

Modeling Radiation-Induced Segregation in Ferritic-Martensitic Steels

A Thesis Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

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May 2015

Abstract

As ferritic-martensitic (FM) steels receive increasing interest, due to the development of Generation IV fission reactors and fusion reactors, it is imperative to understand how the metals will behave under irradiation. Of the radiation effects, radiation-induced segregation (RIS) is of particular concern as it can lead to the formation of intermetallic phases, stress corrosion cracking, and other detrimental effects. However, predicting RIS in FM steels is more complex due to the lack of consistent trends in experimental results. Therefore, we developed a program to simulate RIS in FM alloys. By performing a sensitivity analysis of the input parameters, we found the model to be most sensitive to the defect migration energies. Although the general Chromium (Cr) concentration profile appeared to follow that of experiments, the dose dependence and bulk Cr concentration dependence were not accurately reproduced, and it became obvious that the IK model may be too simple and too sensitive to the input parameters to accurately predict all of the effects of the segregation of Cr.

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Chapter 1

Introduction

Ferritic-martensitic (FM) steels are receiving a renewed interest in research due to the increased development of Generation IV fission reactors and fusion reactors. This stems from an increasing global demand in energy and the proliferation-resistance of nuclear materials. FM steels have shown high strength at intermediate temperatures up to about 500 °C, resistance to thermal stresses, dimensional stability, and radiation resistance, making them excellent candidates for use as structural materials in new reactor designs [24]. However, it is uncertain whether FM steels will maintain these properties through the life of a reactor, as a result of exposure to intense neutron irradiation.

Issues such as creep rupture strength, radiation hardening, phase stability and radiation-induced segregation (RIS) are not well understood for FM steels [32]. Of these issues, the understanding of RIS is of particular importance as it can lead to the formation of intermetallic phases, stress corrosion cracking, and other detrimental effects.

1.1 Radiation Damage

The materials used in nuclear energy are subject to irradiation through the form of high energy neutrons, gamma rays, and charged particles. Neutrons are of the greatest

concern with energies and fluxes exceeding 1 MeV and $10^{14} \frac{n}{cm^2-s}$, respectively. The materials that come in contact with these neutrons experience microstructural changes, and these changes can evolve and conglomerate into macro-scale detrimental effects such as RIS. To understand the mechanisms behind RIS, it is first necessary to understand the formation of primary defects.

The primary radiation damage event is referred to as an atomic displacement cascade, as first proposed by Brinkman in 1954 [13]. The displacement cascade can be thought of as a series of elastic collisions initiated by an atom that is elastically scattered by an energetic neutron [42]. This initial atom is referred to as the primary knock-on atom (PKA) and has an energy that is a fraction of the energy of the scattering neutron. To displace a lattice atom, the neutron must transfer an energy that is greater than the binding energy that is exerted by presence of other atoms within the lattice. This energy is called the displacement energy, E_d , and is on the order of 20 - 40 eV for most structural materials [18]. If an atom receives an energy greater than or equal to E_d , the atom can leave its original lattice site and come to rest as an interstitial in the lattice, referred to as a self-interstitial atom (SIA), and leaving behind a vacant lattice site, referred to as a vacancy. This SIA and vacancy pair is referred to as a Frenkel pair [42]. After the neutron transfers its kinetic energy to a lattice atom, the atom then makes a series of elastic scatters until the excess energy is dissipated. This series of elastic scatters leads to a cascade effect, as the scattered atoms will also go on to scatter other atoms, leaving behind many Frenkel pairs in the process. Most of these Frenkel pairs will recombine, but others will migrate to sinks or aggregate into extended defect structures such as voids or prismatic dislocation loops. It is those defects that migrate to sinks that are of critical importance in the understanding of RIS.

1.2 Radiation Induced Segregation

First predicted by Anthony in 1969, RIS was explained to come from vacancy fluxes and would occur through two processes: the dragging of solute atoms by vacancies, and the reverse atom flux which is a consequence of the vacancy flux [4]. This prediction came from a series of experiments on high-temperature annealed aluminum where, after quenching, Anthony found that vacancy fluxes caused zinc and copper impurity atoms to segregate around voids [6, 5]. Anthony proposed that the size difference between solute and solvent atoms would generate strains around the voids produced by radiation [7].

1.2.1 Early Observations

The first experimental observation of RIS came from Okamoto et al. in 1972 [33]. As predicted by Anthony, strains around voids were observed during the irradiation of an austenitic stainless steel [38]. Figure 1.1 shows the increasing strain effects and precipitation around voids with increasing dose for an austenitic stainless steel [35]. One year later, Okamoto and Wiedersich measured the segregation in irradiated stainless steels utilizing Auger spectroscopy [35].

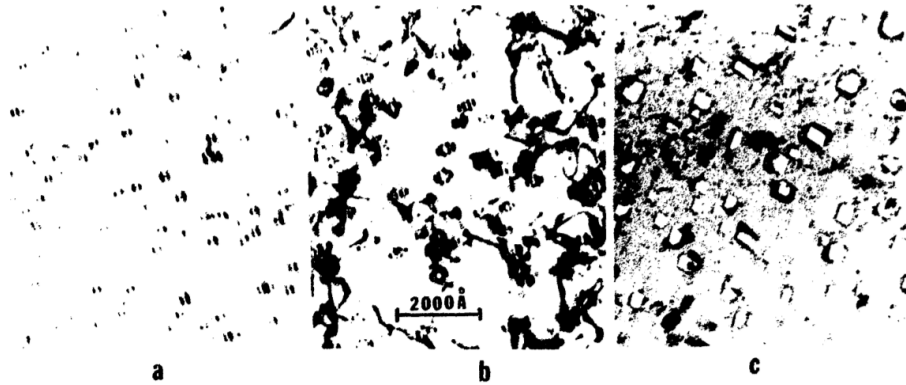


Figure 1.1: Strain effects around voids in austenitic stainless steel after irradiation with 1 MeV electrons (a) at 0.3 dpa, (b) at 1.9 dpa, and (c) precipitation on void surfaces at 4.3 dpa, as reproduced from Ref [35].

Okamoto et al. proposed a possible mechanism where undersized solute atoms are preferentially bound to interstitials, thus driving a segregation of those solutes to point-defect sinks, and oversized solute atoms are bound to vacancies leading to a depletion from sinks [35]. There is competition between the uphill diffusion of the solute, driven by the interstitial flux, and the back diffusion of the solute, which arises from high concentrations of interstitials and vacancies at the sink, and when these two mechanisms are equivalent, there is no segregation.

A few years later, Marwick proposed a mechanism where the solute coupled with the vacancy flux drives RIS, called the inverse Kirkendall effect (IKE) [29]. The Kirkendall effect refers to the flux of defects created by a gradient of solute and solvent atoms [41]. Within the context of the Kirkendall effect, the defect flux arises from thermal vacancies, which are generated due to thermal agitation. Thus, the IKE is the mechanism of a defect flux driving the flux of solute atoms. These two mechanisms are illustrated in Figure 1.2 [14].

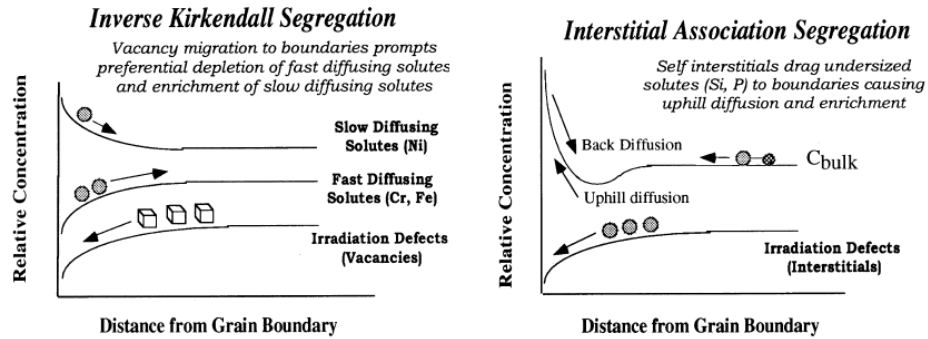


Figure 1.2: Illustrations of the two proposed RIS mechanisms [14]. The figure on the left illustrates the IKE as proposed by Marwick et al. where a flux of vacancies drives an enrichment of slow moving solute atoms and a depletion of fast moving solute atoms [29]. The figure on the right illustrates the interstitial associated diffusional mechanism as proposed by Okamoto et al. where undersized solute atoms migrate with the interstitial flux and enrich at sinks [35].

Since these first observations, many studies have been carried out to study RIS in many different alloys. Of these, austenitic stainless steels have received considerable attention due to their use as structural materials in nuclear applications.

1.2.2 RIS in Austenitic Steels

In irradiated austenitic alloys, Nickel (Ni) enrichment and Cr depletion is consistently observed at grain boundaries [43]. A typical segregation profile is shown in Figure 1.3 [14]. Another consequence of RIS is radiation-induced precipitation (RIP), and a review by Maziasz found γ and G phases, as well as M_2P and M_3P phosphides.

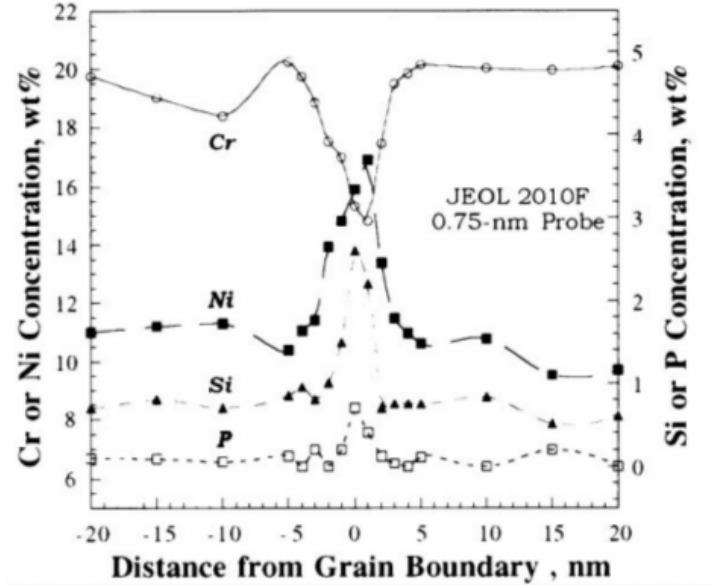


Figure 1.3: RIS concentration profiles for a neutron-irradiation 300-series stainless steel, as reproduced from Ref [14].

T.R. Allen et al. determined the primary RIS mechanism in austenitic alloys is the IKE, and models using the interstitial binding mechanism do not accurately reproduce the measured segregation concentration profiles [1]. Using the IKE mechanism proposed by Marwick [29], Perks et al. developed a model using differences in atom-vacancy jump rates to predict radiation-induced segregation in ternary alloys [37]. Allen and Was modified the Perks model to include composition dependence of diffusion parameters and obtained accurate predictions for RIS in austenitic Fe-Cr-Ni alloys, as shown in Figure 1.4 [2].

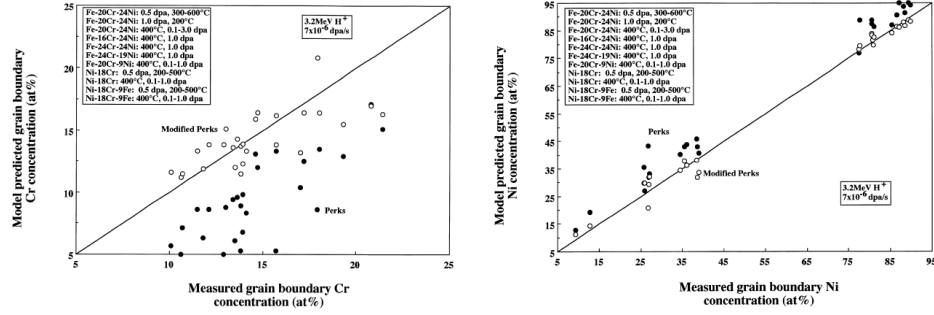


Figure 1.4: Comparing the Perks and Modified Perks model predictions of RIS concentration profiles of Cr and Ni for an austenitic Fe-Cr-Ni alloy, as reproduced from Ref [2].

1.2.3 RIS in Ferritic-Martensitic Steels

Predicting RIS in FM steels is more complex due to the lack of consistent trends observed in experimental results. A literature review by Lu et al. reported on RIS in 15 different experiments in FM steels where 8 showed Cr enrichment and 7 showed Cr depletion [26]. However, there were no systematic studies, making it difficult to draw any definite conclusions. More recently, a systematic study of 3 different alloys was performed by Was et al. by irradiating these alloys to doses from 1 to 10 dpa at 400°C and 500°C with 2.0 MeV protons at a rate of 1.3×10^{-5} dpa/s [43]. The grain boundary compositions were measured using scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM/EDX) and they found that one alloy showed Cr enrichment, one showed Cr depletion, and yet another showed enrichment for one dose, and depletion for two other doses, as shown in Figure 1.5.

