NOVEL PRECIPITATE STRUCTURES IN ALLOYS UNDER IRRADIATION

BY

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DISSERTATION

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We investigate the fundamentals of precipitate stability under energetic particle irradiation, towards the goal of better controlling the microstructures of driven alloys. First we focus on an irradiation-induced precipitate-within-precipitate structure, which is referred to as “cherry-pit” structure. We show by computer simulation and analytical modeling that the formation of cherry-pit structure is a special instance of compositional patterning, and that the conditions for compositional patterning and the formation of cherry-pit structures are related, but different from each other. Then we develop a new kinetic Monte Carlo model, which includes the generation, recombination, and sink elimination of irradiation-induced point defects, as well as ballistic mixing. With this tool we explore the possibility of using point-defect sinks to alter the temperature range where compositional patterns are stable. This novel approach for optimizing radiation-resistant materials is then tested experimentally using a Cu-Ag-W model alloy. Lastly we show that the addition of a high density of W nanoparticles dramatically alters the coarsening behavior of precipitate-hardened Cu-Ag alloys. First, the nanoparticles suppress precipitate growth, but far more surprisingly they induce non-equilibrium Ag wetting layers on grain boundaries. This observation is explained using kinetic Monte Carlo simulations, which show that caging of Ag precipitates by the W nanoparticles suppresses their growth and drives the formation of the wetting layers.
To my family
Every now and then, I recall that summer morning when I arrived in Champaign-Urbana. It rained the night before. The moisture in the air reminded me of Hefei, where I spent my college years. Yes, it was love at first sight. The love became deeper and deeper over time, as I met all the good people in this small town. It’s hard to believe that time went by so fast, and now it’s my time to say goodbye. I’m terrified of the thought that years later when I come back, things remain as ever, yet people are here no more.

I can still remember the afternoon when I had the first meeting with my advisors, Prof. Pascal Bellon and Prof. Bob Averback. Pascal and Bob explained to me the general concept of driven alloys, and the methods that the group used to investigate the problems. By that time, I did not know exactly what “plastic deformation” meant, and my understanding of the word “creep” was a reptile crawling slowly, with nothing related to applied stress. Now I’m finishing my PhD. I have grown up, not by myself, but with the help and care of my advisors. In the journey of the past five years, the road wasn’t always straight. But Pascal and Bob always showed me their support, guiding me when I was lost, encouraging me when I felt frustrated. They also showed me what it takes to be a real scholar- curiosity, critical thinking, and dedication. I’m grateful to them.

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and we had beers together at Crane Alley. Both are fun experiences. With them, my life as a graduate
student is much more colorful. I feel blessed to have all of them in my life.

I would like to thank my parents, for all the care and love they gave me in the past twenty seven years.
They have worked hard to bring food to the table, and provided me with good education. They gave me
trust and freedom of choosing my career. I’m proud of them, and I wish I can be the son that they are proud
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Chapter 1

INTRODUCTION

In recent years, great efforts have been made to develop new generation of nuclear reactors, which aim for advances in sustainability, safety and reliability. The new reactors will operate at higher temperatures than current reactors, and the materials will be subjected to higher irradiation doses. As the containment (fuel cladding, reactor pressure vessel, etc.) of nuclear fuel and fission products, new high-performance structural materials will be critical for the success of proposed nuclear reactors. Specially, nanostructured material (NM), a material with microstructural characteristic length scale below 100 nanometers, has drawn great interest. It has been found that the properties of NMs are often superior to their coarse-grained counterparts. For instance, NM exhibits increased strength, which is captured by the Hall-Petch relationship [1, 2], and it is rationalized by the suppression of dislocation movement due to high density of grain boundaries. However, simple NMs are often far from their thermodynamic equilibrium. The high density of interfaces (grain and phase boundaries) increases the Gibbs free energy significantly. As a result, the nano-scale microstructures in NMs are prone to coarsening, which limits their application at high temperatures. In addition, irradiation environments can significantly accelerate the kinetic evolution of materials by introducing a supersaturation of point defects, resulting in radiation enhanced diffusion (RED) [3]. However, at the same time, irradiation also introduces chemical mixing by randomly displacing atoms from their original positions. Previous works have shown that, in immiscible alloy systems, the dynamical competition between the thermally activated decomposition and the chemical mixing forced by irradiation can lead to the stabilization of self-organized steady state compositional patterns, and it has been proposed that this self-organization is a promising approach to maintain the nano-scale microstructures under irradiation [4].

Solid progress has been made in the past 30-40 years to investigate self-organization of alloys under irradiation, with theoretical, computational, and experimental approaches. There has been a series of modeling works by Nelson et al. [5], Frost et al. [6, 7], Martin [8], and Enrique et al. [9, 10], which successively resolved many of the microstructure stability issues in irradiated alloys. While the models by Nelson et
al., Frost et al., and Enrique et al. differ in their treatment of the chemical mixing forced by irradiation, they all predict a maximum temperature for self-organization for a given irradiation condition. Later, it has been experimentally reported that, for a series of Cu alloys investigated in a systematic way, this maximum temperature is inversely related to the diffusion coefficient of the solute atoms, and thus by choosing a slower diffuser, one can maintain self-organization at higher temperatures [10, 11, 4, 12, 13].

However, the evolution of the microstructures of these materials under irradiation is far from being well understood. In this Ph.D. work, we attempt to combine theoretical, computational, and experimental approaches to answer several key questions that need to be addressed for realizing the full potential of self-organized microstructures as radiation-resistant materials. In particular one needs to determine the exact nature of the self-organized precipitates, and to understand how defect fluxes and sinks impact compositional patterning. Also, engineered materials often contains several populations of precipitates and it is thus important to consider how these distinct populations could interact. Specifically, this dissertation covers three particular topics:

- The mechanism responsible for the stabilization by irradiation of a complex precipitate-within-precipitate structures, referred to as “cherry-pit” structures, observed in experimental studies of irradiated Cu-Fe and Cu-V alloys.

- The effect of point-defect sinks on compositional patterning, and the possibility of increasing the maximum temperature for compositional patterning by introducing high density of point-defect sinks.

- The pinning effect of non-wetting nanoparticles on precipitate evolution and the underlying mechanism.

In Chapter 2 we review the key processes of ion-solid interactions and we then discuss the past investigations of self-organization in irradiated alloys. In Chapter 3, we describe a kinetic Monte Carlo (KMC) model which takes into account both thermal diffusion and ballistic mixing, and we use this simulation tool to systematically investigate the effect of thermodynamic and kinetic asymmetry on the stability of cherry-pit structures. An analytical model is developed to rationalize the results of both simulations and experiments. In Chapter 4 we extend the above KMC model to take into account non-conserved point defects, by introducing the generation of Frenkel pairs, and their elimination by recombination and by annihilation on sinks. Then we use the model to study the effect of point defect sinks on compositional patterning. In Chapter 5 we use a model Cu-Ag-W ternary alloy to validate experimentally the predictions of the model discussed in Chapter 4, using room-temperature irradiation as a first processing step to induce a high density of W nanoparticles, which will serve as point defect sinks. We also discuss in chapter 5 the possibility of using non-wetting nanoparticles to slow the coarsening kinetics during annealing, as well as inducing non-equilibrium...
grain boundary wetting layers, using both a Cu-Ag-W model alloy and KMC simulations. We summarize
the work and discuss future research directions in Chapter 6.

Some of the results presented in this dissertation have been published [14, 15, 16, 17], or prepared for
publication [18].
Chapter 2

BACKGROUND

2.1 Ion-solid interactions

2.1.1 Radiation damage and spikes

Bombardment of a crystal with energetic (KeV to MeV) heavy ions produces regions of disorder. As an ion enters the crystal, it makes a series of collisions with the lattice atoms. The incident ion slows down and finally comes to rest in the crystal, or passes through if the target crystal is thin enough. In these collisions, lattice atoms can be knocked out of their original lattice site and gain part of the energy of the incident ion. These lattice atoms displaced by incident ions are called primary knock-on atoms (PKAs). The PKAs can then pass on their energy to other lattice atoms, which can further displace more lattice atoms. The series of collision and the process of energy transfer result in a collision cascade. Seeger [19] described many processes in the cascade, as shown in Fig. 2.1, which illustrates replacement collision sequences [20], focusons [21], exchange collisions, and channeling events.

During the process of a collision cascade, irradiation damage happens. An important quantity in determining the spatial distribution of irradiation damage is the mean free path of an energetic particle between displacement collisions. It is suggested that when the mean free path of energetic particles in a cascade approaches the atomic spacing of the target atoms, a highly damaged region is formed, which is characterized by the formation of a underdense region (enriched in vacancies) in the center of the cascade, and an overdense region (enriched in interstitials) around it [22], caused by the injection of atoms from the cascade core. This highly damaged volume of material is referred to as a thermal spike. If the kinetic energy of atoms inside the spike is converted into temperature, it can be found that the typical temperature is on the order of $\sim 10000$ K, much higher than the melting point of normal metallic materials [23, 24]. Thus the region can be viewed as a local melt, which persists for several picoseconds and then cools down [25].
2.2 illustrates the liquid Au atoms in a thermal spike, simulated using molecular dynamics (MD) simulation [26]. The volume of the cascade can be approximated by

\[ V_{\text{cascade}} = \frac{4\pi}{3} (\frac{(\delta \Delta X)^2 + 2(\delta Y)^2}{2})^{2/3}, \]  

(2.1)

where \((\Delta X)^2\) and \(Y^2\) are the longitudinal and the transverse moments of the deposited damage energy distribution for an individual cascade, and \(\delta\) is a contraction factor that accounts for the difference between an individual cascade and the average cascade determined by transport theory [27]. The calculated volume leads to a cascade size on the order of several nanometers. Then, during the cooling down stage, the local melted zone returns to the condensed stage, and thermodynamic equilibrium is established, with stable point defects or defect clusters forming. At a longer time scale, thermally activated diffusion of mobile defects happen, until they annihilate by local recombination or escape the cascade zone. The cascade development can then be divided roughly in four stages: collisions, thermal spike, quenching, and annealing. As for defect production, since the core of the thermal spike region is enriched by vacancies, only those interstitials that escape the core region via low index replacement sequences eventually survive recombination. The surviving vacancy-interstitial pairs are referred to as Frenkel pairs.

To determine the number of point defects generated in a cascade, Kinchin et al. proposed an analytical model [28], which assumed that the number of point defects generated by a primary recoil is proportional to
the energy transferred from the ion to the PKA. Norgett et al. modified the original Kinchin-Pease model, and proposed the modified Kinchin-Pease, or NRT model [29], which gives the number of Frenkel-Pairs generated by a PKA

\[ N_d = \frac{0.8E_D}{2E_d}, \]  

(2.2)

where \( E_D \) is the damage energy, which is the amount of PKA energy lost through nuclear collisions, and \( E_d \) is the average displacement energy, which is directional dependent. King et al. [30] measured \( E_d \) for Cu, obtaining \( E_d(110) = 23 \) eV, \( E_d(100) = 19 \) eV, and \( E_d(111) = 76 \) eV.

![Figure 2.2: Liquid atoms in 10 keV cascades in Au. Adapted from Ref. [26].](image)

The NRT formula however ignores collective effects, and it has been estimated that only a small fraction of the point defects initially created in the spike can survive when the melt cools down. This fraction is defined as the displacement efficiency, \( \xi \). Typical values of \( \xi \) range from a few percent to 30%.

A commonly used measure of irradiation damage is displacements per atom or dpa. If we say that a material experiences a damage of 1 dpa, it means that, on average, each atom in the material has been displaced once. The measure of the irradiation damage rate, or dpa rate, is the number of displacements per atom happened in unit time, i.e., dpa/s. This rate ranges from \( \sim 10^{-6} \) for neutron irradiation to \( \sim 10^{-2} \) for heavy ion irradiation.
2.1.2 Ion-beam mixing

Ion-beam mixing (IM) is the atomic intermixing and alloying that can occur at the interface separating two different materials during ion irradiation [31]. The interface can be separating two planar multilayer, or between the matrix and a precipitate, in which case the details of mixing often involve the effect of the curvature of the interface.

Depending on the properties of the incident ion (mass, energy, etc.), there can be different mechanisms for IM: recoil mixing and cascade mixing. For recoil mixing, near a interface the incident ion strikes a local atom, which can recoil far from the initial location and cross the interface, causing mixing. For example, a helium atom can be re-injected into the matrix from the gas bubble by an incident ion. For heavy ion implantations, cascade mixing is more important. As discussed previously in this section, a collision cascade involves a collection of energy transferring collisions. After several such collisions, the momenta of the incident ion and recoil atoms become randomized, and the the relocation of most displaced atoms is a stochastic process [27]. Accurate results of the mixing during the cascade can be obtained from TRIM simulations [32]. The number of atomic jumps in a cascade can be estimated by the modified Kinchin-Pease expression described in Sec. 2.1.1. By assuming that there are $b$ replacements per atomic displacement (typical values range from $\sim 10^0$ to $10^2$), we can write the mixing as

$$n = \frac{0.8bE_D}{2E_d}.$$  \hfill (2.3)

2.1.3 Radiation-enhanced diffusion

Diffusion coefficient of lattice atoms via the vacancy mechanism in a pure $A$ metal is given by

$$D_A^v = f_v D_v C_v,$$  \hfill (2.4)

where $f_v$ is the correlation factor, $D_v$ is the vacancy diffusion coefficient, and $C_v$ is the vacancy concentration. If there exists other mechanisms of diffusion, such as interstitial mechanism, di-vacancy mechanism, etc., the $A$ diffusion coefficient can be written as

$$D_A = f_v D_v C_v + f_i D_i C_i + f_{2v} D_{2v} C_{2v} + \cdots$$  \hfill (2.5)

As discussed in Sec. 2.1.1, under irradiation, point defects will be introduced in excess of their equilibrium concentration, increasing $C_v$, $C_i$ and $C_{2v}$ compared to non-irradiated situation. Thus the $A$ diffusion co-
efficient under irradiation is expected to increase, which lead to radiation-enhanced diffusion (RED). The radiation-enhanced diffusion coefficient is denoted as $D_A^{RED}$. Next we use reaction rate theory to reveal how irradiation can affect diffusion within different temperature ranges.

