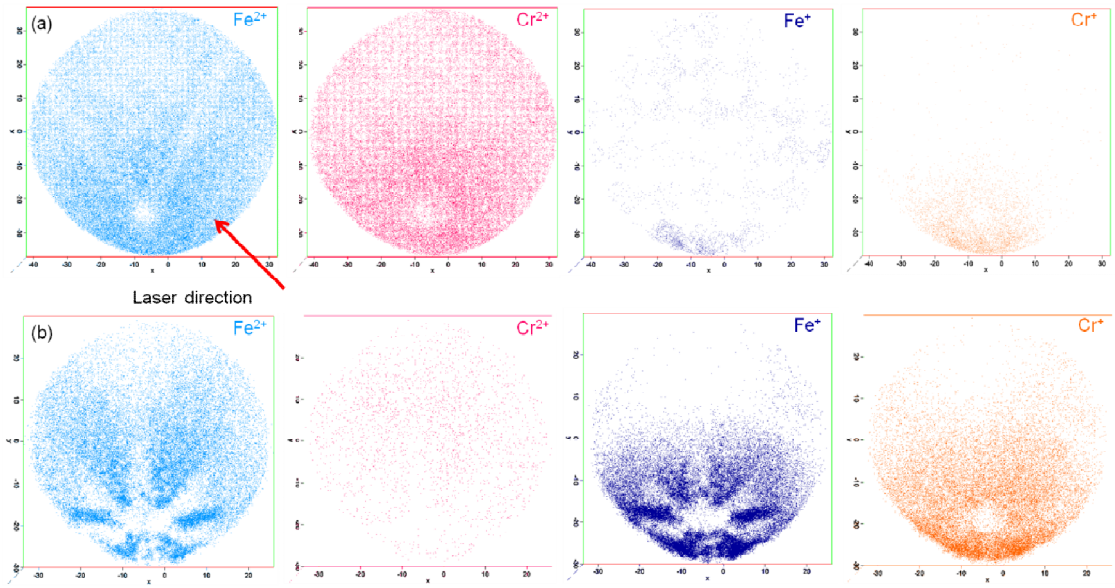


Fig.4.6 Atom maps of Fe and Cr ions in singly and doubly charged states of Fe-12.8%Cr with target evaporation rate set at 0.002ions/pulse in laser mode, 50K (a) pulse energy at 0.2nJ (b) pulse energy at 0.7nJ

By studying the effective pulse fraction PF_{eff} , the range of appropriate laser pulse energy can be further narrowed down. The PF_{eff} was calculated for the laser energies used in test No.2 using equation 3-3 discussed in section 3.4.2.2. As in the method used by Gault and co workers [12], all the data in test No.2 were collected by varying only the laser energy while the target evaporation rate was fixed. After the tip of the specimen had reached a stable shape and the target evaporation rate was maintained at a constant value, the specimen voltage V used in the calculation at each point was taken as an average value over the detection of 500,000 ions. There is no satisfactory theory to suggest what form the relationship should be. However comparing with a second order polynomial fit, a linear fit was found to be a good first order approximation with smaller standard error. So a linear fit was chosen and gave an equation as below:

$$y = \text{intercept} + B_1X \quad (4 - 1)$$

$$\text{intercept} = 8384.11 \quad B_1 = -4282.06$$

The voltage required at zero laser energy was determined by the intercept value, which extrapolated from the linear fit. It was taken as the reference standing DC voltage V_{ef} . The linear fit plot and the PF_{eff} calculation are shown in Fig.4.7.

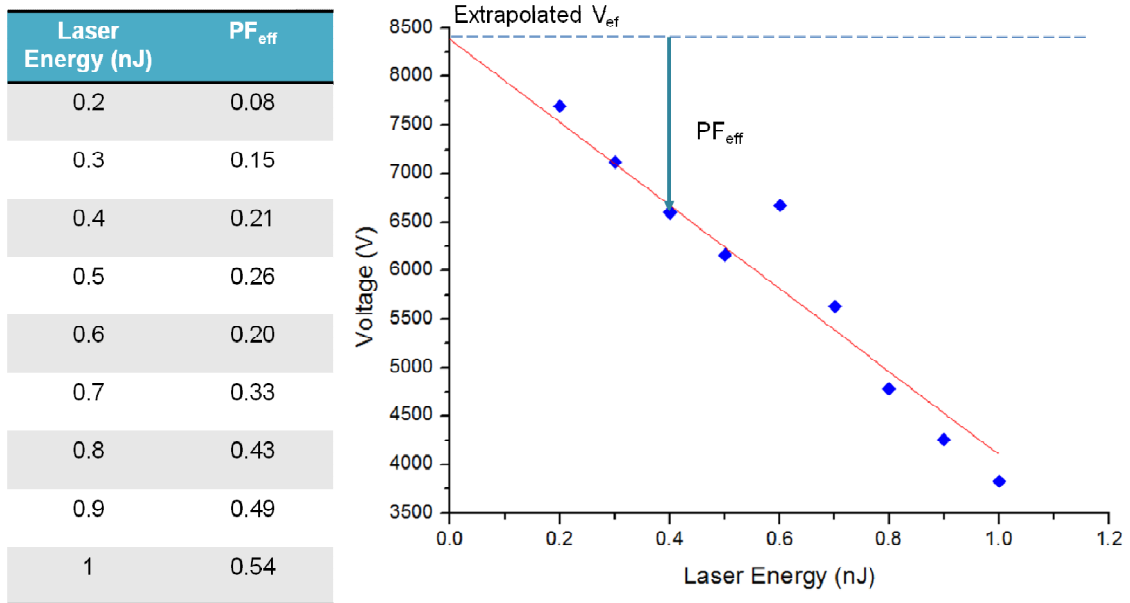


Fig.4.7 Specimen voltage plotted as a function of laser energy, with a linear fit and calculated effective pulse fraction, data obtained from test No.2.

Selection of the right effective pulse fraction is very important in pulsed-laser atom probe experiments. Insufficient effective pulse fraction could cause preferential evaporation/retention and also will result in the application of a higher standing potential to maintain the required rate of field evaporation. This increases the stress on the specimen which might cause frequent specimen fracture. On the other hand, an excessive effective pulse fraction may lead to overheating of the specimen and introduces artifacts such as surface migration of atoms as discussed in Fig.4.6 (b) [7,

13]. Bunton et al. [5] did a series of tests on Si dissolved in stainless steel and suggested that an effective pulse fraction of between approximately 0.10 and 0.15 is suitable for most materials. From this point of view, the appropriate effective pulse fraction in our experiment can only be achieved when the laser energy is set lower than 0.4nJ. Therefore the pulse energy should not exceed 0.3nJ to avoid overheating the specimen, optimize the mass spectrum resolution and ensure approximately uniform evaporation of atoms.

4.5 Temperature

The concept of temperature discussed here, refers to the cryostat temperature which is measured on the specimen stage in the analysis chamber, and can be directly controlled by the LEAP computer. It is not the actual specimen apex temperature, especially under pulsed-laser mode due to the specimen temperature rise caused by the laser heating.

From the discussion in section 4.3, the optimum setting of pulse fraction was defined to be between 15%-25%. Therefore, test No.3 was performed on Fe-12.8%Cr under voltage mode using 5 different cryostat temperatures between 30K and 110K. These tests were performed using a voltage pulse fraction set at 15% and then repeated using a pulse fraction of 20%. All experiments were performed using a target evaporation rate at 0.002ions/pulse as before. Fig.4.8 shows the comparison between measured Cr concentration, multiple hits and background count rate.

When the pulse fraction was set at 15%, the measured Cr concentration gradually decreased from nearly 14% to 10% as the temperature was increased from 30K to 110K. The multiple hits also decreased from over 20% to 11%, while the background level increased from 8.19ppm/ns to 87.68ppm/ns. When the pulse fraction was set at 20%, the Cr concentration also showed the highest value at 30K, and the lowest value at around 10% at both 70K and 110K. The multiple hits dropped from 20.4% at 30K and had the lowest value at 70K. The background level also demonstrated a tendency to increase with temperature. The mass resolution $M/\Delta M$ using a pulse fraction 15%, was 1132.2 (FWHM) and 533.4 (FWTM) at 30K, and gradually decreased to 988.5 (FWHM) and 470 (FWTM) at 110K; at pulse fraction 20%, the $M/\Delta M$ was 1132 (FWHM) and 538.9 (FWTM) at 30K, and

decreased to 978.8 (FWHM) and 480.1 (FWTM) at 110K. Similar tendencies of decreasing mass resolution with temperature were found at different pulse fractions.

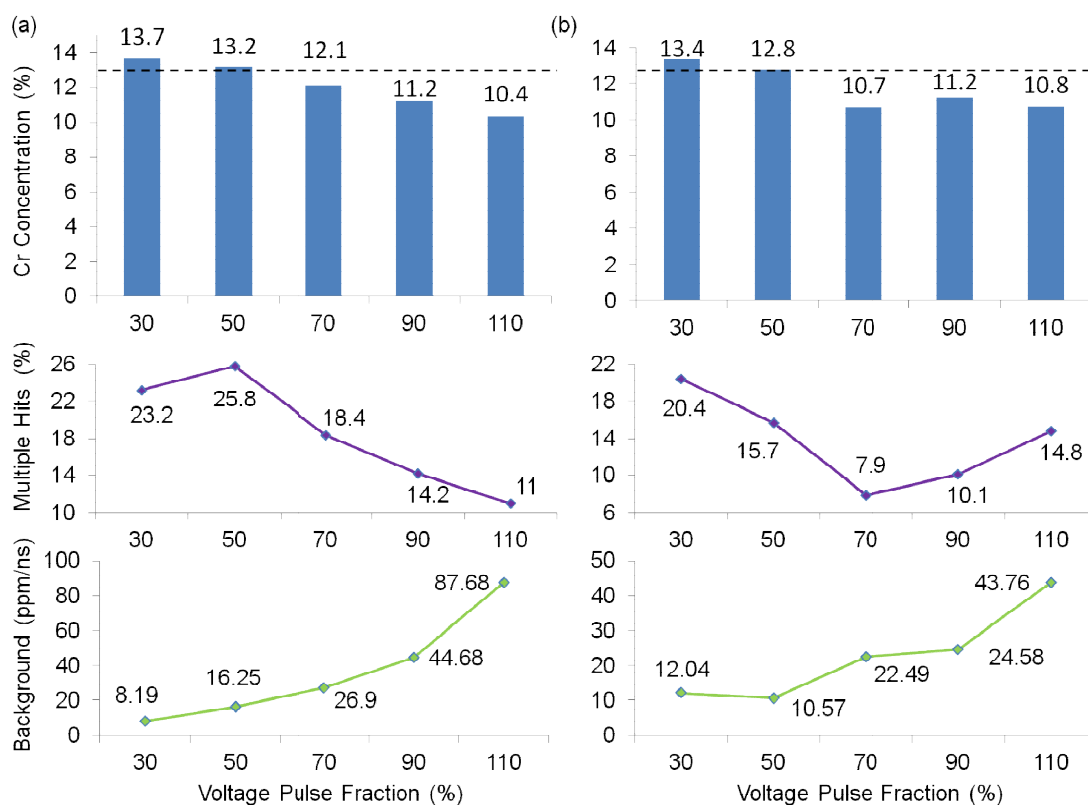


Fig.4.8 The comparison of measured Cr concentration, multiple hits and background count rate when the temperature was varied from 30K to 110K with target evaporation rate set at 0.002ions/pulse in pulsed-voltage mode on a Fe-12.8%Cr, (a) pulse fraction at 15%, (b) pulse fraction at 20%, bulk concentrations are indicated as black dashed lines.

The dramatic change of measured Cr concentration obtained using different temperatures shows that the temperature has a large effect on the accuracy of chemical measurement. The overestimation of Cr concentration at low temperature (30K) is considered to be caused by the higher proportion of multiple-hits. Statistically more Fe ions are lost by multiple events than Cr ions and this

potentially results in a decrease of the measured Fe concentration and an increase of the measured Cr concentration. At different pulse fractions, the plots of multiple hits show similar general tendencies to the changes in measured Cr concentration. This also clearly demonstrates that multiple hits play an important role in chemical concentration measurement.

Fig.4.9 shows two-dimensional density maps of Cr multiple hits and single hits using the data obtained in test No.3, when the voltage pulse fraction was set at 20% and with the target evaporation rate at 0.002ions/pulse. At 30K, the multiple events occurred not only on the crystallographic features such as poles or lines, but also on the entire evaporation surface of the specimen. As temperature was increased, the majority of the multiple events occurred on crystallographic features such as low index poles. Furthermore single events also have the highest density around the low index pole. This phenomenon becomes worse with increasing temperature.

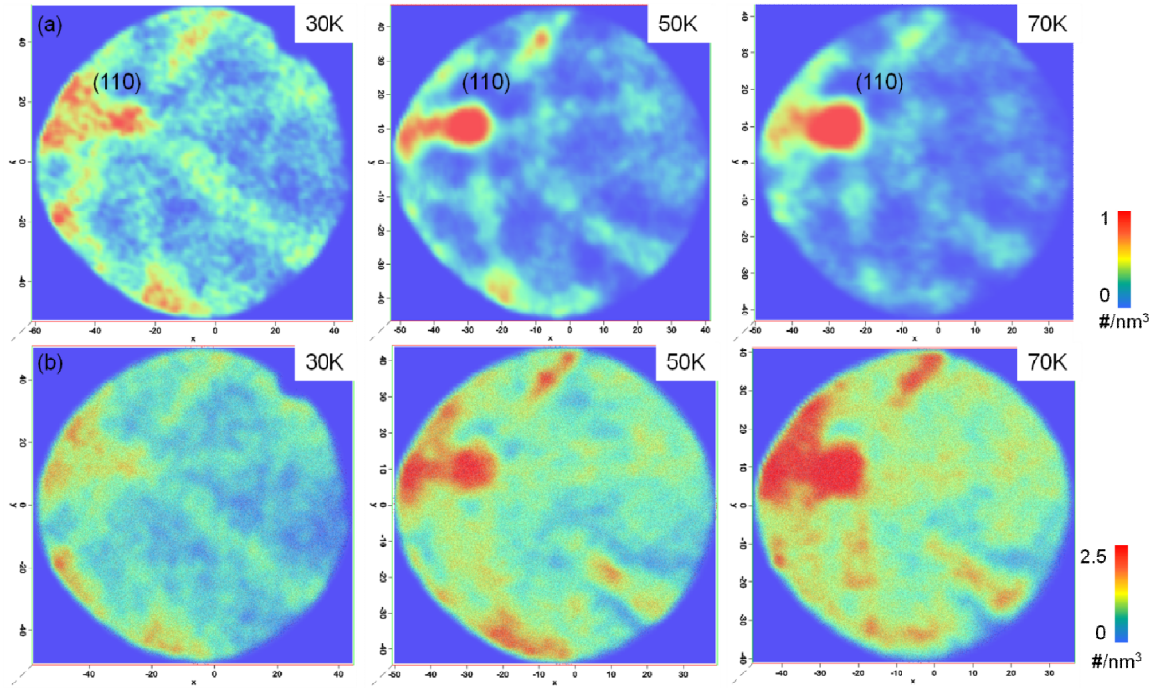


Fig.4.9 (a) Two-dimensional density maps of Cr multiple-hits distribution and (b) Two-dimensional density maps of Cr single hits distribution at 30K, 50K and 70K under pulsed-voltage mode on a Fe-12.8%Cr, at pulse fraction 20% and target evaporation rate 0.002 ions/pulse.

As discussed above, a low cryostat temperature (30K) can provide a higher mass resolution but it also results in an increase in the fraction of multiple hits and hence underestimates Fe concentration. High temperature ($\geq 90\text{K}$) can reduce the occurrence of multiple hits but degrades the mass resolution and may well lead to surface thermal diffusion. Therefore, to balance the multiple hits and mass resolution whilst maintaining a relatively uniform evaporation, the best temperature range under pulsed-voltage mode is between 50K and 70K.

Test No.4 was performed using pulsed-laser mode. 5 different temperatures between 30K and 110K were selected. Following the discussion in section 4.4, the pulse energy was selected to be 0.2nJ and the target evaporation rate was set at

0.002ions/pulse. Fig.4.10 shows the results for measured Cr concentration, multiple hits and background level.

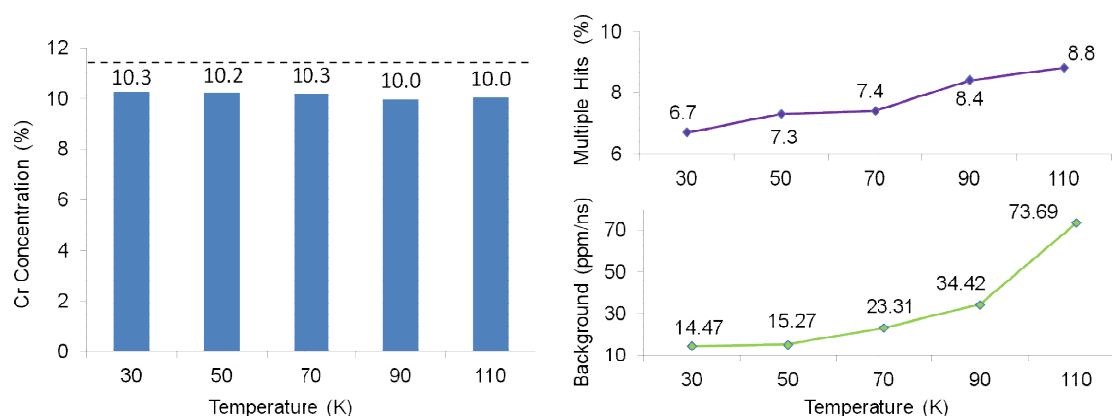


Fig.4.10 The comparison between measured Cr concentration, multiple hits and background count rate of Fe-11.7%Cr when temperature was varied from 30K to 110K, pulse energy at 0.2nJ with target evaporation rate at 0.002ions/pulse in pulsed-laser mode, bulk concentration is indicated as black dashed line.

The measured Cr concentrations are quite similar indicating that the cryostat temperature does not have much effect on the measurement of chemical composition. This is reasonable because the specimen apex is heated by the laser under the pulsed-laser mode; therefore it is thermal energy from the laser energy rather than from the cryostat temperature which dominates the field evaporation process. The multiple hits are also maintained at relatively low values below 10%. However, the background level rose from around 14ppm/ns to almost 74ppm/ns as the temperature was increased from 30K to 110K, which is consistent with results obtained under pulsed-voltage mode. The mass resolution $M/\Delta M$ was 1104.5 (FWHM) and 525.6 (FWTM) at 30K, and gradually decreased to 1087 (FWHM) and 470.8 (FWTM) at 110K.

A comparison between the results obtained from test No.3 and test No.4 shows that the mass resolution obtained under pulsed-voltage mode is slightly better than that obtained under pulsed-laser mode, therefore this result suggests the thermal diffusivity of Fe-Cr alloy is poor, especially at higher temperatures. A similar conclusion was reached by Sha et al. [4] in a study of an Al-Mg-Si-Cu alloy. These authors found that the mass resolution obtained under voltage mode was better than laser mode and suggested this resulted from the poor thermal diffusivity of the material. This is consistent with the reported thermal diffusivity of 304A stainless steel, which is $0.44\text{cm}^2/\text{s}$ at 25K, $0.138\text{cm}^2/\text{s}$ at 50K and decreases to $0.047\text{cm}^2/\text{s}$ at 100K [14]. At low temperature, the thermal diffusivity of the specimen is better while the background level is lower, so it is reasonable to assume that low-temperature analysis should have a positive effect on the mass resolution. Such a conclusion is indeed consistent with the results obtained in test No.3 and No.4 that the best mass resolution is always obtained at the lowest temperature (30K) under both pulsed-voltage mode and pulsed-laser mode.

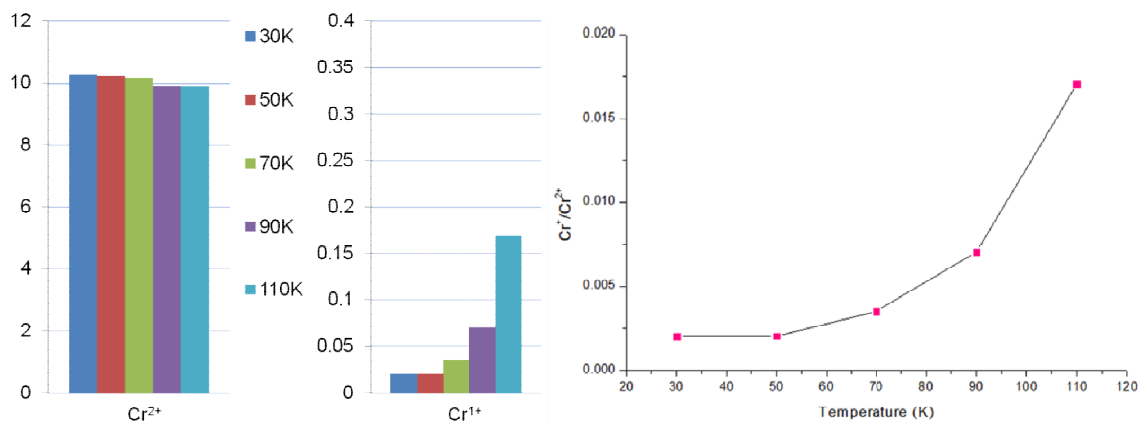


Fig.4.11 The concentration and ratio between Cr singly and doubly charged ions, data obtained in test No.4 on a Fe-10.6%Cr.

Fig.4.11 shows a comparison of Cr singly and doubly charged ions collected in test No.4, and the two-dimensional density maps of Cr atoms are shown in Fig.4.12. The ratio between Cr^+ and Cr^{2+} gradually increases with temperature, however even at 110K, the Cr^+ ions only contribute less than 0.2% to the total Cr concentration and the ratio between singly and doubly charged ions is less than 0.02. This indicates that the effect of cryostat temperature on the charge state of Cr ions can be negligible for laser pulsing. In Fig.4.12, when the temperature was varied from 30K to 110K, the two-dimensional density maps all demonstrate self-consistent distributions of Cr atoms as judged from crystallographic features. Apart from the inevitable high density of Cr at the major pole and in the regions directly heated by the laser, no obvious effect of thermally induced surface diffusion is observed.

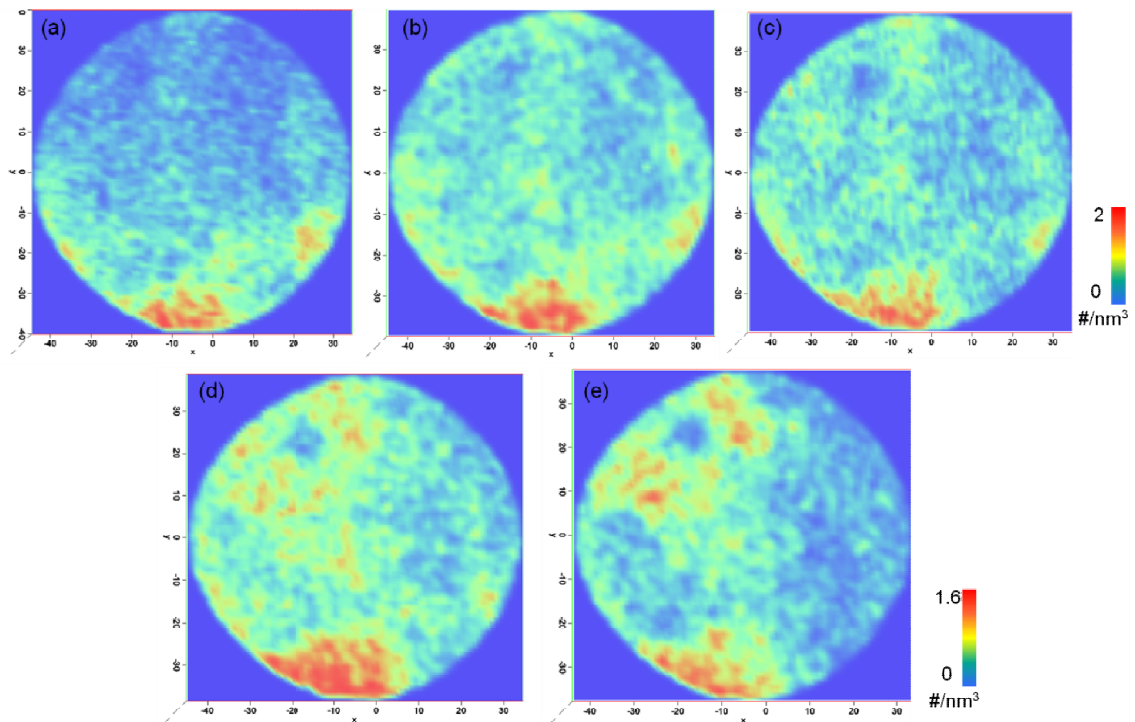


Fig.4.12 Two-dimensional density maps of Cr distribution, at (a) 30K, (b) 50K, (c) 70K, (d) 90K and (e) 110K, data obtained in test No.4 on a Fe-10.6%Cr.

Taking into account the discussion of pulse laser energy in section 4.4, it is very clear that in the pulsed-laser mode it is the laser energy rather than the cryostat temperature which dominates the actual temperature of the specimen apex and hence the relative abundance of evaporated ions with different charge states as well as the surface thermal diffusion. Though the effect of cryostat temperature is more limited than that of the laser energy, a low temperature is found to have a positive effect in reducing the background and increasing the mass resolution. Therefore it is better to keep the cryostat temperature between 50K and 70K to lower the background level whilst maintaining a reasonable mass resolution and reducing the risk of specimen fracture which increases at low temperatures (e.g. 30K).

As the temperature was increased from 30K to 110K, the concentration of H was also found to increase by more than 1% as shown in Fig.4.13. Fig.4.13 also shows two-dimensional atom maps of H distribution obtained in test No.4. As the temperature was increased, more and more H atoms appeared in the region which is directly heated by the laser. It is possible that H evaporates from the surrounding area of the tip. The H ions could also evaporate with other atoms by forming hydride molecular ions, which frequently desorb as singly charged species. For example, FeH^+ molecular ions have been found in the H-rich region. For the doubly charged Cr ions, the main peak is at 26 on the mass spectrum. Combined with one or more H ions, some Cr hydride molecules would result in peaks at 26.5 (CrH^{2+}) or 27 (CrH_2^{2+}). A peak at 27 would overlap with one of the isotope peaks of the doubly charged Fe ion, and therefore be interpreted as Fe. This would further reduce the measured Cr concentration. This explanation is consistent with the lower Cr concentration measured at high temperature (110K) in test No.4 and also the reason to limit the cryostat temperature to the range 50K to 70K as discussed above.

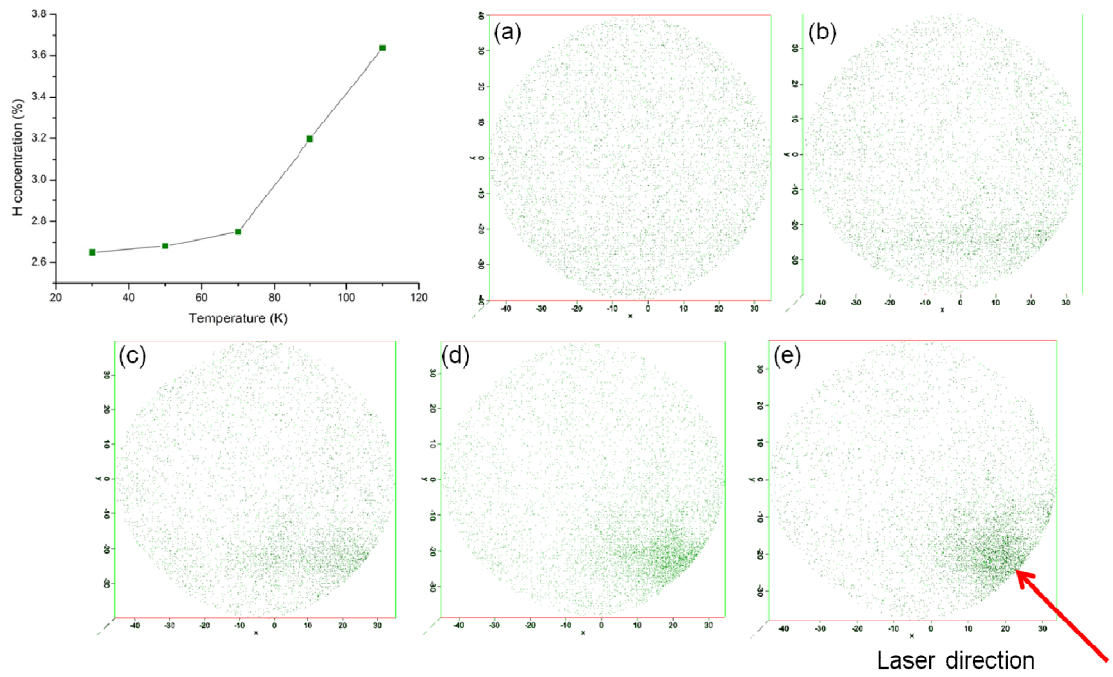


Fig.4.13 Plot of H concentrations as a function of temperature, and two-dimensional atom maps of H distribution, at (a) 30K, (b) 50K, (c) 70K, (d) 90K and (e) 110K, data obtained in test No.4 on a Fe-10.6%Cr.

4.6 Target Evaporation Rate

The target evaporation rate is defined in terms of the desired average number of ions evaporated per voltage pulse (pulsed-voltage mode) or laser pulse (pulsed-laser mode). It depends on the shape of the specimen tip as well as the field of view, which makes it difficult to compare with historic data obtained using different atom probe instruments. Test No.5 and test No.6 were carried out using optimum values for pulse fraction, pulse energy and cryostat temperature as defined in the previous sections.

Test No. 5 was carried out on a Fe-13.8%Cr sample. 5 different target evaporation rates between 0.002ions/pulse to 0.01ions/pulse were selected, with a pulse fraction of 20% and a cryostat temperature of 50K. The measured Cr concentration, multiple hits and background level obtained in test No.5 are shown in Fig.4.14.

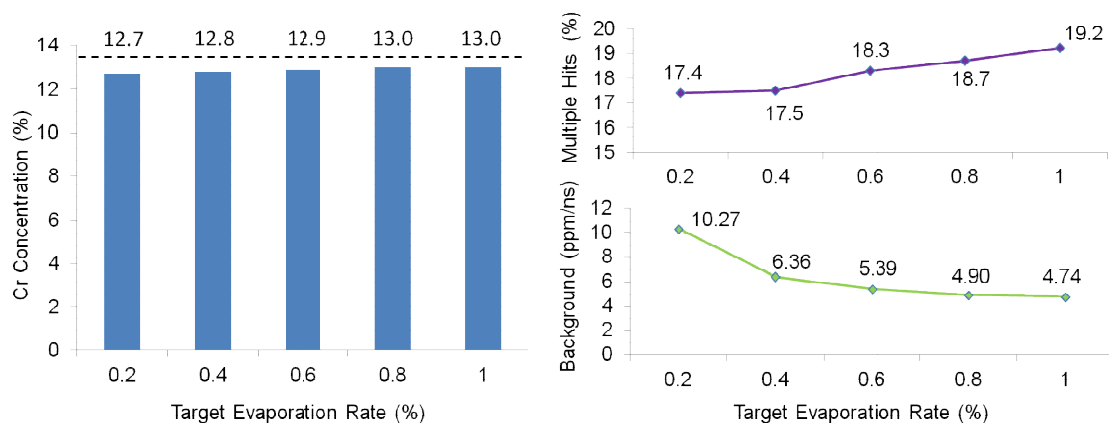


Fig.4.14 The comparison between measured Cr concentration, multiple hits and background level of Fe-13.8%Cr when the target evaporation rate was varied from 0.002ions/pulse to 0.001ions/pulse, with temperature at 50K, pulse fraction at 20% in pulsed-voltage mode, bulk concentration is indicated as black dashed line.

As the target evaporation rate was increased from 0.002 to 0.01ions/pulse, the measured Cr concentrations between different experiments remained quite similar, indicating the target evaporation rate does not have much effect on the chemical composition measurement. The multiple hits also increased slightly, though were still consistent with other experiments carried out under pulsed-voltage mode, such as test No.1 and No.3. The background level slightly decreased as the target evaporation rate increased. In the two-dimensional density maps of Cr distribution shown in Fig.4.15, as the target evaporation rate increased, more and more Cr atoms were found to segregate at crystallographic lines and poles. The most non-uniform distribution occurred when the target evaporation rate was set at 0.01ions/pulse, though the differences were not very large.

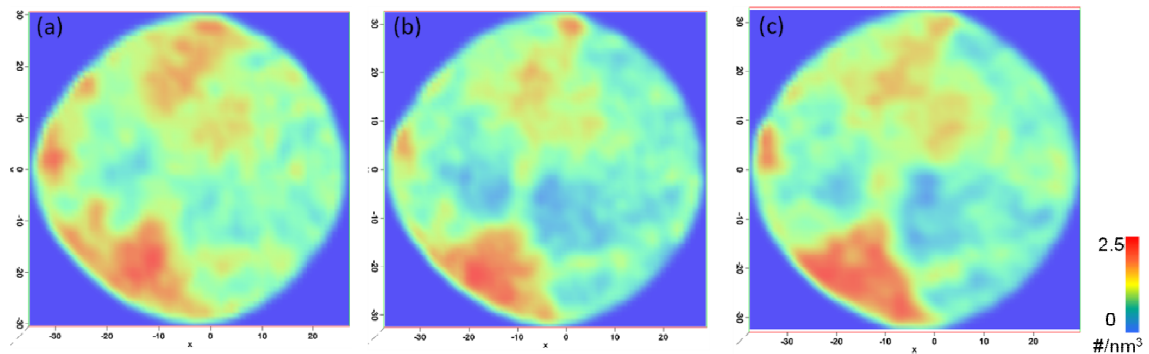


Fig.4.15 Two-dimensional density maps of Cr distribution, when the target evaporation rate was set at (a) 0.002ions/pulse, (b) 0.006ions/pulse, (c) 0.01ions/pulse, and data obtained in test No.5 on a Fe-13.8%Cr.