Thus, while there is no clear trend, dose and irradiation temperature do appear to have an effect on Cr segregation or depletion. J.P. Wharry et al. measured RIS using STEM/EDX in FM alloy T 91 irradiated with 2.0 MeV protons for several doses and found that Cr, Ni, and Si segregate to grain boundaries at low doses, but segregation ceased and redistribution of atoms was observed for doses over 3 dpa as shown in Figure 1.6 [44]. They also found the solute segregation was much less

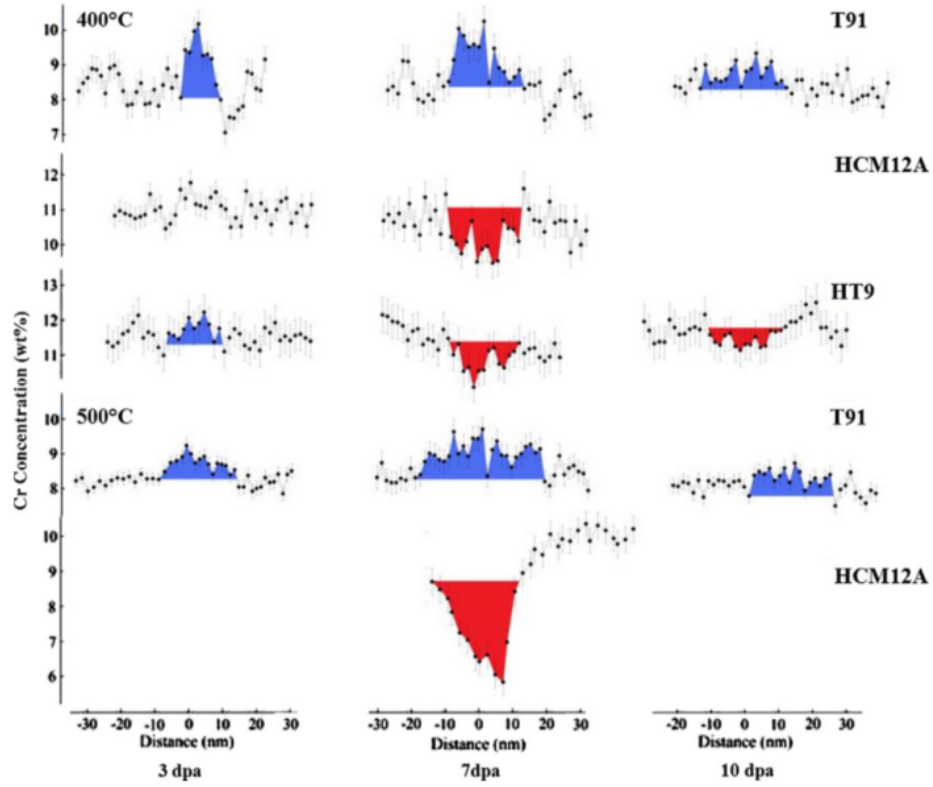


Figure 1.5: Dose, temperature and alloy dependence of grain boundary segregation of chromium following irradiation with 2 MeV protons for T91, HCM12A, and HT9 at 400°C, and T91 and HCM12A at 500°C, as reproduced from Ref [43].

pronounced at 500°C than 400°C. Clausen et al. also observed this temperature effect in HT-9 martensitic steel, finding strong segregation of Cr, Ni, Si, and P for irradiation at 400°C but relatively little segregation at irradiation temperatures of 520°C and 565°C [17]. Marquis et al. irradiated an Fe-15.1 at.% Cr alloy with 0.5 and 2 MeV Fe⁺ at 350 °C at a rate of 2.5×10^{15} ions/m²/s [28]. They measured RIS using atom-probe tomography (APT) for several doses and found the amount of Cr at the boundary plane decreased with increasing dose, while C concentrations remained constant, as shown in Figure 1.7. They concluded that the Cr concentration was changing from a 'W-shaped' profile to a 'V-shaped' depletion profile with increasing dose, stating that carbon segregation may slow down the depletion of Cr by retaining Cr atoms at the grain boundary.

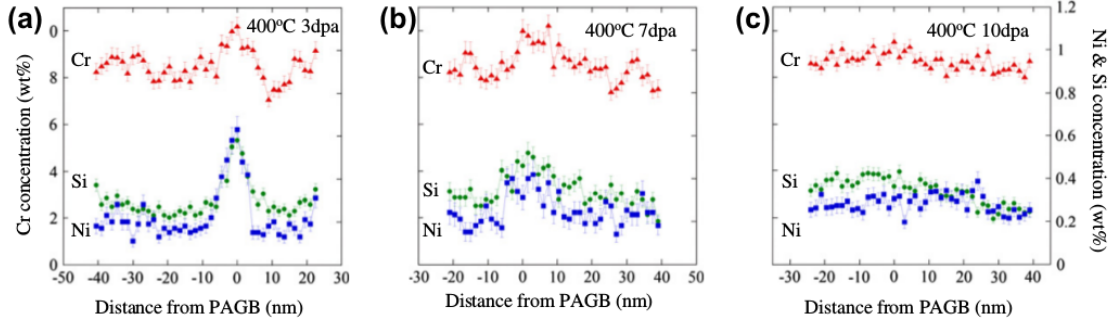


Figure 1.6: RIS profiles of Cr, Ni, and Si at (a) 3, (b) 7, and (c) 10 dpa at 400° C, as reproduced from Ref [44].

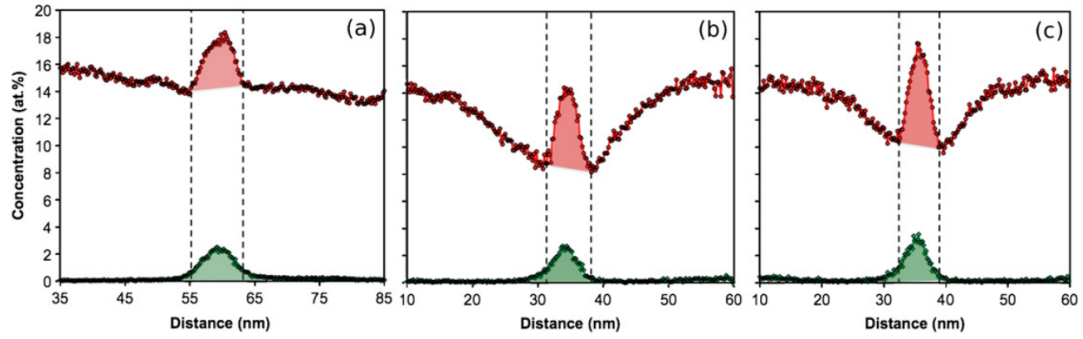


Figure 1.7: RIS profiles of Cr (red) and C (green) at (a) 0 dpa, (b) 0.5 dpa, and (c) 2 dpa, as reproduced from Ref [28].

The Cr segregation also appears to be dependent on the bulk Cr concentration of the alloy. Bachhav et al., using scanning electron microscopy with electron back-scattered diffraction (SEM/EBSD) to measure RIS in neutron irradiated alloys, found Cr enrichment of about 6 at.% for a Fe-6 at.% Cr alloy and only about 2 at.% for a Fe-15 at.% Cr alloy, as shown in Figures 1.8 and 1.9 [11, 10]. Wharry et al. measured RIS using STEM/EDX in several different alloys irradiated with 2.0 MeV protons to 3 dpa at 300°C [45]. The amount of Cr enrichment decreased with increasing bulk Cr concentration as shown in Figure 1.10.

The amount of Cr enrichment or depletion is also dependent on the type of grain boundary. Cr depletion has been observed in high-angle grain boundaries in some experiments [21, 25, 28]. However, Bachhav et al. found Cr enrichment of about 6

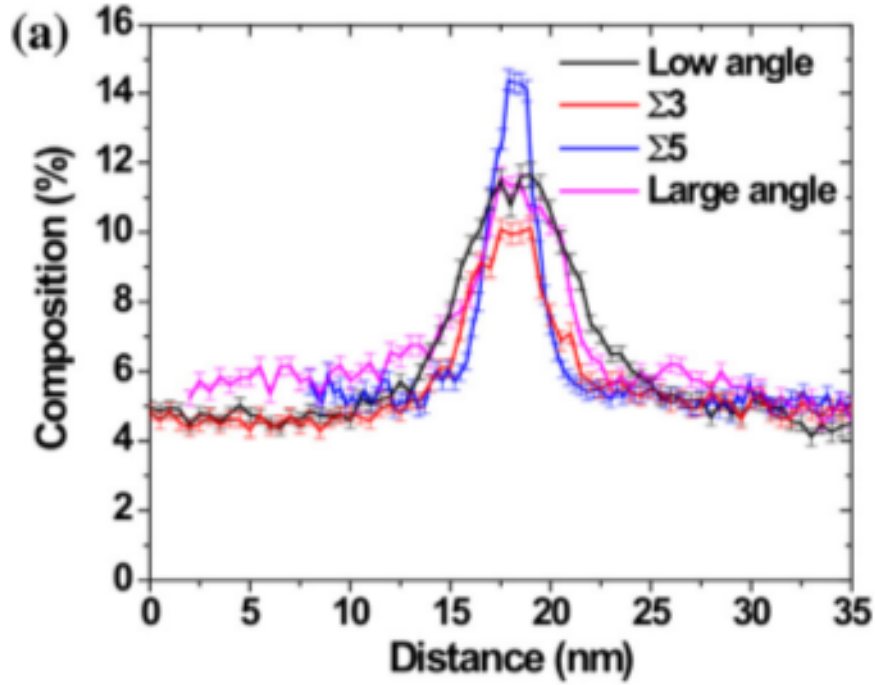


Figure 1.8: Cr enrichment of about 6 at.% was measured for a Fe-6 at.% Cr alloy after neutron irradiation, as reproduced from Ref [11].

at.% for a random high angle boundary [11]. Hu et al. observed a slight Cr enrichment for a $\Sigma 3$ grain boundary and a significant Cr enrichment for a $\Sigma 5$ grain boundary [21]. This effect was also observed by Bachhav et al. as shown in Figure 1.8 [11].

As compared to the relatively small number of phases observed in austenitic steels, Maziasz reviewed several studies and found that the irradiation of FM steels can induce precipitation of M_6C (η), χ , α' , G, σ , Cr_2X , Cr_3P , and MP phases [31]. Hu et al. observed thin carbide precipitates in Fe-15.2 at.% Cr alloy. α' precipitation is expected for Cr concentrations higher than 9 at.% [9]. The large variation in precipitates further adds to the complexity of predicting RIS in FM steels.

To summarize, there is a lack of consistency in the experimental data, but a few trends have been observed. It appears that the segregation decreases with increasing temperature and increases with increasing dose, however there is insufficient data to determine the dose for the onset of segregation and if and at what dose saturation

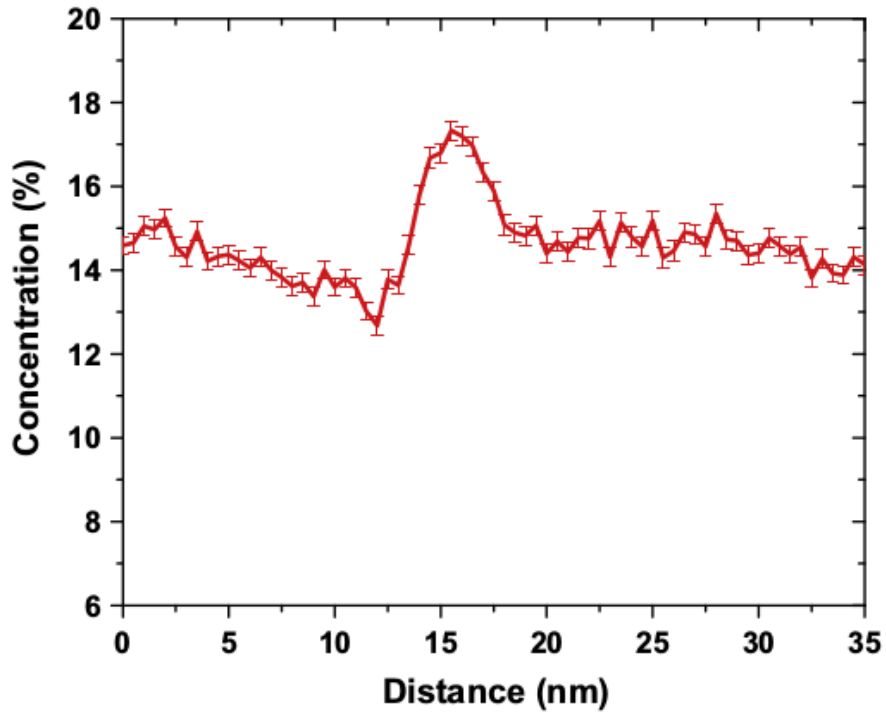


Figure 1.9: Cr enrichment of about 2 at.% was measured for a Fe-6 at.% Cr alloy after neutron irradiation, as reproduced from Ref [10].

will occur. It appears that the Cr segregation may decrease with increasing bulk Cr concentration, and depending on the alloy, many different precipitates may form.