The evolution of point-defect concentration is a result of a competition between defect creation, mutual recombination, and sink elimination. The surviving point defects from the thermal spikes can migrate thermally, either finding an opposite defect and undergo recombination with it, or being absorbed by a point-defect sink, such as grain boundaries, semi-coherent or incoherent precipitate/matrix interfaces, or voids, etc.

These processes can be described using the following rate equations [3, 33],

$$\frac{dC_v}{dt} = K_0 - K_{iv}C_iC_v - K_{vs}C_vC_s,$$

$$\frac{dC_i}{dt} = K_0 - K_{iv}C_iC_v - K_{is}C_iC_s,$$

(2.6)

where $C_v$ and $C_i$ are the concentrations of vacancy and interstitial, $K_0$ is the defect production rate, $K_{iv}$ is the recombination rate coefficient, $K_{vs}$ and $K_{is}$ are the defect-sink reaction rate coefficients for vacancies and interstitials. Eq. (2.6) assumes uniformity, i.e., both the point defects and the sinks are uniformly distributed in the system. If one desires to consider a local sink explicitly, a net flow of point defects will be present, and a diffusion term $\nabla \cdot D_x \nabla C_x$ needs to be added to the r.h.s. of Eq. (2.6), where $x$ is either $v$ or $i$ for the two equations. Otherwise, it can be assumed that $\nabla C_v \approx 0$ if the mean defect separation is greater than the mean distance between sinks. Solving Eq. (2.6) and use Eq. (2.5), we can obtain the atomic diffusion coefficient for a pure metal. As pointed out in Ref. [33], doing this requires several approximations: correlation effect is neglected, i.e., $f = 1$; the sinks do not evolve, and are unsaturable; defect clustering is neglected; sinks are un-biased and there is no preferential absorption of a certain species of defect for the sinks; thermal defects are neglected.

The rate constants are given as follows:

$$K_{iv} = 4\pi r_{iv}(D_i + D_v)$$

$$K_{is} = 4\pi r_{is}D_i,$$

$$K_{vs} = 4\pi r_{vs}D_v.$$  

(2.7)

We focus here on steady states, i.e., $dC_v/dt = dC_i/dt = 0$, and the situation of $\nabla C_v \approx 0$. Solving Eq. (2.6) yields the steady state defect concentration as follows,
\[ C_s^v = -\frac{K_{is}C_s}{2K_{iv}} + \left[ \frac{K_0 K_{is}}{K_{iv}K_{vs}} + \frac{K_{vs}^2 C_s^2}{4K_{iv}^2} \right]^{1/2}, \]
\[ C_s^i = -\frac{K_{iv}C_s}{2K_{iv}} + \left[ \frac{K_0 K_{iv}}{K_{iv}K_{is}} + \frac{K_{is}^2 C_s^2}{4K_{iv}^2} \right]^{1/2}. \]

(2.8)

For the case of low temperature and low sink density, \( C_s \) is small, defects annihilate mainly by mutual recombination, i.e., the system is in the recombination regime. The vacancy and interstitial concentrations described in Eq. (2.8) can be approximated as

\[ C_s^v \approx \sqrt{\frac{K_0 K_{is}}{K_{iv}K_{vs}}}, \]
\[ C_s^i \approx \sqrt{\frac{K_0 K_{iv}}{K_{iv}K_{is}}}. \]

(2.9)

In case of high temperature and high sink density, the high defect annihilation rate at sinks keeps the concentration of interstitials low, and recombination does not contribute much. The system is then in the sink elimination regime, yielding the steady state solution

\[ C_s^v \approx K_0 \frac{K_{vs}}{C_s}, \]
\[ C_s^i \approx K_0 \frac{K_{is}}{C_s}. \]

(2.10)

Making use of Eq. (2.7), taking advantage of the fact that \( D_i \gg D_v \), and only considering diffusion by vacancy mechanism for simplicity, we obtain the atomic diffusion coefficient in recombination regime:

\[ D_A = D_v C_v = D_v \sqrt{\frac{K_0 K_{is}}{K_{iv}K_{vs}}} \approx \sqrt{\frac{K_0 r_{vs} D_v}{4\pi r_{iv} r_{vs}}} \propto (D_v)^{1/2}. \]

(2.11)

In sink elimination regime, the atomic diffusion coefficient is

\[ D_A = D_v C_v = D_v \frac{K_0}{K_{is} C_s} = \frac{K_0}{4\pi r_{vs}} \propto (D_v)^0. \]

(2.12)

Since \( D_v \propto \exp\left(-\frac{E_{\text{mig}}}{kT}\right) \), we see that in recombination regime and sink elimination regime the atomic diffusion coefficient has different temperature dependence. These two relationships are illustrated in Fig. 2.3, which shows the effect of different combination of defect production rate and sink density (linear sinks like dislocations) on radiation-enhanced diffusion in pure Cu [34].

9
2.2 Irradiation-induced self-organization

In some complex equilibrium systems, there exists a competition between interactions, with different characteristic length scales, for example when short-range attractive chemical interactions compete with long-range repulsive electrostatic or elastic interactions [35, 36, 37]. These competitions can result in nanoscale self-organization, and produce highly stable microstructures. For an non-equilibrium situation, like materials under irradiation, the two competing processes are the radiation-enhanced diffusion, which tends to reorder the system, and the irradiation-induced chemical mixing, which continuously disorders the system.

Several models have been developed to describe systems under irradiation and predict the possible steady-state configurations. Some models relied on an approximation that treats ballistic mixing as a “uni-directional” process, i.e., the mixing is restricted to the resolution of solute atoms from the precipitates to the matrix. Using this strategy, Nelson and coworkers [5] developed a model, which predicts that a single steady-state precipitate size is stable under a given irradiation condition. Apart from the “uni-directional” mixing approximation, the model made another critical assumption, assuming that the average relocation distance $R$ can be arbitrarily large, which is unphysical. Frost and Russell [6, 7] improved the model by assuming that an atom in the precipitate is displaced by a vector of random magnitude and direction within a sphere with radius $R$. For a given temperature and relocation distance $R$, the Frost-Russell model predicts a critical irradiation flux, above which the system undergoes “inverse coarsening”, i.e., unlike the classi-
Ostwald ripening description, precipitates with smaller radius would coarsen at the expense of larger precipitates. This critical flux is given by

$$\phi_{\text{F-R critical}} = \frac{48 D_{\text{solute}} c_{\infty} r_{\text{cap}}}{R^3},$$  \hspace{1cm} (2.13)

where $D_{\text{solute}}$ is the irradiation-enhanced solute diffusivity, $c_{\infty}$ is the equilibrium interface solute concentration for a planar interface, and $r_{\text{cap}}$ is the capillary length.

While the models described above can explain some of the experimental observations, neglecting the transport of solute atoms from the matrix to the precipitates leads to some incorrect predictions. Details can be found in Ref. [38]. There are further modeling efforts that uses correct description of the irradiation-induced chemical mixing. Next we will briefly review the model by Martin [8] and the model by Enrique and Bellon [9].

### 2.2.1 Theory of effective temperature

Martin [8] proposed a mean-field description of solid solutions in the presence of irradiation-induced chemical mixing. Treating the short-range ballistic mixing as a forced diffusion process, Martin looked for steady-state solutions of the diffusion equation in the presence of ballistic diffusion. Under the framework of this model, ballistic effects can be captured by a law of corresponding states: at a given temperature $T$ and irradiation flux $\phi$, the steady-state configuration of the system would be the same as a system outside irradiation ($\phi = 0$) at a temperature of $T' = T(1 + \Delta)$, where $\Delta$ is a function of the irradiation flux and temperature as well as of materials parameters. Specifically,

$$\Delta = \frac{D_b}{\bar{D}_{\text{irr}}},$$  \hspace{1cm} (2.14)

where $D_b$ is the ballistic diffusion coefficient, $\bar{D}_{\text{irr}}$ is the interdiffusion coefficient, accelerated by irradiation. For a crystal with cubic symmetry, $D_b = R^2 \Gamma_b / 6$, where $\Gamma_b$ is the frequency of ballistic replacements per atom, which is proportional to the irradiation flux. Therefore, a non-zero irradiation flux leads to positive value of $\Delta$, and the system behaves as if it is at equilibrium at a higher temperature. $T'$ is thus referred to as the *effective temperature*. Fig. 2.4 shows typical variations of $T'$ as a function of different $\Delta$ values, assuming that point defects are in the recombination regime.

This model can predict the irradiation-increased solubility, i.e., the solvus temperature under irradiation,

$$T_{\text{solvus}}^{\text{irr}} = T_{\text{solvus}}^{\text{thermal}} / [1 + \Delta],$$  \hspace{1cm} (2.15)
where \( T_{\text{thermal}} \) is the equilibrium solvus. This is illustrated in Fig. 2.5, which plots different solvus with different values of \( \Delta \).

Figure 2.5: Solubility limit under irradiation, as a function of \( \Delta \) (\( \Delta = 10^{-8}, 10^{-6}, 10^{-4} \)). Adapted from Ref. [8].

Thus, for an immiscible alloy, the effective temperature model predicts that precipitates will not be stable under irradiation if the effective temperature exceeds the solvus temperature. This critical flux is given by

\[
\phi_{\text{critical}} = \frac{\bar{D}_{\text{arr}} [4c(1-c)T_c - T]}{T R^2},
\]

\[(2.16)\]
where $\sigma_r$ is the replacement cross section, $T_c$ is the critical temperature for the immiscible system, and $c$ is the composition at the critical temperature. This critical flux for dissolution scales as $1/R^2$, unlike the critical flux for inverse coarsening, described by Eq. (2.13), which scales as $1/R^3$. Note that the $1/R^3$ dependence is not in Martin’s model. Fig. 2.6 illustrates the different characters of these two critical fluxes.

Figure 2.6: Schematic plot of the dynamical boundary separating macroscopic coarsening from inverse coarsening and from precipitate dissolution. Adapted from Ref. [38].

The different dependences of these boundaries with the irradiation flux lead to the existence of a threshold value $R_c$ for the relocation distance for inverse coarsening to take place.

2.2.2 Compositional patterning under irradiation

The models described so far suffer from important limitations. For instance, Frost-Russel model predicts the regime of inverse coarsening, but $R_c$ is absent from it (see Fig. 2.6). The Martin model, while more complete in physics, fails to predict inverse coarsening, since it only considered ballistic mixing between nearest neighbors. These limitations were overcame by a model developed by Enrique and Bellon [9], as described in this section.

Enrique and Bellon’s model is based on a phase-field-type description, considering a one-dimensional system which has short-ranged thermally driven diffusion competing with finite-ranged athermal atomic exchanges. The equation describing the temporal evolution of local deviation from the nominal concentration $\psi(x) = c(x) - \bar{c}$ is composed of two terms, one for thermal diffusion and another one for ballistic mixing [8]:

$$\frac{\partial \psi}{\partial t} = \frac{\partial \psi^{\text{th}}}{\partial t} + \frac{\partial \psi^{\text{bal}}}{\partial t}.$$  (2.17)

The first term is given by $M \nabla^2 \left( \frac{\delta F}{\delta \psi} \right)$, where $M$ is the solute mobility, $F$ is the global equilibrium free
energy. The second term is given by

\[
\frac{\partial \psi_{\text{bal}}}{\partial t} = -\Gamma \sum_j w_j (\psi_i - \psi_{i+j}) = -\Gamma (\psi_i - \langle \psi \rangle),
\]

(2.18)

where \(w_j\) is a normalized weight function describing the distribution of ballistic exchange distances, and the brackets denote the corresponding (discrete) weighted spatial average. Thus we obtain the governing equation as

\[
\frac{\partial \psi}{\partial t} = M \nabla^2 \left( \frac{\delta F}{\delta \psi} \right) - \Gamma (\psi - \langle \psi \rangle_R).
\]

(2.19)

For \(F\) a Ginzburg-Landau free energy is used,

\[
F = \frac{1}{\Omega} \sum (-A \psi^2 + B \psi^4 + C |\nabla \psi|^2) dx.
\]

(2.20)

The relocation distances of ballistic jumps is given by a distribution \(w_R\). If chosen as an exponential decay, it allows analytical treatment of the minimization problem. Using a variational analysis, one can obtain a map of the stable steady states, i.e., the dynamical phase diagram, as shown in Fig. 2.7.

Figure 2.7: Steady-state phase diagram for an equiatomic model immiscible binary alloy. \(R\) is the average relocation distance of ballistic jumps, and \(\gamma\) represents the forcing intensity (see text and Eq. (4.1) for definition). \(R\) and \(\gamma\) are given in units of the A and C Ginzburg-Landau free energy parameters used in Ref. [9]. Adapted from Ref. [9].

As shown in Fig. 2.7, at small \(R\) values, as the forcing parameter \(\gamma = \Gamma_b/M\) increases, the alloy undergoes
a transition from macroscopic phase separation to a solid solution. When the relocation distance is larger than a critical value $R_c$, given by $\sqrt{C/A}$, the system can phase separate at an intermediate length scale, given by the irradiation conditions. This is the so-called “compositional patterning” regime. A series of KMC simulations have been carried out to verify this dynamical phase diagram [9, 10, 14, 16], and they agree well with the model prediction. Typical value $R_c$ ranges to 1 to a few nearest neighbor distances. It is expected that $R > R_c$ for heavy ion or neutron irradiation, but $R < R_c$ for electron or proton irradiation.