Test No.6 was carried out on a Fe-10.6%Cr specimen under pulsed-laser mode. 5 different target evaporation rates from 0.002ions/pulse to 0.01ions/pulse were used, with temperature set at 50K and pulse energy set at 0.2nJ, and a similar phenomenon was observed. Fig.4.16 shows the measured Cr concentration, multiple hits and

background level and Fig.4.17 shows the two-dimensional density maps of Cr distributions from several selected data obtained in this test.

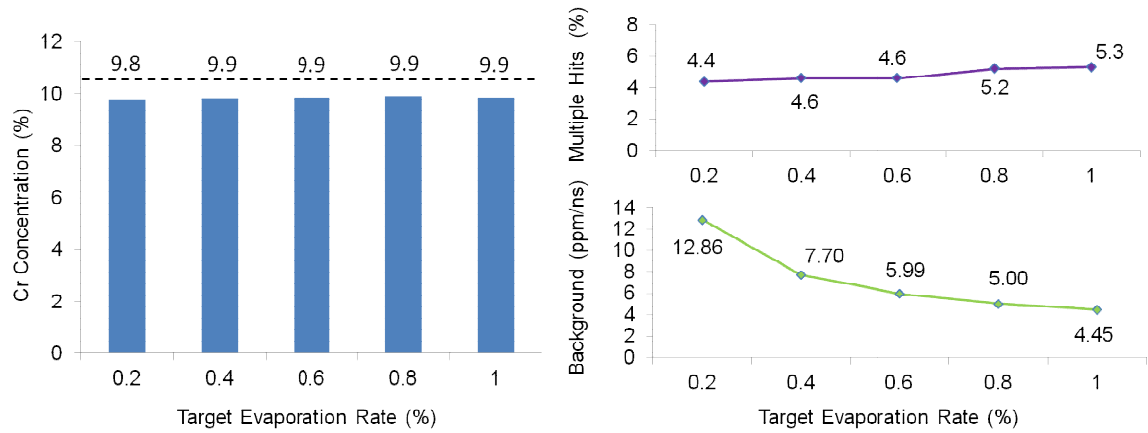


Fig.4.16 The comparison between measured Cr concentration, multiple hits and background of Fe-10.6%Cr when the target evaporation rate was varied from 0.002ions/pulse to 0.001ions/pulse, with temperature at 50K, pulse energy at 0.2nJ in pulsed-laser mode, bulk concentration is indicated as black dashed line.

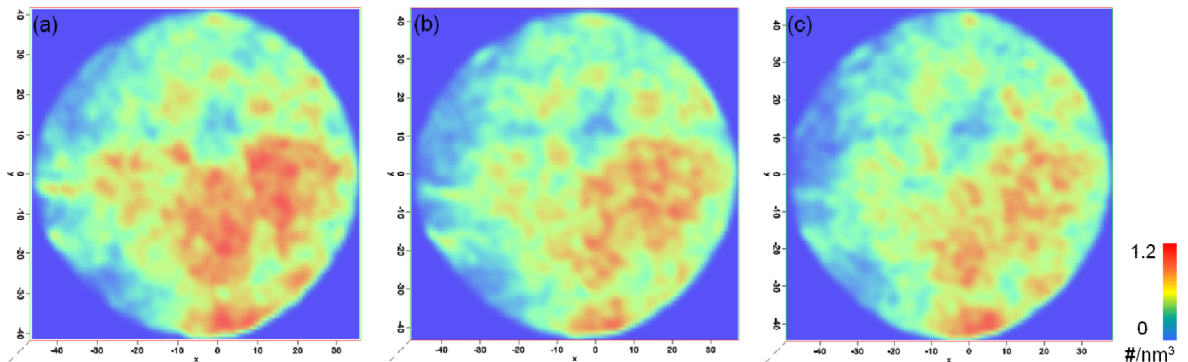


Fig.4.17 Two-dimensional density maps of Cr distribution, when the target evaporation rate was set at (a) 0.004ions/pulse, (b) 0.006ions/pulse, (c) 0.08ions/pulse, and data obtained in test No.6 on a Fe-10.6%Cr.

The measured Cr concentrations are also self-consistent between different experiments, demonstrating very little influence of the target evaporation rate on the

chemical concentration measurement in pulsed-laser mode. A similar fraction of atoms is evaporated as multiple hits in each experiment and this fraction is always observed to be quite low (less than 6%). This is consistent with other experiments carried out under pulsed-laser mode such as test No.2 and No.4. The background level also decrease slightly as the target evaporation rate is increased. Furthermore, the two-dimensional density maps of Cr obtained from three runs with different target evaporation rates demonstrate self-consistent spatial distributions of Cr.

Wagner et.al [15] studied the effect of field evaporation rate on quantitative analysis carried out by atom probe, and found that as the evaporation rate increased, the measured concentration of the less abundant species became greater than the actual bulk concentration. The authors believed such conclusions were applicable to all alloy systems. Very low pulse repetition rates were used in those days (typically less than 200Hz), therefore relatively high evaporation rates per pulse were used (typically above 0.1ions/pulse). The more desirable target evaporation rates of less than 0.01ions/pulse were unobtainable in practice. Instrument developments during the last decade have largely improved the field of view, the pulse repetition rates and the ability to handle high multiplicities. Taking into account the high repetition rates (200KHz) used nowadays, the target evaporation rates we used were actually very low comparing with Wagner's experiments, which can also explain why in our experiment, the influence of target evaporation rate on the chemical composition measurements was found to be quite limited.

In test No.6, it was observed that even at 0.01ions/pulse, multiple hits were still able to be maintained at a quite low level. Therefore, generally the target evaporation rate is best kept between 0.002ions/pulse to 0.004ions/pulse under both pulsed-voltage mode and pulsed-laser mode to maintain a relatively uniform distribution of

evaporated ions. However it may be necessary to increase the target evaporation rate to around 0.008ions/pulse to satisfy the requirement of collecting large amounts of data in a relatively short time period.

4.7 Conclusions

As a conclusion, the optimum ranges of pulse fraction, pulse energy, cryostat temperature and target evaporation rate discussed in this chapter are shown in Table 4.3 below. Note that this general experimental parameter range is valid for binary Fe-Cr alloys for specimens prepared by two-stage electropolishing. There are some special requirements when running FIB prepared specimens and these will be discussed in Chapter 5.

Table 4.3 Optimum experimental parameters for LEAP

Mode	Material	Pulse Fraction (%)	Base temperature (k)	Target Evaporation Rate (ions/pulse)
Pulse-voltage	Binary Fe-Cr alloy	15-20	50, 70	0.002-0.008

Mode	Material	Pulse Energy (nJ)	Base temperature (k)	Target Evaporation Rate (ions/pulse)
Pulse-laser	Binary Fe-Cr alloy	0.2, 0.3	50, 70	0.002-0.008

References

1. Miller, M.K., J.M. Hyde, M.G. Hetherington, A. Cerezo, G.D.W. Smith, and C.M. Elliott, *Acta Metallurgica et Materialia*, 1995. **43**: p. 3385-3401.
2. Miller, M.K. and R. Jayaram, *Surface Science*, 1992. **266**: p. 458-462.
3. Cerezo, A., P.H. Clifton, S. Lozano-Perez, P. Panayi, G. Sha, and G.D.W. Smith, *Microscopy and Microanalysis*, 2007. **13**: p. 408-417.
4. Sha, G. and S.P. Ringer, *Ultramicroscopy*, 2009. **109**: p. 580-584.
5. Bunton, J.H., J.D. Olson, D.R. Lenz, and T.E. Kelly, *Microscopy and Microanalysis*, 2007. **13**: p. 418-427.
6. Cerezo, A., P.H. Clifton, A. Gomberg, and G.D.W. Smith, *Ultramicroscopy*, 2007. **107**: p. 720-725.
7. Miller, M.K., A. Cerezo, M.G. Hetherington, and G.D.W. Smith, *Atom Probe Field Ion Microscopy* 1996, Oxford, UK: Oxford University Press.
8. Thompson, K., J. Sebastian, and S. Gerstl, *Ultramicroscopy*, 2007. **107**: p. 124-130.
9. Morley, A., G. Sha, S. Hirosawa, A. Cerezo, and G.D.W. Smith, *Ultramicroscopy*, 2009. **109**: p. 535-540.
10. Miller, M.K. and G.D.W. Smith, *Journal of Vacuum Science & Technology*, 1981. **19**: p. 57-62.
11. Kingham, D.R., *Surface Science*, 1982. **116**: p. 273-301.
12. Gault, B., M. Muller, A. La Fontaine, M.P. Moody, A. Shariq, A. Cerezo, S.P. Ringer, and G.D.W. Smith, *Journal of Applied Physics*, 2010. **108**.
13. Kellogg, G.L. and T.T. Tsong, *Journal of Applied Physics*, 1980. **51**: p. 1184-1193.

14. Jensen, J.E., W.A. Tuttle, R.B. Stewart, H. Brechna, and A.G. Prodell, eds. *Brookhaven National Laboratory Selected Cryogenic Data Notebook*. 1980, National Technology Information Service, US Department of Commerce: Springfield, VA.
15. Wagner, A. and D.N. Seidman, *Journal de Physique*, 1986. **47**: p. 415-424.

Chapter 5

A Systematic Approach to Analyze Radiation Induced Grain Boundary Segregation/Depletion on a Single Grain Boundary

5.1 Introduction

The concept of radiation induced segregation/depletion (RIS/RID) and the currently established mechanisms were described in Chapter 2. Many studies [1-3] have been devoted to understanding RIS/RID in austenitic steels, where it has been generally observed that Cr is depleted at grain boundaries, which is in agreement with the size effect mechanism suggested by Okamoto et al. [4]. However, both segregation and depletion of Cr in grain boundaries have been reported in ferritic steels with no clear dependency on irradiation condition or alloy type, and the mechanistic understanding is far from complete [5, 6].

Most publications on RIS/RID do not study all the potential contributing factors which could explain the Cr variation at grain boundaries after irradiation and the conclusions drawn from the literature are often based on incomplete data. While grain boundary misorientation is known to affect the segregation levels and RIS/RID behaviour, it is very rarely taken into account in the studies of austenitic steels [7-9] or ferritic steels. For example, Watanabe et al. [9] suggested that the sink strength variations between grain boundaries with different misorientations could affect the RIS/RID behaviour of Cr and Ni in austenitic steel. Was et al. [6] also state that grain boundary character should be taken into account in future research to quantify the RIS/RID tendency in ferritic alloys. Furthermore, the chemical compositions of the grain boundaries before irradiation are not always reported. It is well known that heat treatments will cause chromium segregation [10, 11] while the formation of carbides can lead to Cr depletion at grain boundaries before irradiation [12]. The initial state of grain boundaries is an important parameter that could affect their subsequent response upon irradiation. Finally, the presence of impurities, such as

carbon, silicon, nitrogen, and phosphorus has been observed to affect RIS/RID phenomena [10, 13], however their effects are not yet fully understood. Kano et al.[13] studied the effect of different concentrations of C on the radiation induced depletion of Cr in SUS 304 and SUS316L stainless steels and found that C can suppress the Cr depletion. But the distribution of C at grain boundaries was not discussed possibly due to the difficulty of detecting C using TEM-EDX. Another report is provided by Ohnuki et al.[14] who observed Cr segregation after irradiation in Fe-13%Cr. However the authors applied C^+ ion irradiation and therefore introduced a significant quantity of excess C which may have influenced the segregation phenomenon since there is an interaction between Cr-C complexes and the vacancy flow towards sinks.

RIS/RID at grain boundaries have been studied by AES and more recently by using STEM/EDS. The limitations of these techniques have also been discussed in Chapter 2. On the other hand, atom probe tomography has already been proven to be very useful in studying local chemical composition variations with near atomic resolution [15]. APT has the ability to detect all elements, including those that are difficult to detect by STEM/EDS such as minor elements and low-atomic-number elements. Since the data are presented in three dimensions after reconstruction, the atom distribution and chemical composition information are also available in a three-dimensional form. For example, the distribution of solute atoms within a grain boundary plane can be directly observed by atom probe in three-dimensional form, which is much advanced than the one-dimensional line profile provided by STEM/EDS. Furthermore when combined with FIB specimen preparation, precise sampling and the quantitative analysis of a designated region becomes possible.

In order to develop an understanding of the mechanism of RIS/RID as well as irradiation behaviour of Cr in the grain boundaries in ferritic steels, a systematic approach has been developed, combining Electron Backscatter Diffraction (EBSD), Focused Ion Beam (FIB) specimen preparation and Atom Probe Tomography (APT) analysis. This approach enables one to consider all factors which could contribute to the RIS/RID phenomenon, such as chemistry before irradiation, grain boundary orientation, existence of impurities and precipitates.

5.2 The Design of the Systematic Approach

The key feature of this systematic approach is to combine the advantages of different microstructural techniques and make it possible to analyse the distributions of atoms and variation in chemical composition as a function of irradiation in a selected small region in three dimensions.

The as-received samples were first cut, heat treated and polished using the method discussed in section 3.1 until the surfaces were flat with grain boundaries clearly revealed under an optical microscope. EBSD was then performed on a JEOL 6300 SEM to identify several grain boundaries with special orientations, such as low sigma ones and high angle ones. Ideally these boundaries should be straight and long ($\sim 100\mu\text{m}$) which later would be useful in FIB specimen preparation. The irradiation details are listed in Table 3.1.

5.2.1 FIB specimen preparation on a silicon coupon

The basic principle of FIB specimen preparation was introduced in Chapter 3, and the method provided by Miller et al. [16] has been modified by Thompson et al. [17] to be more productive. The method used in this thesis was developed based on the discussion by Thompson et al. [17]. A silicon coupon was used as specimen holder as shown in the SEM image in Fig.5.1, and (c) shows the top of a micro tip with a diameter of $2\mu\text{m}$. 36 micro tips were aligned on a single silicon piece and the piece was mounted on a T-shape stub using conductive silver glue and a clip.

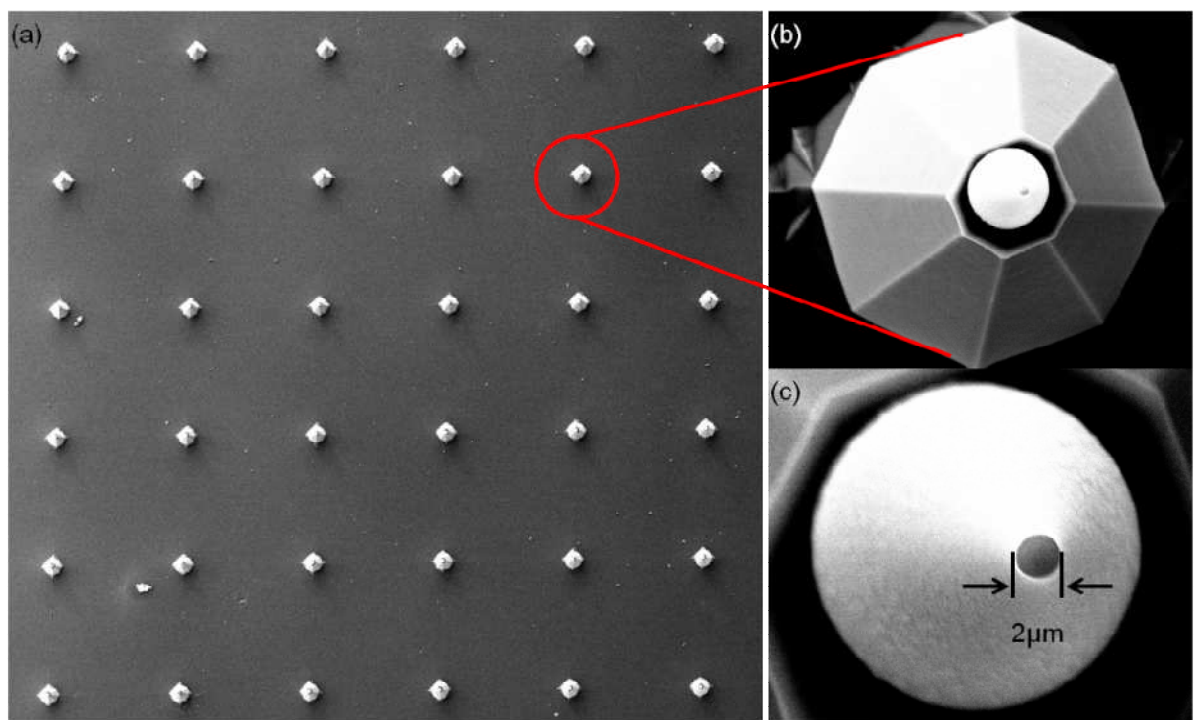


Fig.5.1 SEM images of silicon coupon, (a) 36 micro tips, (b) one micro tip viewed from above and (c) the top of a micro tip with diameter of $2\mu\text{m}$

FIB lift-out was performed on each selected grain boundary to obtain specimens before irradiation. As shown in Fig.5.2, instead of lifting-out a small pillar, the entire

triangular-shape beam was lifted-out using a micromanipulator. Normally the beam is about 30 microns in length and 5-7 microns in depth. One end of the beam was attached with a micromanipulator using W deposition as shown in Fig.5.2 (a). The beam was then cut free and lifted-out, and a cross section view is shown in Fig.5.2 (b). Fig.5.3 (c) shows a small pillar with a $4 \times 4 \mu\text{m}$ square area in top view was mounted on top of the micro tip, which would be later finished by annular milling as shown in Fig.5.2 (d). Using the same method, 5 or 6 specimens could be prepared from one single lift-out beam. The lift-out procedure, especially the final annular milling had to be carefully controlled to ensure that each specimen contains part of the specified grain boundary.

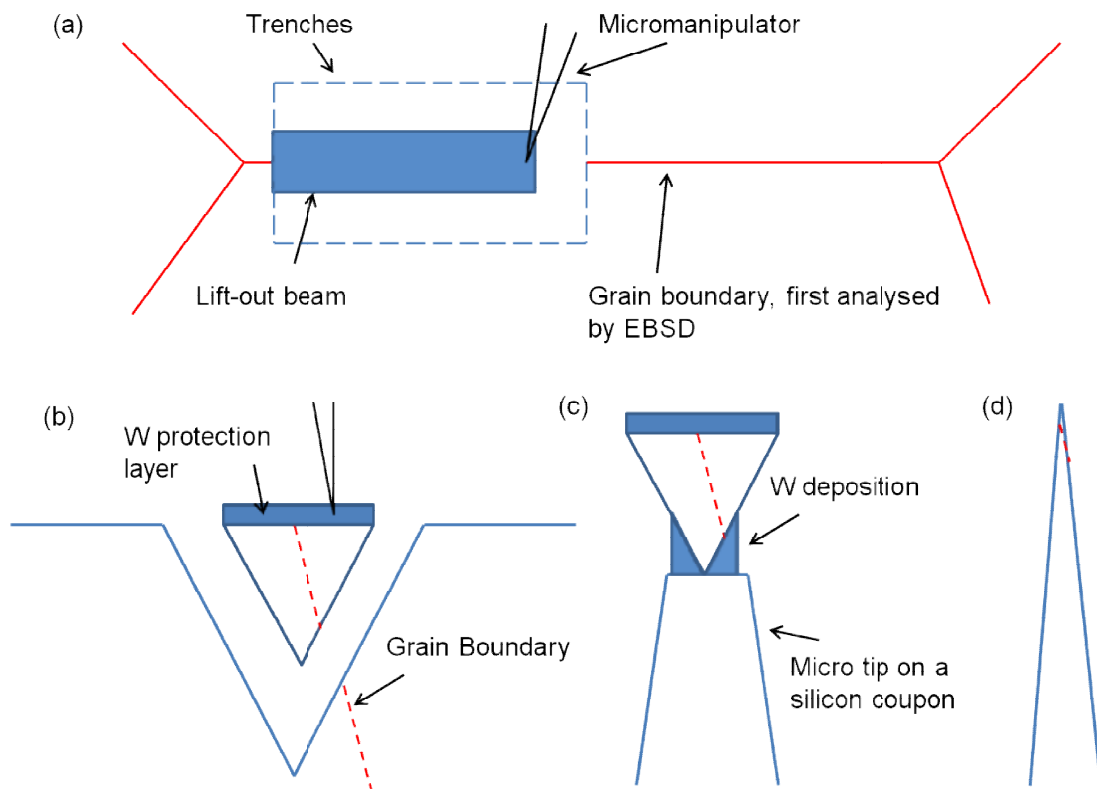


Fig.5.2 Illustration of the FIB lift-out specimen preparation technique before irradiation

After enough specimens containing the selected grain boundaries had been prepared, the block samples were sent to the ion beam facility in the University of Surrey for ion irradiation. After the samples been retrieved, a similar FIB lift-out was performed on the same grain boundaries near the regions where a batch of atom probe specimens had already been prepared before irradiation. It was very easy to locate these boundaries due to the presence of trenches left on the boundaries by the previous FIB lift-out procedure. Then another batch of atom probe specimens containing the same grain boundaries after irradiation was prepared on the silicon coupon using the procedure shown in Fig.5.3. Fig.5.3 (a) shows that a new lift-out beam was cut next to the trenches left by previous cut. The procedure shown in Fig.5.3 (b), (c) and (d) was similar as Fig.5.2.

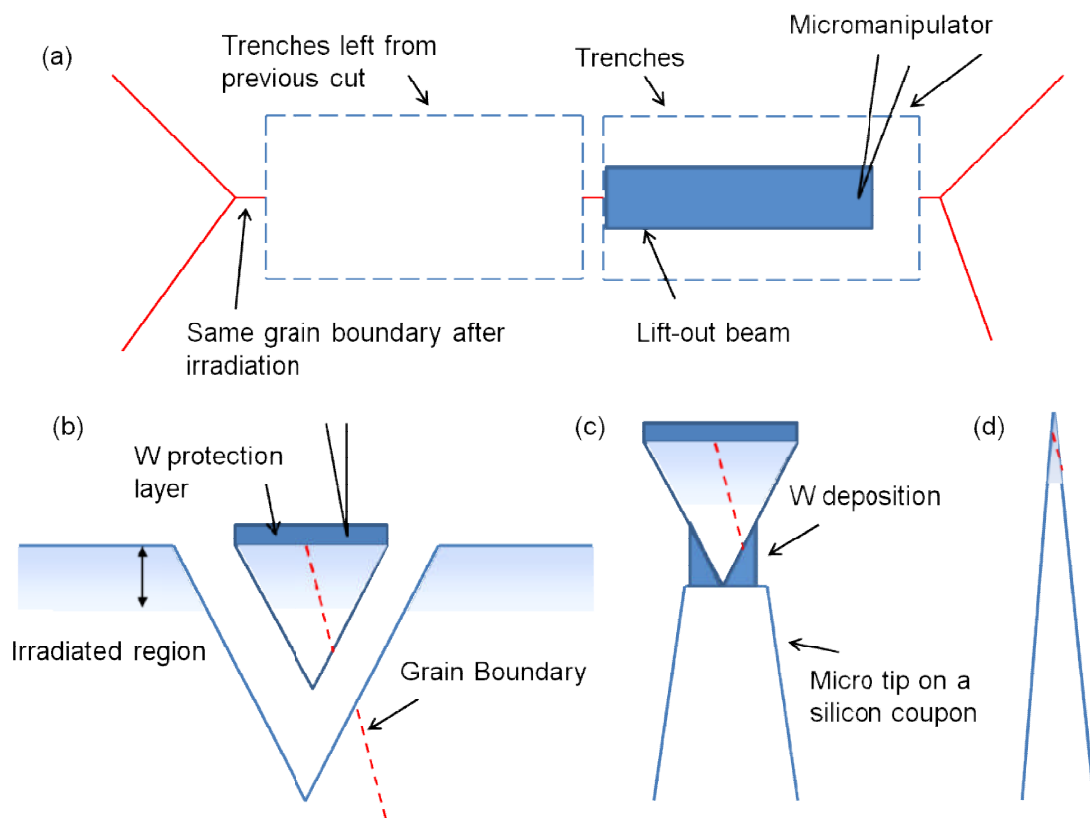


Fig.5.3 Illustration of the FIB lift-out specimen preparation technique after irradiation

Ideally the first batch of specimens should be prepared before the sample had been irradiated; however by slightly modifying the method, it was also possible to produce the first batch of specimens from un-irradiated regions even after the block sample has been through the irradiation experiment. The SRIM calculation discussed in section 3.1.3 demonstrated that even under the highest dose condition, the ions only penetrate a depth of about 1 micron from the surface of the block samples. Therefore, it was possible to perform a FIB lift-out and extract a beam which contained the undamaged region as shown in Fig.5.4. By controlling the length of the specimen during the final sharpening procedure, the irradiated area could be totally removed and APT specimens which only contained un-irradiated grain boundary could be prepared. The data obtained from this region was also representative of the condition of the grain boundary before irradiation.

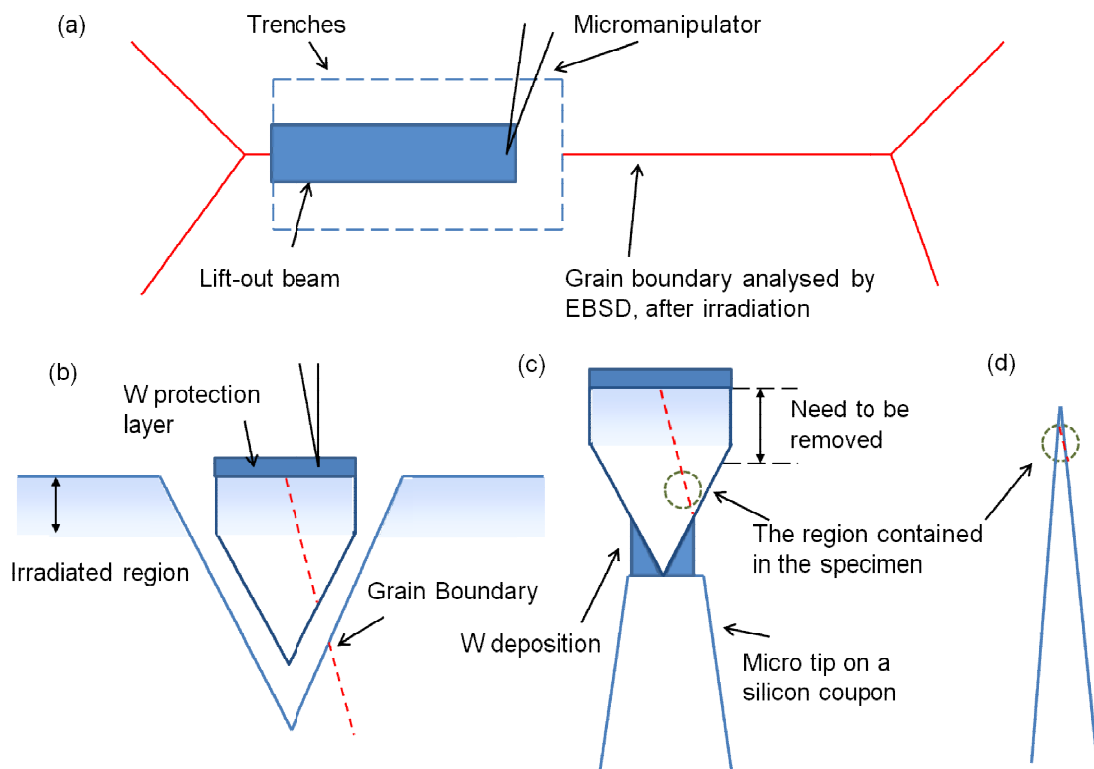


Fig.5.4 Illustration of an alternative FIB lift-out method of preparing specimen containing grain boundary in the un-irradiated region after irradiation

After the annular milling was finished, a 2KV low energy mill was applied to remove the Ga^+ contamination and to remove the unwanted top region which contained the capping W layer or just matrix. The length of grain boundary contained in each atom probe specimen depended on the tilt angle between the grain boundary plane and the surface of the block samples. Specimens containing a long grain boundary could only be prepared if the tilt angle was relatively large or the grain boundary plane was perfectly perpendicular with the surface of the block sample. As shown in the SRIM calculation in section 3.1.3, the dpa value was plotted as a function of irradiation depth. Therefore, a specimen containing a straight and long grain boundary was ideal for studying the irradiation effect as a function of depth. If the tilt angle was relatively small (less than $\sim 70^\circ$), it was better to control the depth of the atom probe specimen to ensure that the grain boundary for subsequent APT was included the maximum damage region as identified from the SRIM calculation.

5.2.2 Atom probe experiment and special requirements on coupons

After the specimens mounted on the top of the micro tip had been sharpened, the coupon could be transferred into the LEAP for atom probe experiments. The general optimum ranges of experimental parameters have been discussed in Chapter 4, however it is still necessary to pay attention to several extra points when using coupon samples to ensure the best analysis conditions are used and to maximize success of atom probe experiments.

Unlike the electropolished specimens, the FIB lift-out specimens are mounted on top of the micro tips by W deposition. After final sharpening, the welds between specimens and micro-tips are fragile and sometimes quite narrow. Therefore it is better to run these kinds of specimens under pulse-laser mode rather than pulse-voltage mode to avoid adding too much stress on specimens and frequent specimen fracture. The distance between each tip is only several hundred microns. Consequently one fractured specimen could easily affect the neighboring ones since the broken fragments can hit and destroy the neighboring specimens.

When the coupon specimens are examined using pulse-laser mode, the specimen voltage must be kept lower than 10,000V. If the voltage is too high, it is possible to generate sufficient field on the neighboring micro-tips due to their narrow separation to cause field evaporation if the neighboring tips are very sharp. Since the micro-tip specimens are sharpened by annular milling, the diameters always gradually increase from apex to bottom. As the diameter increases during analysis, the specimen voltage will also increase to maintain a consistent target evaporation rate. This sometimes limits the volume of material that it is possible to analyse. An alternative strategy is to increase the laser energy slightly by 0.05nJ which reduces the required

potential for field evaporation. However as discussed in section 4.4, it is better to restrict the laser energy to below 0.4nJ to avoid overheating the specimen and thus maintain uniform evaporation and adequate mass resolution.

5.2.3 Reconstruction and quantitative analysis

The collected data was then reconstructed using IVASTM 3.4.3. The commonly used reconstruction parameters, such as materials parameters, specimen parameters and instrument parameters, have been discussed in section 3.4.4. To ensure that a consistent methodology was applied, specimen parameters such as initial tip radius and shank angle were treated as variables to take into account differences in specimen to specimen geometry.

5.2.3.1 One-dimensional concentration profiles

A 1D concentration profile is very useful in describing the distribution and variation of chemical composition of Cr and C atoms across a grain boundary. The method involves sampling a cylindrical or cubical region of the data which contains the region of interest (ROI). The concentration is then calculated as a function of distance through the sampled volume. Composition measurements are usually taken over 1-2nm slices. However the initial 1D profile is only a preview intended to be used for positioning of the ROI. For quantitative analysis, either a fixed bin width profile or a fixed sample count profile can be computed. A fixed bin width profile computes concentrations in constant distance increments with a given bin width (thickness of sample slices along the analysis axis), while a fixed sample count profile calculates concentrations in constant ion number blocks sliced along the analysis axis. Due to the possible lensing effect at grain boundaries, the fixed bin width profile is a better method to plot 1D concentration profiles across grain boundaries.

5.2.3.2 Gibbsian interface excess calculation

To do a further quantitative analysis with a 1D concentration profile, a calculation of the Gibbsian Interface Excess, as defined below, was carried out. The Gibbsian Interface Excess method has been applied in the atomic scale studies of grain boundaries by Seidman et al. [18, 19]. They combined this method with TEM and atom probe field ion microscopy (APFIM) to measure quantitatively the interfacial excess of solute atoms at grain boundaries.

The theory was established by considering a two phase system, where a heterophase interface ζ (Gibbs dividing surface) exists at the boundary as illustrated in Fig.5.5. Fig.5.5 plots the cumulative number of atoms of element i as a function of cumulative number of all atoms. Hence the gradient at any point yields the local concentration of element i . The Gibbsian Interface Excess Γ for solute i is defined as:

$$\begin{aligned}\Gamma_i &= \frac{N_i^{excess}}{A} = \frac{1}{A} (N_i^{vol} - N_i^\alpha - N_i^\beta) \\ &= \frac{1}{A} N^{vol} [C_i^{vol} - C_i^\alpha \xi - C_i^\beta (1 - \xi)]\end{aligned}\quad (5 - 1)$$

Where N_i^{excess} is the number of excess solute atoms i within the interface ζ , and A is the interface area. N_i^{vol} is the number of atoms of element i in the actual system containing the interface, and N_i^α , N_i^β , C_i^α , C_i^β are the number of atoms and concentration of element i in phases α and β separately. Fig.5.5 shows this calculation diagrammatically. Therefore, Γ_i is found by comparing the total number of atoms of element i in the system containing the interface to a reference system where the two phases α and β making up the interface extend to the position of ζ [19]. However, there is one problem in defining the Gibbs dividing surface ζ . Since

C_i^α does not necessarily equal C_i^β , changing the position of ζ would also affect the value of Γ_i . For a simpler case such as in a grain boundary, where $C_i^\alpha = C_i^\beta$, such a problem does not exist. The study in this thesis only involves this simpler situation when the interface is a grain boundary.