1.2.4 Modeling RIS in FM Steels

The first modeling of RIS in dilute alloys was performed by Johnson and Lam in the late 1970s [22, 23]. Their kinetic model included the effects of vacancy and interstitial diffusional encounters with solute atoms and diffusion of vacancy-solute and interstitial-solute complexes. RIS models for concentrated alloys are based on Manning's relations [27]. Marwick developed a model utilizing the vacancy-solute coupling [29], and Wiedersich et al. went on to develop a model that incorporated solute coupling for both vacancies and interstitials [47].

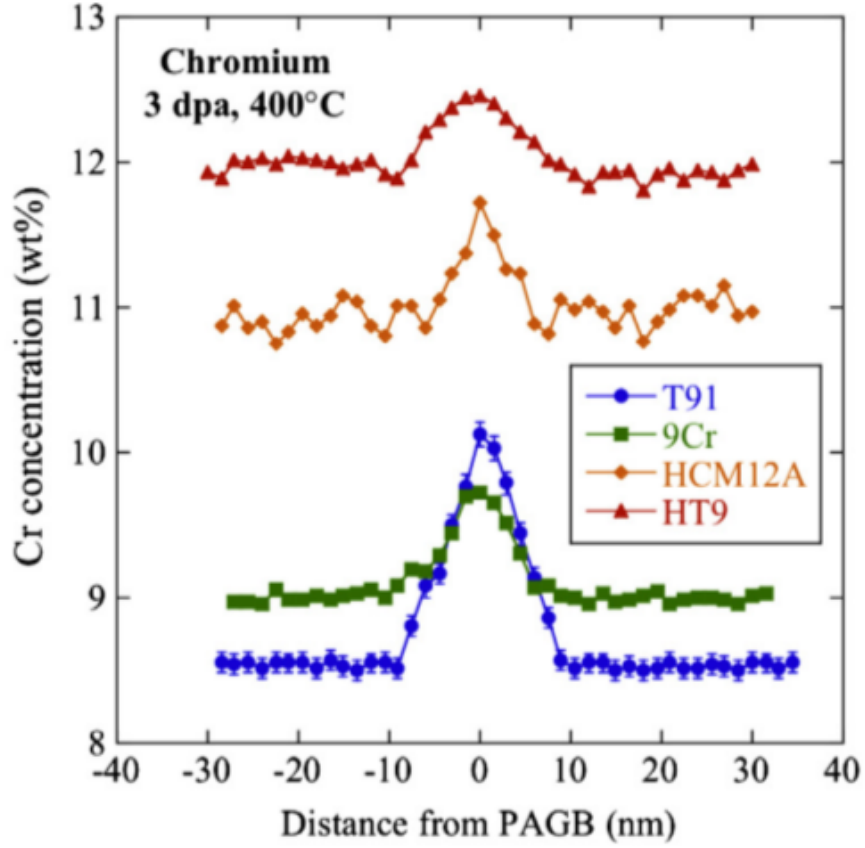


Figure 1.10: Cr enrichment decreases with the increasing bulk Cr concentration of the alloy, as reproduced from Ref [45].

There have been relatively few attempts at modeling RIS in FM steels. Frisbie and Wirth developed a kinetic lattice Monte Carlo (KLMC) model to simulate RIS by a vacancy-mediated mechanism [43]. Cr was either enriched or depleted at the sink by changing the the relative ratio of Fe to Cr diffusivity. Figure 1.11 shows results from these KLMC simulations. Consistent with the IKE, Cr was enriched when it diffused slower than Fe ($D_{\text{Fe}}/D_{\text{Cr}} > 1$), and Cr was depleted when it diffused faster than Fe ($D_{\text{Fe}}/D_{\text{Cr}} < 1$).

Field et al. modified a model developed by Barnard et al. to predict RIS in FM steels using a rate theory model that was parameterized from *ab initio* calculations, incorporating grain boundary structure into the rate equations [19, 12]. The results

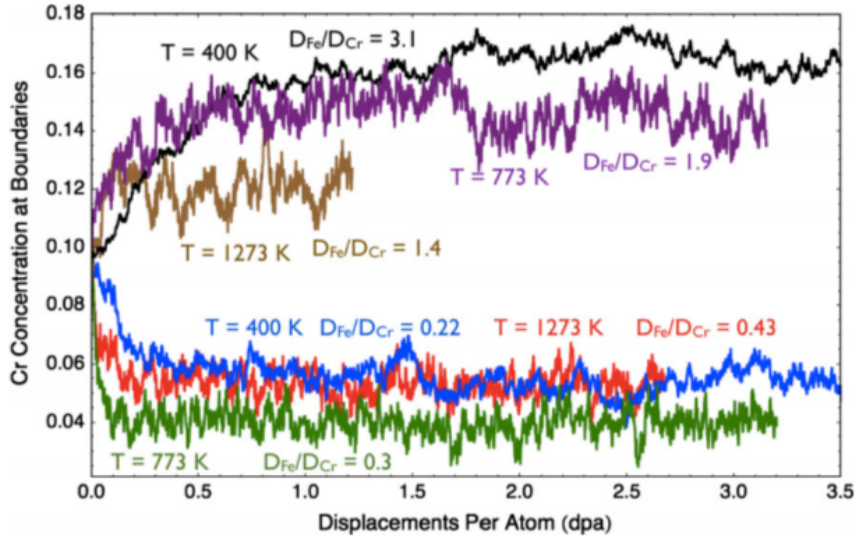


Figure 1.11: Results from KLMC simulations predicting the Cr concentration at grain boundaries as a function of dose, as reproduced from Ref [43].

from the model accurately matched experimental results and led Field et al. to conclude that Cr segregation is dependent on grain boundary structure with the highest enrichment occurring at high angle grain boundaries and a general suppression at low angle and special grain boundaries. Further, Field et al. determined that Cr enrichment increased monotonically with increasing dose up to 3 dpa and segregation decreased at higher irradiation temperatures due to changes in defect diffusivities. Figure 1.12 shows this temperature effect [19].

Most recently, Wharry et al. implemented the Perks model to investigate the mechanism of RIS in FM alloys [46]. First, a sensitivity analysis performed on the input parameters of the model revealed that the model is most sensitive to the values chosen for the migration energies. Then, after a careful selection of input parameters, the model was compared to experimental results. The model produced results that were comparable to experimental results for the concentration of Cr at the boundary as a function of temperature, as shown in Figure 1.13 [46], with the temperature dependence more accurately modeled with a Fe-vacancy migration energy of 0.60 eV. Figure 1.14 shows the concentration of Cr at the sink as a function of dose.

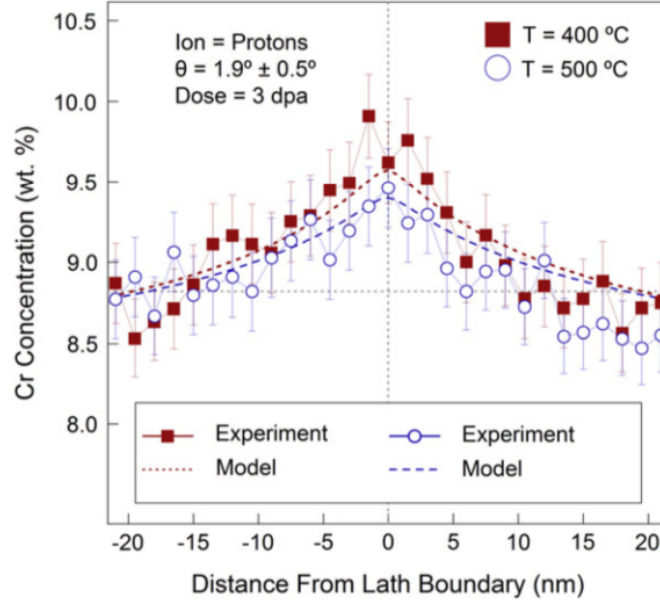


Figure 1.12: Results from experiments and *ab initio* based rate theory calculations showing the decrease in Cr enrichment with increasing temperature, as reproduced from Ref [19].

Initially, the model used a dose independent dislocation density of $7.5 \times 10^{14} \text{m}^{-2}$ and it did not appear to match the experimental results, with the onset of segregation and the steady state RIS occurring at doses much lower than those from experiments [46]. Implementing dose dependent dislocation densities, they were still unable to match the experimental results. They attributed this inconsistency to microstructural evolution, where the nucleation and growth of dislocation loops provide alternate sinks for point defects, reducing the flux to grain boundaries and increasing the dose required to cause segregation.

Consistent with the Inverse Kirkendall (IK) mechanism, Cr was enriched at sinks by interstitial migration over a large temperature range. At high temperatures, Cr was depleted by vacancy migration. Wharry et al. compared results from their model to several experimental values and found the IK model to be in good agreement for the crossover temperature from enrichment to depletion. They explained the cross-over temperature by plotting of the ratio of the diffusivities of Fe and Cr as

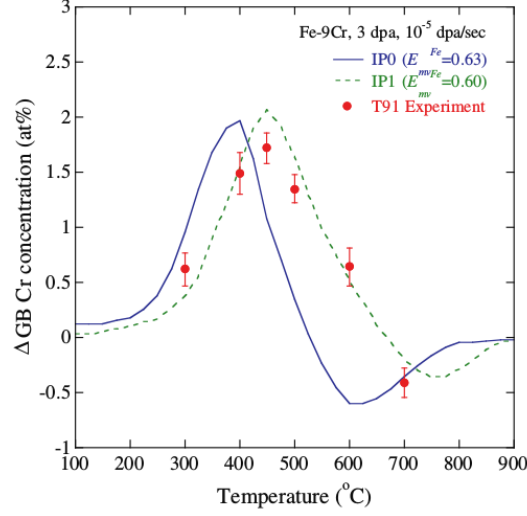


Figure 1.13: Results from the IK model showing the concentration of Cr as a function of temperature, as reproduced from Ref [46].

a function of temperature, as shown in Figure 1.15 [46]. When the ratio of the interstitial diffusivities of Cr to Fe is higher than that of the vacancies, as in the lower temperatures, the contribution of Cr enrichment by interstitials dominates depletion by vacancies; conversely, when the ratio of the vacancy diffusivities of Cr to Fe is higher than that of the interstitials, as in the higher temperatures, the depletion of Cr by vacancies dominates [46].

Wharry et al. also found the enrichment of Cr at sinks to be dependent on the initial Cr concentration in the bulk [46]. Their IK model first showed an increasing enrichment of Cr with increasing Cr concentration. However, this was the opposite effect of experimental results, showing a decreasing Cr enrichment with increasing concentration. After including concentration dependent interstitial migration energies, they were able to reproduce experimental results.

To summarize, there have been relatively few attempts to model RIS in FM alloys. The KLMC simulations lend credibility to the IK model by predicting Cr enrichment when it diffused slower than Fe and depletion when it diffused faster. The rate theory models generally predict Cr enrichment at sinks, saturation of RIS at doses ranging

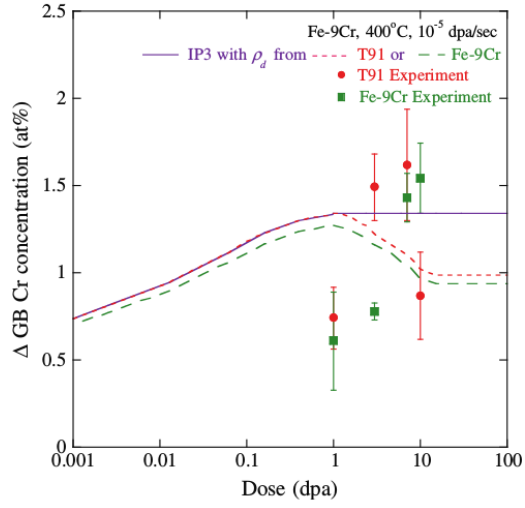


Figure 1.14: Results from the IK model showing the concentration of Cr as a function of dose, as reproduced from Ref [46].

1 - 3 dpa, and decreasing Cr segregation at higher temperatures, and have assumed Cr segregation to be a competition between vacancy and interstitial transport.

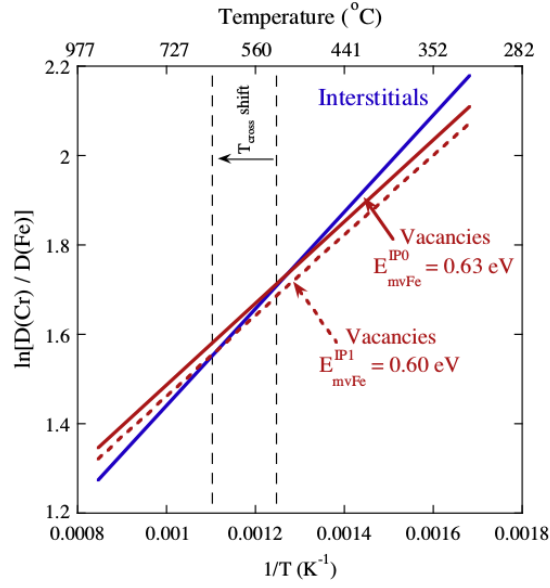


Figure 1.15: Ratio of the diffusivities of Cr to Fe as a function of temperature, where the intersection of the interstitial and vacancy lines define the temperature at which the segregation of Cr cross over from enrichment to depletion, as reproduced from Ref [46].