2.2.3 Experimental study of self-organization in binary Cu alloys

Experimental studies have been carried out to study self-organization under irradiation in binary Cu alloys. Cu alloys are particularly useful in the study of self-organization, because Cu is immiscible with many transition metals, but the degree of the immiscibility varies from very small (Ni) to very high (W). In addition, diffusion data is readily available for many elements in Cu matrix [39, 40, 41]. These properties of Cu alloys reduce the complexity of analysis, and enable a systematic study. In the next two subsections, we next review past experiments on two series of Cu alloys: one set with solutes that are moderately immiscible with Cu, such as Ag, Fe, Co; the other set with solutes that are extremely immiscible with Cu, such as Mo and W.

Moderately immiscible binary Cu alloys

The moderately immiscible binary Cu alloys are characterized by a miscibility gap in the solid phase, and a full miscibility in liquid phase at high temperatures. An example of such systems is Cu-Ag. The equilibrium phase diagram is shown in Fig. 2.8 [42]. For moderately immiscible Cu alloy, it is assumed that full mixing (truly ballistic mixing) will take place in the cascade, since $\Delta H_{\text{mix}} \ll \Delta E_{\text{cascade}}$. The system can be driven to a solid solution under irradiation at low enough temperature.

Enrique et al. [10] studied Cu-Ag multilayered thin films irradiated by MeV Kr ion, from room temperature to 225 °C, using cross-sectional electron microscopy. They found that the grain growth and phase separation are decoupled, and that semicoherent decomposition happens at a scale of several nanometers. This finding shows indirect evidence of self-organization in the system. Chee and coworkers further studied the Cu-Ag system, irradiating samples starting from solid solutions at temperatures varying from room temperature to 300 °C, using 1.8-MeV Kr ions. They used both X-ray diffraction and TEM to examine the Ag precipitate evolution, and found out that the maximum temperature for self-organization is 175 °C. Fig. 2.9 shows the evolution of Ag precipitate sizes with increasing dose for temperatures from 150 °C to 200 °C, around the transition from compositional patterning to macroscopic phase separation.
Krasnochtchekov et al. [11] studied self-organization in Cu$_{1-x}$Co$_x$ (10% ≤ x ≤ 20%) alloys under 1-MeV Kr irradiation, using magnetization measurements to determine the precipitate size. Fig. 2.10 plots the Co precipitate size dependence on temperature for a Cu$_{65}$Co$_{15}$ alloy. They found out that below 140 °C the alloy is driven to a solid solution, while above ~ 300 °C the system would enter the macroscopic phase separation regime.
Figure 2.10: Evolution of Co precipitate sizes with increasing irradiation dose for a Cu$_{85}$Co$_{15}$ alloy. Data are from magnetization measurements. Adapted from Ref. [4].

Similar experiments were performed on a Cu$_{88}$Fe$_{12}$ alloy, and atom probe tomography (APT) was used to determine the Fe precipitate size. The maximum temperature for compositional patterning was found to be 250 $^\circ$C.

**Highly immiscible binary Cu alloys**

For alloy systems like Cu-Mo and Cu-W, the two alloying elements are so immiscible that even at liquid phase they would keep phase separated. To illustrate this point, we show the Cu-W phase diagram in Fig. 2.11, in which we see a miscibility gap above 3414 $^\circ$C, in the liquid phase. In this case, it is probably no longer correct to neglect chemical effects in thermal spikes, and the Enrique-Bellon model is no longer applicable. The consequences on precipitation reaction will be discussed below.

To study the stability of Mo and W precipitates under irradiation, Chee et al. and Vo et al. [4, 12] studied dilute Cu-Mo and Cu-W alloys both experimentally and computationally. The microstructural stability of Cu$_{90}$Mo$_{10}$ and Cu$_{90}$W$_{10}$ alloys under irradiation is remarkable. The core results of the studies are shown in Fig. 2.12. Mo and W begin to precipitate thermally at $\sim$ 400 $^\circ$C and $\sim$ 550 $^\circ$C, respectively. Significant thermal coarsening occurs only above $\sim 0.6T_m$ for Cu$_{90}$Mo$_{10}$ and $\sim 0.8T_m$ for Cu$_{90}$W$_{10}$, as the thermal diffusion becomes important. Precipitation growth in the same samples irradiated to a dose of $\sim 3 \times 10^{16}$ cm$^{-2}$ show different behavior. Both Mo and W precipitate during irradiation at room temperature, but they show little coarsening until higher temperatures. For both alloys, the precipitate size increases from $\sim 3$ to $\sim 5$ nm as the temperature is increased from RT to 550 $^\circ$C. However, at a given temperature, the precipitate
size saturates, i.e., stops growing after $\sim 10$ dpa. The precipitates only start to coarsen at temperatures at which thermal diffusion dominates.

Figure 2.12: Precipitate size vs. temperature during thermal annealing or irradiation at high temperature in CuMo and CuW alloys. Adapted from Ref. [12]
For alloys such as Cu-Mo and Cu-W, the effect of IM is different from that on moderately immiscible alloy systems, where IM can lead to complete dissolution of precipitates. As discussed previously in this chapter, IM comprises both recoil mixing and cascade mixing. Since Mo and W are strongly immiscible in Cu, only recoil mixing contribute to IM. The effect of recoil mixing is relatively small, resulting in slow dissolution rates. MD simulations [12] suggests that precipitates nucleate in the thermal spike and then grow by cluster aggregation in subsequent cascade events. After precipitates grow to the approximate dimensions of the cascade melt, they can no longer diffuse in the thermal spike, and further coarsening is then suppressed. Note that this picture provides an upper limit of the precipitate size, but it does not give the steady state size of the solute precipitates.

Combining the results in the past two sections, we summarize the effect of alloying element on self-organization in various binary Cu alloys by plotting the maximum temperature for compositional patterning as a function of solute thermal diffusion coefficient in Cu.

![Figure 2.13: A comparison of the maximum temperature for self-organization during irradiation with 1.8 MeV Kr with the solute diffusion coefficient in Cu at 900 K. Adapted from Ref. [4]](image)

Fig. 2.13 clearly shows that the maximum self-organization temperature is inversely related to the thermal diffusion coefficient of the solute species. For moderately immiscible alloys, the Enrique-Bellon model [9] can be used: at low temperatures \( \gamma \) is large, and the system is in the solid solution regime; at high temperatures \( \gamma \) is large, and the system enters macroscopic phase separation regime; at intermediate temperatures with the relocation distance exceeding the critical value, there is a compositional patterning regime. For extremely immiscible alloys, due to the ineffective cascade mixing (Enrique-Bellon model is no longer valid), the
maximum temperature for self-organization is even higher.
Chapter 3

“CHERRY-PIT” NANOPRECIPITATE STRUCTURES INDUCED BY IRRADIATION IN IMMISCIBLE ALLOY SYSTEMS

3.1 Introduction

As discussed in Chapter 2, materials subjected to external forcing are known to develop non-equilibrium phases and patterns in a wide variety of situations [44]. These findings have particular importance for materials that are subjected to energetic particle irradiation, for example in nuclear reactors [45]. The primary concern is that non-equilibrium phases and microstructures often impact negatively the performance of these materials during their service life. Irradiation, however, can also be used to stabilize novel microstructures through self-organization reactions, with the potential of improving materials properties. The present work focuses on the fundamental processes responsible for self-organization under irradiation and reports on a novel structure, where matrix atom precipitates form within solute-rich precipitates in dilute binary alloys.

The stabilization of nano-structures by irradiation was first reported by Nelson and co-workers [5] for Ni-Al alloys. These authors showed that after ion irradiation at intermediate temperature ($T = 550 \, ^\circ C$) the alloy had reached a steady state microstructure comprised of nanometer-size ordered precipitates in a Ni-rich matrix. The origin of this mesoscale organization was attributed to the fact that the mixing forced by energetic ions takes place over distances far exceeding the typical length scale for thermally activated atomic jumps, which is typically one nearest neighbor distance in the host lattice, $a_{nn}$. Compositional patterning induced by irradiation has since been reported in several immiscible binary Cu alloys [11, 4], and in systems comprised of metallic precipitates in silica [46, 47]. In particular, Krasnochtchekov et al. [11] used magnetic measurements to carry out a systematic investigation of the evolution of Co precipitates in dilute Cu-Co alloys subjected to Kr irradiations using various irradiation temperature, doses, and initial microstructures. They confirmed that the stabilization by irradiation of finite size precipitates only occurs within a specific range of irradiation temperatures. At too low of temperature the alloys homogenize and at too high of temperature, precipitates coarsen. Chee et al. [4] reported similar results for other dilute Cu-
base alloys, including Cu-Ag, investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) and Cu-Fe, characterized by atom probe tomography (APT). The atomic reconstruction maps in Cu-Fe showed, quite surprisingly, that the Fe-rich precipitates contained a significant amount of Cu and that these Cu atoms would often form precipitates within the Fe-rich precipitates [13], as illustrated in Fig. 3.1. These unusual precipitate structures are akin to core shell structures found in ternary alloys after thermal annealing [48, 49, 50], but here the core consists host matrix atoms. We refer to these structures as “cherry-pit” nanostructures. We note that morphologically similar nanostructures, known as double emulsions, have also been reported in immiscible liquids [51]. While compositional patterning induced by irradiation is reasonably well understood from a fundamental perspective, as we will detail in the next paragraph, the stabilization of cherry-pit nano-structures by irradiation has not been discussed previously. The main objective of the present work, therefore, is to elucidate how these cherry-pit nano-structures develop, and to identify the irradiation conditions required for their stabilization.

The stabilization of cherry-pit structures during irradiation is closely related to compositional patterning, therefore we briefly review some key results previously obtained by modeling and atomistic simulations. As indicated above, Nelson et al. [5] recognized that an essential physical parameter for patterning was the long range recoil of atoms. Frost and Russell [6, 7] later proposed a model for the evolution of precipitates in a
binary immiscible alloy where irradiation forces the relocation of atoms to a distance $R \gg a_{nn}$, and they found that, when this finite-range forced mixing competes with thermodynamically driven phase separation, finite size precipitates could be stabilized. An important simplification introduced in this model, however, is that the ballistic jumps transfer solute atoms from precipitates to the matrix, but not from the matrix to the precipitates. This simplification can sometimes lead to unphysical results [38], particularly for electron and light ion irradiations for which the average recoil distances are comparable to $a_{nn}$, and recoil-induced back diffusion should be important. Indeed, according to the Frost-Russell model, even for low values of $R$, compositional patterning is always predicted in some region of the irradiation parameter space, whereas compositional patterning induced by electron or light ion irradiations has never been reported experimentally [45, 52].

Enrique and Bellon later introduced a kinetic model that accounts for the full contribution of ballistic jumps [9]. This model predicts that the competition between finite range ballistic mixing and thermal decomposition can stabilize three different steady states, namely a homogeneous single-phase state, a phase-separated state where phases co-exist at a macroscopic scale, and a phase-separated state where phases co-exist at a finite length scale, also referred to as compositional patterning (see Fig. 2.7). For a given average composition, the domains of existence of these three distinct steady states were calculated as a function of the mixing distance $R$ and the reduced forcing parameter $\gamma = \Gamma/M$, where $\Gamma$ is the ballistic jump frequency, and $M$ is the thermal mobility, possibly enhanced by radiation. Note in particular that compositional patterning is only found when the relocation distance $R$ exceeds some critical value $R_c$. The above three steady states and their corresponding transitions were confirmed by kinetic Monte Carlo (KMC) simulations on a rigid face centered cubic (fcc) lattice [9, 10, 53]. One important feature of the patterning regime for what follows is that the steady state size of the precipitates increases continuously with decreasing $\gamma$, until undergoing a first-order transition to macroscopic phase separation.

In the present work, we employ similar KMC simulations to investigate more broadly the stabilization of nanostructures by irradiation in a generic $A_{1-c}B_c$ alloy on an fcc lattice. In particular we vary systematically the composition of the alloy, from the dilute compositions investigated by Krasnochtchekov [11] to the equiatomic composition investigated by Enrique et al. [53]. We also consider the effect of the asymmetries in thermodynamic interactions and diffusion coefficients in the $A$-$B$ alloys. Indeed, while past simulations on compositional patterning induced by ballistic mixing only considered $A_{1-c}B_c$ binary alloy systems that are invariant under the transformation $c \leftrightarrow (1-c)$, it is well documented that thermodynamic and kinetic asymmetries can significantly affect kinetic pathways during thermal annealing [54, 55, 56, 57], as well as under irradiation [57]. Furthermore these asymmetries are always present in real alloy systems, and it is
thus important to evaluate their effect on self-organization. By varying composition and asymmetries, we find that there exists in fact five distinct steady states for alloys under irradiation: the three noted above, plus two associated with cherry-pit structures. We show that these five regimes can be rationalized by extending the Frost-Russell model [6, 7] and combining it with the dynamical phase diagram predicted by the Enrique-Bellon model [9]. Lastly we show that our simulations provide the basis for understanding the new experimental results on cherry-pit structures in irradiated Cu-Fe and Cu-V alloys.

3.2 KMC simulations

The KMC simulations are based on the model described by Enrique and Bellon [10]. In this model, atoms migrate by two distinct mechanisms: thermally activated jumps assisted by nearest neighbor atom-vacancy exchanges, and athermal ballistic relocations arising from atomic collisions. An immiscible binary A-B alloy is created on a rigid fcc lattice using periodic boundary conditions. A single vacancy is introduced into the system for the thermally activated atom jumps. Nearest-neighbor atomic pair interactions ($\epsilon_{AA}, \epsilon_{AB}, \epsilon_{BB}$) and atom-vacancy interactions ($\epsilon_{AV}, \epsilon_{BV}$) are used to model cohesion and vacancy formation energies of the system. Pure A and B cohesive energies are defined as $E_{A}^{coh} = \frac{Z}{2} \epsilon_{AA}$ and $E_{B}^{coh} = \frac{Z}{2} \epsilon_{BB}$; $Z$ is the nearest neighbor site coordination number ($Z = 12$ here). The ordering energy is defined as $\omega_{AB} = 2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}$. Therefore a positive value of $\omega$ corresponds to an alloy system that is immiscible and phase separates at low enough temperature. Effective vacancy-atom interactions $\epsilon_{XV}, X = A, B$ are used to adjust the vacancy formation energy [58], which is defined by $E_{fot}^{XY} = Z\epsilon_{XV} - \frac{Z}{2}\epsilon_{XX}$.