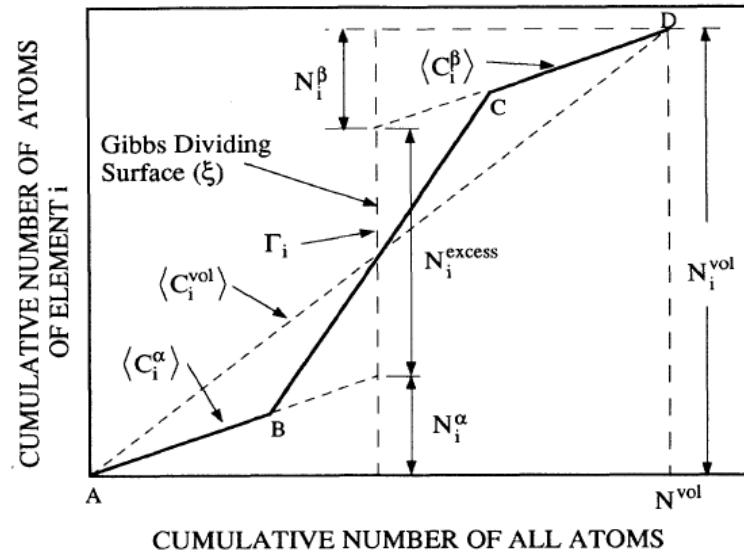


Fig.5.5 Hypothetical integral profile showing how to determine the excess number of solute atom i from an APFIM analysis, reference [18]. There is a difficulty in defining the precise position of the interface (the Gibbs dividing surface ζ) in the case of a heterophase interface. This is discussed further in the main text.

5.3 An Example of an Irradiated Fe-12.8%Cr Alloy

The systematic approach was applied to an irradiated Fe-12.8%Cr alloy from the first batch of material. Several atom probe specimens were prepared by FIB lift-out technique on a single grain boundary after irradiation. No result before irradiation was obtained because the grain boundary was insufficiently long to extract specimens for APT from an unirradiated region. Though unable to take the condition before irradiation into consideration, the quantitative comparison between several results obtained after irradiation still demonstrate the high practicality, reliability and reproducibility of this approach.

The irradiation performed was the implantation type 1 as shown in Table 3.1. Judging from the SRIM calculation in Fig.3.4, the average amount of damage between 100nm to 700nm was about 6dpa, and the entire irradiated region was less than 1 micron in depth from the surface. EBSD analysis confirmed that the selected grain boundary was a high angle boundary with 40° misorientation and rotation axis [331]. Four APT specimens from the irradiated grain boundary were successfully prepared from a single lift-out beam less than 25nm long. Therefore it is reasonable to assume that the distance between each analysed section of grain boundary was less than 5 microns. The depths of each specimen were also carefully controlled in the final stage of FIB preparation to try to make sure all the grain boundary segments contained in the specimens were from the maximum damage region. Fig.5.6 contains several SEM images showing the FIB specimen preparation procedure. The atom probe analyses were performed under the pulse-laser mode using optimum experimental conditions: temperature at 50K, pulse energy at 0.3nJ with target evaporation at 0.004ion/pulse or 0.005ion/pulse.

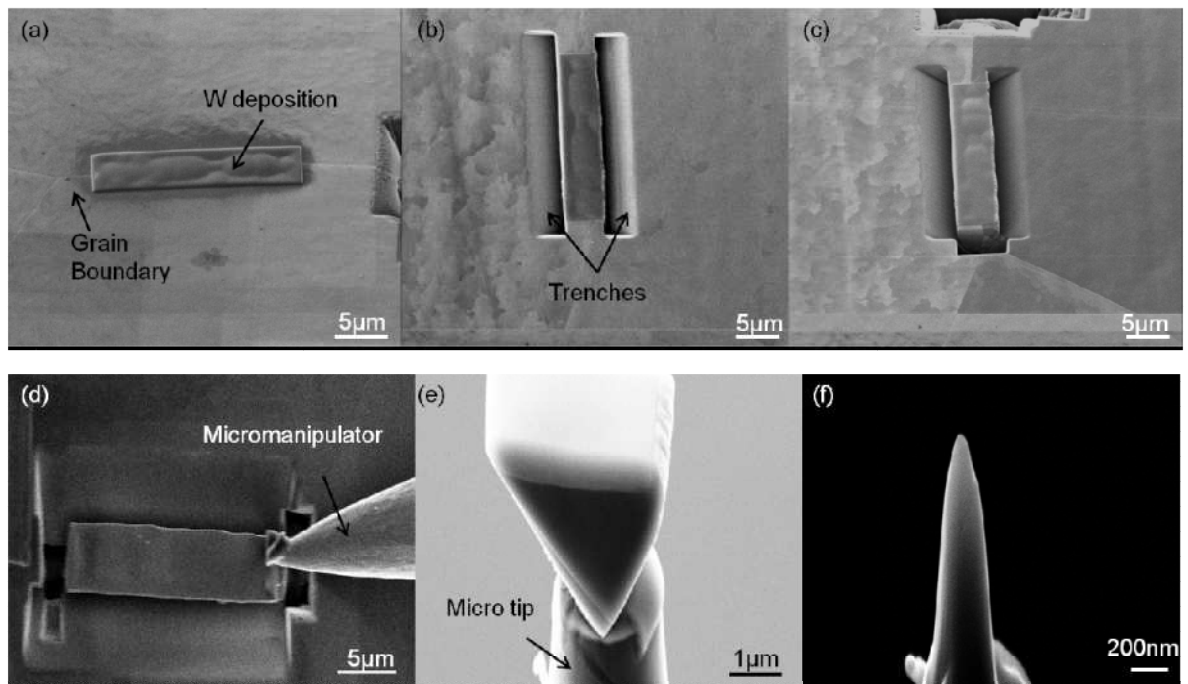


Fig.5.6 SEM images showing the FIB specimen preparation procedure.

5.3.1 Calibrating the image compression factor

The image compression factor determines how the atom positions detected at the detector are projected back to specimen tip space. It affects the shape of the reconstructed volume, however it does not change the density of atoms in the reconstructed data. The default value of the image compression factor used in the reconstruction was 1.65 in IVAS 3.4.3. However, comparing the results with SEM images obtained during FIB specimen preparation, it has been found that the default value was not suitable for the reconstruction of Fe-Cr alloys.

Fig.5.7 shows two atom maps of one specimen reconstructed using two different image compression factors, 1.65 and 1.2. The grain boundaries are marked by black dashed lines. The grain boundaries are at a certain angle α to the centre axis of the specimen. When the image compression factor is set at 1.65, α is 32°. However, when the factor is set at 1.2, α is about 16°. An SEM image of the same specimen taken during the FIB specimen preparation is shown in Fig.5.6 (c), and the grain boundary is again marked by a black dashed line. The estimated shape of the finished specimen is marked with red lines. The reason for choosing an image showing an unfinished specimen rather than a finished specimen is that during the milling process, the contrast between two grains gradually decreases until it becomes totally invisible when the diameter of specimen is reduced to a certain level (less than 200nm). The SEM image shows that the true value of α is about 14°. Therefore when the image compression factor was set at 1.2, the reconstructed results represent the actual specimen geometry. The value 1.2 was also used as image compression factor in all the data reconstruction of atom probe experiments carried on Fe-Cr alloys instead of 1.65.

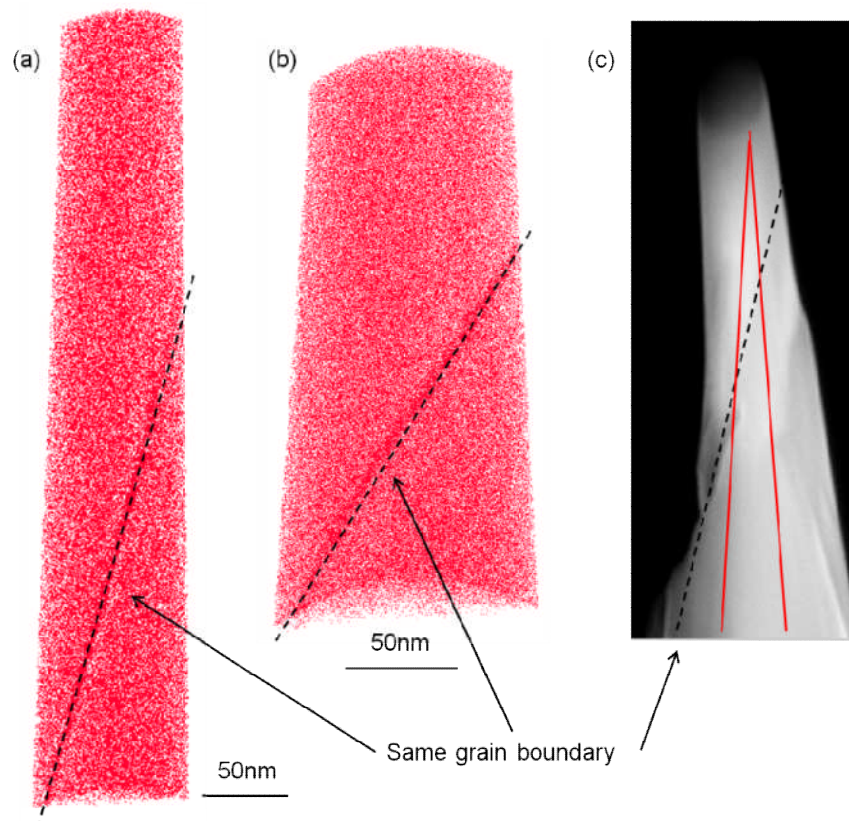


Fig.5.7 Atom maps of Cr of one specimen reconstructed using two different image compression factors, (a) 1.65, (b) 1.2, (c) SEM image of the specimen during FIB preparation

5.3.2 Atom maps

The reconstructed atom maps of Cr and C from four specimens containing the same irradiated grain boundary in the Fe-12.8%Cr alloy are shown in Fig.5.8. The grain boundary region in specimen A is very long, about 250nm in length while the boundary regions in specimen B, C and D are also long enough for analysis, about 150nm. The difference between the lengths of the grain boundary regions contained in each specimen was due to the difficulty of precise control during FIB specimen preparation. However, it is clear that the grain boundaries in four specimens are at the same angle from the central axis of each tip.

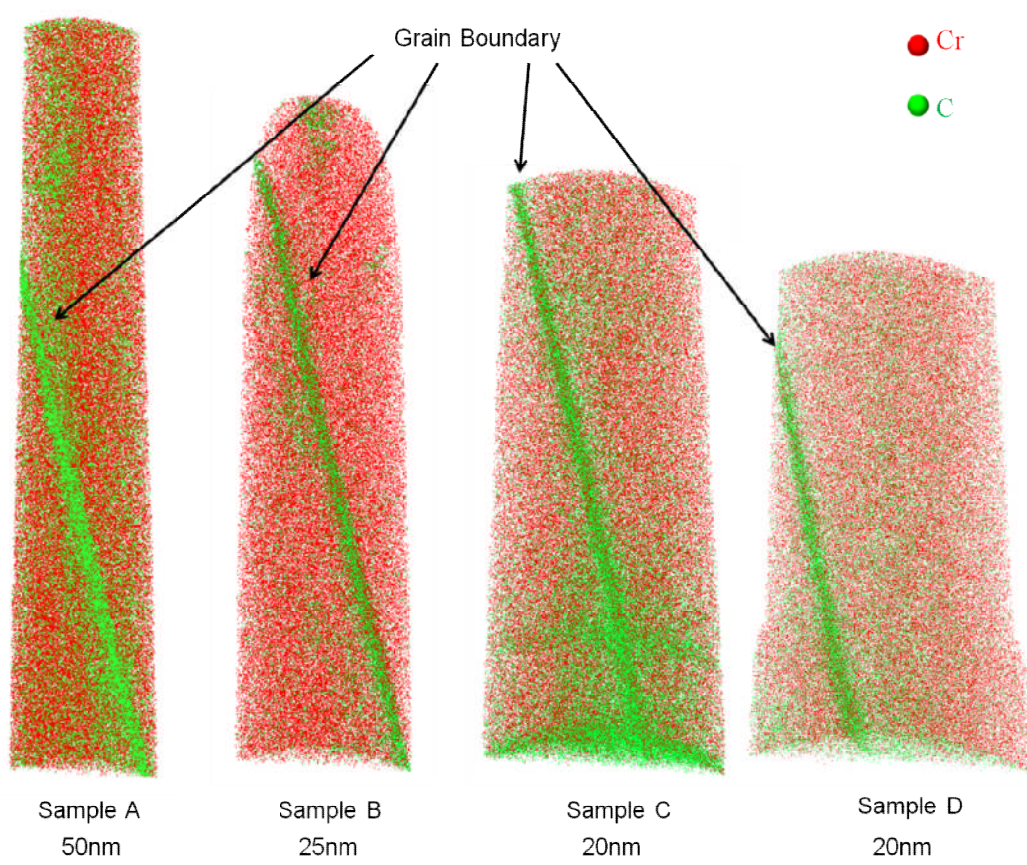


Fig.5.8 Atom maps of Cr and C of four specimens containing the same irradiated grain boundary in the Fe-12.8%Cr alloy

5.3.3 1D concentration profile

The 1D concentration profile was plotted along the Z axis of a cylinder with 25nm in diameter with bin width of 0.1nm. The cylinder was positioned perpendicular to the grain boundary plane on the atom maps.

Fig.5.9 shows typical 1D concentration profiles obtained from specimen A, B, C and D. The shapes of concentration profiles were affected by the presence of prominent poles, crystallographic zone lines and also the selection of region of interests analyzed by the analysis cylinder. Still the shape of 1D concentration profiles of Cr and C obtained from different specimens are all quite similar. The segregation of Cr and C at the grain boundary is observed in all the concentration profiles within a width of less than 8nm, while Cr also shows a slight depletion in the matrix adjacent to the grain boundary (1-2nm) to form a 'W-shape' profile. The rest of the profiles are quite flat with small fluctuations of composition around the bulk concentration of 12.8%, indicating the irradiation has only affected the chemical composition variation in a small region across the grain boundary.

In the profiles obtained from specimen B, there are some fluctuations on the left side of the grain boundary region. This shows that the shape of concentration profiles can be affected by poles or crystallographic zone lines. As discussed in Chapter 4, Cr atoms tend to segregate at the centre of the low index poles. Therefore it is believed that the analysis cylinder in specimen B also sampled data from a low index pole and its position was indicated by the region where the Cr concentration was higher than the profile average. It is also clear that though the appearance of poles or crystallographic zone lines in the analysis cylinder could affect the shape of the

concentration profile, the effect on the segregation/depletion phenomenon of Cr and C across the grain boundary region was minimal.

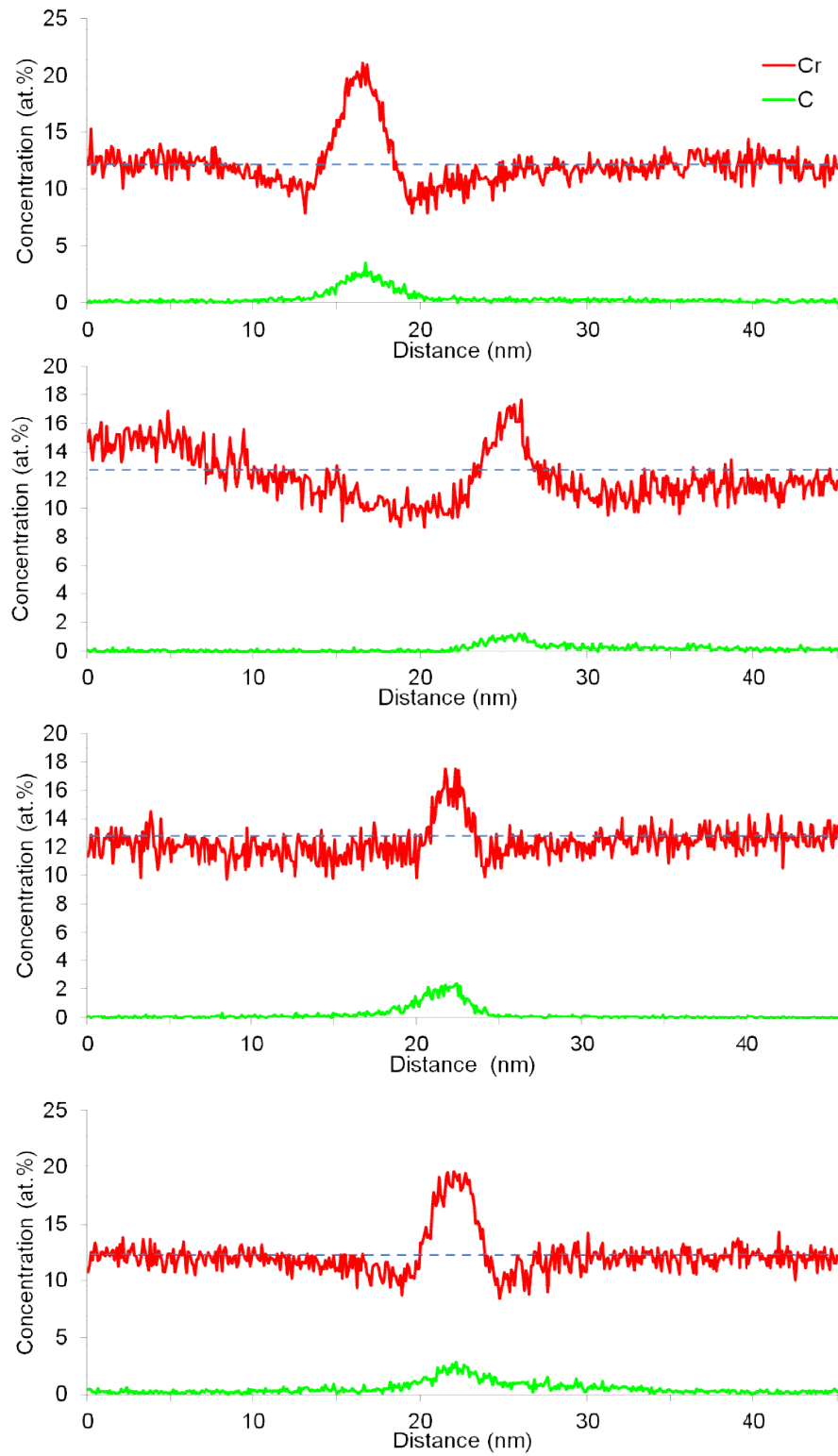


Fig.5.9 1D concentration profiles of Cr and C across the grain boundary of four specimens, from top to bottom are specimen A, B, C and D

5.3.4 Gibbsian interface excess calculation

The Gibbsian interface excess calculation used in this thesis is slightly different to the original method of Seidman et al. [18, 19] though the basic definitions are still the same. The method of using 1D concentration profiles to calculate Gibbsian Interface Excess is illustrated in Fig.5.10.

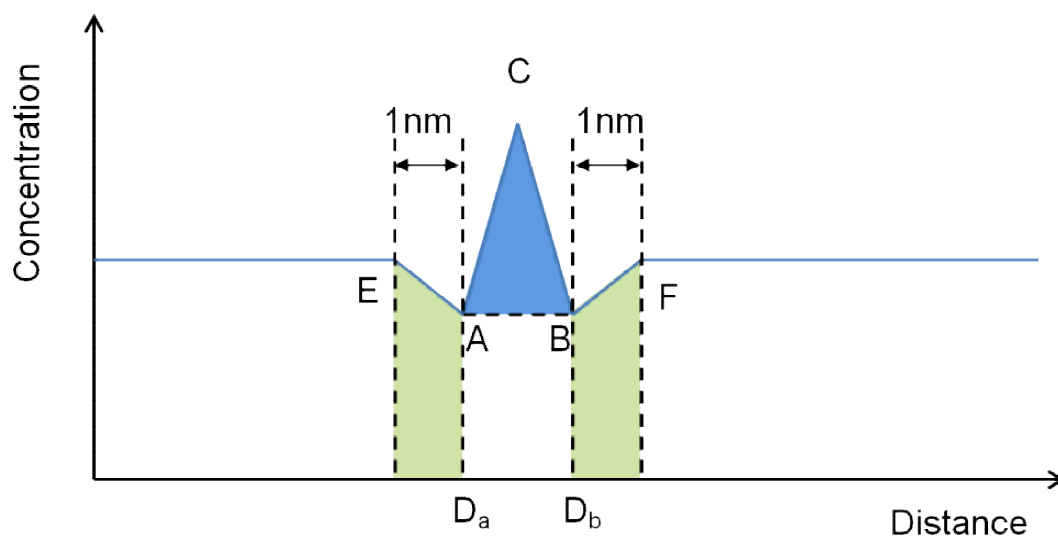


Fig.5.10 Illustration of calculating Gibbsian interface excess using a 1D concentration profile

A typical ‘W-shape’ profile is obtained in an analysis cylinder with diameter a and z axis is the analysis axis along which the 1D concentration profile is plotted. It also indicates the direction of the profile, which is the same as the x axis in Fig.5.10. Point C indicates the peak concentration value in the grain boundary region and points A and B show the lowest points in the depletion regions in the adjacent matrix of the grain boundary. If the entire region between A and B is defined as the actual system containing the interface, by subtracting the rectangular area below line

AB, the triangle marked by point A, B and C then can be defined as the region which contains the total number of excess atoms of element i in the interface.

To subtract the area below line AB, two background regions are identified as coloured green in the figure (areas below the line AE and line BF). Since the depletion regions on either side of the boundary are less than 1-2nm, the widths of the background regions are defined to be 1nm. The background can be calculated as the average concentration or number of atoms of element i . However due to the trajectory aberrations at grain boundaries, the number of atoms in each bin in the background may be affected by the local magnification [20]. Therefore, the background was calculated as the average concentration of element i , and the value C_n^{back} of each point D_n on line AB can be found as below:

$$C_n^{back} = \frac{C_{ae}^{aver} - C_{bf}^{aver}}{D_a - D_b} (D_n - D_a) + C_{ae}^{aver} \quad (5 - 2)$$

Here D_a and D_b are the distances of points A and B on the analysis axis of analysis cylinder and C_{ae}^{aver} and C_{bf}^{aver} are the average concentrations in the two background regions. The area of the interface is calculated from the cross section area of the analysis cylinder with diameter a . Then the Γ_i of element i can be calculated as:

$$\Gamma_i = \frac{\sum_{n=a+1}^{b-1} N_n (C_n - C_n^{back})}{A} = \frac{\sum_{n=a+1}^{b-1} N_n (C_n - C_n^{back})}{\pi \cdot (\frac{a}{2})^2} \quad (5 - 3)$$

A is the area of the cross section of the analysis cylinder. Since the detector efficiency of the LEAP is 37%, the corrected Γ_i^{corr} then will be:

$$\Gamma_i^{corr} = \frac{\Gamma_i}{0.37} \quad (5 - 4)$$

The Gibbsian excess calculation method applied in this thesis only considers the excess solute atoms at the centre of a grain boundary, as in the area between points C, A and B on the ‘W-shape’ profile shown in Fig.5.10. Note that as the irradiation temperature or dose is varied, the slope of line EA and BF on the ‘W-shape’ profile could also change. This aspect of the data may provide additional information about RIS/RID of Cr.

The lengths of the irradiated grain boundaries contained in each specimen were different. For a relative long grain boundary such as in specimen A, it is possible to calculate Gibbsian Interface Excess values at different depths. Therefore, a series of analysis cylinders with 25nm diameter was positioned perpendicular across the grain boundary from the top to bottom to plot a series of 1D concentration profiles. Fig.5.11 shows the Gibbsian Interface Excess values calculated and plotted as a function of depth along the grain boundary in specimen A. Except for the top 2 points, relatively constant Excess values were observed along the grain boundary. This indicates that the irradiation damage on the grain boundary was relatively uniform within this region. For the shorter grain boundaries contained in specimen B, C and D, the average values of Excess were calculated and are shown in Table 5.1.

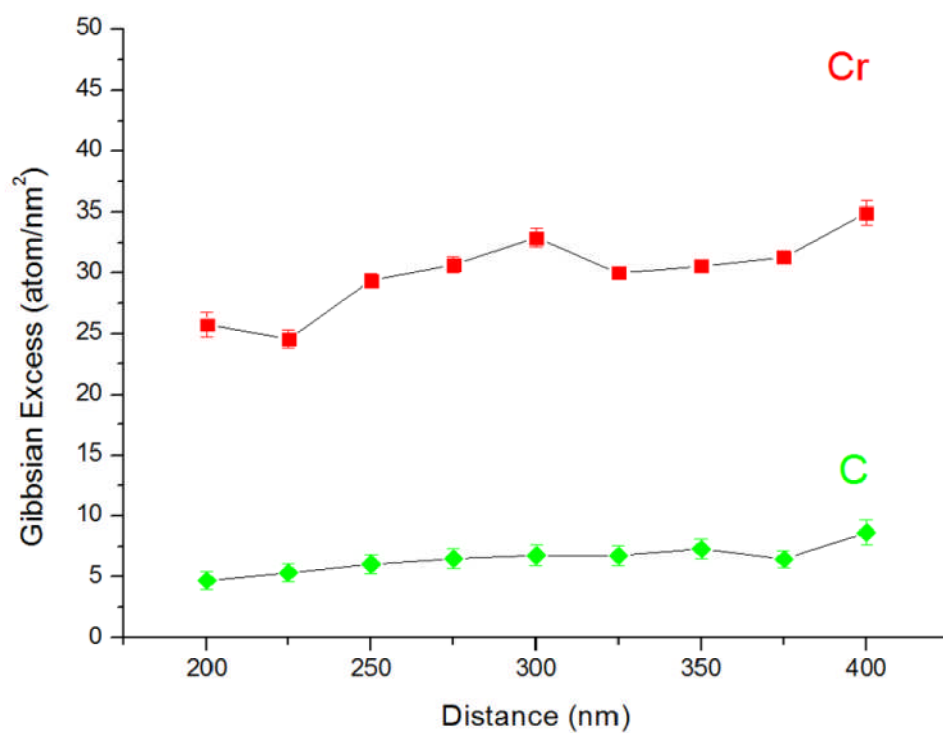


Fig.5.11 Gibbsian interface excess calculated and plotted as a function of depth along the grain boundary in specimen A

Table 5.1 Average Gibbsian Excesses Calculated in Grain Boundaries Region for Samples A, B, C and D

Gibbsian Interface Excess	Sample A	Sample B	Sample C	Sample D
Cr (atom/nm ²)	30.0±3.2	16±3.1	27.1±2.4	20.3±1.2
C(atom/nm ²)	6.5±1.1	6.9±1.4	11.5±2.1	8.4±1.1

5.3.5 Discussion

A significant effort was devoted during the FIB specimen preparation process to try to make sure that the grain boundaries contained in each specimen were from the maximum damage region, and that the specimens were sharpened using the same criteria. However it was still very difficult to identify the exact depth of the boundary contained in each specimen during FIB milling, especially if the grain boundary was not perpendicular with the surface of the bulk sample (which actually happened in many cases). It was also impossible to judge the exact depth of the grain boundaries using a reconstructed atom map, because the top of each tip did not necessarily represent the surface of the bulk sample. Some depths could be lost during the annular milling process or be intentionally removed by the final 2KV low energy mill, and the loss is difficult to be estimated.

On the other hand, with the combination of the Gibbsian Interface Excess value and SRIM calculation, it is possible to roughly identify the depth region of grain boundaries contained in each specimen. For example the relatively self consistent Gibbsian Interface Excess values in Fig.5.11 from depth 200nm to 400nm in specimen A indicate that this region had been affected by similar irradiation damage and was most likely from the maximum damage region. The small variation between values obtained at different distances can be explained as follows:

First, the SRIM calculation is a simulation and only provides an average estimation. Although SRIM indicates an average damage about 6dpa between 100nm and 700nm (maximum damage region), it is still possible that the effect of irradiation and the level of segregation/depletion could be slightly different at different depths in the grain boundary, even in the 100-700nm maximum damage region. Second, the

shape of the 1D concentration profiles, and hence the Gibbsian Interface Excess values, can be affected by the position of the cylinder. Despite ensuring that the centre of each cylinder was aligned on the same line inside the grain boundary plane, some errors and fluctuations could still be introduced. Finally when 1D concentration profiles extend to the very edge of the reconstructed atom map, fewer sampling planes can be used in the calculation at one end of the cylinder and could introduce certain errors as well.

Furthermore, the average Gibbsian excess values of four APT specimens may also suggest that the grain boundaries contained in specimen A, B, C and D were affected by slightly different irradiation damage. It is possible that the grain boundaries contained in these four specimens are from different depths of the original boundary; however it is highly likely that all are in the maximum damage region. Such results also prove the attempt to use FIB to prepare all the APT specimens containing the grain boundaries from the maximum damage region was successful. Considering that the distances between grain boundaries contained in four specimens were less than 5 microns, these results provide three dimensional information that the irradiation damage was relatively uniform not only in depth within the maximum damage range (100-700nm), but also along a single grain boundary at least within the analysed length (20-30 μ m).

5.4 Conclusions

A systematic approach combining EBSD, FIB specimen preparation, APT and data analysis to analyse the effect of irradiation on a single grain boundary has been designed and successfully applied to an irradiated Fe-12.8%Cr alloy. With careful control, it is possible to use FIB specimen preparation techniques to prepare specimens containing a specific grain boundary within the maximum damage region. This was demonstrated by producing four specimens from a single high angle grain boundary. The image compression factor of 1.2 was used for consistency with SEM data. The reconstructed atom maps show that all the grain boundary segments are aligned at the same angle from the centre axis of each specimen. Enrichment of Cr and C in the grain boundary and depletion of Cr in the adjacent matrix to form a 'W-shape' 1D concentration profile had been observed separately for each specimen. Relatively consistent Gibbsian Interface Excess values calculated from each specimen demonstrated the high repeatability and reliability of this approach.

The development of this systematic approach makes it possible to analyse RIS/RID in a specific grain boundary with a known grain boundary orientation and to then experimentally determine the distribution of solute elements both on the grain boundary and within the adjacent grains. It also provides a unique opportunity to have multiple atom probe sampling from a single grain boundary and to analyse all grain boundary data to produce a whole picture rather than the selected snapshots obtained by previous methods.

References

1. Kenik, E.A., T. Inazumi, and G.E.C. Bell, *Journal of Nuclear Materials*, 1991. **183**: p. 145-153.
2. Kato, T., H. Takahashi, and M. Izumiya, *Journal of Nuclear Materials*, 1992. **189**: p. 167-174.
3. Allen, T.R., J.I. Cole, E.A. Kenik, and G.S. Was, *Journal of Nuclear Materials*, 2008. **376**: p. 169-173.
4. Okamoto, P.R. and L.E. Rehn, *Journal of Nuclear Materials*, 1979. **83**: p. 2-23.
5. Lu, Z., R.G. Faulkner, G. Was, and B.D. Wirth, *Scripta Materialia*, 2008. **58**: p. 878-881.
6. Was, G.S., J.P. Wharry, B. Frisbie, B.D. Wirth, D. Morgan, J.D. Tucker, and T.R. Allen, *Journal of Nuclear Materials*, 2011. **411**: p. 41-50.
7. Duh, T.S., J.J. Kai, F.R. Chen, and L.H. Wang, *Journal of Nuclear Materials*, 1998. **263**: p. 2064-2068.
8. Duh, T.S., J.J. Kai, and F.R. Chen, *Journal of Nuclear Materials*, 2000. **283**: p. 198-204.
9. Watanabe, S., Y. Takamatsu, N. Sakaguchi, and H. Takahashi, *Journal of Nuclear Materials*, 2000. **283**: p. 152-156.
10. Lu, Z., R.G. Faulkner, N. Sakaguchi, H. Kinoshita, H. Takahashi, and P.E.J. Flewitt, *Journal of Nuclear Materials*, 2006. **351**: p. 155-161.
11. Schaublin, R., P. Spatig, and M. Victoria, *Journal of Nuclear Materials*, 1998. **258**: p. 1350-1355.
12. Lundin, L. and B. Richarz, *Applied Surface Science*, 1995. **87-8**: p. 194-199.

13. Kano, F., K. Fukuya, S. Hamada, and Y. Miwa, *Journal of Nuclear Materials*, 1998. **258**: p. 1713-1717.
14. Ohnuki, S., H. Takahashi, and T. Takeyama, *Journal of Nuclear Materials*, 1982. **103**: p. 1121-1125.
15. Miller, M.K., J.M. Hyde, M.G. Hetherington, A. Cerezo, G.D.W. Smith, and C.M. Elliott, *Acta Metallurgica et Materialia*, 1995. **43**: p. 3385-3401.
16. Miller, M.K., K.F. Russell, and G.B. Thompson, *Ultramicroscopy*, 2005. **102**: p. 287-298.
17. Thompson, K., D. Lawrence, D.J. Larson, J.D. Olson, T.F. Kelly, and B. Gorman, *Ultramicroscopy*, 2007. **107**: p. 131-139.
18. Krakauer, B.W. and D.N. Seidman, *Physical Review B*, 1993. **48**: p. 6724-6727.
19. Seidman, D.N., B.W. Krakauer, and D. Udler, *Journal of Physics and Chemistry of Solids*, 1994. **55**: p. 1035-&.
20. Miller, M.K., *Journal de Physique*, 1987. **48**: p. 565-570.

Chapter 6

A Study of Radiation Induced Grain Boundary Segregation/Depletion in a Fe- 15.2%Cr Alloy

6.1 Introduction

The systematic approach developed in Chapter 5 is dedicated to gain a better understanding of Cr behaviour at grain boundaries in ferritic alloys under irradiation, while considering as many factors as possible including irradiation depth, grain boundary misorientation, the initial grain boundary chemistry and the presence of minor elements or impurities. An example of the successful application of this approach was presented in Chapter 5. In this chapter, this approach has been fully applied on a Fe-15.2%Cr alloy from the second batch of materials.

The as-received material was cut and polished as discussed in section 3.1.2. Three irradiation experiments were performed to produce a high-dose material condition (6dpa) and two low-dose material conditions (0.6dpa) with different irradiation rates, as detailed in Table 3.1. The corresponding SRIM calculations are shown in Fig.3.4.

For the high-dose irradiated sample, four grain boundaries with different misorientations were selected as shown in Fig.6.1. These were two low sigma boundaries, $\Sigma 1$ with 12° misorientation and $\Sigma 3$ with 72° misorientation, and two high angle boundaries, $\Sigma 39$ with 50° misorientation and a randomly selected high angle boundary with 23° misorientation. APT specimens were produced from irradiated and un-irradiated regions of the four boundaries by the modified method discussed in section 5.2.3. TEM specimens were prepared using the *in-situ* lift-out method described in section 3.2.1 on $\Sigma 3$ boundary.