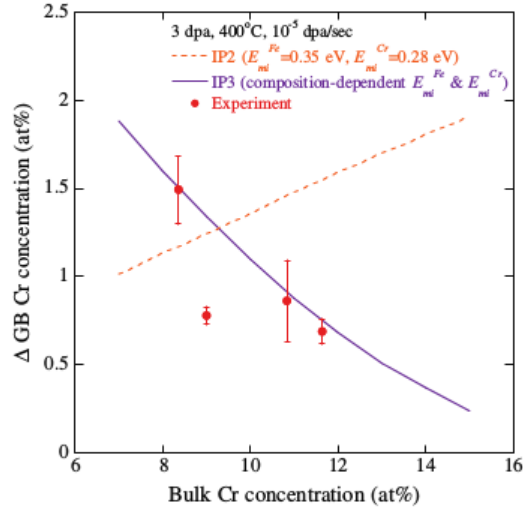


Figure 1.16: Change in Cr concentration at the free surface as a function of initial Cr concentration irradiated to 3 dpa at a dose rate of 1×10^{-5} dpa/s and at 400°C, as reproduced from Ref [46].

Chapter 2

Model Overview

To simulate RIS, we implemented a spatially dependent, reaction-diffusion model using a formulation originally developed by Wiedersich et al. [47]. This model, as well as other current models, only takes into account single interstitials and vacancies and does not consider cascade effects or clustering of interstitials and vacancies. This model accounts for the coupling of defect and atom fluxes through the use of preferential migration of interstitials and vacancies to Fe and Cr atoms in a binary Fe-Cr alloy. By defining the atom fluxes as occurring through vacancies and interstitials, the defect and atom fluxes are expressed in terms of concentration gradients and partial diffusivity coefficients of both the defects and the Fe and Cr atoms. Three coupled partial differential equations describe the one-dimensional (1-D) time and spatial dependence of the concentrations of interstitials, vacancies, and one of the alloying components under irradiation conditions.

2.1 General Rate Equations

The first two partial differential equations are the rates of change of the concentrations of interstitials (C_I) and vacancies (C_V) as a function of time are described by the following equations:

$$\frac{\partial C_I}{\partial t} = -\nabla \cdot J_I + K_0 - R \quad (2.1)$$

$$\frac{\partial C_V}{\partial t} = -\nabla \cdot J_V + K_0 - R \quad (2.2)$$

The first terms on the right hand side (RHS) of equations (2.1) and (2.2), $\nabla \cdot J_I$ and $\nabla \cdot J_V$ are the divergence of the fluxes of interstitials and vacancies, respectively. The second term and third terms on the RHS of equations (2.1) and (2.2), K_0 and R , account for the production of defects from irradiation and the recombination of interstitials and vacancies, respectively, and are equal for interstitials and vacancies.

The conservation equations for the alloying elements Fe and Cr are described by

$$\frac{\partial C_{Cr}}{\partial t} = -\nabla \cdot J_{Cr} \quad (2.3)$$

$$\frac{\partial C_{Fe}}{\partial t} = -\nabla \cdot J_{Fe} \quad (2.4)$$

where $\nabla \cdot J_{Cr}$ and $\nabla \cdot J_{Fe}$ are the divergence of the flux of Cr atoms and Fe atoms, respectively. However, equation (2.4) is not independent and may be omitted because $C_{Fe} = 1 - C_{Cr}$.

2.2 Diffusion Coefficients

To accurately describe the fluxes of the defects and alloying atoms, the diffusion coefficients must be defined. The diffusion coefficients are written as the sum of the partial diffusion coefficients for the various species. The partial diffusion coefficients are written as follows:

$$D_I^{\text{Cr}} = d_{\text{CrI}} N_{\text{Cr}} \quad (2.5)$$

$$D_V^{\text{Cr}} = d_{\text{CrV}} N_{\text{Cr}} \quad (2.6)$$

$$D_I^{\text{Fe}} = d_{\text{FeI}} N_{\text{Fe}} \quad (2.7)$$

$$D_V^{\text{Fe}} = d_{\text{FeV}} N_{\text{Fe}} \quad (2.8)$$

$$D_{\text{Cr}}^{\text{I}} = d_{\text{CrI}} N_{\text{I}} \quad (2.9)$$

$$D_{\text{Cr}}^{\text{V}} = d_{\text{CrV}} N_{\text{V}} \quad (2.10)$$

d_{CrI} and d_{CrV} are the interstitial and vacancy diffusivities for Cr and d_{FeI} and d_{FeV} are the interstitial and vacancy diffusivities for Fe. N_{Cr} is the atomic fraction of Cr atoms, N_{Fe} is the atomic fraction of Fe atoms, N_{I} is the atomic fraction of interstitials, and N_{V} is the atomic fraction of vacancies. The equation for the diffusivities follow the Arrhenius law and are defined as

$$d_{\text{FeI}} = D_{0,\text{I}}^{\text{Fe}} \exp \left(-\frac{E_{\text{mI}}^{\text{Fe}}}{k_B T} \right) \quad (2.11)$$

$$d_{\text{FeV}} = D_{0,\text{V}}^{\text{Fe}} \exp \left(-\frac{E_{\text{mV}}^{\text{Fe}}}{k_B T} \right) \quad (2.12)$$

$$d_{\text{CrI}} = D_{0,\text{I}}^{\text{Cr}} \exp \left(-\frac{E_{\text{mI}}^{\text{Cr}}}{k_B T} \right) \quad (2.13)$$

$$d_{\text{CrV}} = D_{0,\text{V}}^{\text{Cr}} \exp \left(-\frac{E_{\text{mV}}^{\text{Cr}}}{k_B T} \right) \quad (2.14)$$

where D_0 is the pre-exponential factor for interstitial or vacancy diffusion via Fe or Cr atoms, E_{m} is the migration energy interstitial or vacancies via Fe or Cr atoms, k_B is the Boltzmann constant, and T is the temperature.

Using equations (2.5) through (2.14), the diffusion coefficients are defined as

$$D_I = d_{CrI}N_{Cr} + d_{FeI}N_{Fe} \quad (2.15)$$

$$D_V = d_{CrV}N_{Cr} + d_{FeV}N_{Fe} \quad (2.16)$$

$$D_{Cr} = d_{CrV}N_V + d_{CrI}N_I \quad (2.17)$$

However, the atomic fractions can be converted into volumetric concentrations by $N_i = \Omega C_i$. Further, the concentration of Fe atoms can be written as $C_{Fe} = 1 - C_{Cr}$. Making these substitutions, equations (2.15) - (2.17) can be rewritten as

$$D_I = \Omega(d_{CrI} - d_{FeI})C_{Cr} + d_{FeI} \quad (2.18)$$

$$D_V = \Omega(d_{CrV} - d_{FeV})C_{Cr} + d_{FeV} \quad (2.19)$$

$$D_{Cr} = \Omega(d_{CrV}C_V + d_{CrI}C_I) \quad (2.20)$$

Now that the diffusivities and diffusion coefficients have been defined, the flux equations can be introduced.

2.3 Flux Equations

The strongest coupling between defect and atom fluxes comes from the flux of interstitials driving a flux of Cr atoms and Fe atoms in the same direction of the interstitial flux. Similarly, the flux of vacancies drives a flux of Cr atoms and Fe atoms in the opposite direction of the vacancy flux. This is given by

$$J_I = J_{Cr}^I + J_{Fe}^I \quad (2.21)$$

$$J_V = -(J_{Cr}^V + J_{Fe}^V) \quad (2.22)$$

where J_{Cr}^{I} and J_{Fe}^{I} are the fluxes of Cr atoms and Fe atoms, respectively, occurring via the interstitial flux, and the terms J_{Cr}^{V} and J_{Fe}^{V} are the fluxes occurring via the vacancy flux. Using equations (2.21) and (2.22), we can further define the flux of interstitials and vacancies by

$$J_{\text{I}} = -d_{\text{CrI}}\alpha\Omega C_{\text{I}}\nabla C_{\text{Cr}} - d_{\text{FeI}}\alpha\Omega C_{\text{I}}\nabla C_{\text{Fe}} - D_{\text{I}}\nabla C_{\text{I}} \quad (2.23)$$

$$J_{\text{V}} = d_{\text{CrV}}\alpha\Omega C_{\text{V}}\nabla C_{\text{Cr}} + d_{\text{FeV}}\alpha\Omega C_{\text{V}}\nabla C_{\text{Fe}} - D_{\text{V}}\nabla C_{\text{V}} \quad (2.24)$$

The first and second terms on the RHS of equations (2.23) and (2.24) are the defect fluxes that arise from the concentration gradients of Cr atoms and Fe atoms. The third term is the defect flux driven by the interstitial of vacancy gradient. However, because $\nabla C_{\text{Cr}} = -\nabla C_{\text{Fe}}$, equations (2.23) and (2.24) can be rewritten as

$$J_{\text{I}} = -(d_{\text{CrI}} - d_{\text{FeI}})\alpha\Omega C_{\text{I}}\nabla C_{\text{Cr}} - D_{\text{I}}\nabla C_{\text{I}} \quad (2.25)$$

$$J_{\text{V}} = (d_{\text{CrV}} - d_{\text{FeV}})\alpha\Omega C_{\text{V}}\nabla C_{\text{Cr}} - D_{\text{V}}\nabla C_{\text{V}} \quad (2.26)$$

In equations (2.25) and (2.26), the first term on the RHS describes the Kirkendall effects for interstitials and vacancies, respectively, where the difference in constituent atom fluxes are made up by appropriate defect fluxes. The flux of Cr atoms is defined as

$$J_{\text{Cr}} = -D_{\text{Cr}}\alpha\nabla C_{\text{Cr}} + d_{\text{CrV}}\Omega C_{\text{Cr}}\nabla C_{\text{V}} - d_{\text{CrI}}\Omega C_{\text{Cr}}\nabla C_{\text{I}} \quad (2.27)$$

The first term on the RHS of equation (2.27) is the atom flux created by the concentration gradient. The second term and third terms on the RHS of (2.27) are the atom fluxes induced by the interstitial and vacancy gradients, respectively.

The thermodynamic factor, α , accounts for the difference between the chemical potential gradient and concentration gradient and is given by

$$\alpha = 1 + \frac{\partial \ln \gamma_{\text{Cr}}}{\partial \ln N_{\text{Cr}}} = 1 + \frac{\partial \ln \gamma_{\text{Fe}}}{\partial \ln N_{\text{Fe}}} \quad (2.28)$$

where γ_{Cr} and γ_{Fe} are the activity coefficients of Cr and Fe, respectively, and N_{Cr} and N_{Fe} are the atomic fractions. This thermodynamic factor is equal to one for ideal systems, and can be calculated using thermodynamic software.

2.4 Production Rate

The second term on the RHS of equations (2.1) and (2.2), K_0 , is the production rate of interstitials and vacancies due to irradiation. Since we assume that a collision between a lattice atom and an incoming particle would produce interstitials and vacancies in equal numbers, the production rate is the same for interstitials and vacancies and is written as [48]

$$K_0 = \frac{\Phi \times \text{damage} - \text{production}}{N} \quad (2.29)$$

where Φ is the fluence in ions/nm², damage-production is in interstitials/ion/nm or vacancies/ion/nm, depending on the defect type, as determined from SRIM, and N is the atomic number density in atoms/nm³. The model does not account for cascade effects, only considering the production of single interstitials and single vacancies.