In addition, we have extended this model in order to explore the effect of asymmetric thermodynamic interactions by including triplet atomic interactions are introduced. An interaction energy is assigned to the equilateral triangles formed by three common nearest neighbor atoms. Direct counting of bonds and triplets shows that, in mean-field point approximation (Bragg-Williams), the mixing enthalpy of a homogeneous system $\Delta E_{mix}$ with triplet atomic interactions takes the form

$$\frac{\Delta E_{mix}}{N} = \frac{Z}{2} c_A c_B [2\epsilon_{AB} - \epsilon_{AA} - \epsilon_{BB}]$$

$$+ \frac{Z_t}{6} c_A c_B [3(-\epsilon_{AAA} - \epsilon_{BBB} + \epsilon_{AAB} + \epsilon_{ABB})]$$

$$+ (c_A - c_B)(-\epsilon_{AAA} + \epsilon_{BBB} + 3\epsilon_{AAB} - 3\epsilon_{ABB})],$$

where $N$ is the total number of atoms in the system, $Z_t = 24$ is the number of first nearest neighbor triangles sharing one summit. We note that the functional dependence of the mixing enthalpy with composition is
identical to the Redlich-Kister expansion used in sub-regular solution models [59]. For simplicity, we set the triplet atomic interactions \( \epsilon_{\text{AAA}} \) and \( \epsilon_{\text{BBB}} \) to be zero, so that the cohesive energies of pure A and B systems remain identical to the ones calculated with pairwise interactions. Moreover, we assume that \( \epsilon_{\text{AAB}} = -\epsilon_{\text{ABB}} \), so that when \( c_A = c_B \), we recover the same mixing enthalpy as in the case with pairwise interactions. When \( c_A \neq c_B \), however, the mixing enthalpy deviates from the value obtained with pairwise interactions. An important consequence is that, with non-zero \( \epsilon_{\text{AAB}} \) and \( \epsilon_{\text{ABB}} \), the equilibrium phase diagram is no longer invariant under the transformation \( c_A \leftrightarrow c_B \), and thus the solubilities of A and B atoms are no longer equal. The frequency of thermal jumps is determined using standard-rate theory, with the activation energy calculated using a broken-bond model,

\[
\Delta E_{VX} = E_{SPX}^S - \sum_m \epsilon_{mX} - \sum_n \epsilon_{nV} - \sum_{p,q} \epsilon_{pqX},
\]

where \( E_{SPX}^S \) is the saddle point energy, \( m \) and \( n \) label the nearest neighbor sites of \( V \) and \( X \), respectively, and \( p, q, \) and \( X \) are the sites forming first nearest neighbor triangles.

As in previous works, irradiation induced mixing is simulated by randomly picking one atom and switching it with another atom according to a predetermined distribution of relocation distances. Here this distribution is chosen to be a decay exponential, \( \exp(-r_{ij}/R) \), where \( r_{ij} \) is the pair separation distance, and \( R \) is the characteristic relocation distance. If not specifically noted, \( R = 1.08a_{nn} \) is used in the simulations, following molecular dynamics simulation results of energetic cascades in Cu-Ag alloy irradiated with 1 MeV Kr ions [53]. Note that such a distribution of relocation distances includes a non negligible fraction of relocation events to sites farther than nearest neighbor ones. These short-to-medium range relocations are at the origin of the stabilization of compositional patterns under irradiation.

Time evolution is followed using the residence-time algorithm [45], where the frequencies of vacancy exchanges are weighted against the frequencies of random atomic relocations. The pre-exponential factor for the thermal jump is set to \( 10^{14} \text{s}^{-1} \), and \( \Gamma(\text{s}^{-1}) \) is the frequency of random atomic relocation. At each KMC step, a thermal jump or a ballistic jump is randomly chosen according to their relative probabilities, and time is incremented by the residence time of the current configuration, which is given by the inverse of the sum of frequencies for all possible events. Because of the possible trapping of vacancy on solute atoms and solute clusters, we followed the approach proposed by Soisson and coworkers [60], to rescale the KMC time \( t_{\text{MC}} \) to obtain a physically meaningful time \( t \). For alloy compositions such that the matrix phase is highly concentrated in A atoms, as in the present work, this re-scaling assumes that the physically correct vacancy concentration in a pure A phase should match the equilibrium vacancy concentration in that phase,
leading to the following rescaling:

\[ t = t_{MC} \frac{C_{MC}^V(A)}{C_{eq}^V(A)}, \quad (3.3) \]

where \( C_{MC}^V(A) \) is the fraction of the time spent by the vacancy when surrounded with 12 \( A \) nearest neighbors times the nominal vacancy concentration, here \( 1/64^3 \). \( C_{eq}^V(A) \) is the equilibrium vacancy concentration in pure \( A \) at the specific temperature. Such rescaling of time guarantees that the \( B \) diffusivity in the matrix remains constant during precipitation. This rescaling does not take into account radiation-enhanced diffusion (RED), for which one would need to use KMC simulations that explicitly include point defect production, migration, recombination, and elimination on sinks [61]. As a consequence of the simpler KMC model used here, forcing values of \( \gamma \) cannot be directly compared to experimental ones. Nevertheless, the sequence of steady states predicted by the present simulations when \( \Gamma \) or \( T \) are varied can be directly compared to experiments.

Four parameter sets are used in this study, see Table. 3.1. Parameter set 1 corresponds to the model and values used by Enrique and Bellon [10]; in particular this set has only pairwise interactions, the same cohesive energy for \( A \) and \( B \) solids, and the same self-diffusion coefficients in pure \( A \) and pure \( B \) phases. To investigate a system with asymmetric thermodynamic properties, parameter set 2 has \( \epsilon_{AAB} \) set to \( \pm 0.005 \) eV, leading to asymmetric equilibrium phase diagrams, which will be discussed in Section 3.3.2. In parameter sets 3 and 4, the triplet atomic interactions are set back to zero but we introduce asymmetric diffusivities for \( A \) and \( B \) elements; this is achieved by assigning different values to the \( A \) and \( B \) cohesive energies. This kinetic asymmetry is much more pronounced in parameter set 4 than in parameter set 3, as will be detailed in Section 3.3.3. For all parameter sets, the vacancy formation energy was taken as equal for the two elements, with a value typical of pure Cu: \( E_{AV}^{for} = E_{BV}^{for} = 1.28 \) eV. The ordering energy \( \omega = 0.0553 \) eV is typical of alloy systems with moderately immiscibility, e.g., Cu-Ag. These parameters yield a positive heat of mixing of \( 8 \) \( kJ \cdot mol^{-1} \) when triplet interactions are ignored, which results in a miscibility gap with a critical temperature \( T_c = 1573 \) K [62, 63], at the equiatomic composition. The saddle point energy of the vacancy jump, \( E_{SP}^X \) is taken as a constant independent of the nature of the jumping atom \( X \), \( X = A \) or \( B \). In this study, \( E_{SP}^X \) is set to -10.217 eV for both elements, which corresponds to a vacancy migration energy of 0.80 eV for parameter sets 1 and 2. All the simulations were carried out at the temperature of 0.036 eV. The standard simulation system used in this work contains 64×64×64 sites, although some simulations were run with 128×128×128 to evaluate possible finite size effects.

Simulations were run well beyond the time required to reach steady state, which was based on the evolution of internal energy and structure factor with time. Typically, up to 600 iterations of \( 2 \times 10^9 \) jumps were employed for each run (counting both thermal and ballistic jumps), thus representing \( \approx 5 \times 10^6 \) jumps
Table 3.1: Different energetic parameters used in the study.

<table>
<thead>
<tr>
<th>Parameter set</th>
<th>$E_{coh}^A$</th>
<th>$E_{coh}^B$</th>
<th>$\epsilon_{AAB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-4.34 eV</td>
<td>-4.34 eV</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>-4.34 eV</td>
<td>-4.34 eV</td>
<td>±0.005 eV</td>
</tr>
<tr>
<td>3</td>
<td>-4.34 eV</td>
<td>-4.30 eV</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>-4.34 eV</td>
<td>-4.20 eV</td>
<td>0</td>
</tr>
</tbody>
</table>

per atom. Furthermore, two different initial configurations were employed, namely a random solid solution and a single pure $B$ precipitate embedded in a pure $A$ matrix, in order to confirm that the systems have reached steady state.

Cluster analysis is used in this study to identify and calculate the size of precipitates. A cluster is comprised of atoms that are connected by at least one first nearest neighbor bond. The number and possible clustering of matrix atoms inside a precipitate is also analyzed by the same cluster analysis algorithm.

The structure factor $S(k)$, defined as the Fourier transform of the pair-correlation function, is calculated to determine the characteristic length of the microstructure in the patterning regime. Since microstructures in this study are statistically isotropic, we used a spherically averaged structure factor:

$$ S(k) = \frac{1}{4\pi} \int S(k)d\Omega. \quad (3.4) $$

The peak position of the $S(k)$ curve is used to identify the system’s steady state regime in the dynamical phase diagram [10]. When $S(k)$ is maximum for the first non-zero $k$ point, the system is decomposed at the largest possible length scale available in that run. This is characteristic of macroscopic phase separation. In that state, the intensity of the peak of $S(k)$ scales with the simulation volume. In contrast, in the compositional patterning regime, $S(k)$ exhibits a maximum for a finite $k$, and the intensity of that peak is independent of the system size. Since the characteristic relocation distance $R$ that we use here is much smaller than the system size, it is relatively easy to distinguish these two possible steady states solely based on the peak position of the structure factor. For a few ambiguous cases, we ran simulations with larger system sizes to determine the size dependence of the $S(k)$ peak and resolve the ambiguity. Lastly, the solid solution steady state is characterized by a small and size-independent $S(k)$ that decays monotonously with $k$. 

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3.3 Results

3.3.1 Novel cherry-pit nanostructures

$A$-$B$ alloys with $B$ concentration $0.10 \leq c_B \leq 0.50$ have been studied in this work. Results shown in Sections 3.3.1, 3.3.2, 3.3.3 and 3.3.4 were obtained for $c_B = 0.15$ as it provides a basis to describe all steady states when only one of the two phases is connected, and thus when the matrix and precipitate phases can be unambiguously distinguished. The effect of composition is discussed in Section 3.3.5.

In this section, we first report results obtained for an $A_{85}B_{15}$ alloy using parameter set 1, that is for a system where all thermodynamic and kinetic properties are invariant under the transformation $c_A \leftrightarrow c_B$. Upon increasing $\Gamma$, while keeping other parameters constant, analysis of the structure factor shows that the system undergoes a transition from macroscopic phase separation regime to a compositional patterning regime when $\Gamma$ exceeds $0.1 \text{s}^{-1}$. This transition is in agreement with previous results reported by Enrique and Bellon [9] for $c_B = 0.50$ and by Krasnochtchekov et al. [11] for $c_B = 0.10$. The novel result however is that in the patterning regime a significant number of the precipitates, particularly larger ones, possess a sub-structure, as seen in Fig. 3.2 (b). These precipitates are comprised of a nearly pure-$A$ core covered by a nearly pure-$B$ shell. In order to investigate the formation and stability of these cherry-pit structures, we employ cluster analysis, and illustrate the results of that analysis in Fig. 3.2 (a) for $\Gamma = 0.7 \text{s}^{-1}$.

For simplicity, we plot here only the evolution of the size of the largest $B$ precipitate in the simulation cell, and the number of $A$ atoms in that $B$ precipitate, as a function of KMC iterations. As seen in Fig. 3.2(a), while the precipitate size remains stable, the number of $A$ atoms inside the $B$ precipitate evolves in a cyclic manner. We point out that, during most of a cycle, the $A$ atom concentration inside the largest $B$ precipitate greatly exceeds the equilibrium solubility limit, which is $\approx 10^{-4}$.

This large number of matrix atoms have in fact precipitated and formed the $A$-rich core, as seen in Fig. 3.2 (b). A sequence of atomic configurations separated by a small number of iterations, see Fig. 3.3, reveals that cores first nucleate near the center of the larger $B$ precipitates, then grow, until they make contact with the matrix phase, at which point the precipitates undergo a morphological reconstruction, leading to precipitates that are core-free. The sequence then repeats itself, unless the precipitate size changes significantly, for instance through coagulation with another precipitate, or through dissolution into the matrix. The volume fraction occupied by pits in precipitates was measured using our cluster analysis. In the present case, clusters containing 10 $A$ atoms or more were counted as pits, but the results are not sensitive to the choice of this threshold, and a nearly identical volume fraction is obtained if we use a threshold of 30 $A$ atoms. At steady state, for $\Gamma = 0.7 \text{s}^{-1}$, the pit volume fraction was 4.0%. This fraction is thus small but
Figure 3.2: (a) “Cherry” and “pit” size evolution as a function of KMC time. Data points begin from a time during steady state, and the time is set to zero. $\Gamma = 0.7 \text{s}^{-1}$. (b) Structure factor and the microstructure shows that the system is in the patterning regime. A atoms: red, B atoms: yellow. All figures use the same color coding.
easily detectable. Cherry-pit nanostructures persist as part of the stable steady state microstructure until $\Gamma$ exceeds $15 s^{-1}$, at which point the system enters the solid solution regime.

Figure 3.3: Temporal evolution of the cherry-pit structure: (a) a compact $B$ precipitate, (b) nucleation of the “pit”, (c) growth of the “pit”, (d) absorption of the “pit”, (e) recovery of a compact $B$ precipitate. $\Gamma = 0.7 s^{-1}$.

In summary, for the $A_{85}B_{15}$ alloy with parameter set 1, three distinct steady states are observed upon increasing $\Gamma$ as previously reported by Enrique and Bellon[10]. In the patterning regime, however, novel cherry-pit nanostructures are observed, and patterning is not only spatial but temporal, as these cherry-pit structures undergo cyclic formation and elimination.