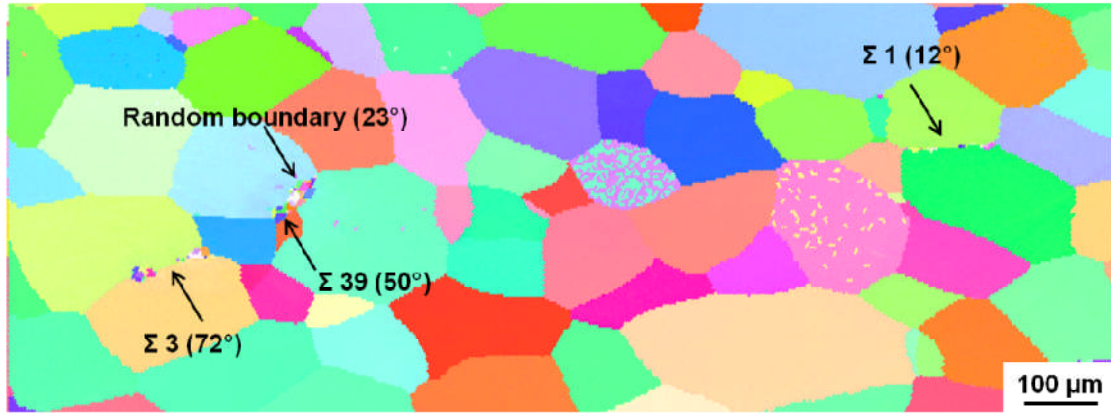


Fig.6.1 EBSD map for the high-dose irradiated sample, showing four identified boundaries with their misorientations.

For the sample irradiated by implantation No.2 (0.6dpa with fast rate), two grain boundaries were selected. One was $\Sigma 1$ with 10° misorientation and the other was a randomly selected high angle boundary with 40° misorientation. For the sample irradiated by implantation No.3 (0.6dpa with slow rate), only a random boundary was selected, with 33° misorientation. APT specimens were prepared from both irradiated and un-irradiated regions of these three boundaries. All APT results were reconstructed and analyzed using the methods discussed in section 5.2 and 5.3.

6.2 Results on High-Dose Irradiated Samples

6.2.1 Grain boundary chemistry before irradiation

APT results were obtained from the irradiated and un-irradiated regions of the randomly selected high angle boundary, $\Sigma 1$ boundary and $\Sigma 3$ boundary, therefore these three boundaries are discussed and compared here. Because no results were obtained from the un-irradiated region of the $\Sigma 39$ boundary, this boundary is only discussed in the section on carbides in grain boundaries.

Before irradiation, Cr and C segregation was observed at the $\Sigma 1$, the $\Sigma 3$ and the high angle boundary, which is consistent with previously reported thermal ageing results [1, 2]. Fig.6.2 shows atom maps of Cr, Fe and C obtained from the randomly selected high angle boundary. Since the boundary was nearly perfectly perpendicular to the surface of the block sample, it was possible to obtain a very extensive section of the boundary within the FIB milled APT sample. A very long and straight grain boundary segment about 450nm in extent was successfully preserved in an APT specimen. The $\Sigma 1$ and $\Sigma 3$ boundary segments were shorter than the high angle one, about 100nm and 250nm respectively.

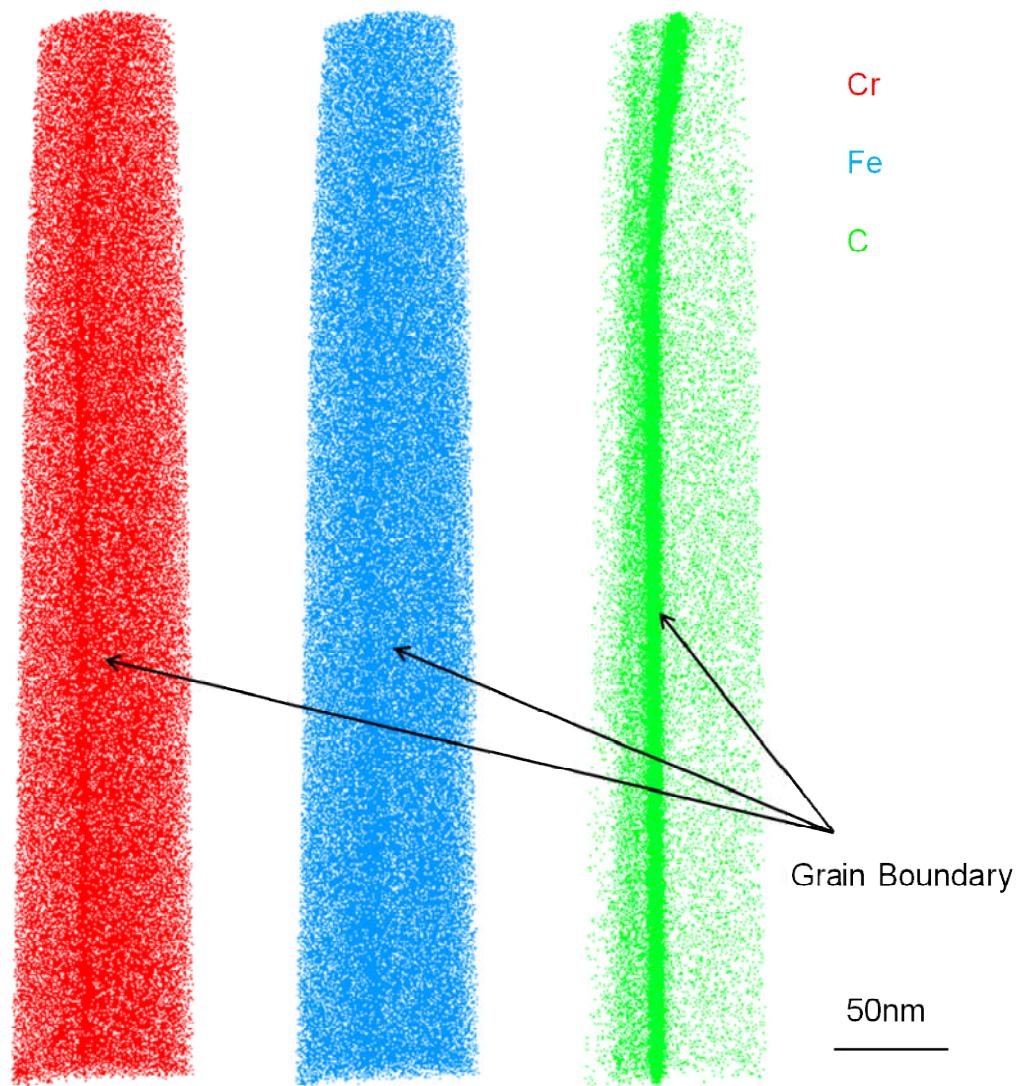


Fig.6.2 Atom maps of Cr, Fe and C obtained from the high angle grain boundary before irradiation.

1D concentration profiles were plotted across the three grain boundaries, in each case sampling the composition as a function of distance through a cylinder of diameter 25nm. The cylinders were placed carefully to avoid the concentration artefacts associated with zone lines and crystallographic poles. The concentration profiles of Cr and C are shown in Fig.6.3. Profiles obtained from the three boundaries are plotted together for comparison. The measured segregation width of

Cr on each profile is less than 8nm. The $\Sigma 1$ boundary shows the narrowest segregation width, about 5nm, while the high angle one shows the widest. The segregation of C (peak concentration and width of measured enriched region) is similar on all three boundaries. The maximum concentration of C is about 2%. Considering the average grain size ($\geq 100\mu\text{m}$), the bulk concentration of C is higher than the nominal as-received alloy concentration. Excess C was possibly introduced in the furnace during the heat treatment.

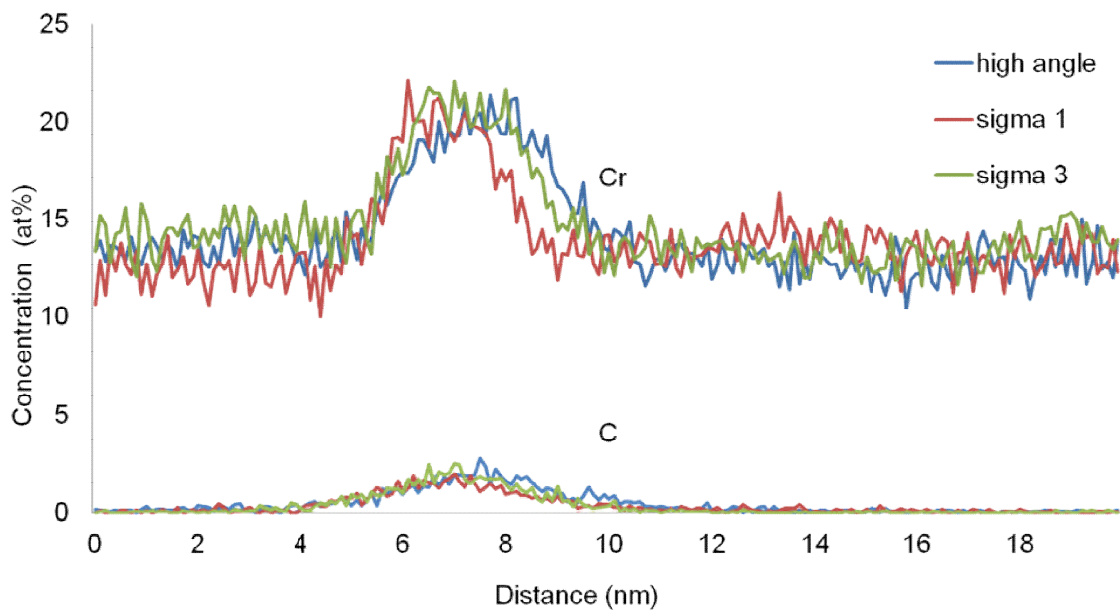


Fig.6.3 1D concentration profiles of Cr and C from high angle, $\Sigma 1$ and $\Sigma 3$ boundaries before irradiation.

Gibbsian excess values were calculated from the top to the bottom of each boundary, based on the 1D concentration profiles. Fig 6.4 shows Gibbsian excess value plotted as a function of depth from the start of analysed data of the high angle boundary before irradiation. Both Cr and C demonstrate similar excess values with distance,

indicating that the segregation distribution resulting from the heat treatment is relatively uniform along the grain boundary. Table 6.1 shows the average Gibbsian excess values of these three boundaries.

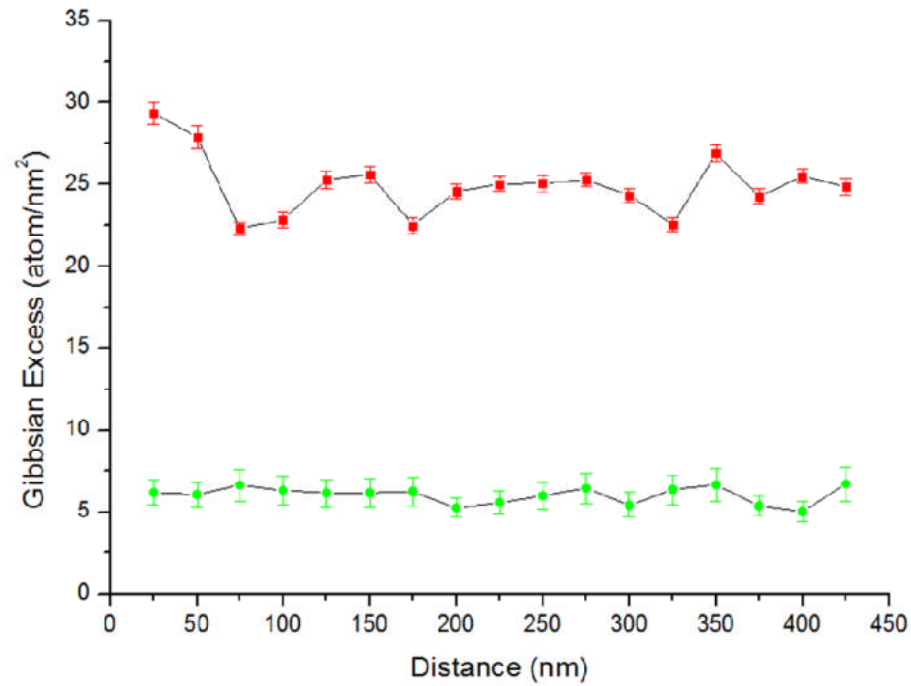


Fig.6.4 Gibbsian excess value plotted as a function of distance along the high angle boundary before irradiation.

Table 6.1 Average Gibbsian excess values of three grain boundaries before irradiation

	Average value		
	High angle boundary	Sigma 1	Sigma 3
Γ_{Cr} (atom/nm ²)	24.9±1.9	17.9±3.3	22.5±4.4
Γ_C (atom/nm ²)	6.1±0.5	5.8±1.8	5.6±1.1

6.2.2 Grain boundary chemistry after irradiation

The grain boundary chemistry after irradiation of the three boundaries was also quantified. Again 1D concentration profiles, 25nm in diameter, perpendicular to the grain boundaries were analysed. Fig.6.5 shows an atom map of Cr and C from the high angle boundary (longer than 600nm in length) with several 1D concentration profiles plotted at different depths from the start of the reconstructed data.

All profiles show that Cr and C are locally segregated within a width of less than 8nm, but Cr is slightly depleted in the immediate adjacent matrix of the grain boundary to form 'W-shape' profiles. The Cr distribution exhibits a dynamic evolution that is a function of depth and therefore irradiation dose, although the SRIM calculation in Fig.3.4 suggests that the irradiation damage was approximately uniform in the maximum damage region. With the black dashed line as an indication of bulk concentration of Cr, the peak concentration in the segregation region across the grain boundary gradually increases while the width of the vicinity depletion region decreases from around 10nm to 5nm. Meanwhile, the width of C segregation is about 5nm and the maximum concentration is about 2% on all profiles.

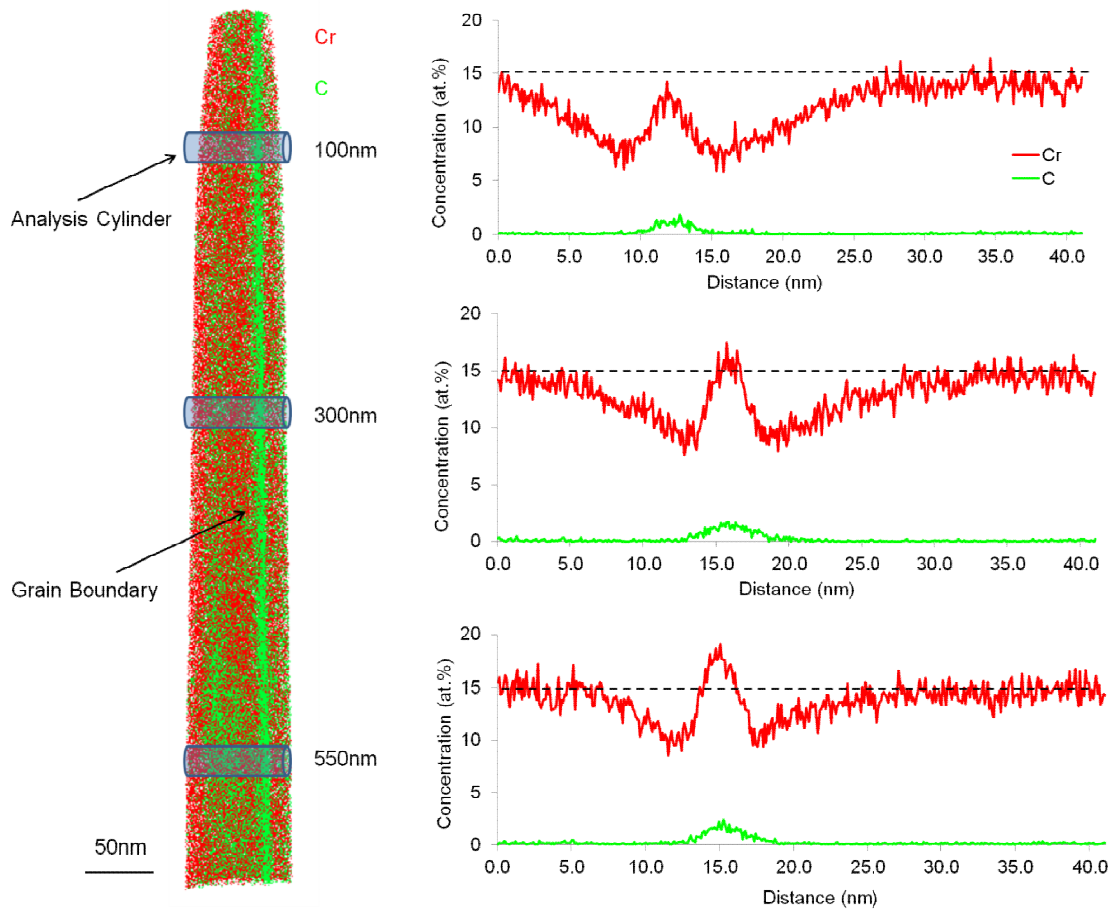


Fig.6.5 Atom map of Cr and C of the high angle boundary after high-dose irradiation (6dpa) with 1D concentration profiles plotted at different depth. Three analysis cylinders indicate the regions where the 1D concentration profiles were plotted and the black dashed lines show the bulk concentration of Cr.

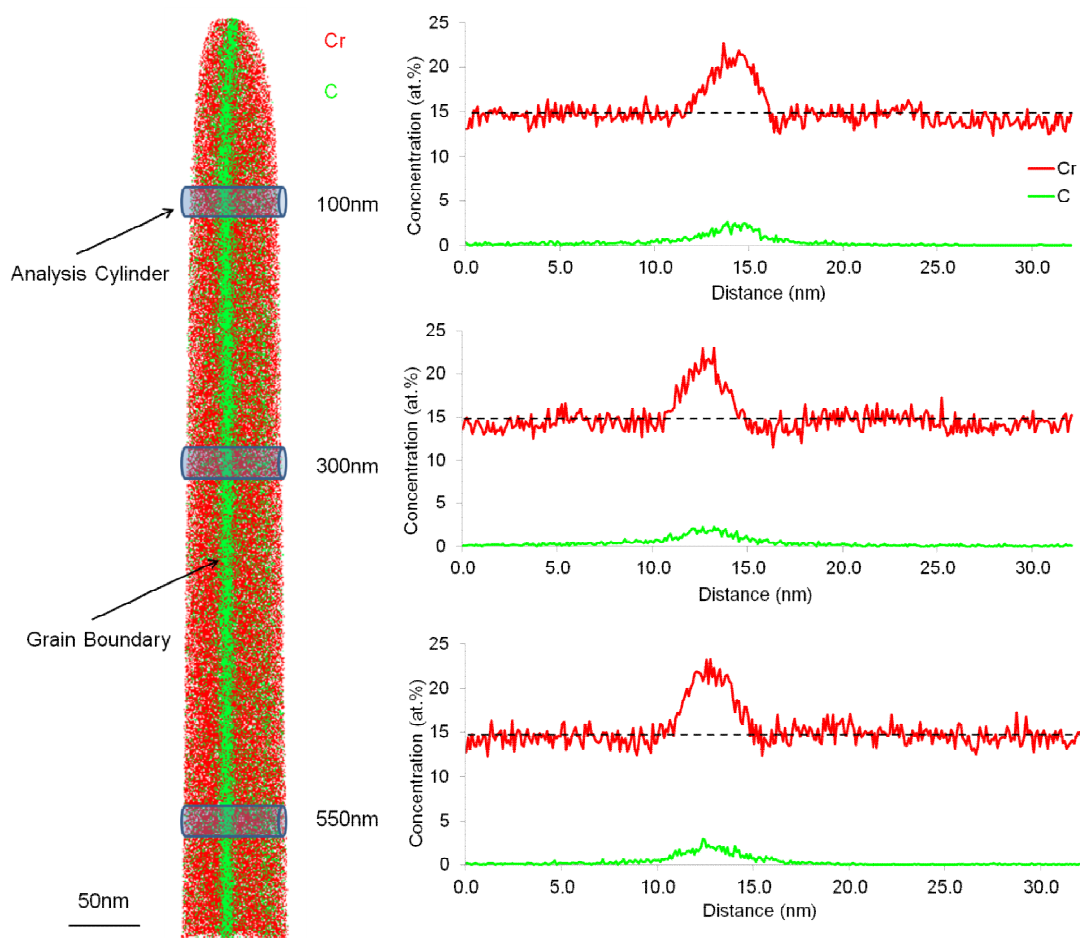


Fig.6.6 Atom map of Cr and C of the $\Sigma 1$ boundary after high-dose irradiation (6dpa) with 1D concentration profiles plotted at different depth. Three analysis cylinders indicate the regions where the 1D concentration profiles were plotted and the black dashed lines show the bulk concentration of Cr.

For the $\Sigma 1$ and $\Sigma 3$ boundaries, Cr segregation still exists after irradiation. Fig.6.6 shows an atom map of Cr and C from the $\Sigma 1$ boundary and three 1D concentration profiles from different depths. These profiles show no sign of depletion in the matrix adjacent to the grain boundary. No dynamic evolution of Cr distribution as a function of depth is observed. Fig.6.7 shows a 1D concentration profile obtained from the $\Sigma 3$ boundary. Cr segregation is clearly present. C segregation is also found on the two sigma boundaries after irradiation.

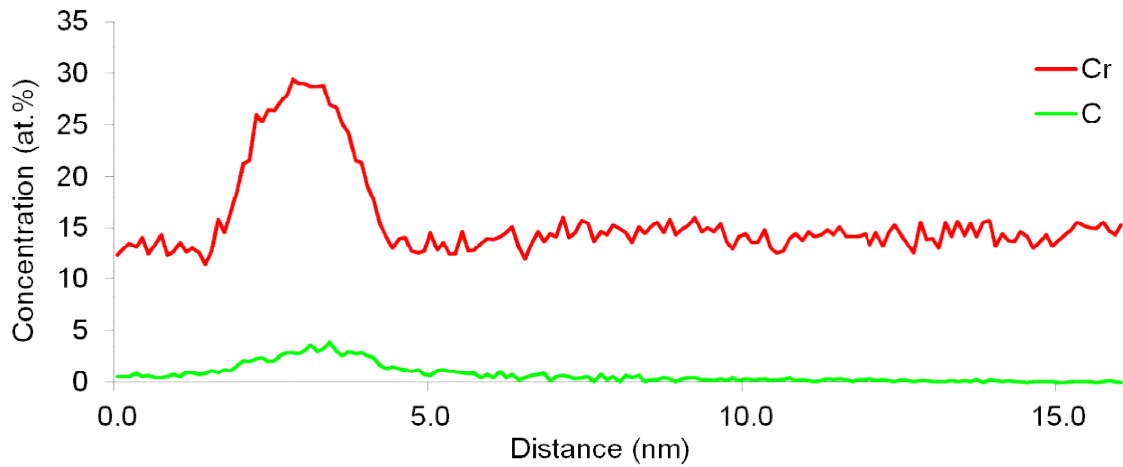


Fig.6.7 1D concentration profiles of Cr and C plotted across the $\Sigma 3$ boundary after high-dose irradiation (6dpa).

Gibbsian excess values were also calculated from the 1D concentration profiles for each boundary, using the method discussed in section 5.3.4. Fig.6.8 shows the Gibbsian excess values plotted as a function of distance for the high angle boundary and the $\Sigma 1$ boundary. The average Gibbsian excess values of Cr and C for each boundary are listed in Table 6.2.

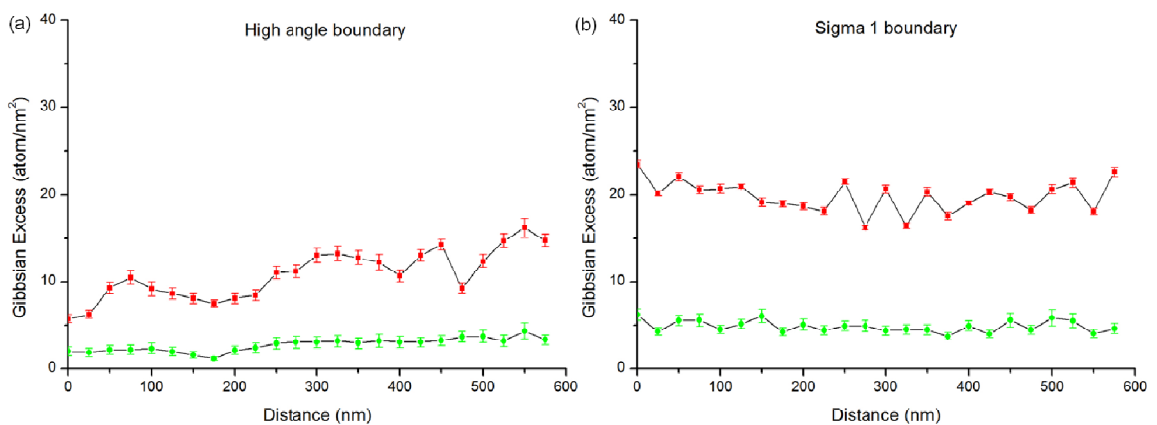


Fig.6.8 Gibbsian excess value plotted as a function of depth for (a) the high angle boundary and (b) the $\Sigma 1$ boundary after high-dose irradiation (6dpa).

Table 6.2 Average Gibbsian excess values of three grain boundaries after high-dose irradiation (6dpa)

	Average value		
	High angle boundary	Sigma 1	Sigma 3
Γ_{Cr} (atom/nm ²)	10.8±2.9	19.8±1.8	36.9±3.5
Γ_C (atom/nm ²)	2.7±0.7	4.8±0.7	6.1±0.7

6.2.3 Carbides

Occasionally, thin carbide precipitates were observed at some grain boundaries. In Fig.6.9, the green C isosurface drawn with C concentration as 8% illustrates such a carbide particle at the $\Sigma 39$ grain boundary. To measure the chemical composition inside the carbide, the mass spectrum has been analyzed within the isosurface. Different C-containing species could appear on the same position on the mass spectrum, for example, $^{12}\text{C}^+$ or $^{12}\text{C}_2^{++}$ at 12, $^{12}\text{C}_2^+$ or $^{12}\text{C}_4^{++}$ at 24 [3]. Even assuming the highest value of C concentration (such as marking $^{12}\text{C}_3^{++}$ at 18, $^{12}\text{C}_4^{++}$ at 24, $^{12}\text{C}_3^+$ at 36, $^{12}\text{C}_4^+$ at 48 and so on), the measured C concentration in the carbide is about 14.2%, slightly lower than in M_{23}C_6 (M=Fe, Cr). Such a result is an average value in the entire region inside the interface, which also depends on where the isosurface has been drawn. The concentration in the centre of the particle should be higher, roughly about 20%, which can be confirmed from the plot showing the ratio $\text{C}/(\text{Cr}+\text{Fe})$ and also the concentration of C, Cr and Fe as a function of distance in Fig.6.9. A concentration profile plotted across the carbide is also included in Fig.6.9, indicating two small regions of Cr depletion on both sides of the particle.

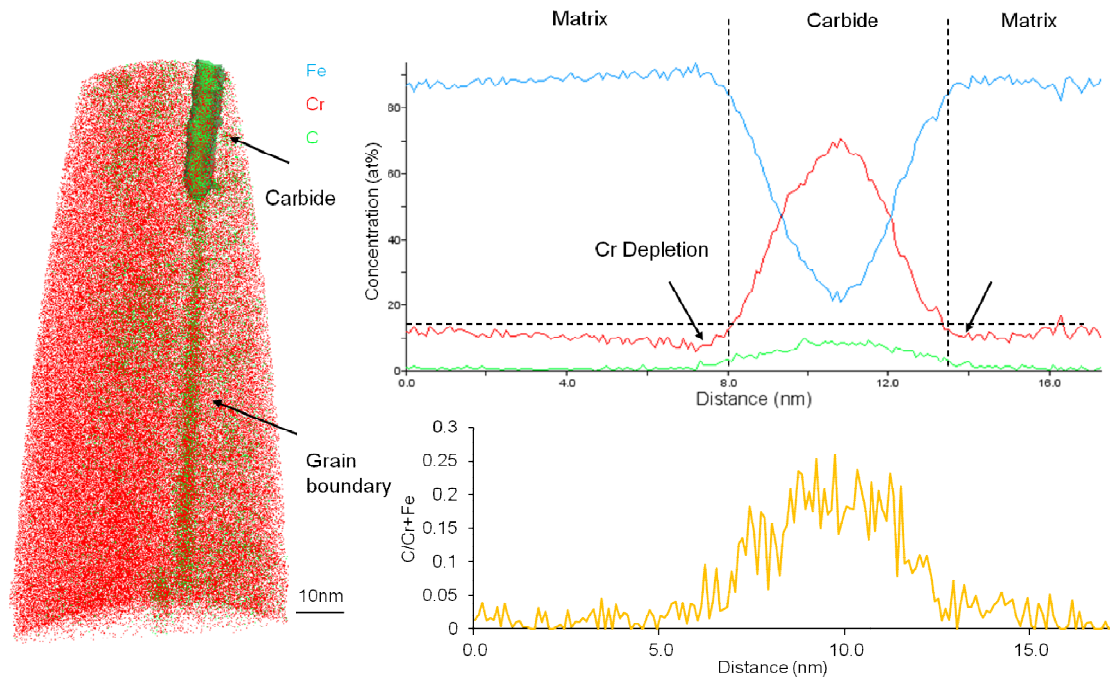


Fig.6.9 Atom map of Cr and C of the $\Sigma 39$ boundary after high-dose irradiation (6dpa), with the green C isosurface indicating a thin carbide particle. The isosurface is drawn with C concentration as 8%. 1D concentration profile of Fe, Cr and C plotted across the carbide and C/(Cr+Fe) concentration ratio plotted as a function of distance.

Another 1D concentration profile plotted across the grain boundary immediately beneath the carbide is shown in Fig.6.10. It still shows the 'W-shape' shape for the Cr concentration, however with much larger depletion regions in the adjacent matrix of grain boundary than the ones observed in the high angle boundary as shown in Fig.6.5. The C/Cr concentration ratio is also plotted as a function of distance. The ratio is about 0.3 in the centre of the grain boundary plane.

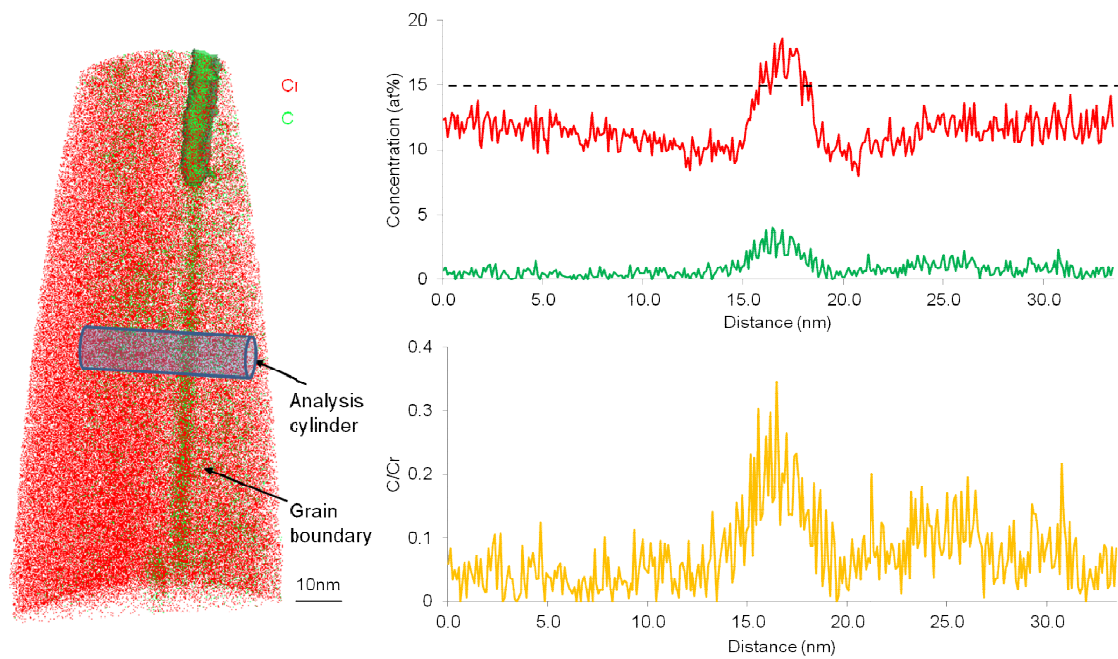


Fig.6.10 Atom map of Cr and C of $\Sigma 39$ boundary after high-dose irradiation (6dpa), with analysis cylinder showing the region where the 1D concentration profile of Cr and C was plotted. Black dashed line indicates Cr bulk concentration. The C/Cr concentration ratio is plotted as a function of distance.

6.2.4 TEM observation on the $\Sigma 3$ boundary

Fig.6.11 is a TEM bright field image of the FIB lift-out specimen from the $\Sigma 3$ boundary. As observed during FIB milling, 300nm has been lost in the thinning process and marked as the region between the two white dashed lines. The red dashed line which is 700nm from the edge of the specimen marks the approximate boundary between the irradiated region and the un-irradiated region. The grain boundary between the irradiated region and the un-irradiated region. The grain boundary is clearly revealed due to the different contrast of the two grains. The green dashed lines mark the regions where EELS line profiles were mapped. Line 1 is in the irradiated region while line 2 is in the un-irradiated region. Carbon contamination resulted from the absorption of the contamination already existing in the column when a very fine probe illuminated the specimen, and was therefore clearly visible in the same area where an EELS spectrum or a line profile was mapped. These features were used to monitor, and hence to correct, spatial drift whilst obtaining line profiles.