2.5 Recombination Rate

The third term on the RHS of equations (2.1) and (2.2), R , is the rate of recombination of interstitials and vacancies, is the same for interstitials and vacancies, and is given by [48]

$$R = 4\pi(r_I + r_V)(D_I + D_V)C_IC_V \quad (2.30)$$

where r_I and r_V are the trapping radii of interstitials and vacancies, respectively, D_{Cr} is the diffusion coefficient of Cr and D_{Fe} is the diffusion coefficient of Fe. Using the definition for D_{Cr} and D_{Fe} , the equation for the recombination rate becomes

$$R = 4\pi(r_I + r_V) [\Omega(d_{CrV} - d_{FeV} + d_{CrI} - d_{FeI})C_{Cr} + (d_{FeV} + d_{FeI})] C_IC_V \quad (2.31)$$

2.6 Final equations

Using the definitions described above, the three partial differential equations can be written as

$$\begin{aligned} \frac{\partial C_I}{\partial t} = & \nabla((d_{CrI} - d_{FeI})\alpha\Omega C_I \nabla C_{Cr} + [\Omega(d_{CrI} - d_{FeI})C_{Cr} + d_{FeI}] \nabla C_I) + K_0 \\ & - 4\pi(r_I + r_V) [\Omega(d_{CrV} - d_{FeV} + d_{CrI} - d_{FeI})C_{Cr} + (d_{FeV} + d_{FeI})] C_IC_V \end{aligned} \quad (2.32)$$

$$\begin{aligned} \frac{\partial C_V}{\partial t} = & \nabla(-(d_{CrV} - d_{FeV})\alpha\Omega C_V \nabla C_{Cr} + [\Omega(d_{CrV} - d_{FeV})C_{Cr} + d_{FeV}] \nabla C_V) + K_0 \\ & - 4\pi(r_I + r_V) [\Omega(d_{CrV} - d_{FeV} + d_{CrI} - d_{FeI})C_{Cr} + (d_{FeV} + d_{FeI})] C_IC_V \end{aligned} \quad (2.33)$$

$$\frac{\partial C_{Cr}}{\partial t} = \nabla((d_{CrV}C_V + d_{CrI}C_I)\Omega\alpha \nabla C_{Cr} + \Omega C_{Cr}(d_{CrI} \nabla C_I - d_{CrV} \nabla C_V)) \quad (2.34)$$

2.7 Initial Conditions

The initial concentrations of interstitials and vacancies are set to their thermal equilibrium values as shown in (2.35) and (2.36), and the concentration of Cr atoms is set uniformly across the spatial coordinate at the applicable volumetric concentration.

$$C_I(0, x) = \exp(-E_{\text{IFe}}^f/kT) \quad (2.35)$$

$$C_V(0, x) = \exp(-E_{\text{VFe}}^f/kT) \exp(S_{\text{sv}}/k) \quad (2.36)$$

$$C_{\text{Cr}}(0, x) = C_{\text{Cr}}^0 \quad (2.37)$$

2.8 Boundary Conditions

At the foil center ($x=L/2$), symmetry boundary conditions are applied by setting the interstitial, vacancy, and Cr gradients equal to zero.

$$\frac{\partial C_I(t, \frac{L}{2})}{\partial x} = \frac{\partial C_V(t, \frac{L}{2})}{\partial x} = \frac{\partial C_{\text{Cr}}(t, \frac{L}{2})}{\partial x} = 0 \quad (2.38)$$

At the free surface ($x=0$), the interstitial and vacancy concentrations are set to their thermal equilibrium values. Further, the rate of change of the interstitials and vacancies at the free surface are set equal to zero.

$$\frac{\partial C_I(t, 0)}{\partial t} = \frac{\partial C_V(t, 0)}{\partial t} = 0 \quad (2.39)$$

$$C_I(t, 0) = \exp(-E_{\text{IFe}}^f/kT) \quad (2.40)$$

$$C_V(t, 0) = \exp(-E_{\text{VFe}}^f/kT) \exp(S_{\text{sv}}/k) \quad (2.41)$$

Table 2.1: Input Parameter Values

Definition	Symbol	Value	Unit	Reference
Fe Interstitial Formation Energy	$E_{\text{fI}}^{\text{Fe}}$	5.0	eV	[36]
Fe Vacancy Formation Energy	$E_{\text{fV}}^{\text{Fe}}$	1.6	eV	[39]
Fe Interstitial Migration Energy	$E_{\text{mI}}^{\text{Fe}}$	0.35	eV	[46]
Fe Vacancy Migration Energy	$E_{\text{mV}}^{\text{Fe}}$	0.625	eV	[46]
Fe Pre-exponential Factor for Interstitial Diffusivity	$D_{0,\text{I}}^{\text{Fe}}$	6.59×10^{11}	$\frac{\text{m}^2}{\text{s}}$	[19]
Fe Pre-exponential Factor for Vacancy Diffusivity	$D_{0,\text{V}}^{\text{Fe}}$	5.92×10^{12}	$\frac{\text{m}^2}{\text{s}}$	[19]
Cr Interstitial Migration Energy	$E_{\text{mI}}^{\text{Cr}}$	0.28	eV	[46]
Cr Vacancy Migration Energy	$E_{\text{mV}}^{\text{Cr}}$	0.55	eV	[46]
Cr Pre-exponential Factor for Interstitial Diffusivity	$D_{0,\text{I}}^{\text{Cr}}$	6.85×10^{11}	$\frac{\text{m}^2}{\text{s}}$	[19]
Cr Pre-exponential Factor for Vacancy Diffusivity	$D_{0,\text{V}}^{\text{Cr}}$	5.46×10^{12}	$\frac{\text{m}^2}{\text{s}}$	[19]
Vacancy Formation Enthalpy	S_{sv}	1.0	k_{B}	[2]

A Cr conservation condition replaces the boundary condition for Cr at the free surface by integrating over half the length of the spatial coordinate.

$$\int_0^{\frac{L}{2}} C_{\text{Cr}}(x, t) dx = C_{\text{Cr}}^0 \frac{L}{2} \quad (2.42)$$

where C_{Cr}^0 is the initial concentration of Cr atoms.

2.9 Parameters

The selection of accurate values for parameters is critical to obtain meaningful results from this model. The values for the parameters used in this model were chosen from published values taken from experiment and model calculations, and are shown in Table 2.1.

The values for the pre-exponential factor for interstitial or vacancy diffusion via Fe or Cr atoms come from Field et al. who used an Arrhenius fit to values calculated by Choudhury et al. from first principles [19, 16]. The vacancy formation energy value comes from a positron annihilation experiment in α – Fe by Shaefer et al. [39].

The interstitial formation energy comes from ab initio calculations on defects in Fe-Cr systems by Olsson et al. [36]. The values for the migration energies come from Wharry et al. [46].

2.9.1 Thermodynamic Factor

The value of the thermodynamic factor, α , accounts for the difference between the chemical potential and the concentration gradient. Previous models used a value of 1 for this parameter, however, we have implemented a concentration-dependent value for α . To do this, the activity coefficients for the binary Fe-Cr system with atomic concentrations of Cr ranging of 0 at.% to 20 at.% at 700K were calculated using the Thermo-Calc software [3]. Using these activity coefficients along with the atomic fractions, the values of α were calculated as a function of Cr concentration. A curve was fit to this data, as shown in Figure 2.1. The program used this equation to calculate the value of α given the initial Cr concentration.

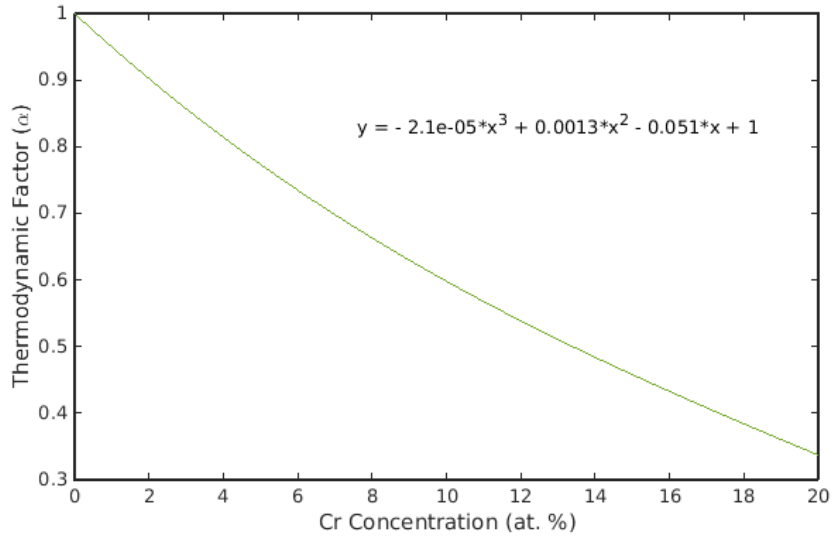


Figure 2.1: Curve fitted to the values of alpha as a function of Cr concentration.

To solve this system of ODEs, we used the *ode15s* solver, a part of the ODE solver suite developed by MATLAB [30]. This ordinary differential equation solver uses the

Numerical Differentiation Formulae (NDF) [40], which is based on the Backward Differentiation Formulae (BDF) [20], to solve stiff differential equations [15]. In Chapter 3 we will describe the results of produced from this model.

2.9.2 Qualitative Analysis

When looking at the flux equations, some qualitative results can be inferred following Wiedersich et al. [47]. First, assuming steady state, the flux of Cr and Fe atoms must be equal to zero.

$$J_{\text{Cr}} = J_{\text{Fe}} = 0 \quad (2.43)$$

Further, because the effect of bias effects are neglected, the flux of interstitials must be equal to the flux of vacancies. This must be true because equal numbers of interstitials and vacancies are generated by irradiation and equal numbers are lost by recombination. Thus, for steady state to be achieved, the flux of interstitials and vacancies to sinks must be equal.

$$J_{\text{I}} = J_{\text{V}} \quad (2.44)$$

Using equations (2.23) and (2.24) along with the steady state requirements in equations (2.43) and (2.44), ∇C_{I} can be eliminated from (2.27) and a relationship between ∇C_{Cr} and ∇C_{V} can be derived.

$$\nabla C_{\text{Cr}} = \frac{\Omega C_{\text{Cr}} C_{\text{Fe}} d_{\text{CrI}} d_{\text{FeI}}}{\alpha (d_{\text{CrI}} C_{\text{Cr}} D_{\text{Fe}} + d_{\text{FeI}} C_{\text{Fe}} D_{\text{Cr}})} \times \left(\frac{d_{\text{CrV}}}{d_{\text{FeV}}} - \frac{d_{\text{CrI}}}{d_{\text{FeI}}} \right) \nabla C_{\text{V}} \quad (2.45)$$

The direction of the gradient of Cr atoms and vacancies is determined from the term in parentheses on the right of the multiplication sign in equation (2.45),

$$\frac{d_{\text{CrV}}}{d_{\text{FeV}}} - \frac{d_{\text{CrI}}}{d_{\text{FeI}}} \quad (2.46)$$

It is clear that the relative ratios of the diffusivities determine the sign of equation (2.46). During irradiation, the concentration of vacancies always decreases toward the sink, e.g. $\nabla C_V > 0$. If $d_{\text{CrV}}/d_{\text{FeV}} > d_{\text{CrI}}/d_{\text{FeI}}$, equation (2.45) will be positive and the concentration of Cr will also decrease toward the sink. This leads to a depletion of Cr at the surface. The qualitative concentration profiles for vacancies and Cr are shown in Figure 2.2 [8]. Conversely, if $d_{\text{CrV}}/d_{\text{FeV}} < d_{\text{CrI}}/d_{\text{FeI}}$, equation (2.45) will be negative and the gradient of Cr will be opposite that of the vacancy gradient, leading to an enrichment of Cr at the surface. This is illustrated in Figure 2.3.

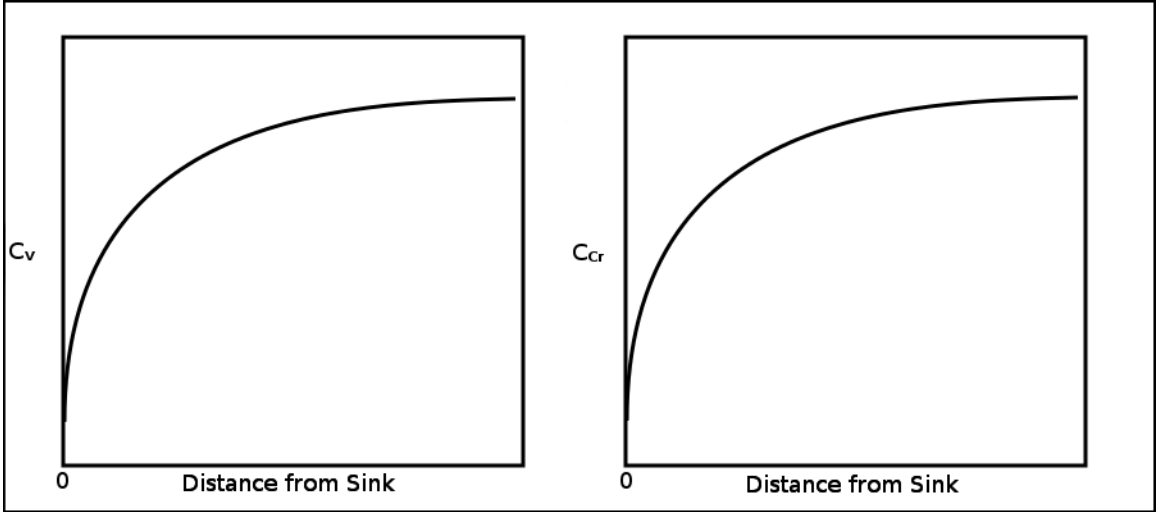


Figure 2.2: The concentration of Cr depletes at the surface when $\left(\frac{d_{\text{CrV}}}{d_{\text{FeV}}} - \frac{d_{\text{CrI}}}{d_{\text{FeI}}} \right) > 0$, based on figures by Ardell et al. [8].