3.3.2 Effect of asymmetric thermodynamic interactions

In this section, we consider the effect of asymmetric thermodynamic interactions by setting the triplet atomic interactions to $\epsilon_{AAB} = \pm 0.005$ eV, see parameter set 2 in Table. 3.1. A consequence of these asymmetric thermodynamic interactions is that the equilibrium solubilities become asymmetric. A positive (resp. negative) triplet interaction decreases (resp. increases) the equilibrium solubility of $B$ in $A$, as illustrated by the low temperature part of the equilibrium phase boundaries calculated with parameter set 1 and 2, see Fig. 3.4. Since the temperature used in the simulations is low, $\approx 0.27 T_c$, we employed a mean field approximation for this calculation, based on the mixing enthalpy given in Eq. (3.1). At $T = 0.036$ eV, the solubility of $B$ atoms in $A$ for $\epsilon_{AAB} = 0.005$ eV is about 780 times smaller than that for $\epsilon_{AAB} = -0.005$ eV, according to the mean field free energy. Note that the equilibrium solubility of $A$ in $B$ is obtained by exchanging $A$ and $B$ everywhere in Fig. 3.4, that is, in the $x$ axis label, and in the subscripts of the triplet
interaction parameters, using the relationship $\epsilon_{BBA} = -\epsilon_{AAB}$. A series of simulations has been carried out by increasing systematically $\Gamma$, so as to identify the sequence of steady states stabilized with parameter set 2. We identified five distinct steady states, instead of three for parameter set 1.

For $\epsilon_{AAB} = 0.005$ eV, the steady state changes from macroscopic phase separation at $\Gamma = 0.05s^{-1}$ to compositional patterning when $\Gamma$ is increased to $\Gamma = 0.1s^{-1}$. This is illustrated by the structure factors and atomic configurations shown in Fig. 3.5 (a) and (b). Note that in both cases, the size of the largest precipitate grows as the systems approach steady state, but it exhibits discontinuities. These discontinuities result from coagulation events, which were confirmed by direct visualization of atomic configurations. More importantly, for the current discussion, the $B$-rich precipitates stabilized for $\Gamma = 0.1s^{-1}$ do not contain $A$-rich cherry pits. Furthermore, the $A$ solubility in the largest $B$ precipitate remains small, $\approx 10^{-2}$. Upon increasing $\Gamma$ to $0.5s^{-1}$, however, cherry-pit structures appear, see Fig. 3.5 (c), and cluster analysis indicates that the steady-state volume fraction of the pits reaches 5.0%.

Turning now to the case where $\epsilon_{AAB} = -0.005$ eV, we observe a stabilization of cherry-pit structures before the transition from macroscopic phase separation to patterning. As illustrated in Fig. 3.5 (d) for $\Gamma = 0.05s^{-1}$, the system is still in the macroscopically decomposed state as indicated by the high intensity of the structure factor and the presence of only one precipitate, but $A$-rich cores are found in this precipitate. Simulations started from configurations with one large precipitate led to a similar steady state.
Figure 3.5: Different steady states and structure factor: (a1) $\epsilon_{AAB} = 0.005$ eV, $\Gamma = 0.05$ s$^{-1}$, no cherry-pit structure (a2) macroscopic phase separation regime; (b1) $\epsilon_{AAB} = 0.005$ eV, $\Gamma = 0.1$ s$^{-1}$, no cherry-pit structure (b2) patterning regime; (c1) $\epsilon_{AAB} = 0.005$ eV, $\Gamma = 0.5$ s$^{-1}$, with cherry-pit structure (c2) patterning regime; (d1) $\epsilon_{AAB} = -0.005$ eV, $\Gamma = 0.05$ s$^{-1}$, with cherry-pit structure (d2) macroscopic phase separation regime. Atomic (111) planes of typical microstructure are shown as inset in the $S(k)$ plots.
In contrast to the cherry-pit structures in the compositional patterning regime, detailed visual inspection of atomic configurations reveal that several pits can simultaneously be present in one macroscopic precipitate, as illustrated in Fig. 3.6. As in the patterning regime, pits are absorbed by the matrix when they make contact with it. The size of the pits, however, remains small compared to the size of the macroscopic precipitate. We checked this point by comparing the pit sizes obtained for system sizes of $64^3$ and $128^3$. In the latter case, the macroscopic $B$-rich precipitate is 8 times more voluminous, but the pit size distributions are nearly identical.

![Figure 3.6: Atomic plane showing the presence of multiple pits in one precipitate in the macroscopic phase separation regime. $\epsilon_{AAB} = -0.005$ eV, $\Gamma = 0.05$ s$^{-1}$. System size is $128\times128\times128$.](image)

In conclusion, with asymmetric thermodynamic interactions, we identified five steady states for an $A_{85}B_{15}$ alloy: macroscopic phase separation without cherry-pit structure; macroscopic phase separation with cherry-pit; patterning regime without cherry-pit; patterning regime with cherry-pit; and disordered solid solution.

### 3.3.3 Effect of asymmetry in diffusion

We turn next to the effect of asymmetry of diffusion, in alloy systems with symmetric thermodynamic interactions, that is with the triplet interactions set back to zero. There are several ways to introduce a kinetic asymmetry in the present model. Following the works of Athènes et al. [54] and Roussel et al. [55], we chose here to vary the relative diffusion coefficients of $A$ and $B$ species by changing their relative cohesive energies, while keeping all other parameters unchanged. As a result, the vacancy jumps faster when it is in a phase enriched with the species with the lower cohesive energy, here the $B$ species. We employ separate kinetic Monte Carlo simulations to measure the thermal diffusivities of $A$ and $B$ monomers and small clusters for parameter sets 3 and 4, as this information plays an essential role on the formation of cherry-pit structures.
For these diffusivity measurements, a single atom or a cluster comprised of \( N \) atoms, with \( N \) ranging from \( \sim 80 \) to \( 800 \), is placed in the appropriate matrix, and the system is allowed to evolve via thermally activated vacancy jumps. The diffusivity of a cluster is measured by calculating the mean squared displacement of its center of mass, according to 

\[
D = \frac{\langle R^2 \rangle}{6t},
\]

using a simulation box of \( 32 \times 32 \times 32 \). In order to account for vacancy trapping effects, time is rescaled according to Eq. (3.3). Note that at the temperature of interest here, \( 0.036 \) eV, the above clusters are fairly stable, losing only a few atoms during the early stage of the simulations. Afterwards, the cluster remains stable, and the average cluster size can be calculated. For parameter set 3, as expected, the diffusion coefficients of \( A \) single atoms and \( A \) clusters migrating in a pure \( B \) matrix are larger than those for the migration of \( B \) atoms and clusters in an \( A \) matrix. For single atom diffusion, we can directly compare our KMC data with the standard five-frequency model [64], and as expected, the agreement is excellent, see Fig. 3.7 (a). With parameter set 3, the \( A \) impurity diffusion coefficient is \( \approx 20 \) times faster than that of the \( B \) impurity. Furthermore, small \( A \) clusters migrate also faster than their \( B \) counterpart. Since the diffusivity of \( A \) clusters decreases significantly with cluster size, one can anticipate that if a pit forms, it will act as a trap for individual \( A \) atoms and small \( A \) atom clusters, thus stabilizing the pit.

Similar cluster diffusivity results were obtained for parameter set 4, but with a larger difference between the diffusivities of \( A \) and \( B \) species since the difference in cohesive energies between the pure metals is much larger than for parameter set 3. The diffusion coefficient of \( A \) monomers, for instance, is five orders of magnitude faster than that of \( B \) monomers, as seen in Fig. 3.7 (b).

We return now to our study of steady states stabilized by irradiation, starting with parameter set 3. Upon increasing \( \Gamma \), the steady state changes from macroscopic phase separation, for \( \Gamma = 0.1 \) \( s^{-1} \), to compositional patterning for \( \Gamma = 0.5 \) \( s^{-1} \). For this moderately low \( \Gamma \) value, no cherry-pit structures are found in the compositional patterning regime, as illustrated in Fig. 3.8 (a1) and (a2). At larger \( \Gamma \) values, however, cherry-pit structures are stabilized, as shown in Fig. 3.8 (b1) and (b2) for \( \Gamma = 2.0 \) \( s^{-1} \). At much larger \( \Gamma \) values, the system is driven into a disordered solid solution. This sequence of steady states is therefore qualitatively identical to the ones observed for parameter set 2 with \( \epsilon_{AAB} = 0.005 \) eV.

In the case of high kinetic asymmetry, that is with parameter set 4, a different sequence of steady states is observed. Namely, cherry-pit structures are never found, and the system simply undergoes transition from macroscopic phase separation to compositional patterning without cherry-pit to solid solution as \( \Gamma \) is increased. In the compositional patterning regime, the \( A \) concentration in the largest \( B \) precipitate remains always small, never exceeding \( \approx 0.01 \). Direct visualization of atomic configurations supports the idea that \( A \) pits could not form because of the very high mobility of the \( A \) atoms in the precipitate compared to the
Figure 3.7: Diffusion coefficients of clusters of $N$ $A$ atoms measured by Kinetic Monte Carlo simulations at 0.036 eV. (a) parameter set 3; (b) parameter set 4. Monomer diffusivities calculated by five-frequency model are also included.

rate of ballistic mixing.
Figure 3.8: Cluster analysis result for simulation with $E_{BB} = -4.30$ eV. (a1) $\Gamma = 0.5$ s$^{-1}$, no cherry-pit structures (a2) Patterning regime (a1) $\Gamma = 2.0$ s$^{-1}$, with cherry-pit structures (a2) Patterning regime. Atomic (111) planes of typical microstructure are inserted in the $S(k)$ plots.

3.3.4 Effect of ballistic jump relocation distance

All the simulation results reported in the previous sections were carried out using a ballistic jump relocation distance of $R = 1.08 a_{nn}$, a value chosen based on MD simulations modeling the ballistic mixing produced by 1 MeV Kr irradiation in equiatomic Cu-Ag alloy [53]. It is nevertheless useful to investigate the effect of the relocation distance on the stability of cherry-pit structures. For instance, for parameter set 2 with $R = 1.08 a_{nn}$ and $\Gamma = 0.1$ s$^{-1}$ cherry-pit structure is not observed. However, if the value of $R$ is increased to $2.16 a_{nn}$ and $3.24 a_{nn}$, as shown in Fig. 3.9, cherry-pit structures form. Simulations were used to determine the boundary in the $(R, \Gamma)$ plane between the regimes where cherry-pit structures were present and absent, for parameter sets 1 and 2, as summarized in Fig. 3.9. This boundary is well approximated by the equation $\Gamma R^n = C_{CP}$ with $n \approx 3.5$, and with $C_{CP}$ a constant. The functional dependence of the stability boundary for cherry-pit structures as well as the value of $C_{CP}$ will be discussed in Section 4.4.
Figure 3.9: Cherry-pit structure formation affected by different relocation distance. Power law fitting of the cherry-pit structure formation boundaries are provided in both plots. (a) parameter set 1; (b) parameter set 2.

3.3.5 Effect of concentration

In previous sections, the KMC simulations were performed for an average $B$-concentration of 15%. This concentration facilitated the identification of the cherry-pit structures as it provided a large volume fraction of isolated $B$-rich precipitates. As the $B$ concentration is increased, the precipitate phase percolates, and one is left with a bi-connected two-phase microstructure, as reported by Enrique and Bellon for equiatomic
compositions [10, 53]. We present here some results obtained for 25% and 40% \( B \) concentration, to illustrate this evolution of the microstructure in the patterning regime. In the case of \( c_B = 25\% \), the \( B \) rich precipitate phase has percolated, as seen in Fig. 3.10 (a). This is not surprising since the static percolation threshold for fcc lattices is \( \approx 20\% \) [65], more importantly the microstructure under irradiation undergoes kinetic roughening under the above conditions [66], leading to non-compact precipitate shapes. While cherry-pit structures can also be identified once the \( B \)-rich phase has percolated, the transition from macroscopic phase-separation to compositional patterning is difficult to identify since the presence of one large \( B \)-rich phase spanning the whole simulation system in the patterning regime leads to a structure factor that is very similar to the one characteristic of macroscopic phase separation. In particular, these structure factors present a peak for the smallest non-zero \( k \) vector, and the intensity of this peak scales linearly with the simulation volume. Percolation and double connectivity of the microstructure become even more evident for simulations performed for \( c_B = 40\% \), as seen in Fig. 3.10 (b). Notice that in this case, the cherry-pit structure has evolved into a three dimensional bi-connected structure, with a finite characteristic length scale. As a result, the corresponding structure factor does display a maximum for a finite \( k \) vector, with an intensity that is independent of the system size, thus making it easy again to distinguish macroscopic phase separation from compositional patterning. In summary, the dynamical stabilization of cherry-pit structures is best observed for compositions ranging from \( c_B \approx 10\% \) to 20\%. These composition boundaries may of course vary with irradiation conditions and with thermodynamic and kinetic parameters of the alloy of interest.

### 3.4 Discussion

The central result presented here is the dynamical stabilization of novel non-equilibrium precipitate structures in alloys subjected to energetic ion irradiation. These novel structures, which we referred to as cherry-pit structures, are observed in KMC simulations of \( A_{1-c}B_c \) binary model alloy systems where ballistic mixing competes with thermally-activated decomposition. These structures are observed near the dynamical transition between the steady states of macroscopic phase separation and compositional patterning. In the compositional patterning regime, the maximum pit size is bounded by the steady-state precipitate size, which maximum size is about \( 2\pi R \) [9, 10], where \( R \) is the characteristic length scale of the ballistic atomic relocations. Interestingly, a similar size limitation is also measured for pit structures forming in macroscopic \( B \)-rich precipitates. In addition, simulations reveal that these cherry-pit structures display temporal organization, and that the pits go through repeated cycles of nucleation, growth, and absorption.
Figure 3.10: Effect of different concentrations on cherry-pit structures. (a) $A_{75}B_{25}$, $\Gamma = 3.0 s^{-1}$, (b) $A_{60}B_{40}$, $\Gamma = 5.0 s^{-1}$.

by the matrix, as illustrated in Fig. 3.2 and Fig. 3.3. Analysis of these dynamical cycles suggests that they are nearly periodic, although a significant scattering is observed from cycle to cycle within one precipitate, and from precipitate to precipitate. This scattering results from the dispersion introduced by variable incubation times for pit nucleation, and from the dispersion of precipitate sizes under steady-state conditions.