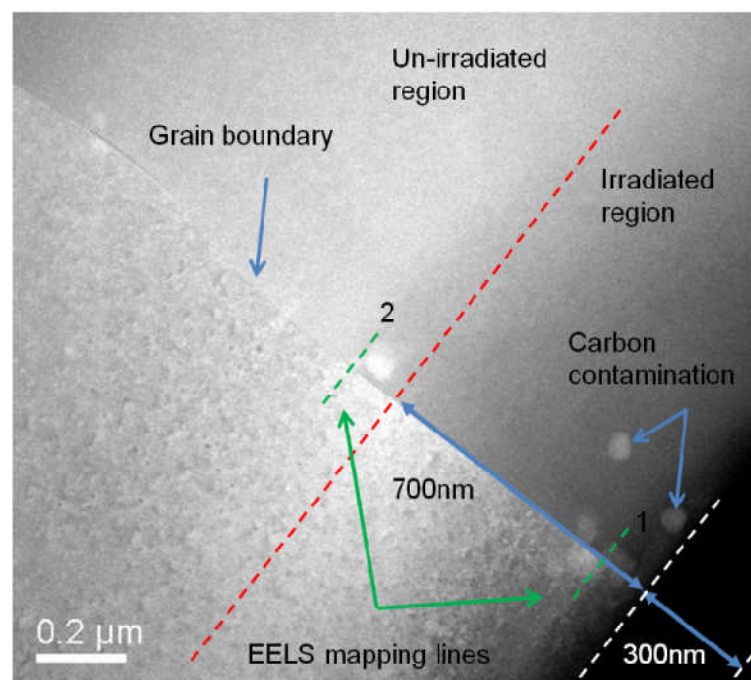


Fig.6.11 TEM bright field image of $\Sigma 3$ boundary after high-dose irradiation (6dpa).

Line 1 and line 2 are both about 80nm in length. They were positioned perpendicular to the grain boundary. Using a probe size of 0.4nm, about 60 individual EELS spectra were measured along the lines. The measuring time of each point was about 0.8s. The results are shown in Fig.6.12. The Cr concentration of each spectrum is plotted as a function of distance across the grain boundary from both the irradiated and un-irradiated regions. These two line profiles both demonstrate the presence of Cr segregation at the grain boundary. They are similar in terms of width of segregation (about 5-6nm) and peak concentration ($\leq 30\%$). The C content was not included due to the C build-up on the specimen surface during the mapping process which would have introduced large errors into the estimated concentrations.

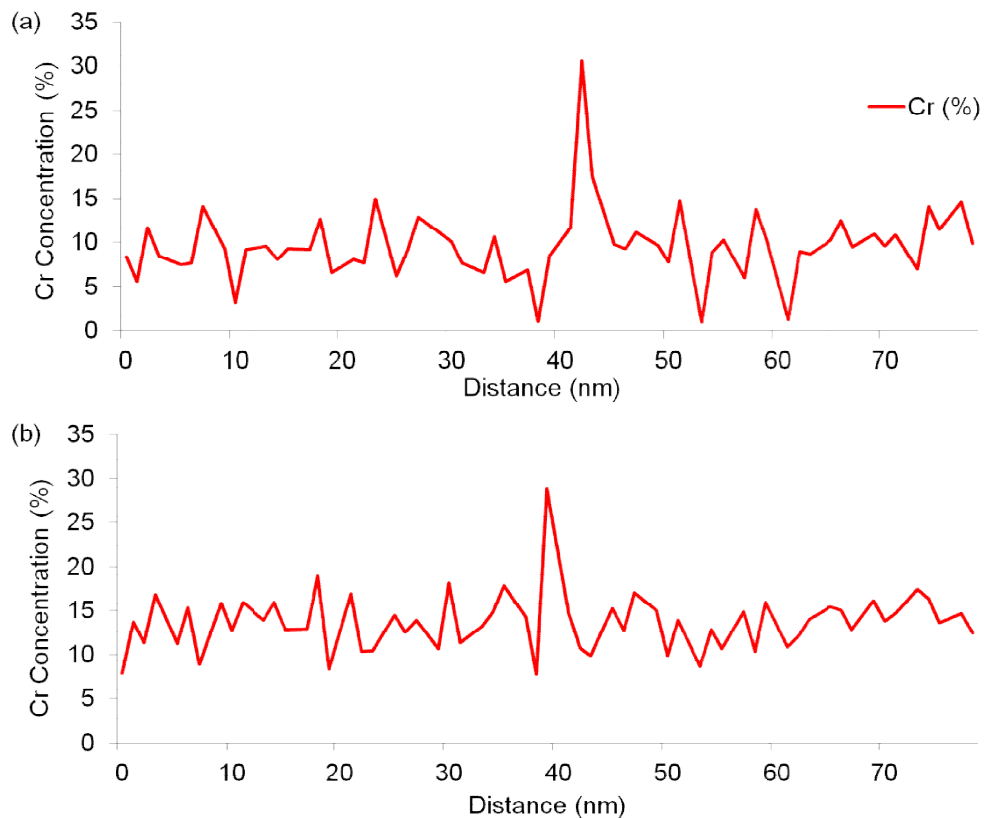


Fig.6.12 EELS line profiles obtained across $\Sigma 3$ boundary after high-dose irradiation (6dpa), (a) line 1 in the un-irradiated region and (2) line 2 in the irradiated region.

6.2.5 Discussion

6.2.5.1 Cr and C segregation induced by heat treatment before irradiation

The observed segregation of Cr at grain boundaries before irradiation is believed to have been accumulated by both equilibrium segregation driven by the thermodynamic factors at 800°C during the heat treatment, and non-equilibrium segregation caused by the supersaturations of vacancies generated during the water quenching from high temperature [4]. Considering the closest packed plane {110} for the BCC structure, the atom density is 17atom/nm². However the Gibbsian excess value calculated before irradiation was about 24.9±1.9atom/nm² for the high angle boundary and 22.5±4.4atom/nm² for the $\Sigma 3$ boundary. This result indicates that there must be more than one monolayer of excess Cr atoms segregated on the grain boundaries before irradiation. For the Fe-15.2%Cr alloy at 800°C, the composition is very close to the α phase boundary on the conventional Fe-Cr binary alloy phase diagram [5] or even possibly within the $\alpha+\alpha'$ two-phase region according to several other models [6]. Even though there are some discrepancies among the studies on the $\alpha-\alpha'$ miscibility gap, when grain boundary segregation occurs, the alloy is clearly in a regime where the Cr-Cr interactions are strongly favourable, therefore the local Cr concentration can build up to multi-layer levels even without the nucleation of a discrete second phase. According to the Gibbsian excess calculation, this phenomenon happens on every grain boundary irrespective of its misorientation. The grain boundary misorientation appears not to have had much effect on the level of Cr segregation. Within experimental error, the Gibbsian Excess values were found to be roughly similar for all three boundaries.

C was also found to segregate at all examined grain boundaries before irradiation. The measured concentration of C in the region of grain boundaries was higher than the nominal bulk concentration, probably because some C was introduced as contamination during the heat treatment. On each boundary the widths of segregation of Cr and C were quite similar, due to the strong binding between Cr and C atoms.

6.2.5.2 “W-shape” Cr concentration profiles across grain boundary planes

Several observations of “W-shape” Cr depletion profiles across grain boundaries have been reported previously [7] [8]. Little [7] proposed that the “W-shape” concentration profiles result from the superimposed, but competing, effects of thermal and radiation-induced segregation. However, Choudhury et al. [9] calculated the tracer diffusion coefficients and suggested that Cr is the fastest diffusion species at all temperatures both for vacancy and interstitial diffusion than Fe and Ni, mainly due to the low migration barriers for Cr atoms. Therefore the observed RIS behaviour of Cr is a balance between two opposing mechanisms. The actual balance depends on the presence and spatial distribution of sinks as well as solute concentration. Therefore it is possible that formation of a “W-shape” profile observed in this thesis arises from a combination of both vacancy and interstitial mechanisms.

Strong C segregation is observed at the grain boundary planes independent of grain boundary misorientation. The depletion of Cr may be suppressed by the strong binding between Cr and C. This mechanism is consistent with the previous observations that C and N suppress the depletion of Cr at grain boundaries in

austenitic steels [10], and hafnium addition was also observed to reduce Cr depletion in ferritic steels [11]. Furthermore, Ohnuki et al. [12], using C^+ ion irradiation of a Fe-13wt.%Cr alloy, observed an increase in Cr segregation at grain boundaries. The presence of interstitial carbon in this case appears to modify the point defect behaviour and lead to Cr drag to the grain boundaries.

In the studies of austenitic steels, “W-shape” profiles have often been observed as a transient state before the steady state of Cr depletion is finally achieved [13]. Nastar et al. [14] proposed a model which suggested that the steady state should be reached at around 1dpa or more dpa. Was et al. [15] suggested that for ion irradiation at 500°C, the steady state of Cr depletion should be established at around 10dpa. For the relatively low temperature and dose used in our experiment, the inhibiting effect of carbon is considered to be a plausible explanation for the “W-shape” profile and it is also possible that with increasing temperature and dose, the Cr profile could gradually evolve through the “W-shape” towards a “V-shape” in an analogous manner to the austenitic steels described above. Furthermore the presence of a “W-shape” profile could also have been missed by others authors due to other reasons such as insufficient spatial resolution or the inability to detect previously existing C by STEM-EDS or inaccuracy of measuring C due to C build up on samples by STEM-EELS.

6.2.5.3 Depth effect

The 1D concentration profiles obtained at different depths in the irradiated region of the high angle grain boundary demonstrate a dynamic evolution of grain boundary chemistry, showing that the Cr distribution is a function of irradiation dose. As

discussed in Chapter 5, the top of the APT specimen does not necessarily represent the actual original surface of the block sample due to the removal of some material by FIB milling. Combining the Gibbsian excess calculation with SRIM calculation, it is possible to roughly identify the irradiation depth of the grain boundary contained in an APT specimen as well as the irradiation damage.

In Fig.6.8 (a), the Gibbsian excess value gradually increases from around 8atom/nm^2 to about 15atom/nm^2 from the top of the reconstructed volume to 600nm in depth. This not only represents the small variation of irradiation damage in the maximum damage region, but also implies a high possibility that the bottom part of this grain boundary in the reconstructed volume is from the tail showing on the SRIM calculation (700-1000nm) rather than the maximum damage region, and is therefore affected by a different level of damage. However the exact actual depth of this section of grain boundary is difficult to determine.

Both Gibbsian excess calculations and 1D concentration profiles indicate that with decreasing irradiation dose, the amount of Cr at the grain boundary plane increases while the segregation level of C remains roughly constant. The increasing extent of the depleted region in the adjacent matrix of grain boundaries as the irradiation dose increases also implies the possibility that the grain boundary is evolving from a 'W-shape' profile to a 'V-shape' profile at higher doses. Eventually Cr would be totally depleted at the grain boundary.

However, for the $\Sigma 1$ boundary, neither 1D concentration profiles nor Gibbsian excess calculations show a clear tendency for the similar dynamic evolution observed in the high angle boundary. This makes it impossible to identify the location that the $\Sigma 1$ grain boundary contained in the APT specimen was originally

from. On the other hand, no clear tendency can be identified over an extensive distance (600nm) which indicates that the level of irradiation damage had little effect on the Cr distribution on this $\Sigma 1$ grain boundary.

6.2.5.4 Effect of grain boundary misorientation

Irradiation-induced Cr depletion in the randomly selected high angle grain boundary is observed, consistent with several previous reports [11, 16]. In contrast, irradiation has very little effect on the $\Sigma 1$ boundary, while it leads to increased segregation of Cr on the $\Sigma 3$ boundary. Although other authors reported similar segregation phenomena, [17-19] the effect of grain boundary misorientation has rarely been taken into account, which makes it impossible to make direct comparisons with results presented in this work. Was et al. [20] suggested that Cr enrichment is likely to occur in ferritic alloys with lower Cr concentration (about 9%) and at lower temperatures (400°C), but the authors were not able to identify unambiguous trends. The data reviewed by Was et al. are also not completely consistent with our experiments which show Cr enrichment observed in alloys with relatively high Cr concentration (15.2%) and at low temperature (350±50 °C).

Watanabe et al. [21] studied the sink strength difference associated with grain boundary misorientation, and found that RID of Cr was enhanced as the tilt angle increased but was suppressed at coherent low sigma grain boundaries such as $\Sigma 9$, $\Sigma 3$ and $\Sigma 1$ in austenitic steels. They suggested that the sink strength for point defects for a randomly selected grain boundary is much stronger than the strength at a coherent/or a low-energy boundary like a small tilt angle boundary. These results are consistent with the present results that the irradiation has the strongest effects on RIS/RID of Cr on the random high angle boundaries and the weakest effects on the low sigma boundaries, especially $\Sigma 1$. Combining with the calculation Choudhury et

al. [9] provided, a reasonable explanation for the high angle boundary is that the sink strength is much stronger, therefore the vacancy mechanism works as a dominant process; however for a coherent/low-sigma boundary such as $\Sigma 3$, fewer sinks are present and the interstitial mechanism is the main process which gives rise to the Cr segregation.

6.2.5.5 Carbide interfaces

When analyzing small particles embedded in a solid solution using APT, the aberrations of ion trajectories and local magnification are issues which could lower the measured solute concentrations of such particles. These effects were first observed in the 1970s' [22]. When one phase evaporates faster than the other, the local surface will be slightly recessed at the interface. The trajectories of ions are also affected by this recessed surface. Ion trajectories from this region will be compressed while ions from the slower-evaporation phase will be locally magnified [23, 24].

C has a higher evaporation field than Fe and Cr and therefore the local magnification effect will result in the carbides appearing larger than they should. Furthermore, in the reconstructed data some of the Fe/Cr atoms that were near the particle interface will appear within the carbide. These effects reduce the measured C concentration in the particle after reconstruction [25]. The C concentration could be further reduced by surface diffusion and imperfect detector efficiency for identifying multiple events (an instrument limitation), even though the APT experimental parameters had been optimized as discussed in Chapter 4. Judging from Fig.6.9, in the centre of the carbide, the highest ratio between C and M is 0.25, which is close to the ratio of

$M_{23}C_6$ ($C/M=0.26$). Therefore it is reasonable to assume that the carbide is $M_{23}C_6$ though further TEM experiments would be necessary to prove this conclusion. Small regions depleted in Cr are also found on both sides of the carbides in the matrix along the grain boundary, suggesting the interface between matrix and carbide also acts as a sink for point defects, which is also consistent with previous reports [26].

At the irradiation temperature considered in this paper, there was not enough time for the carbide to form during irradiation, therefore these carbides were already formed before irradiation. It is well known that the formation of Cr-rich carbides can cause the depletion of Cr at grain boundaries [27], which can explain the much larger extent of depletion regions in the adjacent matrix of grain boundary on the 1D concentration profile in Fig.6.10. This clearly indicates that the carbide increased the overall depletion tendency of Cr in the neighbouring grain boundary and matrix.

The C/Cr ratio inside the grain boundary plane is about 0.25, which indicates the possibility of the formation of a very fine C-rich clusters or phases within the grain boundary plane. The observation of Cr-C clusters will be discussed in Chapter 7.

6.2.5.6 Comparison between TEM and APT

Most if not all recent research on the RIS/RID phenomena of Cr has been conducted using STEM-EDS/EELS analyses of grain boundary chemistry. The accuracy of the measurements (spatially and chemically) depends on the different measuring methods, equipment conditions, electron beam spot size, spatial drift, research materials as well as irradiation conditions. For example, Takahashi et al. [28] studied Fe-5at%Cr and Fe-13at%Cr irradiated at 673K at 3dpa using TEM-EDX, with a minimum beam spot size of 10nm in diameter, and the Cr depletion regions

were found to be within 200nm of the grain boundary. However, Kano et al. [10] showed a Cr depletion region within less than 20nm of the grain boundary using a field emission TEM-EDX with the probe size of 0.5nm in several irradiated SIS304 and SUS316L steels irradiated at 573k to 1dpa. In the present work, with a field emission gun and a probe size of 0.4nm, the observed Cr segregation at the $\Sigma 3$ boundary is within about 5-6nm across the grain boundary.

The present APT-based study on the same $\Sigma 3$ boundary shows that the width of Cr segregation before and after irradiation is also about 5-6nm. While the results obtained by TEM could be affected by beam broadening, trajectory aberrations [25] could also reduce the accuracy of APT measurement. APT can however provide the data with sufficient spatial resolution and accuracy to describe the behaviour of solutes.

The EELS profiles obtained in the un-irradiated region and irradiated region both demonstrated Cr segregation at the grain boundary. However without quantitative analysis, it was impossible to estimate the change in the level of segregation and this made it impossible to compare with the Gibbsian excess results calculated from APT results. While quantification of carbon remains an issue due to specimen contamination in the TEM experiments, the capability to quantitatively detect minor elements such as C and provide 3D information on the distribution of solute atoms within the grain boundary planes is unique to the APT technique.

6.3 Results on Low-Dose Irradiated Samples

6.3.1 Grain boundary chemistry before irradiation

As shown in Table 3.1, the same energies and implantation sequence were used for implantations No.2 and No.3. Therefore they have the same damage profile as shown in Fig.3.4, and the maximum damage is about 0.6dpa. Different dose rates were applied to allow the implantation No.2 to finish in 28.5min and the implantation No.3 to finish in 9.5h (20 times longer than implantation No.2). Therefore, the sample which was fast-irradiated by implantation No.2 is referred to as sample F, and sample which was slow-irradiated by implantation No.3 is referred to as sample S. Furthermore to further reduce the C contamination introduced in the furnace, the sample F sent to implantation No.2 was heated treated in an argon atmosphere and the sample S sent to implantation No.3 was sealed in an argon-filled tube during heat treatment.

Before irradiation, Cr and C were also found to segregate at each boundary observed in all samples. Fig.6.13 shows reconstructed atom maps of Fe, Cr and C of the random selected high angle grain boundary in sample F. Even though the grain boundary is not perpendicular to the surface of the block sample, an APT specimen containing a section of the grain boundary longer than 400nm was still successfully prepared.

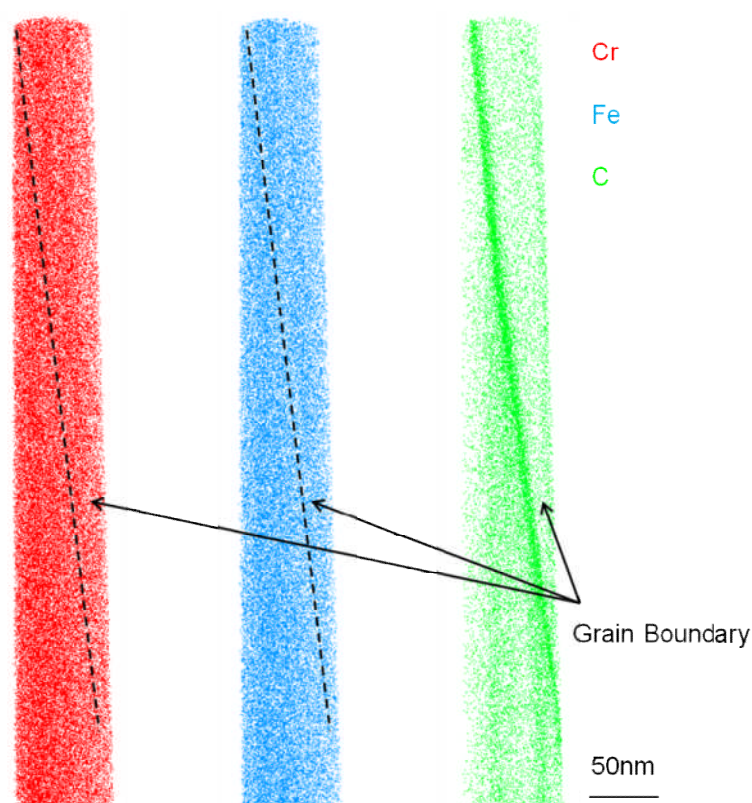


Fig.6.13 Atom maps of Fe, Cr and C of the randomly selected high angle grain boundary from sample F.

1D concentration profiles were plotted in analysis cylinders of diameter 25nm carefully positioned perpendicular with the grain boundaries. Fig.6.14 (a) shows concentration profiles of Cr and C obtained from the high angle boundary and $\Sigma 1$ boundary of the sample F, which are plotted together for comparison. Fig.6.14 (b) shows concentration profiles of Cr and C of the high angle boundary of the sample S. For the sample F, the measured segregation widths (about less than 5nm) and the peak concentrations ($\leq 20\%$) of Cr on two boundaries were quite similar. The measured segregation width of Cr on the sample S was slightly larger, about 6nm. The maximum concentrations of C on these three boundaries were all about 2%.

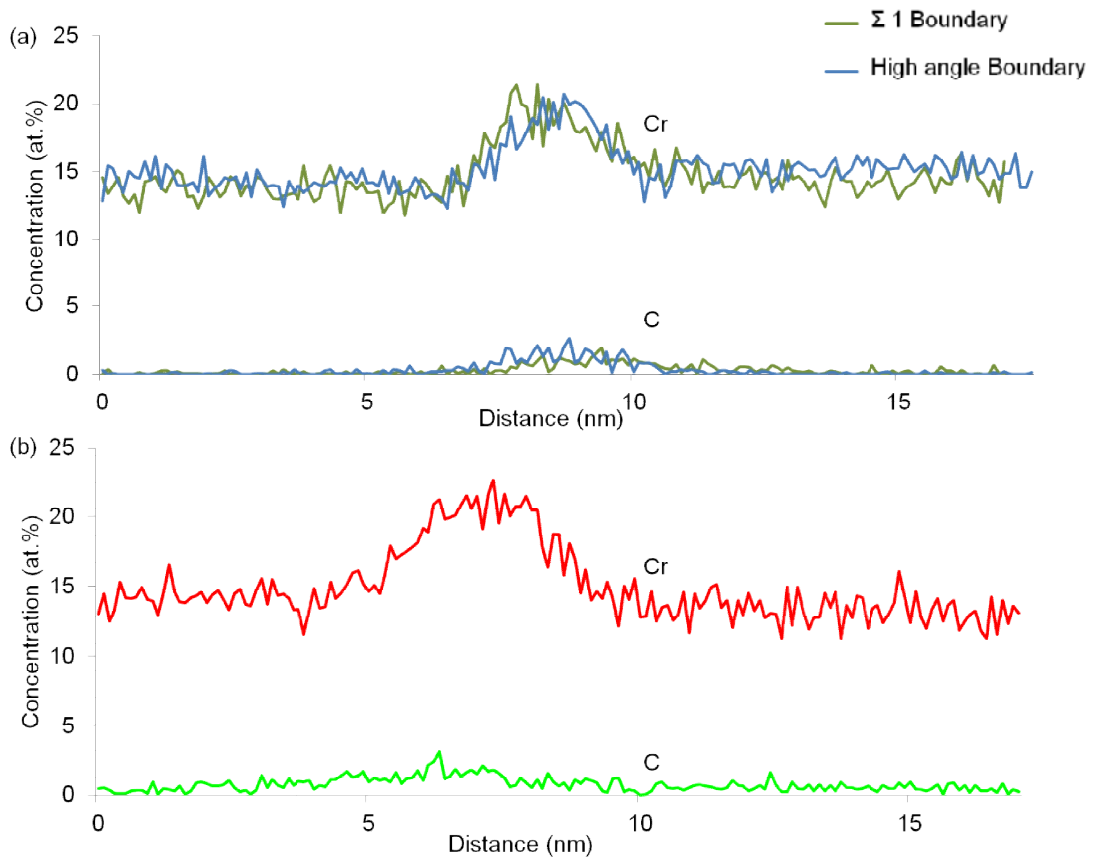


Fig.6.14 1D concentration profiles plotted across (a) the high angle boundary and the $\Sigma 1$ boundary from sample F and (b) the high angle boundary from sample S before irradiation.

Gibbsian excess values were also calculated from top (i.e. nearest the irradiated surface of the original sample) to bottom (i.e. further away from the irradiated surface of the irradiated sample) for each boundary in the reconstructed volume and the average values of three boundaries are shown in Table 6.3. The two boundaries from sample F yielded similar average values, while the one from the high angle boundary from sample S is higher. The differences are believed to result from different batches of heat treatment performed in the furnace before irradiation.

Table 6.3 Average Gibbsian excess values of three grain boundaries before irradiation from sample F and sample S

	Sample F		Sample S
Average value	High angle boundary	Sigma 1	High angle boundary
Γ_{Cr} (atom/nm ²)	10.0±1.1	10.6±2.8	20.3±4.1
Γ_C (atom/nm ²)	1.3±0.2	2.1±1.2	3.9±1.3

6.3.2 Grain boundary chemistry after irradiation

1D concentration profiles were also used to examine the grain boundary chemistry after irradiation. Fig.6.15 shows an atom map of Cr and C of the high angle boundary in the slow-irradiated sample S, with several 1D concentration profiles plotted at different depths from top to bottom along the boundary using identical cylinders (25nm in diameter).

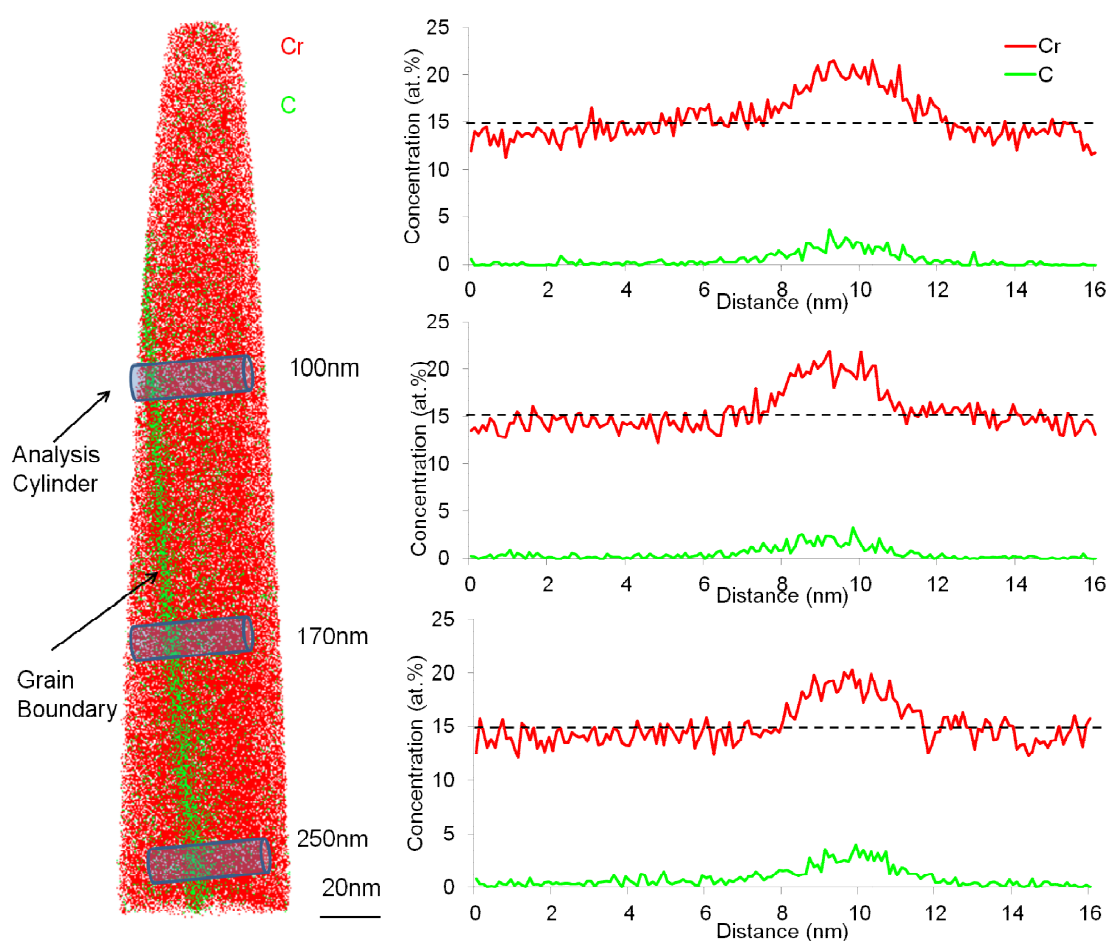


Fig.6.15 Atom map of Cr and C of the high angle boundary from the low-dose (0.6dpa) slow-irradiated sample S, with several 1D concentration profiles plotted at different depths

After irradiation, Cr and C were still segregated at the grain boundary region, with a measured segregation width of about 5nm. 1D concentration profiles plotted from different depths demonstrated similar shape. In contrast to the results obtained on high angle boundaries of the high-dose irradiated sample, neither ‘W-shape’ profiles with depletion regions in the adjacent matrix of the grain boundary nor dynamic evolution as a function of depth are observed. Similar phenomena are also found in the low-dose fast-irradiated sample F. Fig 6.16 shows two 1D concentration profiles plotted across a high angle boundary and a $\Sigma 1$ boundary. Only Cr and C segregation are observed, without any evidence of a depletion region, and the measured segregation widths of Cr on two boundaries are about 5nm. As usual, Gibbsian excess values were calculated for these three boundaries after irradiation based on 1D concentration profiles, and the average values are shown in Table 6.4.

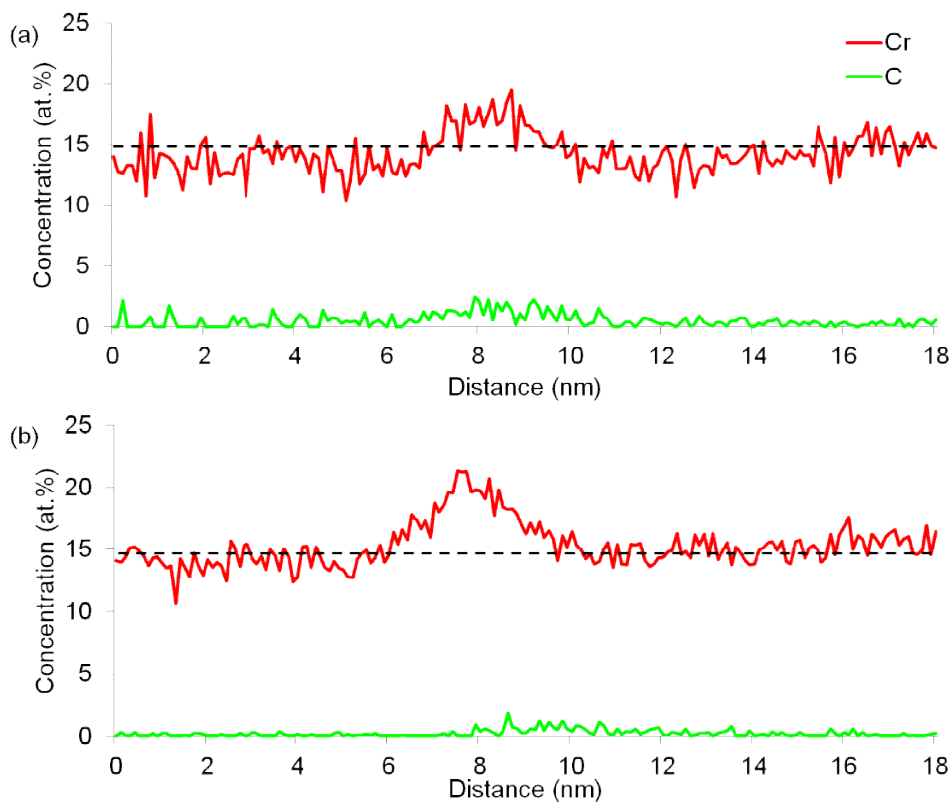


Fig.6.16 1D concentration profiles plotted across (a) the high angle boundary and (b) the $\Sigma 1$ boundary in the low-dose (0.6dpa) fast-irradiated sample F.

Table 6.4 Average Gibbsian excess values of three grain boundaries after low-dose irradiation (0.6dpa) of the fast-irradiated sample F and the slow irradiated sample S

	Fast-irradiated sample F		Slow-irradiated sample S
Average value	High angle boundary	Sigma 1	High angle boundary
Γ_{Cr} (atom/nm ²)	6.8±1.3	9.9±2.9	15.2±2.9
Γ_C (atom/nm ²)	2.8±1.3	1.1±0.6	5.0±0.4

6.3.3 Discussion

Before irradiation, Cr and C were found to be segregated at all three grain boundaries. Gibbsian excess values showed that the levels of segregation of Cr and C were similar for the high angle boundary and the $\Sigma 1$ boundary of the low-dose (0.6dpa) fast-irradiated sample F, indicating that the grain boundary misorientation has little effect on the segregation caused by heat treatment. The high angle boundary of the low-dose slow-irradiated sample S demonstrated a higher segregation level. This may have resulted from different batches and methods of heat treatment as discussed below.

The samples irradiated in implantation No.1 were heat-treated in a sealed vacuum tube and a high level of C segregation (around 6atom/nm²) was found on all examined grain boundaries regardless of their misorientations. Argon atmosphere and an argon-filled tube were used during heat treatment of samples irradiated by implantations No.2 (low-dose fast irradiation) and No.3 (low-dose slow irradiation) respectively. Judging from the Gibbsian excess values, an argon atmosphere appears to be the optimum method of reducing C contamination during heat treatment. Comparing Table 6.1 and 6.3, it is reasonable to believe that a higher C concentration at the grain boundary would give rise to a higher Cr segregation level as well due to the strong binding between Cr and C.

After irradiation, high angle boundaries from both low-dose fast-irradiated and slow-irradiated samples demonstrated Cr and C segregation, without the presence of any depletion region in the matrix adjacent to grain boundaries, which is totally different from the observation made on the high angle boundary of the high-dose irradiated sample. Gibbsian excess values showed that about 25% of Cr had been

depleted from the high angle boundary in the slow-irradiated sample S, and the depletion level of Cr in the fast-irradiated sample F was about 32%. These values are much lower than the results from the high angle boundary of the high-dose irradiated sample (about 57% at maximum damage region and about 39% at the bottom). Such results indicate that the level of Cr depletion is a function of irradiation damage, but is not affected by the irradiation rate. As long as the irradiation reached the same damage level as simulated by SRIM, high angle boundaries from fast and slow-irradiated samples demonstrate similar behaviour. It also suggests that the assumption made in section 6.2.5.3 to estimate the damage region of the bottom of the high-dose irradiated high angle grain boundary shown in Fig.6.5 is correct. The level of depletion of Cr on this boundary gradually decreased from 57% to 39%, which is getting closer to the value seen in the low-dose (0.6dpa) irradiated high angle boundaries. This is correlated with the bottom of this grain boundary lying in the tail of the SRIM calculated damage distribution.