Further, equation (2.46) can be rewritten as

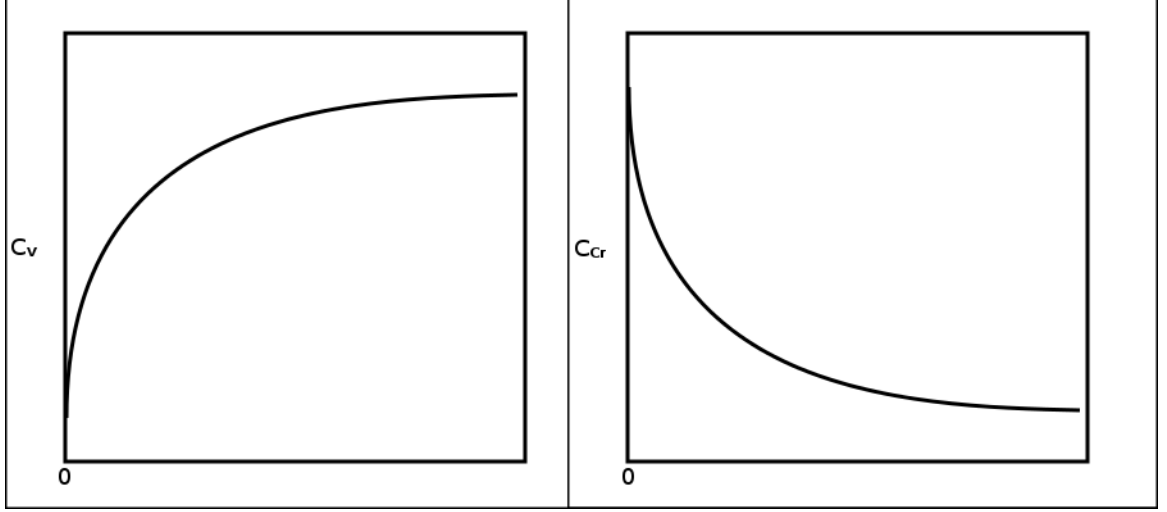


Figure 2.3: The concentration of Cr enriches at the surface when $\left(\frac{d_{\text{CrV}}}{d_{\text{FeV}}} - \frac{d_{\text{CrI}}}{d_{\text{FeI}}} \right) < 0$, based on figures by Ardell et al. [8].

$$\frac{D_{0,V}^{\text{Cr}}}{D_{0,V}^{\text{Fe}}} \exp \left(\frac{E_{\text{mV}}^{\text{Fe}} - E_{\text{mV}}^{\text{Cr}}}{k_B T} \right) - \frac{D_{0,I}^{\text{Cr}}}{D_{0,I}^{\text{Fe}}} \exp \left(\frac{E_{\text{mI}}^{\text{Fe}} - E_{\text{mI}}^{\text{Cr}}}{k_B T} \right) \quad (2.47)$$

By writing the term in this way, it becomes apparent that the real driving force behind the magnitude of this value is the difference between the migration energies for the vacancy and interstitial diffusion mechanism, respectively. This will be referred to as the migration energy gap. From equation (2.47), it becomes apparent that the choice of migration energies will directly affect the behavior of Cr segregation.

Chapter 3

Results

3.1 Radiation Induced Segregation Simulations

We first compare the Cr concentration profile to experimental results. To do this, we simulated an experiment performed by Wharry et al. where a sample of a T 91 FM alloy was irradiated [44]. Following their experiment, we simulated a sample with a Cr concentration of 8.37 at.%, with an initial concentration of interstitials and vacancies equivalent to that at the annealing temperature of 790°C. Using a grain size of 0.3 μm , we simulated proton irradiation of the sample to 3 dpa at an irradiation temperature of 400°C and a dose rate of 1.3×10^{-5} dpa/s. The resulting Cr concentration profile is shown in Figure 3.1. The final Cr concentration profile compares reasonably well with that obtained by Wharry et al., as shown in Figure 3.2 [44]. The amount of Cr enrichment away from the grain boundary is greater in the simulation than in the experiment. However, the concentration of Cr at the boundary is comparable.

The next experiment we simulated was performed by Bachhav et al. on a Fe-15 at.% Cr alloy [10]. After annealing at 750°C, the sample was irradiated to a dose of 1.82 dpa at 290°C and a constant dose rate of 3.4×10^{-7} dpa/s. The Cr concentration profile across a $\Sigma 3$ grain boundary is shown in Figure 3.3. Simulating these conditions for a grain size of 64 nm, we obtained the Cr concentration profile shown in Figure

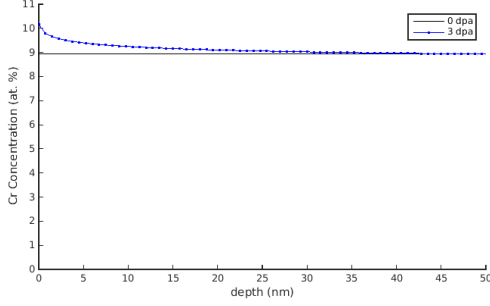


Figure 3.1: Cr concentration profile of a simulation of a Fe-8.37 at.% Cr alloy irradiated to 3 dpa at an irradiation temperature of 400°C and a dose rate of 1.3×10^{-5} dpa/s.

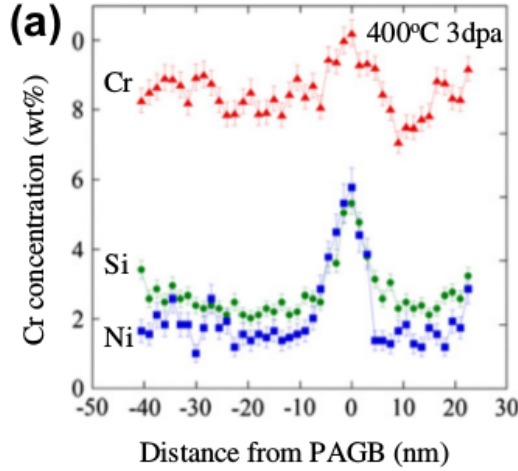


Figure 3.2: Cr concentration as a function of depth from the sink of a T 91 FM alloy irradiated to 3 dpa at an irradiation temperature of 400°C and a dose rate of 1.3×10^{-5} dpa/s [44].

3.4. Comparing this to the results obtained by Bachhav et al., the simulated Cr enrichment is less than the experimental values, but the overall shape of the profile is comparable.

We also simulated an experiment performed by Bachhav et al. on a Fe-6 at.% Cr alloy [11]. Following the same experimental procedure as with the Fe-15 at.% Cr, the sample was annealed at 750°C and then irradiated to a dose of 1.82 dpa at 290°C and a constant dose rate of 3.4×10^{-7} dpa/s. The Cr concentration profile across a random high angle grain boundary is shown in Figure 3.5. Simulating these

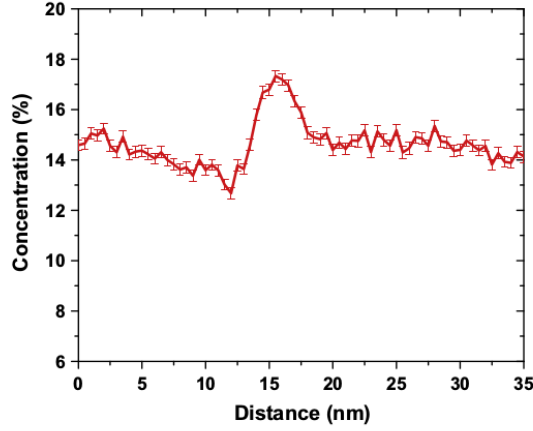


Figure 3.3: Cr concentration profile as a function of depth from the grain boundary of a Fe-15 at.% Cr alloy irradiated to 1.82 dpa at an irradiation temperature of 290°C and a dose rate of 3.4×10^{-7} dpa/s, as reproduced from Ref [10].

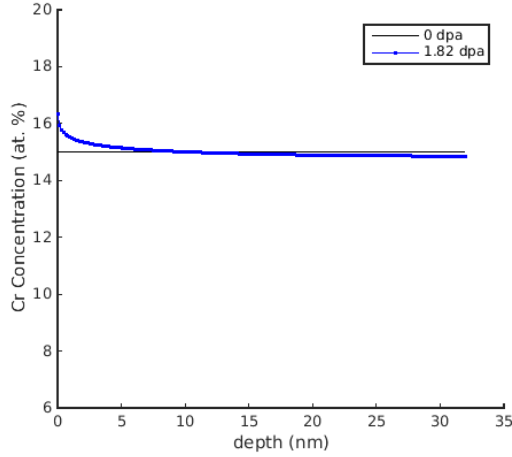


Figure 3.4: Cr concentration profile of a simulation of a Fe-15 at.% Cr alloy irradiated to 1.82 dpa at an irradiation temperature of 290°C and a dose rate of 3.4×10^{-7} dpa/s.

conditions for a grain size of 64 nm, we obtained the Cr concentration profile shown in Figure 3.6. This simulation resulted in a Cr concentration that was much less than in the experiment.

Further, we set out to reproduce results from a set of experiments performed by Wharry et al. performed on four different alloys: T 91, HCM12A, HT9, and a Fe-9 wt.% Cr model alloy [45]. The samples were all irradiated to various doses at 1.2×10^{-5}

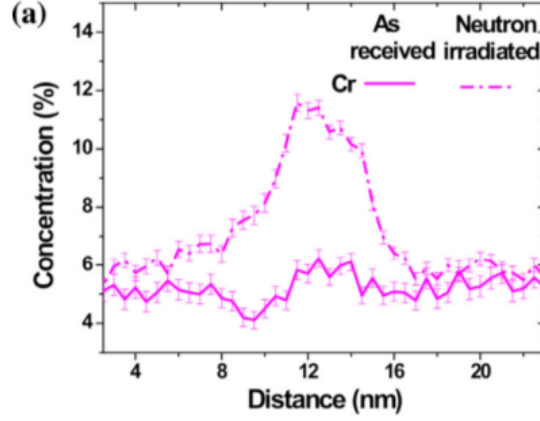


Figure 3.5: Cr concentration profile as a function of depth from the grain boundary of a Fe-6 at.% Cr alloy irradiated to 1.82 dpa at an irradiation temperature of 290°C and a dose rate of 3.4×10^{-7} dpa/s, as reproduced from Ref [10].

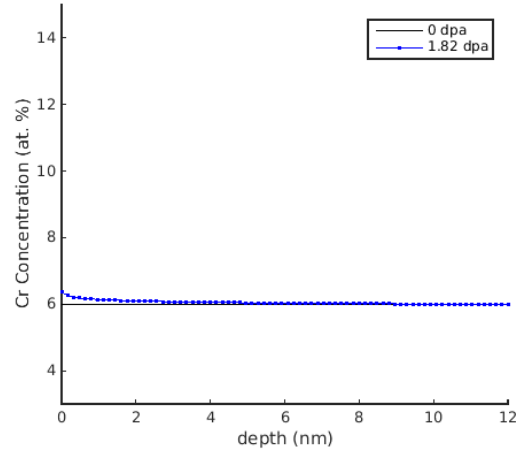


Figure 3.6: Cr concentration profile of a simulation of a Fe-15 at.% Cr alloy irradiated to 1.82 dpa at an irradiation temperature of 290°C and a dose rate of 3.4×10^{-7} dpa/s.

dpa/s at different temperatures. To simulate these experiments, we modeled a grain size of $0.3 \mu\text{m}$. We first simulated an annealing at 790°C for T 91, 750°C for the Fe-9Cr model alloy, 770°C for HCM12A, and 760°C for HT9. Then, we simulated irradiation at the prescribed dose and temperature at a dose rate of 1.2×10^{-5} dpa/s. We then calculated the change in the Cr concentration at the sink and compared

Table 3.1: Results from simulations of experiments performed by Wharry et al. [45]

Alloy	C_{Cr} (wt.%)	Dose (dpa)	Temp. ($^{\circ}C$)	ΔC_{Cr} (wt.%) [45]	ΔC_{Cr} (wt.%), Sim	Difference (wt.%)
T 91	8.37	1	400	0.74	1.15	0.41
		3	400	1.49	1.15	-0.34
		7	400	1.62	1.15	-0.47
		10	400	0.87	1.15	0.28
		3	300	0.62	0.69	0.07
		3	450	1.72	0.81	-0.91
		3	500	1.35	0.37	-0.98
		3	600	0.64	0.02	-0.62
		3	700	-0.43	0.00	0.43
		1	400	0.61	1.27	0.66
Fe-9Cr	9.0	3	400	0.78	1.27	0.49
		7	400	1.43	1.27	-0.16
		10	400	1.54	1.27	-0.27
		3	400	0.86	1.65	-0.79
HCM12A	10.83	3	400	0.69	1.84	-1.15
HT9	11.63	3	400			

it to the average change in Cr concentration at grain boundaries obtained in the experiments. The results from these simulations are available in Table 3.1.

From this series of simulations, certain trends can be determined from the model. The segregation of Cr is already saturated at a dose of 1 dpa, whereas the experimental Cr concentrations continue to increase with increasing dose up to 7 dpa, and then decrease for higher doses for T 91. The Fe-9 wt.% Cr model alloy did not exhibit this saturation behavior at all. The enrichment of Cr compared reasonably well at lower temperatures, but at higher temperatures the predicted Cr concentrations deviated from the experiment. The model overpredicted the Cr enrichment for the high Cr alloys HCM12A and HT9, suggesting there are other concentration dependent factors not accounted for in the model.