In order to investigate the processes controlling the kinetics of pit dynamics, we measured the average pit
life-time as a function of precipitate size. It was found that the pit life-time increased nearly linearly with the precipitate size. A related characteristic of the kinetic evolution of pits is that, after their nucleation, their volume tends to grow nearly linearly in time. Since precipitate sizes are largely constant at the short time scale relevant for pit nucleation, growth and absorption, a linear growth kinetics is consistent with a linear dependence of the pit life-time with precipitate size. These dependencies can be understood by assuming that pits, once nucleated, grow by trapping the $A$ atoms ballistically recoiled from the matrix into the precipitates.

We have shown in Sections 3.3.2, 3.3.3 and 3.3.4 that the conditions required for the stabilization of cherry-pit structures are strongly dependent on thermodynamic and kinetic parameters of the alloy system, as well as of the relocation range $R$. We propose here to rationalize these effects by extending the model introduced by Frost and Russell [6, 7] for irradiation-induced compositional patterning. In that model, one considers pure $B$ precipitates of fixed radius $r_p$ to calculate the solute concentration profile in the matrix in the presence of ballistic relocations of length $R$. One then solves a diffusion equation for the solute atoms, here the $B$ atoms, assuming that their transport between precipitates is purely controlled by thermally activated diffusion. The ballistic mixing is reduced to a source term, resulting from the injection of $B$ atoms from the precipitate into the matrix. This source term is a function of $r$, the distance to the center of the precipitate:

$$G(r) = \frac{\Gamma}{4R^2} \left[ r_p^2 - (r - R)^2 \right] \quad (r > r_p). \quad (3.5)$$

The steady-state solution of this diffusion equation yields the following expression for the steady-state solubility of $B$ atoms in the matrix forced by ballistic mixing:

$$c_B^{bal} = \frac{\Gamma R^2}{12D_B} \left( 1 - \frac{R}{4r_p} \right), \quad (3.6)$$

where $D_B$ is the impurity diffusion coefficient of $B$ atoms in a pure $A$ matrix. As the above model does not include thermal solubility or capillary (Gibbs-Thomson) effects, Frost and Russell proposed to superimpose to the previous solubility the standard thermal contribution expected for a precipitate-matrix system. The resulting total solubility limit under irradiation then writes

$$c_B^{irr} = c_B^{eq,\infty} \left( 1 + \frac{2\sigma V_B}{r_p k_B T} \right) + \frac{\Gamma R^2}{12D_B} \left( 1 - \frac{R}{4r_p} \right), \quad (3.7)$$
where $c_{eq}^B\infty$ is the $B$ equilibrium solubility for a planar interface, $\sigma$ is the interfacial energy and $V_B$ the atomic volume in the precipitate, which is assumed to be pure $B$. As noted by Frost and Russell, two terms contribute to the dependence of the solubility with the precipitate radius, one due to the Gibbs-Thomson effect, and one from ballistic mixing. Since these two terms have identical functional dependence, both scaling as $1/r_p$, they can be grouped together, and recast into an effective Gibbs-Thomson equation, with an effective capillary length. As the ballistic frequency $\Gamma$ increases, the effective capillary length is reduced, and eventually becomes negative. Frost and Russell proposed to identify the $\Gamma$ value at which the capillary length becomes negative as the boundary between equilibrium-like phase separation and patterning. A similar but more detailed analysis of this inverse coarsening can be found in the work of Heinig et al. [67]. This critical value for the transition between these two steady states, $\Gamma_{MPS-CP}$ takes the following expression

$$\Gamma_{MPS-CP} = c_{eq}^B \infty D_B \left( \frac{96\sigma V_B}{k_B T} \right) \frac{1}{R^3}. \quad (3.8)$$

We note that this model predicts that, in the $(R, \Gamma)$ parameter space, the boundary between the two steady states is given a condition $R^3 \times \Gamma = constant$. This functional dependence of the boundary with $R$ and $\Gamma$ is in agreement with the analytical model of Enrique and Bellon in the so-called “strong-segregation” regime [9, 10], that is far from the critical point $(R_c, \gamma_c)$ in Fig. 2.7. In the context of the present simulations, two important conclusions from the above equation are that the critical ballistic frequency for the transition from macroscopic phase separation to compositional patterning scales linearly with the $B$ equilibrium solubility and with the $B$ impurity diffusion coefficient.

We propose now to extend Frost and Russell’s model to atomic diffusion inside a precipitate.\(^1\) We need to consider the flux of $A$ atoms that are ballistically recoiled from the matrix into the precipitate, which are again assumed to be pure $B$. From simple geometric considerations, we derive the corresponding source term

$$G(r) = \frac{\Gamma}{4 R p} \left[ (R + r)^2 - r_p^2 \right] \quad (r < r_p). \quad (3.9)$$

Following the approach employed by Frost and Russell, we calculate an expression for the steady-state solubility of $A$ in the precipitate, and add the expected Gibbs-Thomson contribution, yielding the following expression for the total $A$ solubility

\(^1\)Although the more complete theory of Enrique and Bellon would be preferable, this geometry of precipitates within a sphere does not lend itself to an analytical solution.
\[ c_{irr}^A = c_{A}^{eq,∞} \left( 1 - \frac{2\sigma V_A}{r_p k_B T} \right) + \frac{\Gamma R^2}{12 D_A} \left( 1 + \frac{R}{4r_p} \right). \]  

(3.10)

Notice that this time, the signs of the two terms contributing to capillary effects are opposite to the ones found when solving for \( B \) solubility in the matrix phase, see Eq. (3.7). Again, one can define an effective capillary length. As the ballistic frequency \( \Gamma \) increases, this effective capillary length decreases, then goes to zero, and becomes negative. We propose that a negative capillary length inside the precipitate corresponds to the onset of precipitation of \( A \) atoms inside the \( B \) precipitate, and it corresponds to the formation of a cherry-pit structure. The critical ballistic frequency for the transition from no cherry-pit to cherry-pits is given by

\[ \Gamma_{CP} = \frac{c_{A}^{eq,∞} D_A}{96 \sigma V_A} \left( \frac{k_B T}{R^3} \right). \]  

(3.11)

Figure 3.11: Schematic \( A \) concentration profile in the \( B \) precipitate. (a) positive effective capillary length; (b) negative effective capillary length.

The origin of the stabilization of the \( A \)-rich pits can be understood by considering the \( A \) compositions in local equilibrium with the relevant interfaces, as depicted in Fig. 3.11. When the effective capillary length, deduced from Eq. (3.11), is positive, the local \( A \) solubility in a \( B \)-rich precipitate is larger at the pit-precipitate interface than it is at the precipitate-matrix interface, as illustrated in Fig. 3.11 (a). It is therefore expected that \( A \) atoms will flow from the pit to the matrix, and thus that pits are not stable. Note that this is also the case for systems at thermodynamic equilibrium. In contrast, when irradiation conditions are such that this effective capillary length is negative, as in Fig. 3.11 (b), the situation is reversed, and \( A \) atoms should now flow from the precipitate-matrix interface to the pit-precipitate interface, leading to the
continuous growth of the pit, as observed in the KMC simulations.

Returning to the model, one first notes the similarity between Eq. (3.11) and the one derived by Frost and Russell for the onset of patterning, Eq. (3.8). In particular, the functional dependence of the boundary with respect to $R$ and $\Gamma$ is again given by $R^3 \times \Gamma = \text{constant} = C_{CP}$. We tested this functional dependence using the KMC simulation results presented in Fig. 3.9 for parameter sets 1 and 2. As seen from the figure, the agreement is quite good, with the best fit to the data giving a boundary for $R^n \times \Gamma = \text{constant}$ with $n = 3.52$ for parameter set 1 and $n = 3.46$ for parameter set 2. We note that these values are between the values identified by Enrique et al. [9] of $n = 3$ for the strong segregation regime (i.e., far from $\gamma_c$) and $n = 4$ for the weak segregation regime (i.e., close to $\gamma_c$). Another important result from Eq. (3.11) is that the critical ballistic jump frequency for the stabilization of cherry-pits scales linearly with the $A$ equilibrium solubility and with the $A$ impurity diffusion coefficient. Note that in the Frost and Russell model, and in its extension proposed here, all ballistic events have the exact same relocation distance, $R$. Heinig et al. [67] showed however that an exponential distribution of relocation distances leads to results identical to Eqs. (3.6, 3.7, 3.8), except for different numerical coefficients. These differences do not affect the functional dependences of the transition from macroscopic phase separation to compositional patterning, and of the stability boundary of the cherry-pit regime. It is therefore meaningful to compare these analytical functional dependences with our KMC data.

We can now compare the steady states identified in the KMC simulations with those predicted by this extended patterning model. First, in the case of a fully symmetric alloy system, as for parameter set 1, the equilibrium solubilities and the impurity diffusion coefficients are identical for $A$ and $B$ atoms. We thus expect that, as $\Gamma$ is increased, the onset of compositional patterning (the boundary labeled $\gamma_1$ in Fig. 2.7) coincides with the onset of the formation of cherry-pit structures. This is indeed what was found for parameter set 1, see Section 3.3.1. We turn then to the case of alloy systems that have asymmetric solubilities but symmetric diffusion properties, parameter set 2. When the $B$ equilibrium solubility in $A$ is lower than that of $A$ in $B$, that is for positive values of $\epsilon_{AAB}$, the extended patterning model predicts that, as $\Gamma$ is increased, the system will first undergo a transition from macroscopic phase separation to compositional patterning before entering the domain of cherry-pit formation. This is also in agreement with the KMC results summarized in Fig. 3.5 (a-c). Conversely, when the $B$ equilibrium solubility is larger than that of the $A$ solubility, that is for negative values of $\epsilon_{AAB}$, the extended patterning model predicts that cherry-pit structures will become stable while the system is still in the macroscopic phase separation steady state, again in qualitative agreement with our simulation results, see Fig. 3.5 (d). In both cases, however, the quantitative agreement with the model is limited in the sense that the model predicts that for positive $\epsilon_{AAB}$
values the domain over which compositional patterning would be stabilized without cherry-pit structures should cover three decades in $\Gamma$ according to Eqs. (3.8), (3.11), in contrast to the one decade found in the KMC simulations. We believe that this overestimation is due to the approximations made in the model, in particular the assumption that the matrix and precipitate phases are pure $A$ and pure $B$ phases, respectively, and the fact that the ballistic and thermal solubilities are derived separately.

We turn now to the case of alloy systems that have symmetric thermodynamic interactions but asymmetric impurity diffusion coefficients, as in parameter sets 3 and 4. In this case again, the sequence of steady states predicted by the extended patterning model is in agreement with the simulation results reported in Section 3.3.3. For instance, an increase of $A$ atom diffusivity over that of $B$ atoms is expected to shift the onset of cherry-pit formation to larger $\Gamma$ values than those required for compositional patterning. In this case, the agreement between the KMC simulations and the model is even semi-quantitative, as the ratio of $\Gamma$ values for the transition from macroscopic phase separation to compositional patterning, $\Gamma \approx 0.1s^{-1}$, to the transition for no cherry-pit to cherry-pit, $\Gamma \approx 2.0s^{-1}$, is in the ratio of $D_B(A)$ over $D_A(B)$, as expected from Eqs. (3.8), (3.11). For parameter set 4, this shift is expected to be very large since the $A$ and $B$ diffusivities differ by 5 orders of magnitude. The fact that no cherry-pit structures are observed for parameter set 4 can then simply be understood as a case where the very large diffusional asymmetry shifted the possible cherry-pit formation to $\Gamma$ values larger than the boundary between the compositional patterning and solid solution steady states, the boundary labeled $\gamma_2$ in Fig. 2.7.

The stabilization of cherry-pit structures is reminiscent of the transient formation of small clusters around a precipitate undergoing dissolution, under irradiation [68, 67]. Cherry-pit structures are also reminiscent of the stabilization of similar inverted structures in equilibrium systems with competing interactions. Indeed, following approaches introduced by Martin [8], Vaks and coworkers [69] and Garrido and coworkers [70], Enrique and Bellon [71] showed that the dynamical steady states reached under irradiation can be described as thermodynamic equilibrium states in systems with effective interactions. Specifically, for the alloy systems considered here, the effective interactions between like atoms would be comprised of short-range attractive interactions, due to the thermodynamics of the systems, and long range repulsive interactions, resulting from the finite-range ballistic mixing. Such a competition can be found in physical systems, for instance in the two-phase phospholipid systems studied by McConnell and coworkers [72, 73, 74]. In these thin film systems, a solid-liquid phase co-existence results from a competition between short-range attractive chemical interactions with long-range repulsive dipolar interactions. As shown analytically [74], and observed experimentally [72, 75], this competition generates morphological instabilities of lipid domains, and in particular, above a critical size, spherical domains undergo a first-order transition from a disc to a
torus, which is the two-dimensional equivalent of the transition from compact sphere to cherry-pit structures in three-dimensions.

One remarkable characteristics of the cherry-pit structures reported here is their near periodic cyclic evolution. This can be rationalized by considering the three characteristic time scales relevant for these evolutions, namely the pit nucleation time, the pit growth time, and the precipitate life time. For the parameters employed in this study, KMC simulations reveal that the three time scales are well separated. As a consequence, in the pit formation regime, starting from a pristine precipitate, a pit nucleates quickly, then grows relatively slowly, and is finally absorbed by the matrix when it intercepts the precipitate-matrix interface, which has barely changed over this one cycle. Furthermore, for a given precipitate size, the pit growth rate is nearly identical from one cycle to the next, since this growth rate is controlled by the recoil of \( A \) atoms from the matrix into the precipitate. As a consequence, the pit evolution cycles are nearly periodic.