Furthermore, no clear dynamic evolution of Cr distribution was observed in high angle boundaries in the fast and slow-irradiated samples. Even though the grain boundary shown in Fig.6.15 was much shorter than the one shown in Fig.6.5, the similarity of 1D concentration profiles plotted over a distance of 150nm provides evidence that no depth effect occurred on the low-dose irradiated samples. A plausible explanation could be that the low-dose irradiation was more uniform in the maximum damage region, or the damage was not heavy enough to cause the depth effect.

Meanwhile, $\Sigma 1$ boundaries from high-dose and low-dose fast-irradiated samples demonstrated similar behaviour, with Cr and C segregated at the $\Sigma 1$ grain boundaries both before and after irradiation independent of damage level or damage

rate. The Gibbsian excess values show that irradiations at these doses and dose rates have very little effect on a $\Sigma 1$ boundary; the small fluctuations of average values before and after irradiation are all the same within the range of the error bars.

6.4 Conclusions

This systematic approach developed in Chapter 5, combining EBSD, FIB and APT techniques, has been applied successfully to analysis RIS/RID on specific grain boundaries in an irradiated Fe-15.2%Cr alloy, taking into account all factors such as irradiation depth, grain boundary orientation, microchemistry and impurities, with sufficient chemical and spatial resolution.

Before irradiation, Cr and C both segregated at all examined grain boundaries. C introduced during the heat treatment played a major role in affecting Cr segregation at the grain boundaries. All grain boundaries from the same sample demonstrated similar levels of Cr segregation despite their varying misorientations.

After irradiation, segregation or depletion of Cr were found to be strongly connected with the grain boundary orientation. In the high-dose irradiated sample, the segregation of Cr decreased significantly on the randomly selected high angle boundary. On the 1D concentration profile, two depletion regions appeared in the adjacent matrix of the grain boundary and formed a 'W-shape' profile, and dynamic evolution of the profile was also observed as a function of irradiation depth. On the other hand, although the Gibbsian excess values indicated Cr depletion after irradiation, the 1D concentration profiles plotted across the high angle boundaries in the low-dose irradiated samples still demonstrated Cr segregation without the presence of a depletion region. No dynamic evolution was observed in this case. Furthermore, the level of Cr depletion was a function of irradiation dose, but not related with irradiation rate. The variation of irradiation conditions, despite their different damage levels and damage rates, had very little effect on the $\Sigma 1$ boundary.

However, increased Cr segregation was observed on the $\Sigma 3$ boundary in the high-dose irradiated sample.

Two mechanisms of RIS/RID were summarized by Okamoto and Rehn [29] as a vacancy mechanism, which depletes solute atoms from the grain boundary, and an interstitial mechanism which transports solute atoms towards the grain boundary. Previously these two mechanisms were considered separately and most researchers used only one of these two mechanisms to explain their experimental results. However, the calculation provided by Choudhury et al. [9] has suggested that the observed RIS/RID phenomenon of Cr is a balance of these two opposing mechanisms. The contrasting behaviour of Cr observed on grain boundaries with different misorientations presented in this thesis confirms the suggestion made by Choudhury et al. Two mechanisms are found in both high-dose and low-dose irradiation cases, and the balance depends on the presence and spatial distribution of sinks and the solute concentration. For high angle boundaries, whose sink strength is stronger, the vacancy mechanism plays the major role; while for the more coherent/low-sigma boundaries, the interstitial mechanism appears to be the main process.

C has been found to segregate at all grain boundaries after irradiation, and the level of segregation was not sensitive to the damage level or damage rate. It is believed that C may play a role in retaining Cr in the grain boundary under irradiation and slow down the depletion process due the strong binding between Cr and C atoms. Occasionally, thin-shape carbides had been found on the grain boundary and caused the depletion of Cr in the adjacent matrix and also along the boundary. The chemical composition analysis is consistent with the $M_{23}C_6$ type. The examination of C/Cr

ratio inside the grain boundary plane indicated the possibility of the formation of very fine Cr-rich phase within the grain boundary plane.

References

1. Schaublin, R., P. Spatig, and M. Victoria, *Journal of Nuclear Materials*, 1998. **258**: p. 1350-1355.
2. Lapena, J., M. Garcia-Mazario, P. Fernandez, and A.M. Lancha, *Journal of Nuclear Materials*, 2000. **283**: p. 662-666.
3. Sha, W., L. Chang, G.D.W. Smith, C. Liu, and E.J. Mittemeijer, *Surface Science*, 1992. **266**: p. 416-423.
4. Faulkner, R.G., *Acta Metallurgica*, 1987. **35**: p. 2905-2914.
5. Okamoto, H., P.R. Subramanian, and L. Kacprzak, eds. *Binary Alloy Phase Diagrams (Second Edition)*. ed. T.B. Massalski. Vol. 2. 1990, ASM International, Materials Park: Ohio.
6. Bonny, G., D. Terentyev, and L. Malerba, *Scripta Materialia*, 2008. **59**: p. 1193-1196.
7. Little, E.A., *Journal of Nuclear Materials*, 1993. **206**: p. 324-334.
8. Fukuya, K., M. Nakano, K. Fujii, and T. Torimaru, *Journal of Nuclear Science and Technology*, 2004. **41**: p. 594-600.
9. Choudhury, S., L. Barnard, J.D. Tucker, T.R. Allen, B.D. Wirth, M. Asta, and D. Morgan, *Journal of Nuclear Materials*, 2011. **411**: p. 1-14.
10. Kano, F., K. Fukuya, S. Hamada, and Y. Miwa, *Journal of Nuclear Materials*, 1998. **258**: p. 1713-1717.
11. Lu, Z., R.G. Faulkner, N. Sakaguchi, H. Kinoshita, H. Takahashi, and P.E.J. Flewitt, *Journal of Nuclear Materials*, 2006. **351**: p. 155-161.
12. Ohnuki, S., H. Takahashi, and T. Takeyama, *Journal of Nuclear Materials*, 1982. **103**: p. 1121-1125.
13. Faulkner, R.G., *Journal of Nuclear Materials*, 1997. **251**: p. 269-275.

14. Nastar, M., *Philosophical Magazine*, 2005. **85**: p. 641-647.
15. Was, G.S. and T. Allen, *Journal of Nuclear Materials*, 1993. **205**: p. 332-338.
16. Neklyudov, I.M. and V.N. Voyevodin, *Journal of Nuclear Materials*, 1994. **212**: p. 39-44.
17. Clausing, R.E., L. Heatherly, R.G. Faulkner, A.F. Rowcliffe, and K. Farrell, *Journal of Nuclear Materials*, 1986. **141**: p. 978-981.
18. Gupta, G., Z. Jiao, A.N. Ham, J.T. Busby, and G.S. Was, *Journal of Nuclear Materials*, 2006. **351**: p. 162-173.
19. Wharry, J.P., Z.J. Jiao, V. Shankar, J.T. Busby, and G.S. Was, *Journal of Nuclear Materials*, 2011. **417**: p. 140-144.
20. Was, G.S., J.P. Wharry, B. Frisbie, B.D. Wirth, D. Morgan, J.D. Tucker, and T.R. Allen, *Journal of Nuclear Materials*, 2011. **411**: p. 41-50.
21. Watanabe, S., Y. Takamatsu, N. Sakaguchi, and H. Takahashi, *Journal of Nuclear Materials*, 2000. **283**: p. 152-156.
22. Waugh, A.R., E.D. Boyes, and M.J. Southon, *Surface Science*, 1976. **61**: p. 109-142.
23. Miller, M.K. and M.G. Hetherington, *Surface Science*, 1991. **246**: p. 442-449.
24. Vurpillot, F., A. Bostel, and D. Blavette, *Applied Physics Letters*, 2000. **76**: p. 3127-3129.
25. Blavette, D., F. Vurpillot, P. Pareige, and A. Menand, *Ultramicroscopy*, 2001. **89**: p. 145-153.
26. Lundin, L. and B. Richarz, *Applied Surface Science*, 1995. **87-8**: p. 194-199.
27. Hall, E.L. and C.L. Briant, *Metallurgical Transactions A-Physical Metallurgy and Materials Science*, 1984. **15**: p. 793-811.

28. Takahashi, H., S. Ohnuki, and T. Takeyama, *Journal of Nuclear Materials*, 1982. **103**: p. 1415-1419.
29. Okamoto, P.R. and L.E. Rehn, *Journal of Nuclear Materials*, 1979. **83**: p. 2-23.

Chapter 7

A Study of C/Cr-enriched Clusters in a Fe-15.2%Cr Alloy

7.1 Clustering in Fe-Cr Alloys

7.1.1 Introduction

TEM observations [1-7] have confirmed the formation of α' phase under irradiation in Fe-Cr alloys of composition 5%-15%Cr within the temperature range 600K-800K. Comparing with the literature, the Fe-Cr alloys studied in this thesis have a similar composition and irradiation temperature. Even though no α' phase in any shape could be directly observed in any of the atom maps discussed in Chapter 6, it is interesting to study the microstructural evolution to find out if there is any formation of very early stage α' phase or Cr-enriched clusters which were not visible on the atom maps. Furthermore, the discussion in section 6.2.5.5 implies the possibility of formation of a C-rich phase within the grain boundary plane. Such insight into ultrafine scale microstructural evolution can be inferred from data obtained by APT.

In many studies reported in the literature, the microstructural features of interest are second phase precipitates, often on the scale of a few nanometers. These are usually visible on the reconstructed atom maps. Due to the large amount of data provided by LEAP (at least several million atoms), it is necessary to apply an automatic algorithm to identify and characterize precipitates in terms of parameters such as size, chemical composition, volume fraction and so on, rather than using a time-consuming manual selection method. Such algorithms are also very useful in searching for fine scale clusters which may not be visible in the atom maps.

7.1.2 The maximum separation method

There are many algorithms to define clusters applied by different researchers [8]. The maximum separation method has been proved to be a successful approach in the characterization of solute clusters, and is shown schematically in Fig.7.1 [9]. It is based on the assumption that, within a local region of high solute concentration in the solid solution, such as a second phase precipitate, the spacing between two solute atoms is smaller than in the matrix. Therefore, for all the shaded solute atoms in Fig.7.1 (a), any two atoms having a distance less than a pre-defined parameter D_{max} are considered to be in the same cluster, as shown in Fig.7.1 (b). Another parameter N_{min} is defined as the minimum number of solute atoms in a cluster. Only a cluster with at least N_{min} number of solute atoms is considered to be significant. Furthermore, any other atoms within a distance of L of any core solute atoms are also defined as being in the same cluster, as shown in Fig.7.1 (c). Fig.7.1 (d) shows the last step of erosion, in which atoms which have been found within a distance of E of any other atoms in the matrix are removed.

In summary, there are four key parameters involved in the maximum separation method:

D_{max} - maximum separation distance between core solute atoms

N_{min} – minimum number of core solute atoms in a cluster

L – maximum separation distance of additional elements

E – erosion distance to remove any atoms near cluster interface

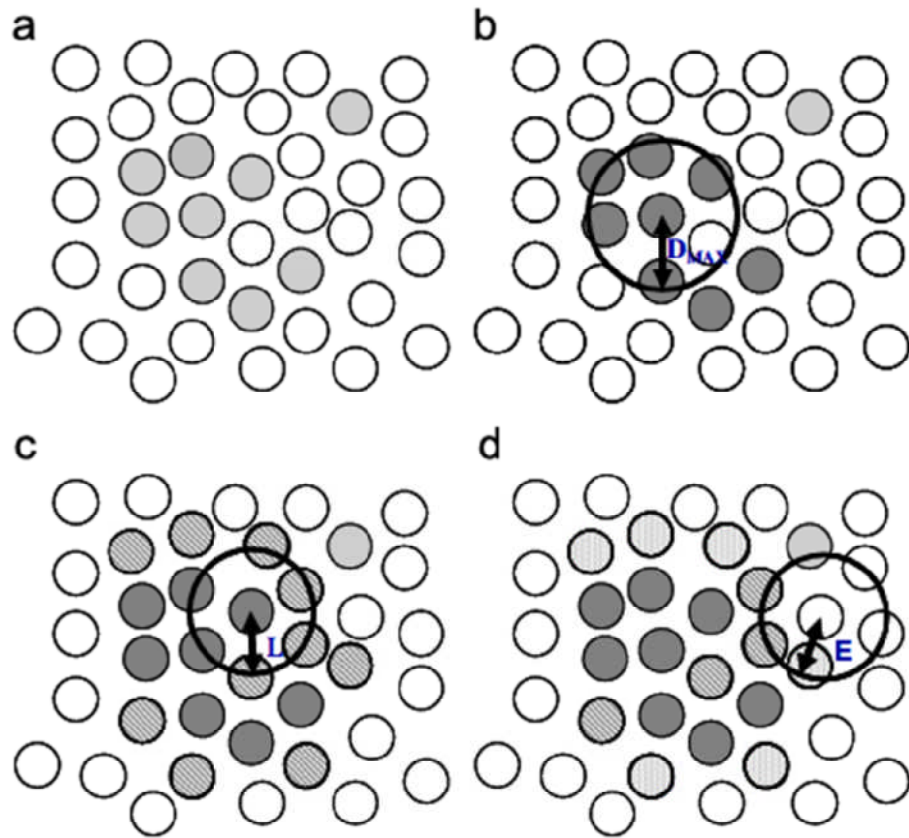


Fig.7.1 Schematic diagrams of the maximum separation method, (a) solute atoms are shown shaded, (b) solute atoms within the distance of D_{max} of each other are identified as core solute atoms in a cluster, shown dark shaded, (c) other atoms within the distance of L of a core solute atom are identified in the same cluster, shown hatched, (d) erosion of atoms within the distance of E of any other atom in the matrix, shown dotted, from reference [9]

7.1.3 Calibration of parameters

The successful application of the maximum separation algorithm depends on the correct combination of these four key parameters. D_{max} is the most important parameter in terms of identifying individual clusters. A larger D_{max} will enable the identification of more dilute solute clusters than a smaller D_{max} . A suitable N_{min} needs to be defined to make sure such clusters are significant and would not be detected in a random solid solution. Furthermore, when the solute concentration is high, if D_{max} is too large, it is possible to identify two neighbouring clusters as a single large one. Hyde et al. [9] showed that for a given dataset, N_{min} depends on D_{max} and the relationship between these two parameters is not trivial. If N_{min} is too large, smaller clusters will be ignored. On the other hand, a smaller N_{min} might pick out the presence of clusters in a random solute solution. The selection of values for these two parameters depends on the solute concentration in each dataset. L and E are less important than D_{max} and N_{min} . L should be less or equal to D_{max} to make sure the solute atoms in the neighbouring matrix of a cluster are not included, and E should be at least equal to L so that the solute atoms in a cluster or the cluster itself would not be eroded.

To estimate a suitable combination of these four parameters, a simple analytical model developed by Cerezo et al.[10] is applied in this work to search for the possibility of finding a random cluster with a given size in a solid solution and the procedure is described as follow:

For an atomic volume Ω and an overall atom fraction X of solute atoms, the number of neighbouring atoms N_s within a distance D_{max} of a given atom is given by:

$$N_s = \frac{4}{3}\pi D_{\max}^3 \cdot \Omega^{-1} \quad (7-1)$$

The probability of finding a number n of solute atoms among the neighbouring atoms is given by the binomial distribution:

$$P(n) = {}^{N_s}C_n X^n (1-X)^{(N_s-n)} = \frac{N_s!}{n! (N_s-n)!} X^n (1-X)^{(N_s-n)} \quad (7-2)$$

To produce a model for a cluster, it is assumed that a solute atom must have at least two neighbouring solute atoms to be part of a cluster. The probability is given by:

$$\begin{aligned} P(n > 1) &= 1 - P(n = 0) - P(n = 1) \\ &= 1 - (1-X)^{N_s} - N_s X (1-X)^{(N_s-1)} \end{aligned} \quad (7-3)$$

For a BCC Fe structure, with a LEAP detector efficiency of 37%, Ω should be:

$$\Omega^{-1} = 31 \text{ atoms/nm}^3$$

The probability of finding a cluster can then be plotted as a function of $D_{\max}$, when $N_{\min}$ varies from different given sizes. Because of the statistical random nature of even an ideal solid solution, this procedure will always lead to the identification of a finite concentration of clusters. Fig.7.2 shows the plots from random solid solution, using C and Cr as solute atoms separately. The Cr concentration is the nominal value of the matrix, and the C concentration is an average measured peak value across the grain boundary as discussed in Chapter 6. Clusters observed in this randomized case are referred as ‘random clusters’ or ‘statistically insignificant clusters’.

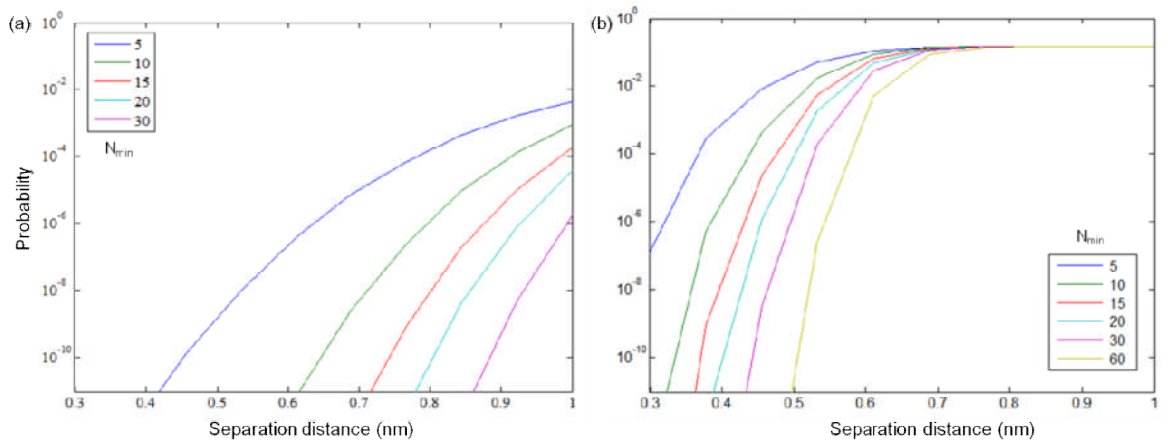


Fig.7.2 Variation in predicted probability for observing clusters of at least N_{min} atoms in a random solute solution, (a) N_{min} varies from 5 to 30, 2%C as solute atom and (b) N_{min} varies from 5 to 60, 15.2%Cr as solute atom

7.1.3.1 C-enriched cluster search in the matrix adjacent to a grain boundary

C was used as the solute atom to start the search for clusters. Assuming a typical atom probe dataset containing 1,000,000 atoms, the possible combinations of values of the search parameters for finding one cluster in an equivalent random solid solution can be determined from Fig.7.2 (a). The objective is to minimize the identification of clusters in a random solid solution, but maximize the chances of characterizing actual clusters. The figure shows that there are a number of possible values of N_{min} and D_{max} that need to be explored since the optimum value of N_{min} depends on D_{max} . Since the reconstruction of atom positions in real data is not perfect, it is necessary to explore ranges of D_{max} and N_{min} to optimize the significance of the results. Relevant combinations are shown in Table 7.1. The selection of L and E can affect the composition measurements of the clusters. For the extreme case, with $L=0$, the clusters will only contain core solute atoms. There are many possible choices, and testing all of them would have required a large

amount of work. The purpose here is to find a suitable combination which could be applied later to the other datasets for comparison. Therefore L and E were selected so that $L = E = D_{max}$ or $L = E \approx 0.5D_{max}$.

Table 7.1 Possible combinations of searching parameters based on Fig.7.2, using C as solute atom

D _{max} (nm)	N _{min}	L (nm)	E (nm)	D _{max} (nm)	N _{min}	L (nm)	E (nm)
0.7	5	0.7	0.7	1	5	1	1
		0.4	0.4			0.5	0.5
0.8	5	0.8	0.8	10	10	1	1
		0.4	0.4			0.5	0.5
	10	0.8	0.8	15	15	1	1
		0.4	0.4			0.5	0.5
0.9	5	0.9	0.9	20	20	1	1
		0.5	0.5			0.5	0.5
	10	0.9	0.9	30	30	1	1
		0.5	0.5			0.5	0.5
	15	0.9	0.9				
		0.5	0.5				
	20	0.9	0.9				
		0.5	0.5				

To choose the most appropriate combination of values for the parameters, it is necessary to apply these parameters to a real APT dataset. A section of data containing about 1,500,000 atoms was cut from the dataset obtained on the irradiated $\Sigma 39$ boundary from the high dose irradiated Fe-15.2%Cr (See Chapter 6 for further details on this dataset). The original atom map and the extracted portion are shown in Fig.7.3. The extract also contains a section of grain boundary, and the grain boundary region and its adjacent matrix need to be treated separately. Therefore, a cuboid was used to cover and separate the grain boundary region so that

the cluster searching could be performed in the grain boundary and its adjacent matrix respectively. From Fig.6.10, the lowest points on the 1D concentration profile indicate a width of roughly 8nm. Therefore, the width of the cuboid was adjusted to be 4nm to cover the centre of the grain boundary. The 1D concentration profiles plotted along the width were used to assist the positioning of the cuboid to make it symmetrical across the grain boundary. Generally the grain boundary planes were flat enough to be totally covered by the cuboid. The atom maps of the centre of the grain boundary and its adjacent matrix are also shown in Fig.7.3. Without the grain boundary region, the adjacent matrix contained about 1,300,000 atoms with a size of 50×50×30nm.

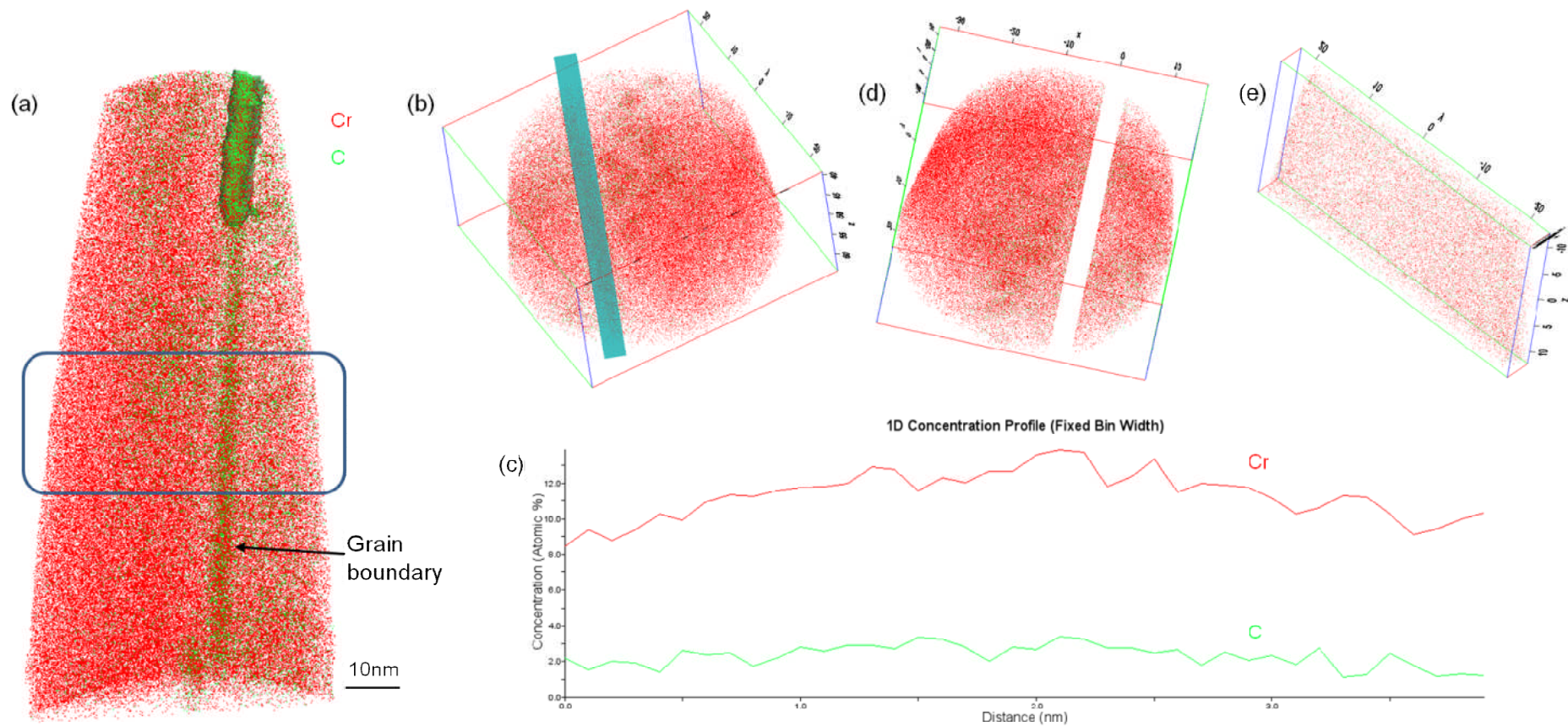


Fig.7.3 Atom maps of Cr and C of (a) the $\Sigma 39$ boundary, (b) an extract from the region indicated by the blue box and a cuboid covers the grain boundary region, (c) 1D concentration profile plotted across the grain boundary, (d) adjacent matrix and (e) the centre of the grain boundary.

The combinations of searching parameters listed in Table 7.1 were first applied on the adjacent matrix and the searching was carried out using Visualisation & Statistical Analysis of Atom Probe Data (VSA) 1.04 [11]. The numbers of clusters found in the data are shown in Table 7.2. The results vary from about 20 to over 400. The atom maps of clusters were also examined as shown in Fig.7.4. In (a) about 358 separate clusters are shown and in (b) about 69 separate clusters are shown. The results clearly indicate that certain combinations of values for the parameters separate a large cluster into smaller ones and increase the observed number density, while other combinations result in neighbouring clusters been identified as a single combined cluster which reduces the observed number density. Such combinations should not be taken into account for further exploration. Only the combinations which gave a result between 70 and 350 were tested further, as marked red in Table 7.2.

Table 7.2 Combinations of searching parameters and the observed number of C-enriched clusters

D _{max} (nm)	N _{min}	L (nm)	E (nm)	Number of Clusters	D _{max} (nm)	N _{min}	L (nm)	E (nm)	Number of Clusters
0.7	5	0.7	0.7	203	1	5	1	1	121
		0.4	0.4	305			0.5	0.5	392
0.8	5	0.8	0.8	181		10	1	1	45
		0.4	0.4	358			0.5	0.5	125
	10	0.8	0.8	49		15	1	1	28
		0.4	0.4	82			0.5	0.5	69
0.9	5	0.9	0.9	153		20	1	1	21
		0.5	0.5	402			0.5	0.5	49
	10	0.9	0.9	48		30	1	1	17
		0.5	0.5	95			0.5	0.5	33
	15	0.9	0.9	32					
		0.5	0.5	51					
	20	0.9	0.9	26					
		0.5	0.5	34					

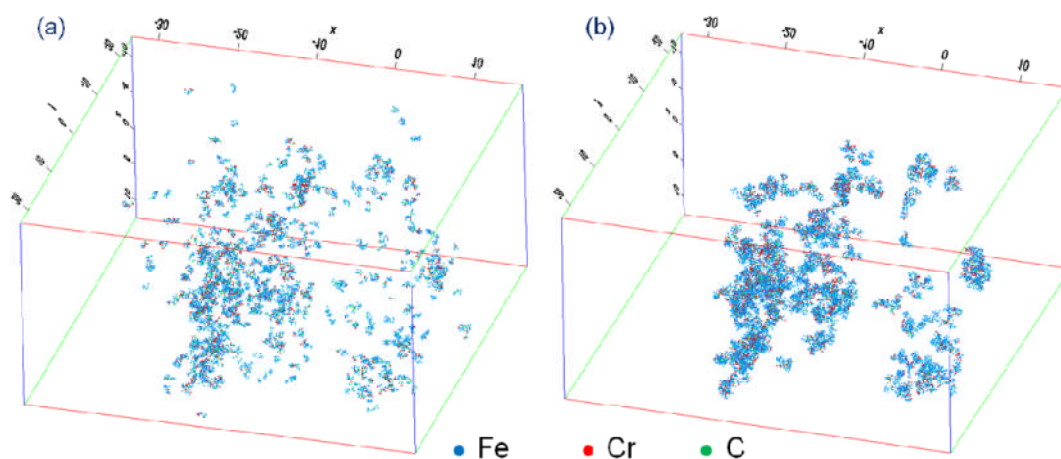


Fig.7.4 Atom maps showing (a) 358 observed clusters and (b) 69 observed clusters.

The next step is to ‘scramble’ the data and do the search using the same combinations again. The word ‘scramble’ here refers to the process of randomly exchanging the positions of pairs of atoms in the dataset. For example, if there are two atoms which have position information (X_1, Y_1) and (X_2, Y_2) and mass information M_1, M_2 separately, after exchange, the first atom has a new position information (X_2, Y_2) with its original mass M_1 ; and the second atom is on position (X_1, Y_1) also with its original mass M_2 . This procedure is important for examining whether observed clusters are significant or not. If a large number of clusters still can be found in the ‘scrambled’ data using the same parameters, it means that clusters found in the original data are not ‘significant’ enough and these parameters are not suitable. The search results on the ‘scrambled’ data are shown in Table 7.3.

Table 7.3 Comparison between the observed number of clusters in the original and scrambled data

$D_{\max}$ (nm)	$N_{\min}$	L (nm)	E (nm)	Number of Clusters (original)	Number of Clusters (scrambled)	Ratio (scrambled/original)
0.7	5	0.7	0.7	203	164	0.81
		0.4	0.4	305	166	0.54
0.8	5	0.8	0.8	181	214	1.18
	10	0.4	0.4	82	12	0.15
0.9	5	0.9	0.9	153	252	1.65
	10	0.5	0.5	95	21	0.22
1	5	1	1	121	285	2.36
1	10	0.5	0.5	125	41	0.33

It is important to minimise the number of statistically insignificant clusters whilst identifying as many significant clusters as possible. It should be emphasised that there is no ‘correct’ combination of values of parameters. One has to make a judgement and select an appropriate combination. One such combination of values for the parameters is $D_{\max} = 0.8\text{nm}$, $N_{\min} = 10$, $L = E = 0.4\text{nm}$.

Furthermore, since it is impossible to plot out all possible $N_{\min}$ in Fig.7.2, only a limited number of plots are shown to give a general estimation of $N_{\min}$. After the separation distance $D_{\max}$ has been decided to be 0.8nm , it is also necessary to examine possible values of $N_{\min}$ to optimize this parameter. Fig.7.5 shows a plot of the observed number of clusters in original and the scrambled data as a function of $N_{\min}$ as it varies from 6 to 15 with $D_{\max}$ set to 0.8nm and with $L = E = 0.4\text{nm}$.

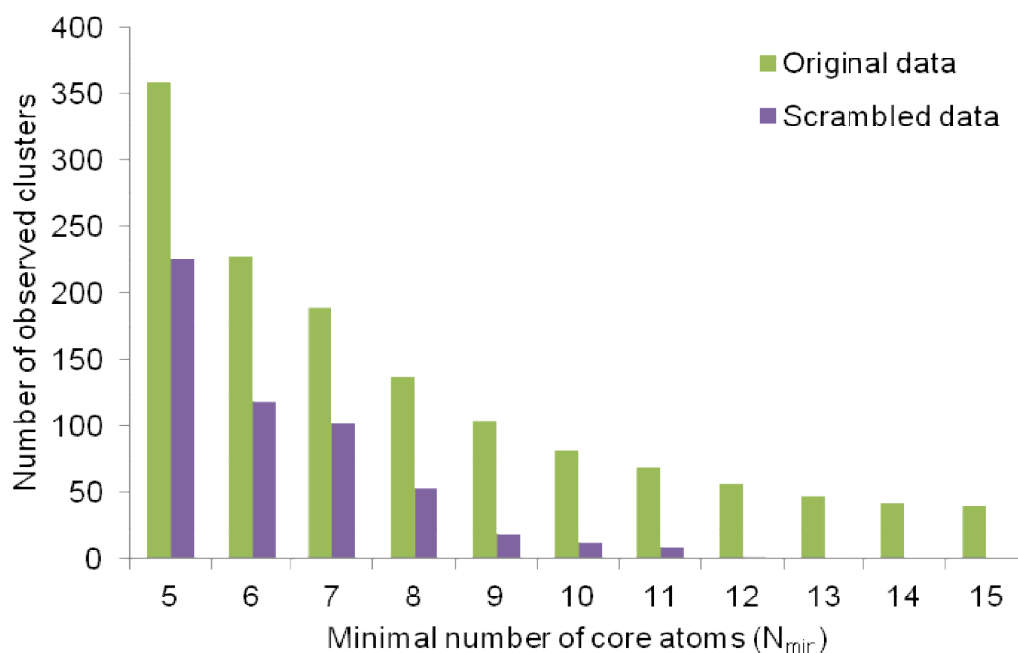


Fig.7.5 Observed numbers of clusters in original and scrambled data plot as a function of N_{min} , with $D_{max} = 0.8\text{nm}$ and $L = E = 0.4\text{nm}$, C as solute atom.

Fig.7.5 indicates that the number of observed clusters in the original and scrambled data decreases as N_{min} increases from 5 to 15. Setting a higher value of N_{min} reduces the number of statistically insignificant clusters, but also removes some genuine significant clusters. It is necessary to choose a precise value for N_{min} , balancing the need to maximize the number of significant clusters whilst minimizing the contribution from insignificant clusters. For this data, as shown in Fig.7.5, with $D_{max} = 0.8\text{nm}$, it is reasonable to choose N_{min} to be 9. The identified C-enriched clusters have average C concentration of 24.4%, a mean diameter of 1.97nm and a volume fraction of 0.49%.