3.2 Sensitivity Analysis

Following the method of Wharry et al., we also performed a sensitivity analysis of the input parameters [46]. To determine the effect each of these parameters had on model predictions, a sensitivity analysis was performed for the various parameters where the model sensitivity was defined as the derivative of the Cr concentration at the free surface with respect to an input parameter, $\frac{\partial C_{Cr}}{\partial P}$ [46]. This sensitivity is approximated as the ratio of the change in the concentration of Cr at the free surface to the change in the value of the parameter, $\frac{\delta C_{Cr}}{\delta P}$.

$$\frac{\partial C_{\text{Cr}}}{\partial P} \approx \frac{\delta C_{\text{Cr}}}{\delta P} = \frac{C'_{\text{Cr}} - C_{\text{Cr,ref}}}{P' - P_{\text{ref}}} \quad (3.1)$$

where C'_{Cr} and P' refer to the varied concentration and parameter value, respectively, and $C_{\text{Cr,ref}}$ and P_{ref} are the reference values. A more meaningful value is the fractional change in the concentration of Cr at the free surface and is referred to as the significance, S_{P}^C [46]. This is expressed as

$$S_{\text{P}}^C = \frac{C'_{\text{Cr}} - C_{\text{Cr,ref}}}{P' - P_{\text{ref}}} \times \frac{P_{\text{ref}}}{C_{\text{Cr,ref}}} \quad (3.2)$$

Using this definition, the significance of the input parameters were calculated by modeling the irradiation of an Fe-9 at.% Cr alloy to 15 dpa at 320°C, and then reducing the value of the parameter in question by 0.01% and re-running the simulation at the same conditions. The significances of the various parameters are shown in Figure 3.7.

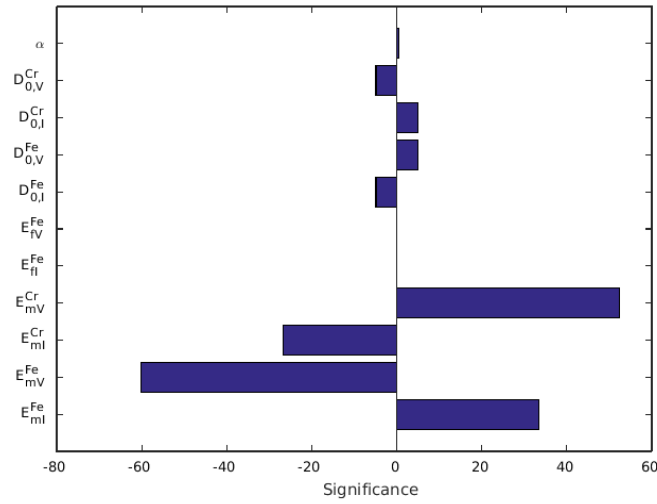


Figure 3.7: Significances for the various parameters in the model, following the method by Wharry et al. [46].

From Figure 3.7, it is clear that the migration energies are the most significant input parameters. Further, the model is more sensitive to the migration energies for vacancies than to the migration energies for interstitials. It is also apparent from Figure 3.7 that a perturbation in the migration energy increases the migration energy gap for one of the elements and decreases it for the other. This is also the case for a perturbation in the migration energy of the two defect types for the same element. This effect is consistent with equation (2.47), where decreasing the Cr-vacancy migration energy increases the migration energy gap and decreasing the Cr-interstitial migration energy decreases the migration energy gap. The opposite holds for the Fe-vacancy and Fe-interstitial migration energies.

After discovering the model's sensitivity to the migration energies, we investigated the effect of small changes on the migration energy gap from equation (2.46). We calculated this value range of values of E_{mV}^{Fe} , as shown in Figure 3.8. The values for the other migration energies were held constant at the values shown in Table 2.1.

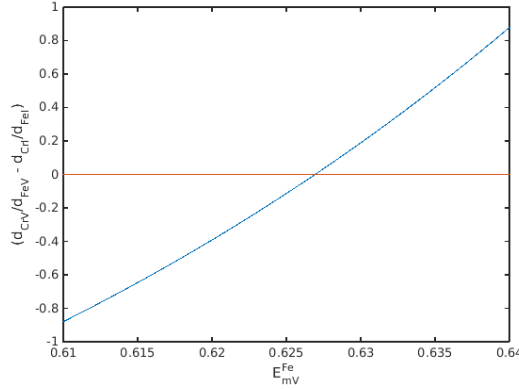


Figure 3.8: Values of $\left(\frac{d_{CrV}}{d_{FeV}} - \frac{d_{CrI}}{d_{FeI}}\right)$ for varying values of E_{mV}^{Fe}

From Figure 3.8, the value is negative for values of E_{mV}^{Fe} less than 0.6264 eV and positive for greater values. Thus, the values chosen for the migration energies will determine the enrichment or depletion of Cr at the surface. To gain a better understanding of how the migration energies affect the final Cr concentration at the surface, simulations were run for various combinations of E_{mI}^{Fe} and E_{mV}^{Fe} , as well as

combinations of $E_{\text{mi}}^{\text{Cr}}$ and $E_{\text{mv}}^{\text{Cr}}$. We simulated a 2 μm thick foil with an initial uniform Cr concentration set to 9 at.%. The foil was irradiated to 3 dpa at 1×10^{-5} dpa/s and 400°C. The input parameters values were the same as shown in table 2.1, with the exception of the values of the migration energies in question. Figures 3.9 and 3.10 show the results obtained from these simulations. The change from depletion to enrichment as predicted by equation (2.47) is also represented in these figures.

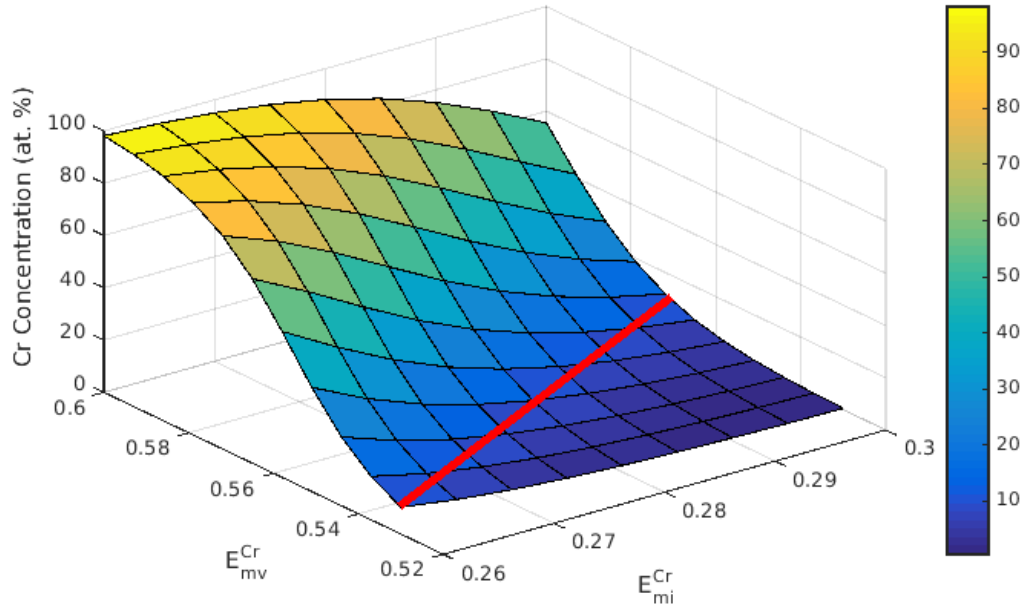


Figure 3.9: Final Cr concentration at the free surface as a function of the migration energy of interstitials and vacancies in Cr. The red line marks the the crossover from depletion to enrichment as predicted by the migration energy gap from equation (2.47).

As predicted by the initial sensitivity analysis, the migration energies had a significant effect on the final Cr concentration at the surface. With changes in migration energies as small as 0.08 eV, Cr concentrations varied from almost complete depletion with 0.54 at.% Cr at the sink to near complete enrichment with 98.14 at.% Cr at the sink. Figures 3.9 and 3.10 show how sensitive this model is to the values chosen for the migration energies. Further, the change from depletion to enrichment as governed by the migration energy gap is consistent with equation (2.47).

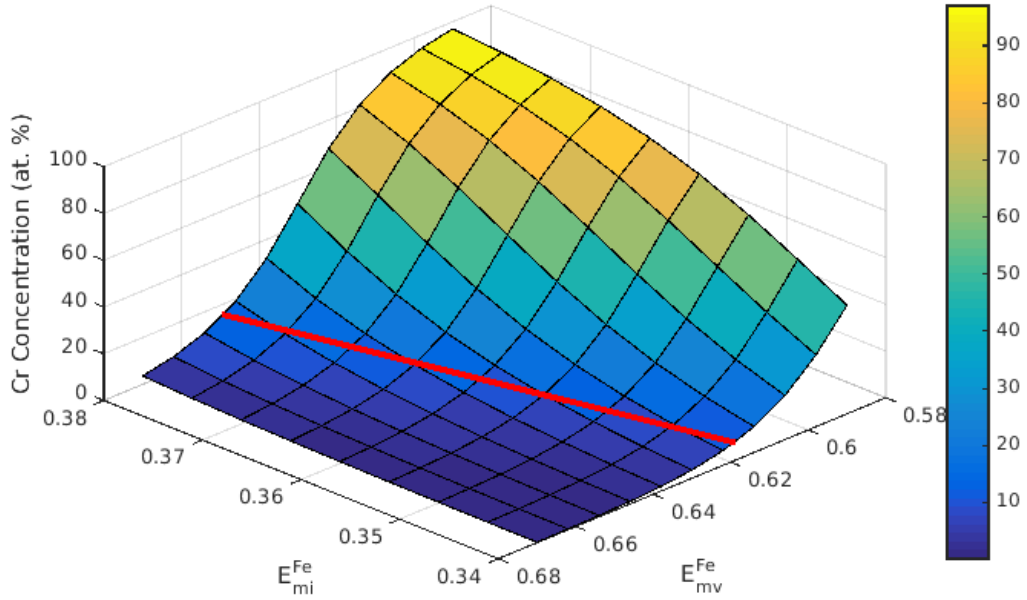


Figure 3.10: Final Cr concentration at the free surface as a function of the migration energy of interstitials and vacancies in Fe. The red line marks the the crossover from depletion to enrichment as predicted by the migration energy gap from equation (2.47).

Using this sensitivity study, we chose values for the migration energies that produce results consistent with reported values of segregation. These values are displayed in table 2.1.

3.2.1 Dose Dependence

To investigate the effect of dose on the segregation of Cr, we simulated a $2\ \mu\text{m}$ grain of an Fe-9 at.% Cr alloy and irradiated it to various doses at 400°C and a constant dose rate of 1×10^{-5} dpa/s. The resulting dose dependence is shown in Figure 3.11. Comparing this plot to the experimental values measured by Wharry et al., it is apparent that our model does not accurately represent the dose dependence observed from experiments, where the onset of Cr enrichment as well as the saturation occurred at a lower dose than experimentally observed [45].

The lack of consistency between the model and the experimental data could be due to the lack of microstructural evolution in the model, where the nucleation and growth of dislocation loops, which act as very strong defect sinks, which reduce the flux of defects to grain boundaries and increase the dose required to cause segregation as well as to reach steady state segregation [46]. The saturation of Cr enrichment is due to reaching a steady-state compositional gradient, and the back diffusion of Cr down this gradient, the first term in Equation (2.27) balances the defect-flux induced flow of Cr toward the sink, the second two terms in Equation (2.27) [34].

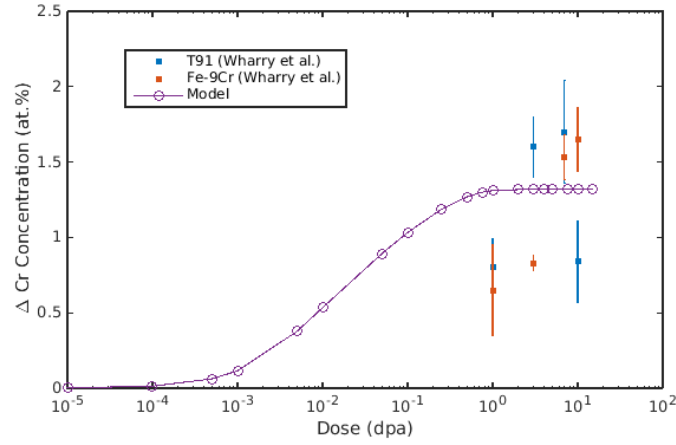


Figure 3.11: Final Cr concentration at the free surface as a function of dose at a dose rate of 1×10^{-5} dpa/s and at 400°C . The experimental values come from the systematic study performed by Wharry et al. [45].