Finally, we point out that in recent experiments on \( \text{Cu}_{1-x}\text{Fe}_x \) and \( \text{Cu}_{1-x}\text{V}_x \) (with \( x \approx 10 \) at\%) thin films subjected to 1.8 MeV Kr ion irradiation, Stumphy et al. [13] observed by atom probe tomography inner precipitate structures similar to the cherry-pit structures reported here from KMC simulations, as illustrated by comparing Fig. 3.1 with Fig. 3.6. Interestingly, these inner precipitate structures are observed in Cu-Fe in the macroscopic phase separation regime as well as in the compositional patterning regime, where as in Cu-V they are only observed in the patterning regime. Our present study indicates that thermodynamic and kinetic asymmetries can be responsible for these differences. As we point out previously in this section, the critical values of \( \Gamma \) for compositional patterning and cherry-pit formation differ from each other, and depend on the asymmetry of the phase diagram, the relative diffusion coefficient and atomic volume of the two elements in the alloy. It is not yet known whether the nanostructures observed experimentally are dynamical, cyclic structures, as the ones revealed by the KMC simulations. A detailed comparison between experimental results and the present simulations and modeling will be offered elsewhere [76].

### 3.5 Conclusion

We investigate by kinetic Monte Carlo simulations in binary \( A-B \) alloys the possible stabilization by irradia-
tion of precipitate-within-precipitate structures, which we refer to as cherry-pit structures. The simulations indicate that these structures should be stable for a broad range of thermodynamic and kinetic parameters, and that the asymmetry of these parameters influence greatly the domain of stability of the cherry-pit structures. Moreover, in the simulations, these structures display a dynamical, near-periodic, behavior, going through cycles of pit nucleation, growth, and absorption by the matrix/precipitate interface. An analytical
model is proposed by extending the model previously introduced by Frost and Russell [6, 7] to include the
dynamics of pit formation and stability inside precipitates. The effect of thermodynamic and kinetic alloy
asymmetry on cherry-pit stabilization is in very good qualitative agreement with the KMC simulations. The
simulations also offer a framework to rationalize the formation of nanostructures within precipitates recently
reported by atom probe tomography in ion-irradiated Cu-Fe and Cu-V alloys.
Chapter 4

ROLE OF POINT-DEFECT SINKS ON IRRADIATION-INDUCED COMPOSITIONAL PATTERNING IN MODEL BINARY ALLOYS

4.1 Introduction

As discussed in previous chapters, materials subjected to continuous irradiation by energetic particles constitute dynamical systems, whereby the disorder introduced by irradiation, in the form of non-equilibrium point defects and forced chemical mixing, competes with thermally activated relaxation toward equilibrium. This dynamical competition can trigger self-organization reactions, such as the formation of void and bubble lattices in pure metals [77, 78], and the stabilization of nanoscale compositional patterns in multi-phase alloys [5, 4]. The latter reaction has been rationalized using atomistic simulations [10, 53] and continuum modeling [9]. The dynamical stabilization of nanoscale compositional patterns results in microstructures with a high density of chemical interfaces under irradiation. These interfaces are of interest since they are potential traps for point defects. These point defect sinks are not included in the model described in Chapter 3. However they are likely to limit long range diffusion, and with it, degradation of the material from swelling, irradiation creep, or radiation-induced segregation and precipitation [79, 80, 81, 82, 83, 78, 84, 85].

Implementation of this approach requires the ability to control and tune the regime where compositional patterns are stable under irradiation. In particular, as many advanced nuclear reactor designs call for very high temperatures of operation [86, 84], a significant challenge is to extend the patterning regime to these high temperatures. We demonstrate in the this chapter that the introduction of a high number density of point defect sinks can dramatically extend the stability of the patterning regime. The influence of sinks on irradiation-induced compositional patterning can be readily seen using as an example the model proposed by Enrique and Bellon [9, 10]. This model employs a phase-field-type approach to calculate dynamical phase diagrams, representing the most stable steady state under given irradiation conditions. For an equiatomic \( A-B \) model alloy, comprised of immiscible elements, two parameters control the evolution and stability of the composition field. The first parameter \( \gamma \) characterizes the forcing intensity, while the second parameter,
$R$, refers to the characteristic relocation distance of atomic mixing events. The forcing intensity is defined as the ratio,

$$\gamma = \frac{\Gamma}{\tilde{D}_{\text{irr}}} \quad (4.1)$$

where $\tilde{D}_{\text{irr}}$ is the chemical diffusion coefficient, typically accelerated by the supersaturation of irradiation-induced point defects, and $\Gamma$ is the ballistic jump frequency. $\Gamma$ is directly related to the atomic displacement rate, $K_0$, through $\Gamma = bK_0$, where $b$ is the number of atoms undergoing ballistic relocation per atomic displacement [8]. We note for completeness that the definition of $\gamma$ in Eq. (4.1) involves here the chemical diffusion coefficient, allowing for a direct comparison with atomistic simulations, instead of the atomic mobility as in Ref. [77]. This alternative choice does not alter the results since, in a mean-field approximation, mobility and chemical diffusion are directly related [10, 8]. At temperatures below the equilibrium critical temperature of the binary alloy $T_c$, three possible steady states were identified in the $(\gamma, R)$ parameter space, as illustrated in Fig. 2.7. At large $\gamma$, ballistic mixing dominates and forces the system into a solid solution, while at low $\gamma$ and $R$ values, thermally activated diffusion wins out and maintains macroscopic phase separation. At intermediate $\gamma$, and with $R$ exceeding a critical value $R_c$, a third steady state evolves, where compositional patterns with a finite length scale are stabilized.

The dependence of $\gamma$ with temperature, and thus the temperature range of the compositional patterning regime, is dictated by the chemical diffusion coefficient, as ballistic mixing is largely independent of temperature. It is well recognized that the dependence of the radiation-enhanced diffusion coefficient on temperature and displacement rate is a function of the alloy microstructure. This dependence can be estimated, for instance, using standard rate theory [3], as described in Sec. 2.1.3. For the simple case of infinitely dilute alloys, the chemical diffusion coefficient entering in the denominator of Eq. (4.1) can be approximated by the radiation-enhanced solute ($B$ atom) diffusion coefficient in an $A$-atom matrix, $D_{irr}^{B}$. At low temperatures and sink densities, recombination is the dominant mechanism of point defect annihilation, and $D_{irr}^{B}$ is proportional to $\Gamma^{1/2}D_{V}^{1/2}$ [3, 8], where $D_V$ is the vacancy diffusivity. In this recombination regime, therefore, the forcing intensity scales as $\gamma \propto \Gamma^{1/2}D_{V}^{-1/2}$, and it thus decreases continuously as the irradiation temperature increases. Eventually, $\gamma$ will cross the $\gamma_1$ boundary and the system will undergo macroscopic precipitate growth. If the alloy microstructure possesses a sufficiently high density of sinks, on the other hand, vacancies and interstitials will be lost predominantly at sinks. Accordingly, the solute diffusion coefficient scales as $D_{irr}^{B} \propto \Gamma(D_{V})^{0}$, and therefore the forcing intensity is independent of both $\Gamma$ and $T$. Therefore, if the alloy microstructure can be tailored to contain a high density of stable sinks, compositional patterning could be stable at high temperatures, as the forcing intensity would never cross the $\gamma_1$ boundary. This prediction is
however quite speculative since diffusion in alloys under irradiation is far more complex than assumed in
the above discussion, owing to the coupling between chemical and defect fluxes [87]. Moreover the sink effi-
ciency of irradiated microstructures is likely to evolve, albeit slowly, as precipitate and dislocation densities
are affected by the irradiation temperature and the displacement rate. In the present work, we overcome
many of these complexities encountered by rate theory in studying compositional patterning by using kinetic
Monte Carlo (KMC) simulations. We note that the KMC model developed here includes both the effects of
radiation-induced ballistic mixing, which plays an essential role in stabilizing compositional patterns, and
the non-conserved character of point defects, which can lead to the redistribution of chemical species under
irradiation. As detailed below, this extended model now makes it possible to investigate the influences of
point defect sinks and radiation-induced solute fluxes on compositional patterning.

4.2 Methods

4.2.1 KMC simulation with non-conserved point defects

The kinetic model employed in the present simulations is a combination of the models developed by Enrique
and Bellon [10] (used in Chapter 3), to study compositional patterning under irradiation, and Soisson [88],
to study the effects of sinks on radiation induced segregation. In particular, the model includes finite-
range ballistic mixing, defect production, and defect annihilation. The main ingredients of the model are
summarized as follows (details of the model are given in Appendix A). Atoms are assumed to migrate either
by thermally activated jumps, mediated by vacancies and interstitials, or by athermal, ballistic relocations
forced by irradiation. Atoms are located on a perfect, rigid, face-centered cubic (fcc) lattice, having periodic
boundary conditions. The resulting simulation volume is a $L_1a_{nn} \times L_2a_{nn} \times L_3a_{nn}$ rhombohedron whose
faces are \{111\} planes of the fcc lattice, $a_{nn} = \sqrt{2}a/2$ being the nearest neighbor distance of the fcc lattice
of lattice parameter $a$. Irradiation induced Frenkel pairs, i.e., vacancies ($V$) and dumbbell interstitials ($I$),
are introduced randomly into the system at a rate specified in units of displacements per atom (dpa) per
second. The model for defect generation, migration, and annihilation on sinks is similar to the one described
by Soisson [88], for a bcc lattice. For simplicity, we ignore point defect clustering, during both defect
production and migration. The impact of this approximation will be discussed in Sec. 4.4.

The internal energy of a given atomic configuration is computed as the sum of nearest neighbor pair inter-
actions, including atom-atom interactions ($\varepsilon_{AA}, \varepsilon_{AB}, \varepsilon_{BB}$) and effective atom-vacancies and atom-interstitial
dumbbell interactions ($\varepsilon_{AV}, \varepsilon_{BV}, \varepsilon_{AI}, \varepsilon_{BI}, I = AA, AB, BB$). These interaction energies determine the co-
hesive energy of the pure elements, the mixing enthalpy of the alloys, and the defect formation energies.
Values of $\varepsilon_{ij}$ were selected to give an ordering energy of $\omega_{AB} = 0.0553 eV$, yielding a critical temperature for phase separation of $T_c = 1573$ K. The frequency of all thermal jumps is determined using standard rate theory, with the activation energy calculated by a broken-bond model,

\begin{align}
\Delta E_{XV} &= E_{XV}^{SP} - \sum_m \varepsilon_{mX} - \sum_n \varepsilon_{nV} \\
\Delta E_{XI} &= E_{XI}^{SP} - \sum_m \varepsilon_{mX} - \sum_n \varepsilon_{nI}
\end{align}

(4.2)

where $m$ and $n$ label the nearest-neighbor sites of point defect ($V$ or $I$) and atom $X$, respectively. The saddle point energies $E_{XV}^{SP}$ and $E_{XI}^{SP}$ are the interaction energies between the atom-defect complex and the surrounding atoms at the saddle point configuration. With a predetermined set of pair interactions, the saddle point energy is set by the activation energy for the migration of the corresponding defect. We assume here for simplicity that these saddle point energies depend on the identity of the jumping atoms, but not on their environment. The parametrization of these saddle point energies is provided later in this section.

Once created, the point defects migrate on the lattice through thermally activated jumps until they either recombine or reach a sink. Sinks are defined as sets of lattice sites where the point defects have a pre-defined, non-zero probability $p$ to be absorbed. Perfect sinks are characterized by $p = 1$. The ballistic mixing forced by nuclear collisions is modeled by randomly exchanging atoms at a certain frequency, which is calculated by multiplying the displacement rate, $K_0$ by $b$, the number of relocations per displacement. Following Enrique et al. [53], the distribution of relocation distances is chosen to be an exponential-decay, $\exp(-r/R)$, where $r$ is the relocation distance, and the average relocation distance, $R$ is set to be $R = 1.5a_{nn}$. This value is slightly larger than the average relocation distance determined by molecular dynamics (MD) simulations for Cu-Ag alloys, $1.09a_{nn}$. We have used this somewhat larger average relocation distance since it increases the region of compositional patterning (see Figure 1), and enhances the effects illustrated in the present parametric study. The kinetic evolution of the system is constructed using the residence-time algorithm [45], considering all possible events at each KMC step. After each time step, the algorithm checks whether recombination or absorption at sinks should take place based on the rules given previously. When recombination or defect elimination at sinks occurs, the KMC time is not changed, since we consider these events to be instantaneous.

The particular thermo-kinetic parameters used in the KMC simulations are listed in Appendix A, Table A.1. As indicated in Sec. 4.1, the present modeling work is motivated in part by experimental work on dilute Cu-base alloys. The parameters of the $A$ metal have thus been chosen to be representative of Cu. We note
that Cu has a fairly small atomic volume, and thus for many copper alloys, such as Cu-Ag and Cu-Nb, the solute species is oversized compared to Cu atom, making mixed dumbbells and solute dumbbells unstable in the Cu matrix. We thus set the formation energies of $AB$ and $BB$ dumbbells in $A$ significantly larger than the other formation energies, see Appendix A Table A.1. Turning next to vacancy-mediated transport, the relative diffusivity of the solute and solvent species can be different from alloy to alloy. For example, in a Cu matrix, the thermal diffusivity of Ag atom is larger than that of Cu; that for Fe is similar; while the diffusivity of Co is smaller [39, 40, 41]. In the present work, we thus employ three different parameter sets, so as to investigate the effect of the relative diffusivity of solute and solvent atoms. These three parameter sets are obtained by varying the saddle point energy for the $B$-vacancy exchange in pure $A$, see Table A.1 in Appendix A. The saddle point energy for the $A$-vacancy exchange in pure $A$ is kept constant, and its value is chosen so that the vacancy migration energy in pure $A$ is 0.8 eV, close to the experimental value for Cu [89]. As seen in Fig. 4.1, in the dilute limit, the ratio of partial diffusivities by vacancy motion, $d_{V}^{B}/d_{V}^{A}$, is less than one, equal to one, and greater than one for the parameter set 1, 2, and 3, respectively. Note also that the ratios of partial diffusivities depend differently on temperature, either increasing, constant, or decreasing with temperature for parameter set 1, 2, and 3, respectively.