7.1.3.2 Cr-enriched cluster search in the matrix adjacent to a grain boundary

Using Cr as the solute atom is much more complicated since the concentration of Cr is much higher than C. Using a similar D_{max} to that described above would probably result in the identification of a large percolated structure. According to Fig.7.2 (b), a number of possible combinations of values of the parameters would result in the identification of one cluster in a random solute solution containing 1,000,000 atoms. Results are summarized in Table 7.4, as well as the search results in the original and scrambled data.

Table 7.4 Combinations of searching parameters based on Fig.7.2 (b), using Cr as solute atom, and the observed number of clusters in the original and scrambled data.

D_{max} (nm)	N_{min}	L (nm)	E (nm)	Number of Clusters (original)	Number of Clusters (scrambled)	Ratio (scrambled/original)
0.3	5	0.3	0.3	955	663	0.69
		0.2	0.2	1025	673	0.66
0.4	10	0.4	0.4	614	502	0.82
		0.2	0.2	1019	629	0.62
	15	0.4	0.4	297	145	0.49
		0.2	0.2	366	156	0.43
0.5	20	0.5	0.5	314	234	0.75
		0.3	0.3	610	813	1.33
	30	0.5	0.5	167	248	1.49
		0.3	0.3	300	424	1.41

It is clear that even using the ‘optimum’ combination of parameters listed in Table 7.4 ($D_{max} = 0.4\text{nm}$, $L = E = 0.2\text{nm}$ and $N_{min} = 15$) would yield a distribution of clusters containing a very high fraction of insignificant clusters which would exist in

a random solid solution. N_{min} was then varied around 15 with D_{max} fixed to be 0.4nm to examine other possible variations of N_{min} . A plot showing the comparison between the clusters observed in the original and scrambled data as a function of N_{min} is shown in Fig. 7.6.

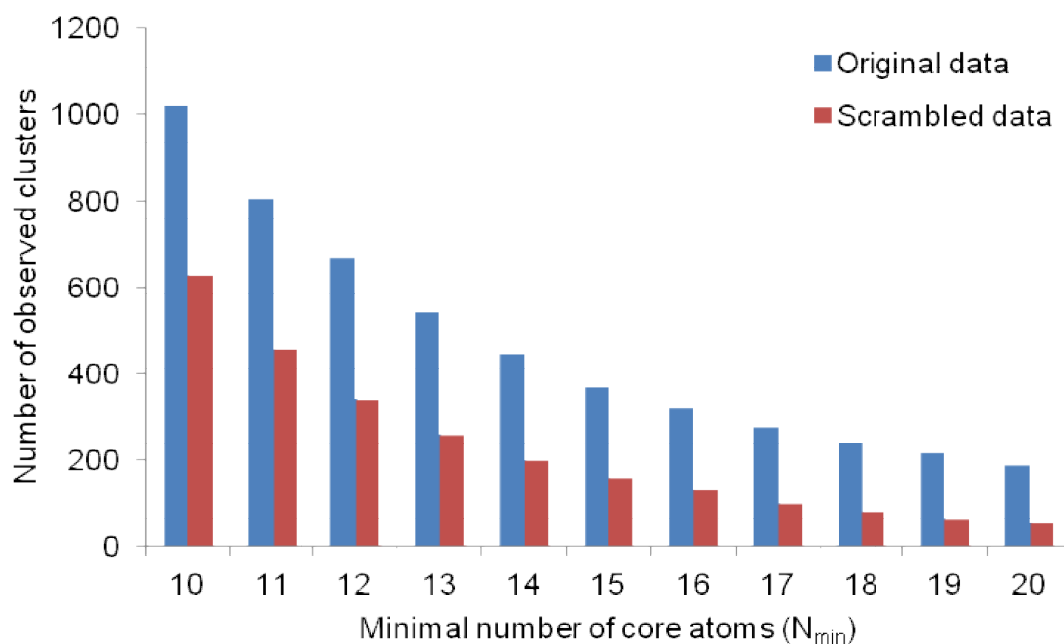


Fig.7.6 Observed numbers of clusters in original and scramble data plot as a function of N_{min} , with $D_{max} = 0.4\text{nm}$ and $L = E = 0.2\text{nm}$, using Cr as solute atom.

When $N_{min} = 20$, the ratio between the number of clusters in the scrambled and original data is around 0.3. Such a combination of parameters is able to identify a large number of significant clusters in the original data. Of course the ratio will further decrease if N_{min} is further increased, however a very large N_{min} will also decrease the possibility of finding clusters and cause the loss of smaller clusters with fewer core atoms, which is not acceptable. From Fig.7.6, $D_{max} = 0.4\text{nm}$, $N_{min} = 15$, and $L = E = 0.2\text{nm}$ would be a proper combination only if the significance of

clusters could be increased by other methods. Therefore due to the high concentration of Cr, an additional ‘tagging’ method is introduced here to help to first locate locally Cr-enriched regions. Then the maximum separation method is applied, based on the location of such regions, to increase the probability of finding significant clusters.

To locate these regions, the neighbouring N_{ne} atoms around each Cr atom in the dataset are examined. If more than N_{ne}^{min} of the neighbouring N_{ne} atoms are Cr, then the centre Cr atom is tagged to indicate the existence of a Cr-enriched region around it. Later on, such tagged Cr atoms are used as core solute atoms in the maximum separation searching method. Since there is no general rule for choosing N_{ne} and N_{ne}^{min} , several possible combinations were tested. Fig.7.7 shows the plots of comparisons between observed numbers of clusters in the original and the scrambled data as a function of N_{ne}^{min}/N_{ne} , and $D_{max} = 0.4\text{nm}$, $N_{min} = 15$, and $L = E = 0.2\text{nm}$. The purpose is not to examine all possibilities but to find one suitable combination which would increase the significance of clusters found by the maximum separation method.

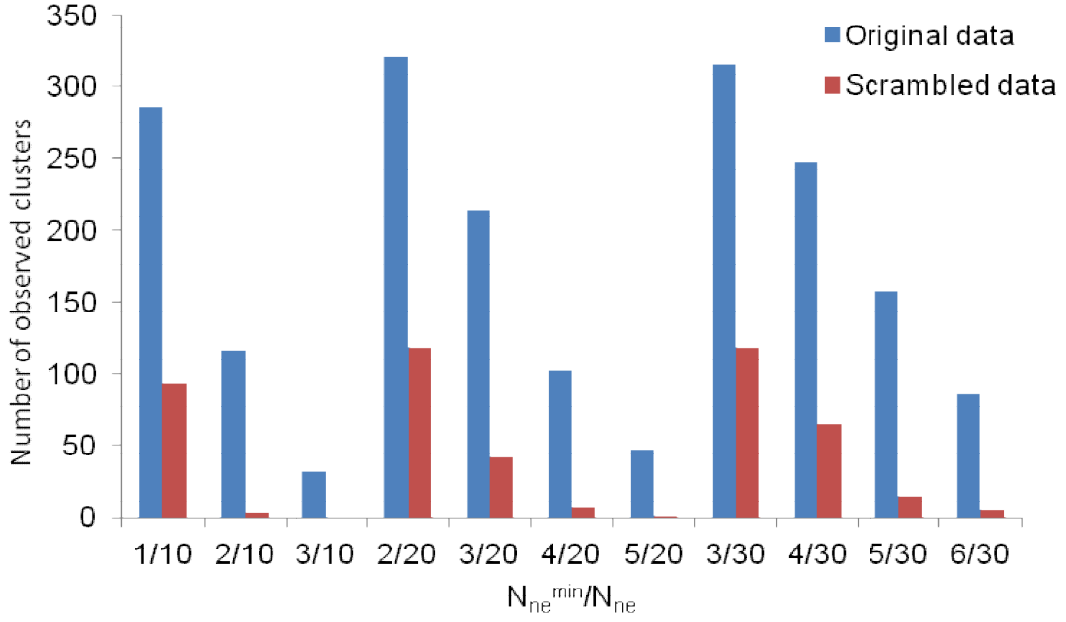


Fig.7.7 Comparisons between observed numbers of clusters in original and scrambled data as a function of N_{ne}^{min}/N_{ne} , with tagged Cr as core solute atom, and $D_{max} = 0.4\text{nm}$, $N_{min} = 15$, and $L = E = 0.2\text{nm}$.

It is clear that only a very small number of clusters was identified in the scrambled data when the ratio between N_{ne}^{min} and N_{ne} is larger than 0.2. An appropriate combination was found using $N_{ne}^{min}/N_{ne}=2/10$ with $D_{max} = 0.4\text{nm}$, $N_{min} = 15$, and $L = E = 0.2\text{nm}$, when 117 clusters were found in the original data and only 3 clusters in the scrambled data. This combination causes the loss of some smaller clusters with fewer solute atoms which are relatively unimportant. In some other cases, for example when $N_{ne}^{min}/N_{ne}=3/10$, no clusters were found in the scrambled data, however such a combination reduced the volume fraction of observed clusters in the original data, suggesting that the algorithm had failed to identify some of the clustering. Using $N_{ne}^{min}/N_{ne}=2/10$ and the other parameters identified above the observed Cr-enriched clusters were found to have an average Cr concentration of

66.7%, C concentration of 0.5%, a mean diameter of 1.72nm and a volume fraction of 0.28%.

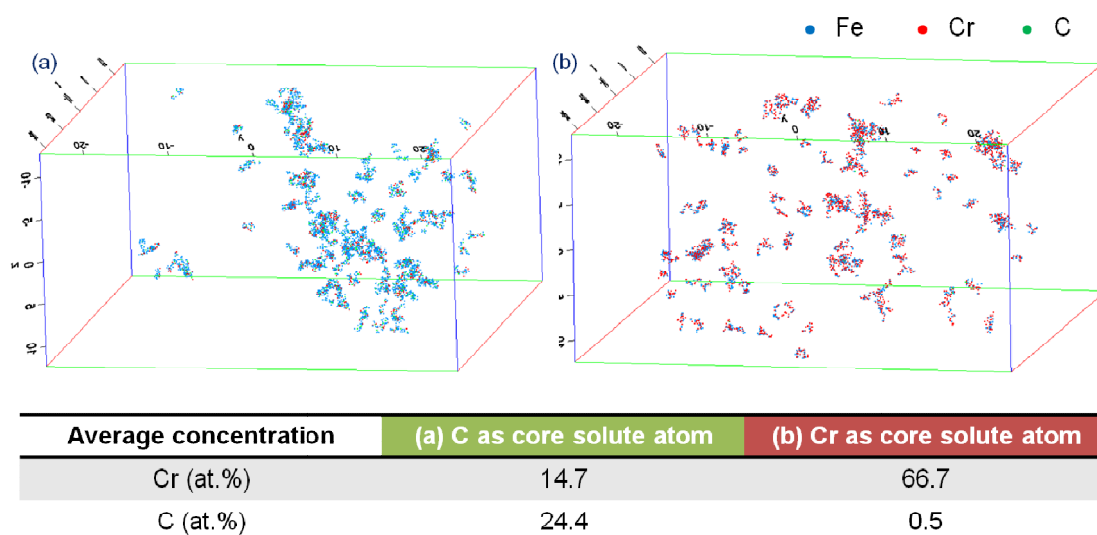


Fig.7.8 Atom maps of observed clusters in the same dataset with the average concentration of Cr and C, (a) C as core solute atom and (b) Cr as core solute atom.

Fig.7.8 shows two atom maps of observed clusters in the same dataset, using C and tagged Cr as core solute atoms separately, together with the average concentration of Cr and C of the observed clusters. It is possible that parts of these two types of observed clusters overlap but it is clear that the majority do not. The C-centered type indicates the presence of very fine carbides, and the Cr-centered type demonstrates the tendency to move towards early stage formation of α' phase.

7.1.3.3 C-enriched cluster search in the grain boundary region

The maximum separation method was then applied to the grain boundary region as shown in Fig.7.3 (e). Using C as core solute atom and the parameters $D_{max} = 0.8\text{nm}$, $N_{min} = 9$, and $L = E = 0.4\text{nm}$, the numbers of observed clusters in the original data and the scrambled data were found to be 64 and 43 respectively. This provided no evidence for clustering. The ‘tagging’ method was also applied to help to locate locally C-enriched region. However due to the existence of multiple carbon-containing species such as $^{12}\text{C}_4^{++}$ or $^{12}\text{C}_4^+$, the ‘tagging’ method readily identifies such species and therefore was not useful in increasing the significance of the observed clusters. Therefore the only way to increase the significance of the observed clusters is to increase the threshold of minimal number of core atoms of the clusters, which has the side effect of sacrificing characterization of the smaller clusters with fewer core atoms. However such loss would be acceptable if the observed clusters could provide evidence of the formation of fine M_{23}C_6 type carbides. Fig.7.9 plots the number of observed clusters in the original and scrambled data as N_{min} increases from 9 to 15, and $D_{max} = 0.8\text{nm}$, $N_{min} \approx 13$, and $L = E = 0.4\text{nm}$ appears to be a suitable combination, which allowed the ratio between scrambled and original data to decrease to 0.43.

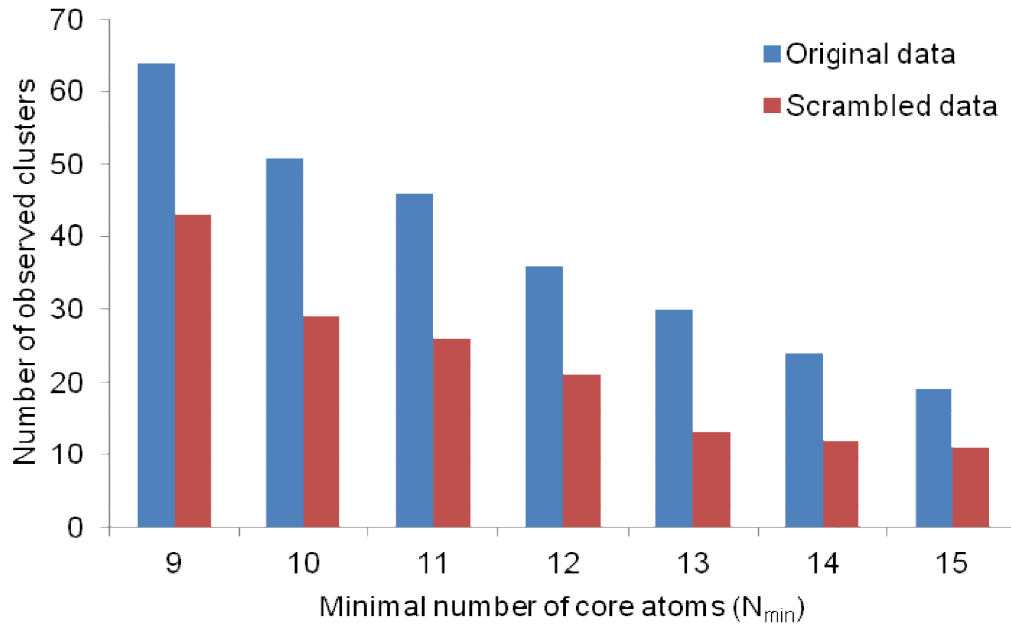


Fig.7.9 Observed numbers of clusters in the original and scrambled data plotted as a function of N_{min} , with $D_{max} = 0.8\text{nm}$ and $L = E = 0.4\text{nm}$, using C as solute atom (without tagging method).

Fig.7.10 (a) shows the atom map of the observed clusters using the parameters $D_{max} = 0.8\text{nm}$, $N_{min} = 13$, and $L = E = 0.4\text{nm}$. The number of clusters is 30. There are still 13 clusters in the scrambled data. Fig.7.10 (b) plots the frequency distribution as a function of Cr concentration of observed clusters in the original and scrambled data. The average C concentration of the observed clusters in the original data is 24.2% which is consistent with the formation of very fine $M_{23}C_6$ type carbides.

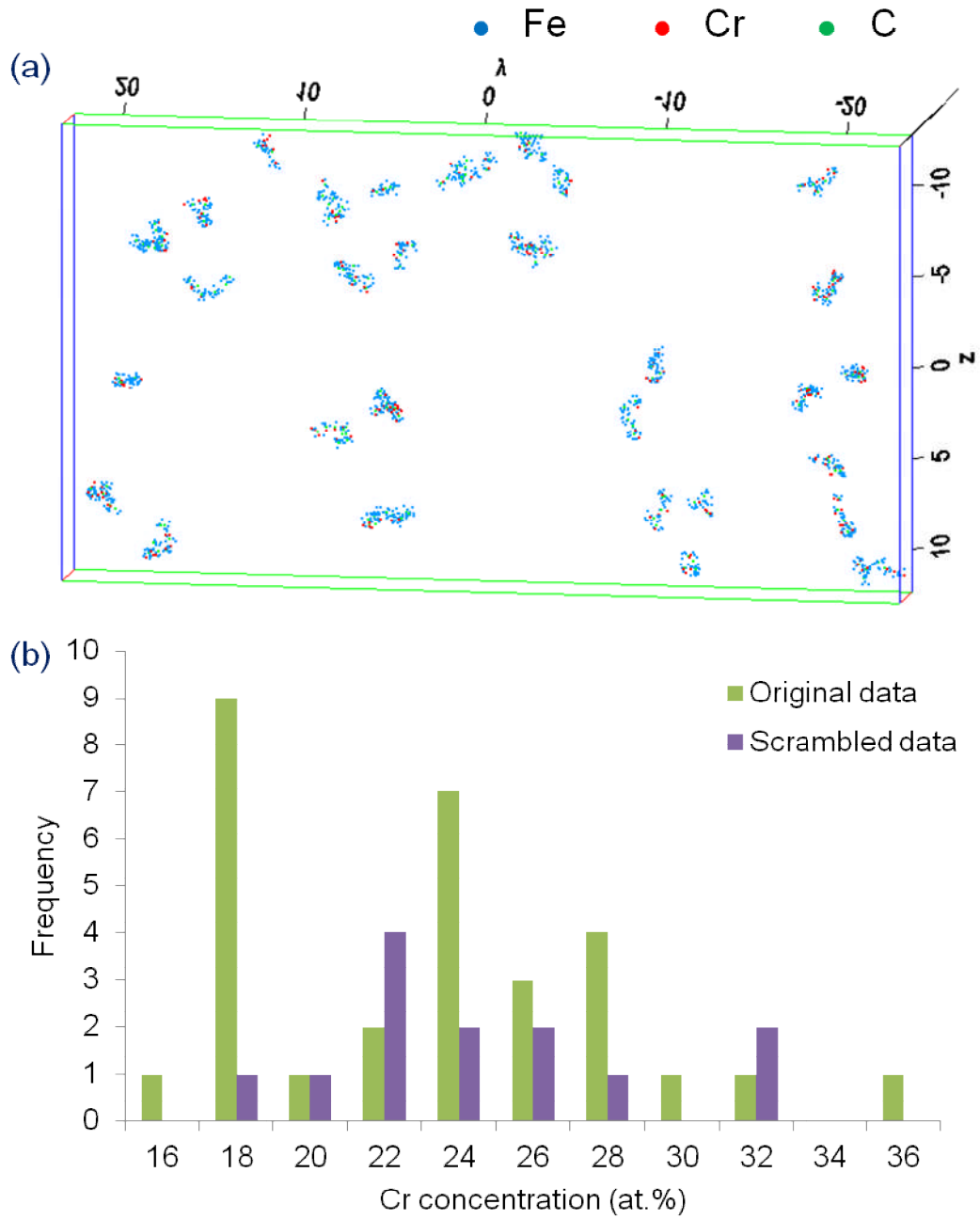


Fig.7.10 (a) Atom maps of the observed clusters using C as core solute atom with parameters $D_{max} = 0.8\text{nm}$, $N_{min} = 13$, and $L = E = 0.4\text{nm}$, (b) frequency distribution as a function of the Cr concentration of observed clusters in the original and scrambled data.

7.2 Searching for Clusters in a Fe-15.2%Cr Alloy

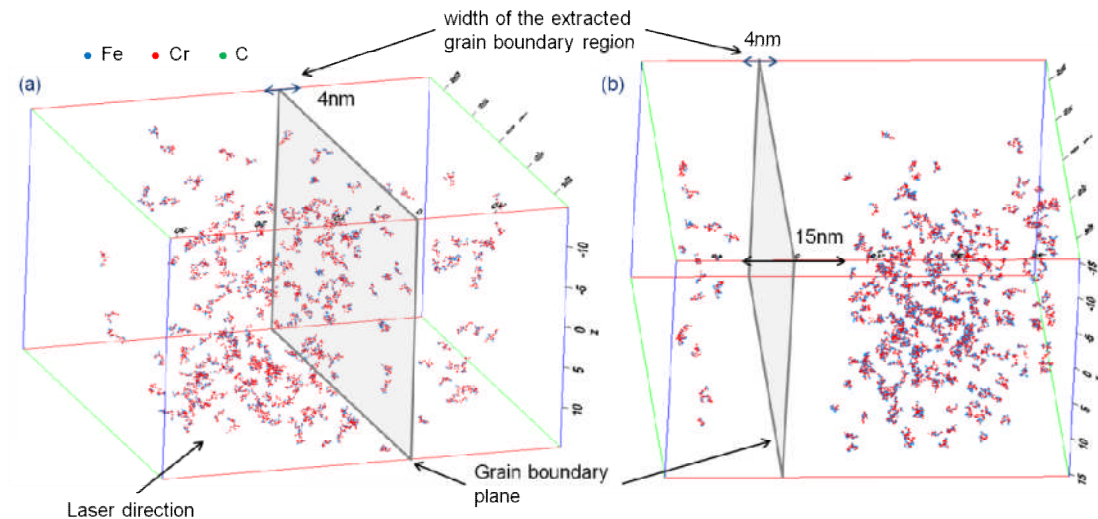
The maximum separation method was applied using VSA 1.04 for the grain boundaries and their adjacent matrix before and after 6dpa/0.6dpa irradiation of the Fe-15.2%Cr alloy. The chemical compositions of these boundaries were discussed in Chapter 6. Due to the large sizes of these datasets, some of which contained more than 100,000,000 atoms, it would take a lot of time to search for clusters in the full datasets. The datasets also vary in size. To compare different datasets on a like for like basis, representative regions were extracted from each dataset. Each region was cylinder shaped with diameter less than 50nm, containing approximately the same number of atoms, roughly 2,000,000, and a section of grain boundary. For some datasets which contained very long grain boundaries, the regions were extracted from the maximum damage region to exclude the possible depth effect on the cluster distribution. The centre of the grain boundaries and their adjacent matrix were separated and the widths of the boundaries were determined from the 1D concentration profiles as discussed in section 7.1.2, generally 4-5nm. To study the cluster distribution in the centre of the grains, one atom probe specimen was specially prepared and analyzed from the centre of a grain after 6dpa irradiation. Since the grain size of this alloy was intentionally enlarged by heat treatment before irradiation and was more than 100 μ m, it is safe to assume that the matrix contained in this specimen was at least 50 μ m away from any grain boundary and had not been affected by any boundary effect.

Exactly the same combinations of parameters were used in the searching of clusters on each dataset as determined in previous section, and so there was no need to apply the ‘scramble’ method. In the centre of the grain boundary, C was used as the core

solute atoms and the searching parameters were $D_{max} = 0.8\text{nm}$, $N_{min} = 13$, and $L = E = 0.4\text{nm}$. In the adjacent matrix, which was less than about 50nm from the centre of the grain boundary, and also for the matrix at the centre of a grain, C and Cr were used as core solute atoms, and the searching parameters were $D_{max} = 0.8\text{nm}$, $N_{min} = 9$, $L = E = 0.4\text{nm}$ and $D_{max} = 0.4\text{nm}$, $N_{min} = 15$, and $L = E = 0.2\text{nm}$ separately. The tagging method with $N_{ne}^{min}/N_{ne}=2/10$ was first applied to locate Cr-enriched regions before applying detailed searching using Cr as the core solute atom.

7.2.1 High dose irradiated samples

7.2.1.1 Randomly selected high angle boundary



Cr-enriched clusters	Before irradiation	After irradiation
Cr Average Concentration (at.%)	67.4	64.0
C Average Concentration (at.%)	0	0
Mean Diameter (nm)	1.68	1.61
Volume Fraction (%)	0.32	0.40

Fig.7.11 Two atom maps of Cr-enriched clusters (a) before and (b) after irradiation, with the grain boundary planes marked, together with comparisons between the average cluster concentrations, mean diameters and volume fractions.

Before irradiation, in the matrix adjacent to the randomly selected high angle grain boundary, very few C-enriched clusters were observed and their volume fraction was less than 0.03%. Cr-enriched clusters were found randomly distributed on both sides of the grain boundary as shown in Fig.7.11 (a). In addition, a local region containing an enhanced level of Cr-enriched clusters was found to coincide with the area directly heated by the laser pulsing. After irradiation, within about 15nm of the grain boundary region, no clusters were observed in Fig.7.11 (b). In the rest of the

matrix, C-enriched clusters were still very rare, while Cr-enriched clusters were randomly distributed. A comparison between average concentrations, mean diameters and volume fractions of the Cr-enriched clusters is shown in Fig.7.11.

Fig.7.12 shows the frequency distributions of Cr concentration and the size of Cr-enriched clusters observed in Fig.7.11. Clearly both the concentration distribution and size distribution were quite similar before and after irradiation, which indicates that the irradiation had little effect in altering the concentration or the size of these Cr-enriched clusters.

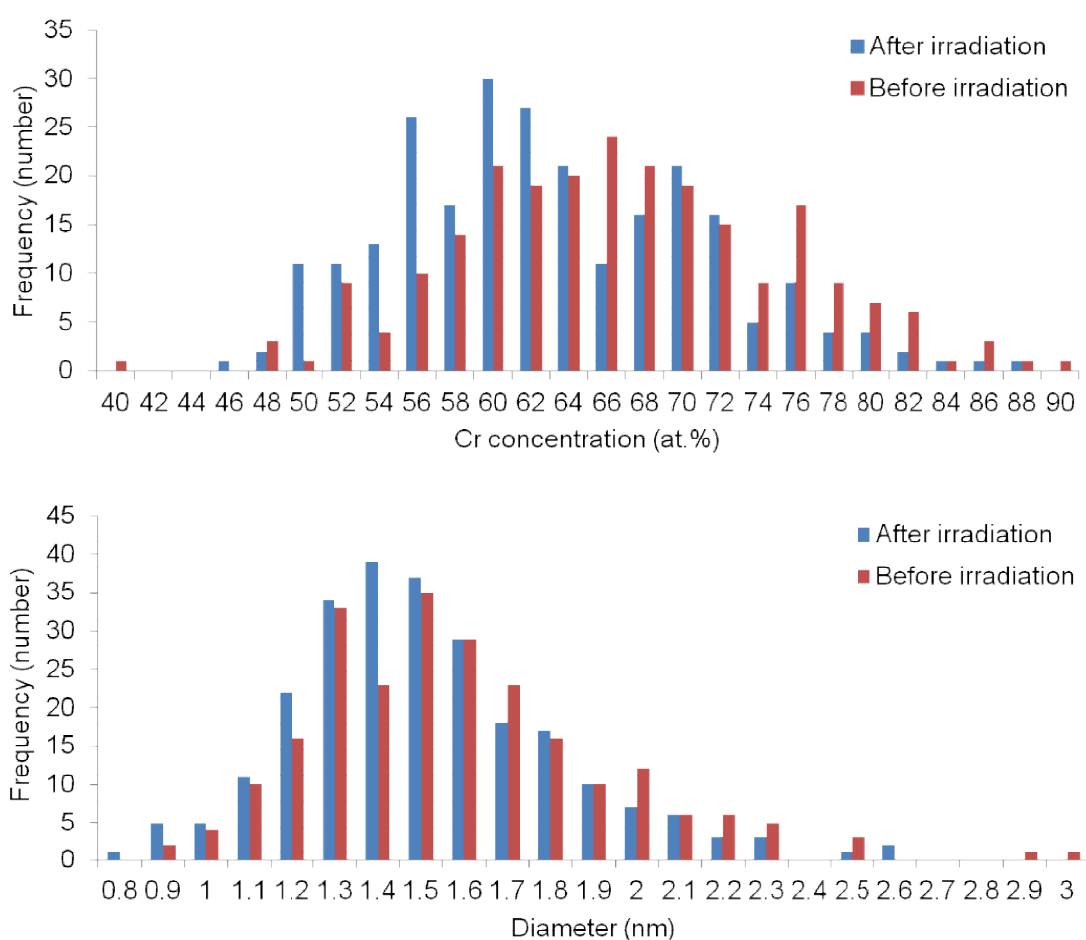


Fig.7.12 Frequency distributions of Cr concentration and size of the Cr-enriched clusters observed in Fig.7.11

On the other hand, many C-enriched clusters were found in the centre of the grain boundary before irradiation, with an average C concentration of 17.7%, and a quite high volume fraction of 4.9%. After irradiation, only a very few C-enriched clusters were observed in the centre of the grain boundary, and the volume fraction dropped to around 0.05%. The Gibbsian excess calculated in Chapter 6 showed that on this boundary, almost 60% of C had been depleted from the grain boundary region due to irradiation, which is believed to be the reason for the significant disappearance of C-enriched clusters.

7.2.1.2 Low sigma boundaries

In the matrix adjacent to the $\Sigma 1$ and $\Sigma 3$ boundaries, very few C-enriched clusters were observed before or after irradiation, and the volume fraction was found to be less than 0.03%. Cr-enriched clusters were found randomly distributed before and after irradiation on both sides of the $\Sigma 1$ and $\Sigma 3$ boundaries. A comparison of average concentrations, mean diameters and volume fractions of the observed clusters in these two boundaries is shown in Table 7.5. Fig.7.13 shows an atom map of observed clusters in $\Sigma 1$ boundary after irradiation and a comparison of the frequency distribution of Cr concentration and size is shown in Fig.7.14. The shape of the frequency distribution, average size and Cr concentration, were quite similar, but the volume fraction was substantially increased after irradiation. The same phenomenon also happened on the $\Sigma 3$ boundary, and the volume fraction was even higher at 0.94%, which is consistent with the highest Gibbsian excess value shown in Table 6.2.

Table 7.5 Comparison of average concentrations, mean diameters and volume fractions of the observed Cr-enriched clusters in the matrix adjacent to the $\Sigma 1$ and $\Sigma 3$ boundaries before and after irradiation

Cr-enriched clusters	Irradiation	Cr Average Concentration (at.%)	C Average Concentration (at.%)	Mean Diameter (nm)	Volume Fraction (%)
$\Sigma 1$	Before	68.8	0	1.64	0.16
	After	64.9	0.1	1.66	0.54
$\Sigma 3$	Before	64.5	0	1.62	0.46
	After	64.4	0.1	1.71	0.94

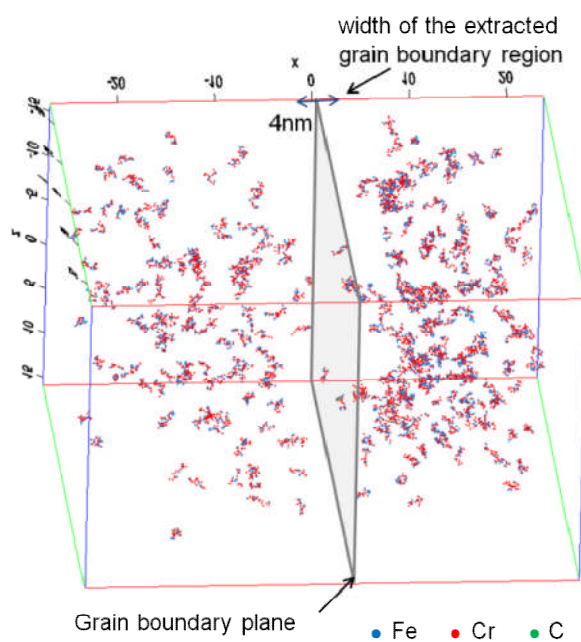


Fig.7.13 Atom map of observed clusters in the matrix adjacent to the $\Sigma 1$ boundary after irradiation

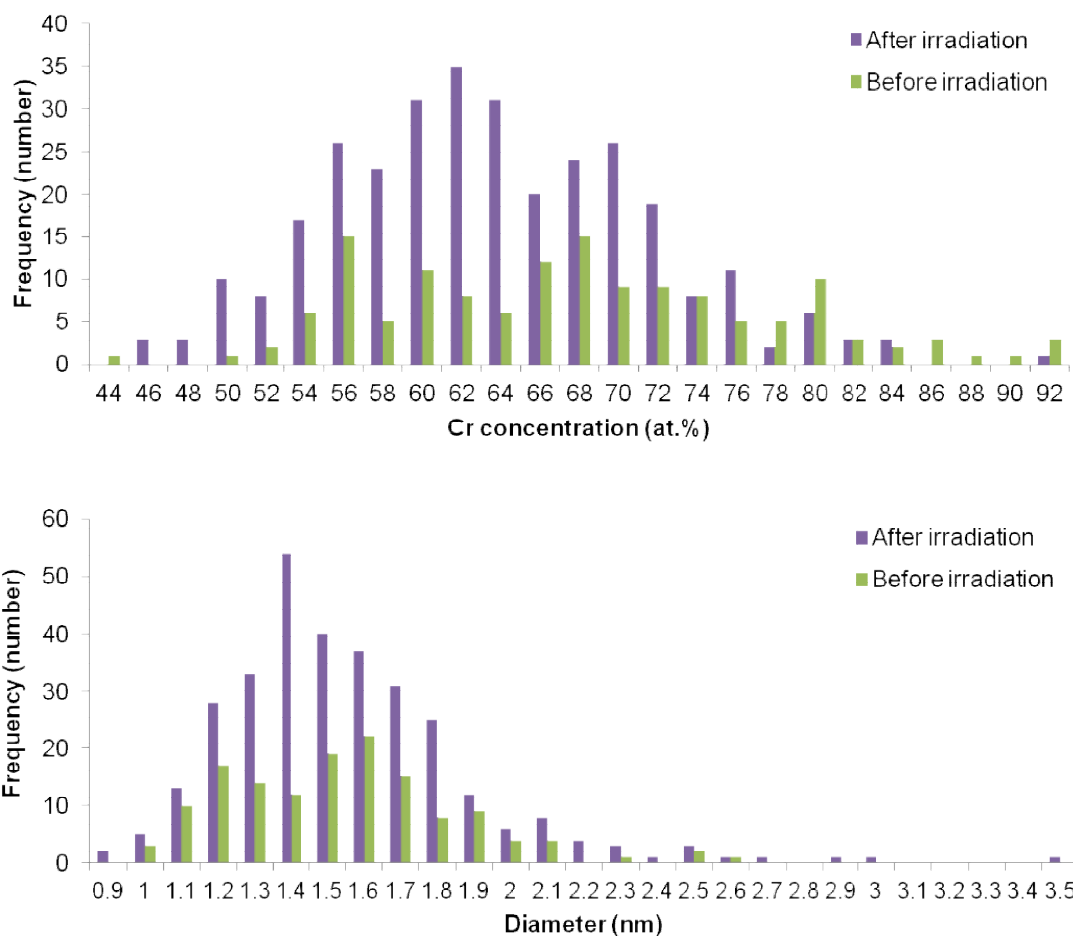


Fig.7.14 Comparison of frequency distribution of Cr concentration and size of the matrix adjacent to the $\Sigma 1$ boundary before and after irradiation

C-enriched clusters were also found on the centre of the $\Sigma 1$ and $\Sigma 3$ boundaries before and after irradiation, and the details are listed in Table 7.6. A common trend was that after irradiation, the C concentration substantially increased in contrast to the behaviour of the randomly selected high angle boundary while the Cr concentration decreased, with a certain fluctuation in size and volume fraction. The highest average C concentration reached over 80%.