3.2.2 Dose Rate Dependence

We looked at the dose rate dependence on the segregation of Cr as well, simulating a $2 \mu\text{m}$ grain of an Fe-9 at.% Cr alloy and irradiating it at various dose rates to 5 dpa at 400°C , as shown in Figure 3.12. The blue line represents the current model, with the thermal equilibrium boundary conditions, and the red line represents the model using a black sink boundary condition, where the interstitial and vacancy concentrations are set equal to zero at the sink. At low doses, the concentrations of interstitials and vacancies introduced through irradiation are not high enough to overcome the

concentrations from thermal equilibrium. Thus, the back diffusion of Cr dominates and there is very little Cr segregation. This behavior is not present when a black sink is modeled, as the concentration of defects at the sink is zero. As the dose rate increases, the concentrations of defects introduced from irradiation becomes greater than those from thermal equilibrium, and the Cr segregation increases. As the dose rate increases to very high doses, the recombination of defects begins to become prevalent as compared to the production of defects, thus the amount of segregation begins to decrease. The ratio of recombination to production as a function of dose rate is shown in Figure 3.13.

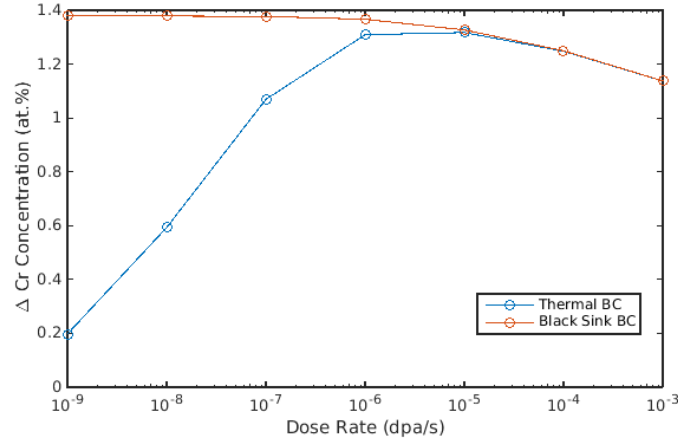


Figure 3.12: Change in Cr concentration at the free surface as a function of dose rate.

3.2.3 Temperature Dependence

To investigate the temperature dependence of Cr segregation, we simulated a 2 μm grain of an Fe-9 at.%Cr alloy and irradiated it at various temperatures to 5 dpa with a constant dose rate of 1×10^{-5} dpa/s, as shown in Figure 3.14. Once again, the blue line represents the current model, with the thermal equilibrium boundary conditions, and the red line represents the model using a black sink boundary condition, where the interstitial and vacancy concentrations are set equal to zero at the sink. At low temperatures, depletion is predicted, as vacancy-mediated diffusion dominates.

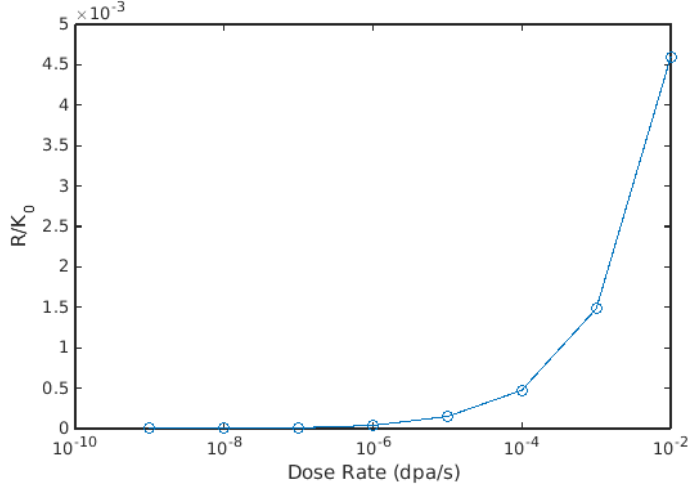


Figure 3.13: Ratio of the recombination rate to the production rate as a function of dose rate.

As the temperature increases, the segregation behavior changes from depletion to enrichment, and the model matches the experimental values reasonably well. As the temperature increases above about 450°C, the amount of segregation begins to decrease. This is due to back diffusion of Cr as the thermal concentrations of vacancies increase and the induce back diffusion of Cr. As such, the first term in Equation (2.27) balances the defect-flux induced flow of Cr toward the sink, the second two terms in Equation (2.27) [34]. Once again, this behavior is not present when a black sink is modeled, as the concentration of defects at the sink is zero. Further, at very high temperatures, the large defect concentrations also lead to high recombination rates, as shown in Figure 3.15.

To understand why we get depletion at low temperatures, we followed the method used by Wharry et al. by making an Arrhenius plot of the ratio of the diffusivities of Cr to Fe as a function of temperature, as shown in Figure 3.16 [46]. At low temperatures, the ratio of the vacancy diffusivity of Cr to Fe is higher than that of the interstitial diffusivity ratio, therefore the vacancy diffusion dominates driving Cr depletion. The ratio of the interstitial diffusion of Cr to Fe is greater at higher temperatures, and interstitial diffusion dominates, leading to Cr enrichment. The

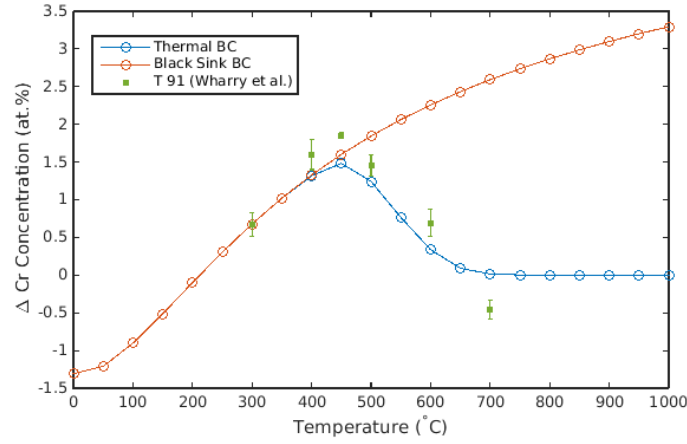


Figure 3.14: Final Cr concentration at the free surface as a function of temperature irradiated to 5 dpa at a dose rate of 1×10^{-5} dpa/s. The experimental values come from the systematic study performed by Wharry et al. [45].

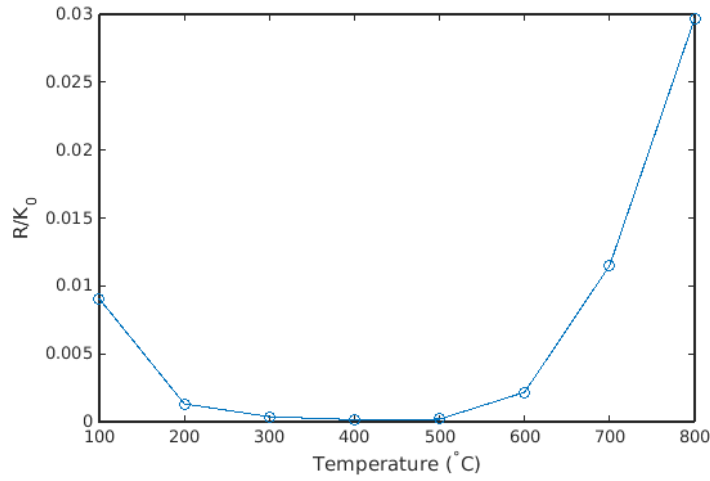


Figure 3.15: The ratio of the recombination rate to the production rate as a function of temperature.

temperature where the segregation of Cr crosses over from depletion to enrichment is predicted to occur around 200°C by the Arrhenius plot, and this is consistent with the plot of the temperature dependence. We also investigated how a small change in one of the migration energies would affect this temperature dependence, and with a change as small as 0.05 eV, the temperature dependence was greatly altered.

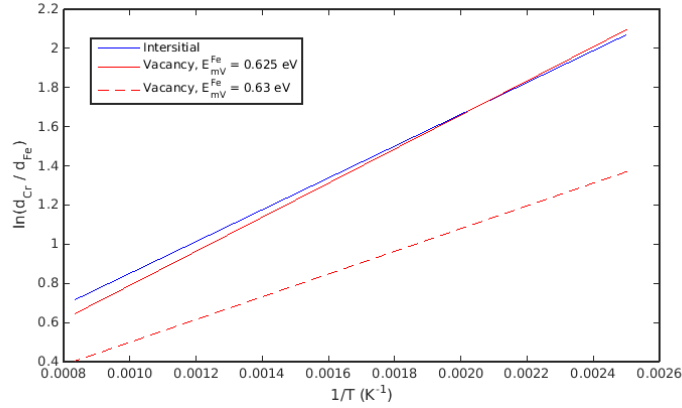


Figure 3.16: Ratio of the diffusivities of Cr to Fe as a function of temperature.

3.3 Concentration Dependence

A series of simulations were run to better understand the dependence of Cr enrichment on bulk Cr concentration. In these simulations, a grain size of $2\ \mu\text{m}$ was modeled for Fe-Cr alloys with varying concentrations of Cr. The alloy was then irradiated to 5 dpa at 400°C at a dose rate of 1×10^{-5} dpa/s. The change in the concentration of Cr at the sink as a function of initial Cr concentration is shown in Figure 3.17. Comparing this to experimental results measured in the systematic study by Wharry et al., the concentration dependence of the model appears to be opposite of these experimental results [45]. The reason for the increasing segregation with increasing bulk Cr concentration is due to the segregation terms in the model scaling with Cr concentration, and the back diffusion terms scaling with its derivative. Therefore a high bulk concentration requires a higher peak at the boundary to achieve balance. The concentration dependent thermodynamic factor was not enough to account for the experimentally observed behavior; thus, other concentration dependent parameters, such as migration energies and diffusivity prefactors, could be the answer.

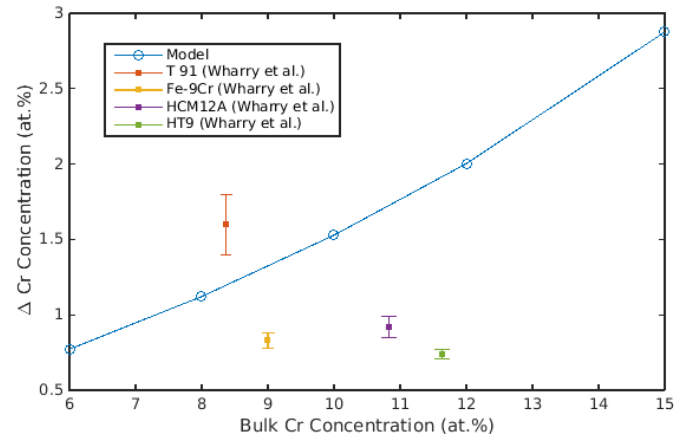


Figure 3.17: Change in Cr concentration at the free surface as a function of initial bulk Cr concentration. The experimental values come from the systematic study performed by Wharry et al. [45].

Chapter 4

Conclusion

The results of experiments to study RIS in FM steels are difficult to understand with qualitative arguments. Therefore, it is necessary to use models to predict this behavior. Using input parameter values obtained from ab initio calculations and a model developed by Wiedersich et al. [47], a program was written to gain insight into the effect of RIS on FM steels.

By performing a sensitivity analysis, it became apparent that the model is extremely sensitive to the input parameters, particularly the values chosen for the migration energies. In further study, by changing the value of migration energies by as little as 0.08 eV, the enriched Cr concentration at the sink could vary by more than 90 at.%.

Within some experimental regimes, the model has reasonable values given the chosen input parameters. For example, at intermediate temperatures, the model appears to compare well to experimental measurements. The temperature dependence of the model compared well with experiments, with a peak segregation occurring at about 450 °C, and a lack of segregation at higher temperatures due to the balancing of the back diffusion and defect flux terms.

The lack of accuracy in the dose dependence is likely due to microstructural evolution, such as the nucleation and growth of dislocation loops, which act as very

strong defect sinks, reducing the flux of defects to grain boundaries and increasing the dose required to cause segregation as well as to reach steady state segregation. The model predicts the dose for the onset of segregation much too low, as well as the dose at which saturation occurs, which is due to the balancing of the back diffusion and defect flux terms. The concentration dependence has the opposite effect from experiments, due to the segregation terms scaling with the Cr concentration and the back diffusion terms scaling with its derivative. Therefore a high bulk concentration requires a higher peak at the boundary to achieve balance. The concentration dependent α value was not enough to account for the experimentally observed behavior. Other concentration dependent parameters, such as migration energies and diffusion prefactors, could provide the solution to this issue. With a careful selection of input parameters, accurate results could be determined from this simple model; however, considering the extreme sensitivity, this model may not be the best choice to model RIS.

4.1 Outstanding Issues

In moving forward with this work, it is necessary to have a more in depth analysis of how concentration dependent parameters, such as migration energies and diffusion prefactors, affect the resulting Cr concentrations. Further, it is important to include other physical characteristics into the model, such as cascade effects, self-clustering of interstitials and vacancies, dislocation loops, voids, and grain boundary misorientations. It is also necessary to look at the effect of precipitates, particularly carbides, on the Cr segregation behavior.

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Vita

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