Table 7.6 Comparison of average concentrations, mean diameters and volume fractions of the observed C-enriched clusters in $\Sigma 1$ and $\Sigma 3$ boundary before and after irradiation

C-enriched clusters	Irradiation	Cr Average Concentration (at.%)	C Average Concentration (at.%)	Mean Diameter (nm)	Volume Fraction (%)
$\Sigma 1$	Before	17.0	16.4	2.36	2.53
	After	9.9	53.6	2.21	2.86
$\Sigma 3$	Before	17.2	20.1	2.43	5.36
	After	5.2	82.3	3.19	2.58

7.2.1.3 Centre of a grain

Fig.7.15 shows an atom map of Cr-enriched clusters in the centre of a grain after high-dose irradiation (6dpa). Only Cr-enriched clusters were found, with an average concentration of 66.1%, mean diameter of 1.66nm and volume fraction of 0.51%. The clusters were observed to be randomly distributed in the matrix except for a slight segregation in the region where was directly heated by the laser during specimen evaporation.

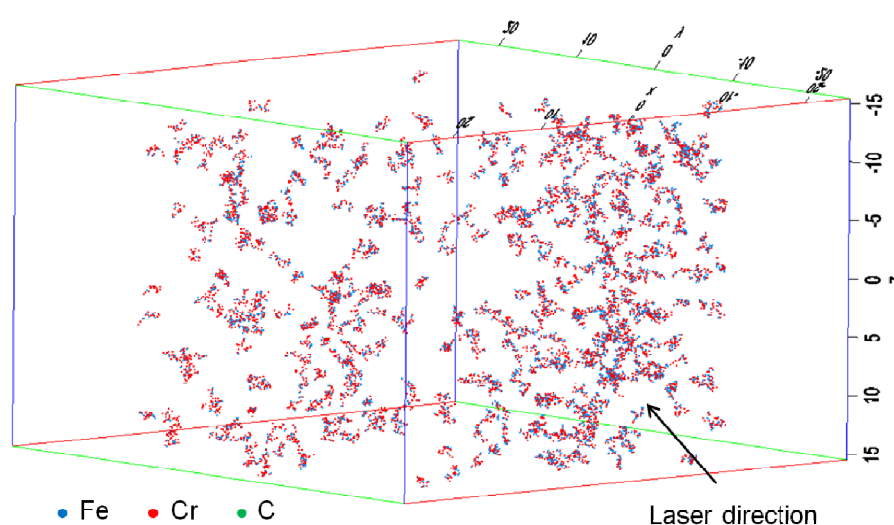


Fig.7.15 Atom map of observed Cr-enriched clusters in the centre of a grain after high-dose irradiation (6dpa), with an indication of laser direction.

7.2.2 Low dose irradiated samples

7.2.2.1 Fast-irradiated sample

In the low-dose (0.6dpa) fast-irradiated sample, no C-enriched clusters were found in the matrix adjacent to the randomly selected high angle boundary or the $\Sigma 1$ boundary, either before or after irradiation. Furthermore, this type of cluster was rarely found in the centre of these two grain boundaries. As discussed in Chapter 6, an argon atmosphere had been applied during heat treatment of this alloy to reduce the C contamination and the Gibbsian excess calculation proved that C had been successfully limited to $\sim 2 \text{ atoms/nm}^2$ in the grain boundary plane, which could explain why very few C-enriched clusters were found either in the grain boundaries or in the adjacent matrix.

Meanwhile, Cr-enriched clusters were discovered in the matrix adjacent to these two boundaries both before and after irradiation, and a comparison of the average concentrations, sizes and volume fractions is shown in Table 7.7. Apparently the 0.6dpa fast irradiation had not affected the average concentrations or sizes of the Cr-enriched clusters; however the volume fraction in the matrix adjacent to the $\Sigma 1$ boundary had doubled. Fig.7.16 shows an atom map of observed Cr-enriched clusters in the matrix adjacent to the high angle boundary. All the clusters were randomly distributed and no cluster free zone was found near the boundary.

Table 7.7 Comparison of average concentrations, mean diameters and volume fractions of the observed Cr-enriched clusters in the matrix adjacent to the $\Sigma 1$ boundary and high angle boundary before and after irradiation of the low-dose fast-irradiated sample

Cr-enriched clusters	Irradiation	Cr Average Concentration (at.%)	C Average Concentration (at.%)	Mean Diameter (nm)	Volume Fraction (%)
Random high angle boundary	Before	65.3	0	1.63	0.56
	After	66.8	0	1.68	0.45
$\Sigma 1$	Before	66.6	0	1.63	0.46
	After	65.2	0	1.70	0.94

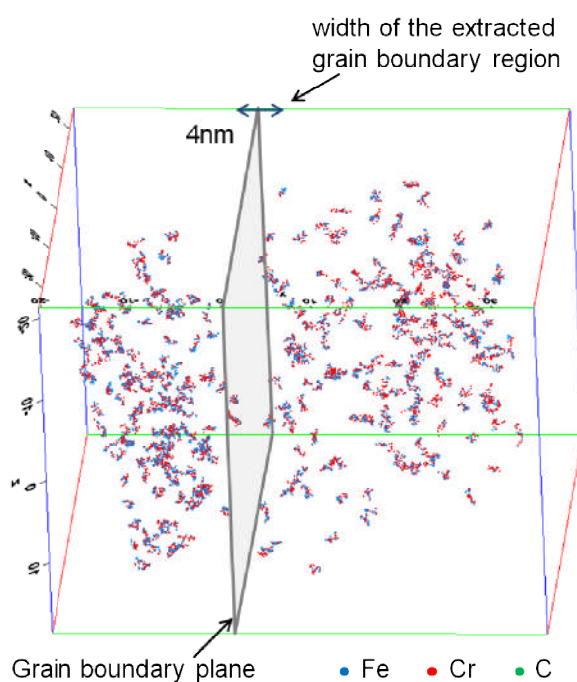


Fig.7.16 Atom map of observed Cr-enriched clusters in the matrix adjacent to the high angle boundary in the low-dose fast-irradiated sample

7.2.2.2 Slow-irradiated sample

Fewer C-enriched clusters were found in the matrix adjacent to the high angle boundary in the low-dose slow-irradiated sample either before or after irradiation. However, this type of cluster was found in the centre of the high angle boundary after irradiation, with a volume fraction of 1.21% and average diameter of 2.24nm. The average C concentration was about 21.0% which was consistent with the $M_{23}C_6$ type carbide. The corresponding atom map is shown in Fig.7.17.

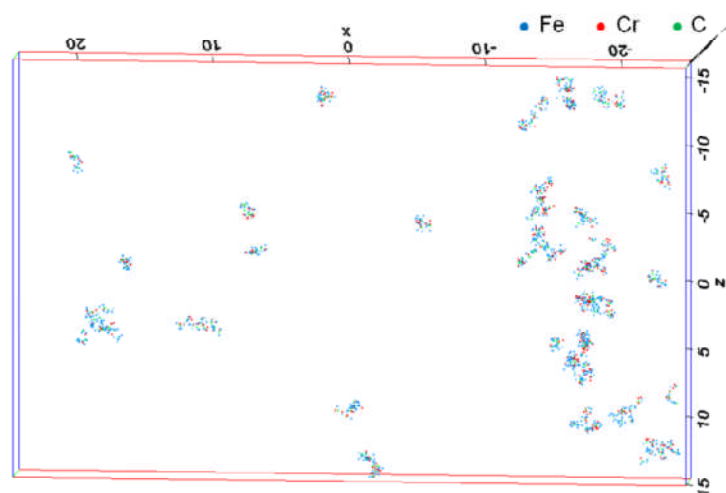


Fig.7.17 Atom map of C-enriched clusters in the centre of the high angle boundary in the low-dose slow-irradiated sample

As expected, Cr-enriched clusters were found in the matrix adjacent to the high angle boundary in the low-dose slow-irradiated sample as well, details are shown in Table 7.8. The average concentration of Cr and the mean size were not significantly changed by irradiation, but the volume fraction was doubled after irradiation. Fig.7.18 shows an atom map of these Cr-enriched clusters after irradiation and Fig.7.19 shows the frequency distributions of Cr concentration and size. There was

no evidence of a cluster free zone and the frequency distributions of Cr concentration and size exhibited similar patterns before and after irradiation.

Table 7.8 Average concentrations, mean diameters and volume fractions of the observed Cr-enriched clusters in the matrix adjacent to the high angle boundary in the low-dose slow-irradiated sample before and after irradiation

Cr-enriched clusters	Irradiation	Cr Average Concentration (at.%)	C Average Concentration (at.%)	Mean Diameter (nm)	Volume Fraction (%)
Random high angle boundary	Before	65.9	0	1.59	0.14
	After	66.3	0.1	1.63	0.69

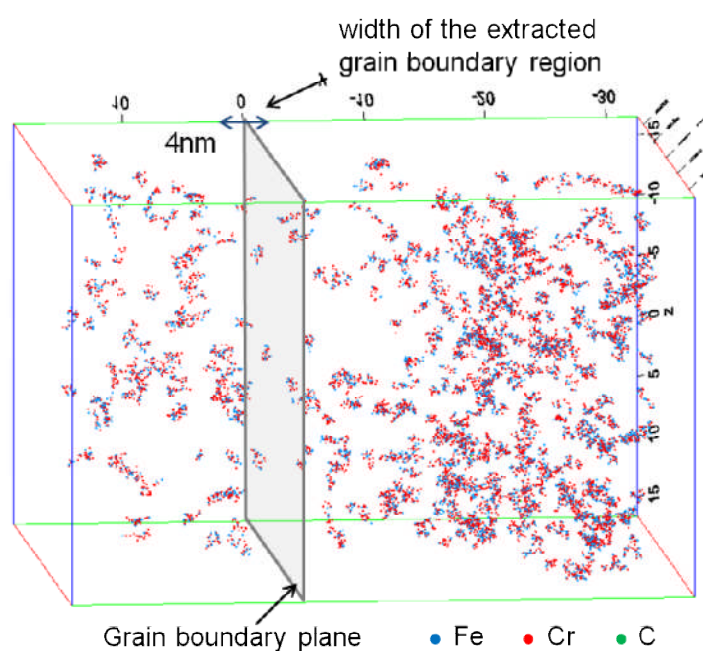


Fig.7.18 Atom map of Cr-enriched clusters in the matrix adjacent to the high angle boundary in the low-dose slow-irradiated sample after irradiation.

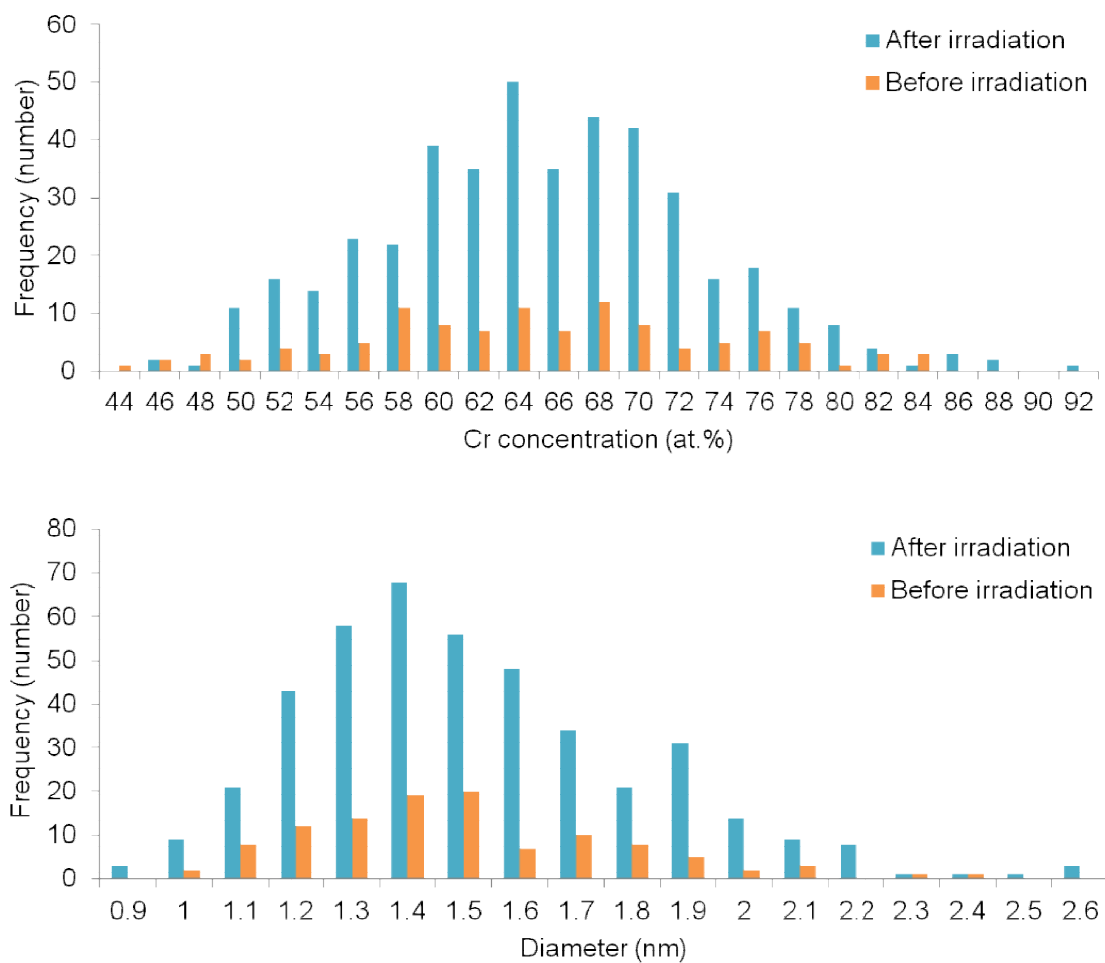


Fig.7.19 Comparisons of frequency distributions of Cr concentration and size of Cr-enriched clusters in the matrix adjacent to the high angle boundary before and after irradiation in the low-dose slow-irradiated sample

7.2.3 Discussion

The observations of Cr-enriched clusters and C-enriched clusters on all grain boundaries and their adjacent matrix are summarized in Table 7.9, along with Gibbsian excess values from Chapter 6 for comparison.

Table 7.9 Summary of Cr-enriched clusters and C-enriched clusters observed in all grain boundaries and their adjacent matrix

High dose irradiation (6dpa)		Gibbsian Excess across the grain boundary (atoms/nm ²)		Volume fraction of Clusters (%)		
Grain boundary type	Irradiation	Cr	C	Grain boundary plane	Adjacent matrix	
				C-enriched clusters	Cr-enriched clusters	C-enriched clusters
High angle boundary	Before	24.9±1.9	6.1±0.5	4.9	0.32	0.03
	After	10.8±2.9	2.7±0.7	0.05	0.4	—
Σ1 boundary	Before	17.9±3.3	5.8±1.8	2.53	0.16	—
	After	19.8±1.8	4.8±0.7	2.86	0.54	≤0.01
Σ3 boundary	Before	22.5±4.4	5.6±1.1	5.36	0.46	—
	After	36.9±3.5	6.1±0.7	2.58	0.94	≤0.03
Centre of a grain	After	N/A	N/A	N/A	0.51	—

Low dose irradiation (0.6dpa)		Gibbsian Excess across the grain boundary (atoms/nm ²)		Volume fraction of Clusters (%)		
Grain boundary type	Irradiation	Cr	C	Grain boundary plane	Adjacent matrix	
				C-enriched clusters	Cr-enriched clusters	C-enriched clusters
Fast-irradiated high angle boundary	Before	10.0±1.1	1.3±0.2	—	0.56	—
	After	5.8±1.3	2.8±1.3	0.1	0.45	—
Fast-irradiated Σ1 boundary	Before	10.6±2.8	2.1±1.2	—	0.46	—
	After	9.9±2.9	1.1±0.6	—	0.94	—
Slow-irradiated high angle boundary	Before	20.3±4.1	3.9±1.3	0.2	0.14	—
	After	15.2±2.9	5.0±0.4	1.21	0.69	—

Cr-enriched clusters were found randomly distributed in the matrix adjacent to every grain boundary examined as well as in the centre of a grain. Meanwhile, slight segregation was also discovered in the region directly heated by the laser. From the discussion in Chapter 4, it is known that laser heating can result in local Cr surface segregation, and such a phenomenon is related to the material thermal diffusivity and the experimental conditions as well as the shape of the specimen. Even using the most controllable FIB method, the shape of APT specimens varied. However since these specimens were all prepared using the same procedure and criteria, they were much more self-consistent in shape than those prepared by electropolishing. Furthermore, all the APT experiments were carried out using the same experimental parameters, which included the base cryostat temperature. Therefore it is reasonable to assume that the laser effect on the distribution of Cr-enriched clusters was similar for all specimens and there is no need to take such effect into account during the comparison between different grain boundaries or irradiation conditions.

Cr-enriched clusters are believed to form during the heat treatment before irradiation. After 6dpa irradiation, a cluster free zone of 15nm in width was found across the high angle boundary. From Fig.6.5, the Cr depletion regions were roughly 15-20nm in width across the grain boundary in the maximum damage region. Therefore it is reasonable to conclude that the irradiation resulted in Cr depletion zones on both sides of the high angle grain boundary, and hence the lack of Cr-enriched clusters in these zones. Although the irradiation affected the distribution of Cr-enriched clusters, it had little effect on the concentration or volume fraction of this type of clusters. Meanwhile, in the matrix near the low sigma boundaries, although the average size and concentration of Cr-enriched clusters remained the same after irradiation, the volume fraction was substantially increased. The frequency distributions of Cr

concentration and size of these clusters demonstrate similar forms, which indicates that irradiation did not accelerate the growth of the Cr-enriched clusters, but may help the formation of such clusters. As discussed in Chapter 6, the chemical distribution across the grain boundary develops as a result of the balance between vacancy and interstitial mechanisms. For low sigma boundaries which are strongly affected by the interstitial mechanism, it is possible that more Cr-enriched clusters could form during the irradiation. Such an effect would be much less obvious on the high angle boundaries which were mainly affected by the vacancy mechanism.

Similar phenomena were observed on the low-dose (0.6dpa) fast-irradiated sample. Since the irradiation damage did not produce any Cr depletion region across the high angle grain boundary, there was also no cluster free zone in the adjacent matrix. However, the volume fraction of Cr-enriched clusters was found to increase in the matrix adjacent to the high angle boundary in the low-dose slow-irradiated sample. The Gibbsian excess calculation demonstrated Cr depletion of this boundary after irradiation. In this case, it is necessary to take thermal diffusion during irradiation into account.

The temperature of the heat treatment before irradiation was always kept at 800°C for all samples, and the temperature of irradiation was also kept at 350±50°C. As discussed by Bonny et al. [12], although there are some discrepancies among different models, the re-determination of α - α' phase boundary by many researchers has indicated that, for Fe-15.2%Cr alloy, the temperatures used in heat treatment and irradiation are within in α + α' phase region. The low dose slow irradiation was carried out for 9 hours at 350±50°C, therefore the Cr-enriched clusters could also form during this process driven by thermal diffusion.

It is reasonable to conclude that the Cr-enriched clusters found in the centre of grains and in the matrix adjacent to grain boundaries are essentially small regions of α' phase, with average Cr concentration of $66.1 \pm 1.3\%$ and mean size of $1.65 \pm 0.04 \text{ nm}$. Kuksenko et al. [13] studied a Fe-12%Cr alloy which was neutron irradiated at 300°C to 0.6dpa. Cr-enriched clusters were observed with a mean radius of $1.1 \pm 0.2 \text{ nm}$ and average Cr concentration of $58.5 \pm 1.1\% \text{ Cr}$. The values are slightly lower than the results discussed in this thesis; however it is understandable since they studied an alloy with lower Cr concentration. Novy et al. [14] studied a Fe-20%Cr thermally aged at 500°C , and found the maximum Cr concentration in the α' phase is about $83 \pm 1\%$. In this thesis, clusters with Cr concentration reaching over 90% were also observed, however with much lower probability. It is also worth noting that there was very little C in the α' phase, indicating that the formation of α' phase is independent of the binding between Cr and C.

Large quantities of C-enriched clusters were found only in the matrix adjacent to the $\Sigma 39$ boundary. It is possible that C-enriched clusters can only form so abundantly in such a local C-enriched region in the vicinity of the large carbide. C-enriched clusters were also found in the centre of several grain boundaries before or after irradiation. Generally the C-enriched clusters are consistent with M_{23}C_6 type carbide, occasionally clusters with higher C concentration (up to more than 80%) were also observed. The formation of C-enriched clusters was linked with the C concentration. It was more likely to find C-enriched clusters in the centre of a grain boundary if the Gibbsian excess calculation indicated C excess about 5 atom/nm^2 .

7.3 Conclusions

The maximum separation method has been successfully applied to search for C/Cr-enriched clusters in a Fe-15.2%Cr alloy. The searching parameters were adjusted according to different cluster type and an additional ‘tagging’ method was also helpful in locating local Cr rich regions to increase the significance of observed Cr-enriched clusters.

Cr-enriched clusters were found distributed randomly in the matrix adjacent to the grain boundaries and in the center of the grains before and after irradiation. This type of cluster is believed to be α' phase, with an average Cr concentration of $66.1 \pm 1.3\%$ and mean size of $1.65 \pm 0.04 \text{ nm}$, which formed during the heat treatment before irradiation. Irradiation had little effect in altering the Cr concentration or the average size of α' phase, however the total volume fraction of α' phase increased in the matrix adjacent to low sigma boundaries. This indicates that irradiation promotes the earliest stage of α' phase formation. The results indicate that the different irradiation doses used in this work have similar effects.

Large amounts of C-enriched clusters were observed only in the matrix adjacent to a carbide aligned along the $\Sigma 39$ grain boundary, and fewer C-enriched clusters were also observed in the centre of several grain boundary planes with high excess C before or after irradiation. Most C-enriched clusters were consistent with M_{23}C_6 type carbide, occasionally clusters with higher C concentration were also found.

References

1. Konobeev, Y.V., A.M. Dvoriashin, S.I. Porollo, and F.A. Garner, *Journal of Nuclear Materials*, 2006. **355**: p. 124-130.
2. Dubuisson, P., D. Gilbon, and J.L. Seran, *Journal of Nuclear Materials*, 1993. **205**: p. 178-189.
3. Horton, L.L., J. Bentley, and W.A. Jesser, *Journal of Nuclear Materials*, 1981. **103-104**: p. 1085.
4. Gelles, D.S., *Journal of Nuclear Materials*, 1995. **225**: p. 163-174.
5. Sagaradze, V.V., Kositsyna, II, V.L. Arbuzov, V.A. Shabashov, and Y.I. Filippov, *Physics of Metals and Metallography*, 2001. **92**: p. 508-517.
6. Kohno, Y., A. Kohyama, T. Hirose, M.L. Hamilton, and M. Narui, *Journal of Nuclear Materials*, 1999. **271**: p. 145-150.
7. Dvoriashin, A.M., S.I. Porollo, Y.V. Konobeev, and F.A. Garner, *Journal of Nuclear Materials*, 2004. **329**: p. 319-323.
8. Marquis, E.A. and J.M. Hyde, *Materials Science & Engineering R-Reports*, 2010. **69**: p. 37-62.
9. Hyde, J.M., E.A. Marquis, K.B. Wilford, and T.J. Williams, *Ultramicroscopy*, 2011. **111**: p. 440-447.
10. Cerezo, A. and L. Davin, *Surface and Interface Analysis*, 2007. **39**: p. 184-188.
11. Hyde, J.M., Private communication.
12. Bonny, G., D. Terentyev, and L. Malerba, *Scripta Materialia*, 2008. **59**: p. 1193-1196.
13. Kuksenko, V., C. Pareige, C. Genevois, F. Cuvilly, M. Roussel, and P. Pareige, *Journal of Nuclear Materials*, 2011. **415**: p. 61-66.

14. Novy, S., P. Pareige, and C. Pareige, *Journal of Nuclear Materials*, 2009.
384: p. 96-102.

Chapter 8

Conclusions

The work in this thesis has focused on the study of RIS/RID phenomena at specific grain boundaries in Fe-Cr binary alloys as well as the determination of the very early stage of α' phase under irradiation conditions.

A systematic approach combining EBSD, FIB and APT technique has been developed on an irradiated Fe-12.8%Cr alloy and applied successfully to specific grain boundaries in a Fe-15.2%Cr alloy, while considering as many factors as possible including initial grain boundary chemistry, grain boundary misorientation, irradiation depth and the presence of minor elements or impurities. Systematic differences have been found between high angle boundaries and low sigma boundaries, and between high dose irradiated specimens and low dose irradiated specimens. The results also help in clarifying the working mechanisms. It is the first time that all factors which are expected to play a role in affecting RIS/RID behavior have been taken into account in the study of ferritic alloys. Furthermore, this systematic approach can be applied to any grain boundary of known character. It demonstrates high reliability and reproducibility and provides a unique way to obtain multiple atom probe specimens from a single grain boundary, to analyze all grain boundary data in a self-consistent manner and to provide comprehensive microstructural data.

With careful calibration of searching parameters, the maximum separation method has been successfully applied to search for C-enriched clusters and Cr-enriched clusters in a Fe-15.2%Cr alloy. Cr-enriched clusters, which are consistent with the early stage of α' phase formation, have been observed in the matrix adjacent to the grain boundaries and also in the centre of the grain before and after irradiation. Irradiation has been found to accelerate the formation rather than growth of these clusters. Even though these features are not visible on the atom maps, the maximum

separation method has been proven to be a powerful tool for extracting such information from the APT data and can provide key knowledge on the re-determination of the phase boundary. It also demonstrates the advantage of applying the APT technique combined with the maximum separation method to the study of the early stage of α' phase.

The energy demand world-wide and the increasing need for developing nuclear power have provided many challenges for materials science. The study of the binary Fe-Cr alloys is of significant importance and fundamental to the development of complex alloys systems as structural materials. Future studies on Fe-Cr alloys with large variations of Cr concentration, for example 9%-15%, would be helpful to provide additional knowledge regarding the completion of the knowledge of RIS/RID phenomena. Furthermore, computer modeling would also be useful to compare with the experimental APT data to establish a better understanding of mechanisms.

Appendix

During the study of the Fe-12.8at%Cr alloy from the first batch of materials, an interesting feature on a grain boundary plane was discovered. This feature was observed on a high angle grain boundary with a 61° misorientation (un-irradiated material). However this is not the same boundary as discussed in chapter 5 and so it was not possible to determine the effect of irradiation or make direct comparison. However this observation is also worth recording, therefore the result is shown in the appendix.

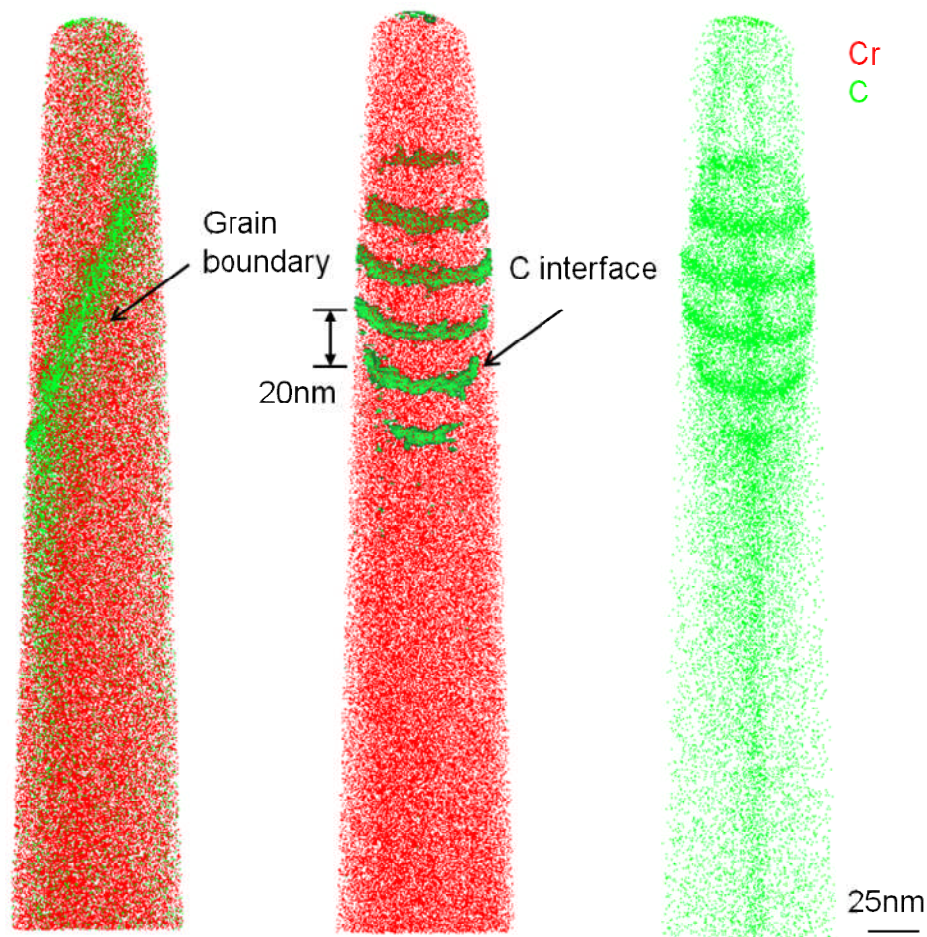


Fig.1 Atom maps of Cr and C on one boundary from Fe-12.8%Cr alloy before irradiation, the C isosurface is mapped as C concentration of 3.3%.

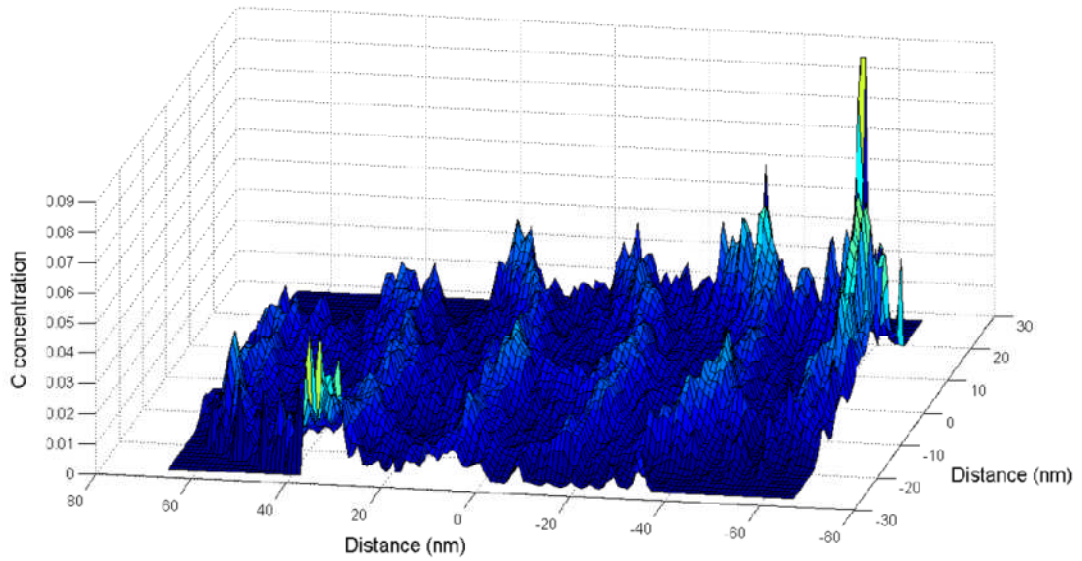


Fig.2 3D contour of the C concentration distribution on the grain boundary plane

As shown in Fig.1, a dislocation array is observed on the grain boundary plane before irradiation. The C atom map clearly indicates the location of the dislocations due to the C segregation. The C isosurface is mapped with C concentration of 3.3%. Each dislocation is arc shaped and the distance between dislocations is about 20nm. Fig.2 plots the 3D contour of the C distribution on the grain boundary plane. The distribution of C concentration is consistent with the dislocation spacing. It is very rare to make direct observation of dislocation arrays on the atom maps of a grain boundary plane, and the result shown in this appendix is the only one found during the entire thesis work.