Figure 4.1: Ratio of partial diffusion coefficients of $A$ and $B$ atoms via vacancy diffusion mechanism, as a function of temperature, for the three alloy parameter sets (see Table A.1 for definitions).
Two sink geometries are considered in this work, planar and spherical. The first situation corresponds to multilayer composites, while the second situation represents semi-coherent or incoherent precipitates. Simulations are run until the system reaches steady state, as monitored by the structure factor. Typically, for systems with spherical sinks, each run is comprised of 800 iterations of $1 \times 10^9$ jumps, which corresponds to $3 \times 10^6$ jumps per atom. For selected simulations, we verified that the system reaches a unique steady state by using two very different initial configurations, a random solution and a single $B$ precipitate embedded in the $A$ matrix.

We first use the simulation to consider a pure metal, using both planar and spherical sinks. This is done to validate the KMC model by comparing the computed defect concentration profiles with analytic results from rate theory. We then examine compositional patterning in alloys using spherical sinks. In this case, we use the structure factor $S(k)$, which is the Fourier transform of the pair correlation function, to distinguish the three possible steady states illustrated in Figure 1 [90]. The simulated microstructures are on average isotropic, and it is thus sufficient to consider the spherically averaged structure factor $S(k)$:

$$S(k) = \frac{1}{4\pi} \int S(k) d\Omega$$  \hspace{1cm} (4.3)

In the case of a solid solution, $S(k)$ decreases monotonously with $k$, following closely a Lorentzian shape. In the patterning regime, the maximum of $S(k)$ is located at a finite $k$ value, and the intensity of that peak is independent of the size of the system [90, 91]. In order to obtain a characteristic decomposition length scale, we calculate the first moment of $S(k)$. In the macroscopic phase separated regime, $S(k)$ is maximum for the first nonzero $k$ point, i.e., the system decomposes at the largest length scale compatible with the simulation cell size.

### 4.2.2 Point defect evolutions from rate theory

As discussed in Sec. 2.1.3, with explicit consideration of a planar sink, the rate equations describing the evolution of point-defect concentration are

$$\frac{dC_v}{dt} = K_0 - K_{iv} C_i C_v - K_{sv} C_s C_v + D_v \nabla^2 C_v$$

$$\frac{dC_i}{dt} = K_0 - K_{iv} C_i C_v - K_{si} C_s C_i + D_i \nabla^2 C_i$$  \hspace{1cm} (4.4)

where $K_0$ is the defect production rate of Frenkel pairs, $K_{iv}$, $K_{sv}$, $K_{si}$ are rate constants for recombination and defect-sink reactions, the subscripts $v$, $i$, and $s$, referring to vacancies, interstitials, and sinks. We focus
here on steady states, i.e., \( \frac{dC_v}{dt} = \frac{dC_i}{dt} = 0 \), and consider two simple situations: planar sinks and spherical sinks.

We first consider in Sec. 4.3 the case of planar sinks, which is relevant for multilayered samples. Demkowicz and coworkers have used this geometry to evaluate the effect of imperfect sinks on both the average defect concentration and the concentration profile \[92\]. In this case, there are no distributed sinks, and thus the \( K_{sv} \) and \( K_{si} \) terms are set to zero and the boundary conditions become

\[
C_v|_{x=0,t} = C_v^e, \quad C_i|_{x=0,t} = C_i^e,
\]

where \( C_v^e \) and \( C_i^e \) are the equilibrium vacancy and interstitial concentration. For an imperfect sink, the sink efficiency \( \eta \) is defined as \[93\]

\[
\eta = \frac{J_{\text{imperfect}}}{J_{\text{perfect}}},
\]

where \( J_{\text{imperfect}} \) and \( J_{\text{perfect}} \) are the defect fluxes into the interface for an imperfect and a perfect sink, respectively. Solving the simplified governing equations numerically with this new imposed boundary conditions, Demkowicz et al. \[92\] obtained the average defect concentrations within the entire cell and concentration profiles along the domain.

4.3 Results

4.3.1 Defect regimes in irradiated pure metal

We first reconsider the case of a layered structure to test our KMC model. We thus introduce a planar sink on one of the 111 planes terminating the rhombohedral simulation cell; owing to the periodic boundary conditions, this represents a layered geometry. The results presented below are for a system size of \( 200 \times 200 \times 96 \); additional results with different system sizes are given in Appendix B. At \( T = 406 \) K, which corresponds to \( \sim 0.25T_c \), a series of simulations was carried out with different absorption probabilities \( p \), simulating sinks of different efficiencies. The defect production rate was set to \( 5 \times 10^{-4} \text{dpa/s} \). The resulting steady state vacancy concentration profiles are compared in Fig. 4.2 with the solutions to the reaction-diffusion Eq. (4.4) Note that in the calculated profiles the sink efficiency \( \eta \) is not fitted, but it is instead obtained directly from the KMC simulations using Eq. (4.2.2) and then used as the flux boundary condition for solving Eq. (4.4).

The profiles illustrate the expected result that less efficient sinks lead to higher vacancy concentrations. The flat portion of the profiles away from the sinks corresponds to a region where the dominant mechanism for defect elimination is recombination.
Figure 4.2: Vacancy concentration profile for a planar sink geometry as a function of sink absorption probability, \( p \). \( \eta \) is the sink efficiency measured in the KMC simulation and used as input for rate theory calculation. Symbols are the KMC simulation results; solid lines are the results of rate theory.

The results shown in Fig. 4.2, along with others using different layer thicknesses (see Appendix B) clearly illustrate that the steady-state vacancy concentration, and thus the sink efficiency as defined by Eq. (4.2.2), is a function of both the sink absorption probability \( p \) and the distance between sinks. As expected, the sink efficiency \( \eta \) varies with the layer thickness for a given absorption probability \( p \). The sink efficiency \( \eta \) defined by Eq. (4.2.2), therefore, is not an intrinsic property of a sink, like \( p \), as its value depends on the layer thickness [92].

We next consider whether defects annihilate primarily by recombination or at sinks, as this will help in understanding the compositional patterning behavior, namely, its dependence on temperature and irradiation flux. The criterion that is often used in rate theory to make this determination is based on the dependence of atomic diffusion coefficients with temperature or displacement rate [3]. We suggest here a simpler approach, one that considers only the fraction of point defects eliminated by recombination; this quantity is readily available in KMC simulations.

A set of simulations was thus carried out at various temperatures, keeping the displacement rate constant, to determine atomic diffusion coefficients and the fractions of vacancies annihilated by recombination
with interstitials. The atomic diffusion coefficient was obtained as the product of the steady-state vacancy concentration measured in the KMC simulations and the vacancy diffusion coefficient \([3]\), the latter being directly calculated using the parameters given in Table A.1. In this calculation, and in the following ones, we ignore the effect of correlation factors on atomic diffusion since they do not vary significantly in the temperature range examined. At low temperatures, the atomic diffusion coefficient increases as temperature increases, see Fig. 4.3 (a) and (b), with an apparent activation energy of 0.4 eV, equaling half of the vacancy migration energy, in agreement with rate theory for the recombination regime. At higher temperatures, the increase of the atomic diffusion coefficient plateaus, which in rate theory corresponds to the sink-elimination regime. As expected in this regime, the plateau value scales linearly with the displacement rate (results not shown here). The transition temperature between the two defect regimes was taken as the point where the two asymptotic behaviors intersect, as illustrated in Fig. 4.3. The KMC measured recombination fractions at this crossover are 28.3 % and 32.1 % for perfect sinks \((p = 1)\) and imperfect sinks \((p = 10^{-3})\), respectively. One can also estimate the intersection of these asymptotic regimes by using the steady-state solutions of Eq. (4.4) for uniform defect concentrations, i.e., without the Laplacian terms, to calculate the diffusion coefficients under irradiation. This procedure yields a cross-over recombination fraction of \(\sqrt{5} - 1)/4 \approx 0.309\), thus in very good agreement with the KMC results. The rate theory calculation suggests that the recombination fraction at the cross-over should be independent of the sink geometry. Results obtained for the case of spherical sinks, detailed in Appendix C, yield a recombination fraction of \(\approx 29\) %, thus supporting the above analysis. In Sec. 4.3.2, we will thus use a recombination fraction of 30 % as the boundary separating the recombination and sink-limited regimes.

### 4.3.2 Effect of sinks on compositional patterning in irradiated alloys

We next examine the effect of sinks on compositional patterning in immiscible alloys. The solute concentration selected for this study is 12 at. % B, as it is high enough compared to the solute solubility under irradiation to result in the formation of precipitates that are easy to identify and characterize, but low enough to prevent the formation of connected precipitates. We begin with patterning in the recombination regime, and then turn to the sink-elimination regime.

#### Patterning in the recombination regime

In this section, we consider a 64\(^3\) simulation cell with one spherical sink. This yields a relatively low sink density, \(3.2 \times 10^{23} m^{-3}\). We also choose a low absorption probability \(p = 0.001\) so that recombination is the dominant mechanism for point defect annihilation. Specifically, the recombination fraction will be
Figure 4.3: The atomic diffusion coefficient and the KMC measured recombination fraction as a function of temperature for planar sink geometry. (a) perfect sinks, $p = 1.0$ (b) imperfect sinks, $p = 0.001$. The dash-dot lines are the asymptotic lines of the recombination and sink-elimination regimes; their intersection corresponds to the transition point.
Figure 4.4: Steady state phase separation length scale as a function of temperature for three parameter sets for the low sink strength case. The length scale is given by the inverse of the first moment of structure factor, in unit of $a$. The largest possible phase separation length scale compatible with the $64^3$ simulation cell equals to $64a/(2\pi\sqrt{3}) \approx 5.88a$. In the figure, for points at high temperatures, the length scale of the circled data points is limited by the size of simulation cell, and would be larger with a larger simulation cell.

greater than 90% for all parameters used in this sub-section. As irradiation temperature is increased while keeping the displacement and the ballistic mixing rates constant, the solute diffusion coefficient increases, and accordingly the value of the forcing parameter $\gamma$ decreases. We expect, therefore, that as the temperature increases the steady-state microstructure will first undergo a transition from solid solution to compositional patterning, and then from compositional patterning to macroscopic phase separation. In order to study the effect of alloy properties on compositional patterning, three different sets of parameters are used, leading to three different relative diffusivities between solute and solvent atoms. For parameter sets 1, 2, and 3, the partial diffusion coefficient of $B$ by vacancy diffusion is smaller than, equal to, and larger than that of $A$, respectively. The number of ballistic relocations per displacement, $b$, is fixed at 20 for each case, a value typical of light to medium mass ion irradiations [94], and the displacement rate is set to $5 \times 10^{-4}$ dpa/s. The evolution of the steady-state decomposition length scale is plotted in Fig. 4.4 as a function of the irradiation temperature. For all three sets of parameters, the steady-state structure factors shows that the systems
undergo a transition from the compositional patterning regime to the macroscopic phase separation regime as temperature increases. The transition temperatures are similar for the three parameter sets, as they all lie between 580 K and 638 K. Fig. 4.5 shows the steady state structure factors and microstructures for parameter set 3 near the transition. At 522 K, the structure factor has a peak at finite wave vector, characteristic of the compositional patterning regime. At 580 K the structure factor has a maximum at the first \( k \) point, however, its intensity is low compared to that of a macroscopically phase separated system and it does not increase with time. This suggests that the system still lies within the patterning regime. In contrast, the structure factor is very large on the first \( k \) point at 638 K, suggesting macroscopic phase separation. Direct visualization of steady-state microstructures provides further support for these conclusions. In particular, at 638 K, the microstructure contains only one precipitate, see Fig. 4.5 (d), and it is thus decomposed at the largest scale allowed by the size of the simulation cell; in contrast, at 522 K and 580 K, multiple finite size precipitates are observed in (b) and (c). Noteworthy in these figures are small \( A \) precipitates inside \( B \) precipitates, which are the focus of Chapter 3.

Figure 4.5: (a) Structure factor evolution near the transition temperature for parameter set 3, \( b = 20 \). The wave vector \( k \) is given in unit of \( 1/a \). (b) Microstructure at 522 K (c) Microstructure at 580 K (d) microstructure at 638 K. Red: \( A \), blue: \( B \).
Figure 4.6: Phase separation length scale as a function of temperature for three parameter sets for high sink strength case. $p = 1$, 8 perfect sinks in the simulation cell. The length scale is given by the inverse of the first moment of structure factor, in unit of $a$. The largest possible phase separation length scale compatible with the $64^3$ simulation cell equals to $64a/(2\pi\sqrt{3}) \approx 5.88a$. In the figure, for points at high temperatures, the length scale of the circled data points is limited by the size of simulation cell.

**Patterning in the sink-elimination regime**

Patterning in the sink limited regime is quite different. This regime is of potential applied interest as it can extend the temperature range of patterning, as discussed in the Introduction. In order to favor annihilation of point defects at sinks, we increase the sink density by a factor 8, to $2.6 \times 10^{24} m^{-3}$, and employ perfect sinks, i.e., $p = 1$. The high sink density and efficiency result in the sink-elimination regime being dominant for irradiation temperatures above $\approx 400$ K. The number of ballistic relocations per displacement, $b$ is set to be 20, 40 and 175 for parameter set 1 to 3. This setting leads to similar phase separation length scale at lower temperatures for the three cases, and allows us to examine the patterning evolution for all three cases at the same temperature range.

In Fig. 4.6, the phase separation length scale is plotted as a function of temperature. The precipitate evolutions are seen to be distinctively different for the three alloys, and in some cases they depart from the simple predictions obtained using rate theory for estimating the forcing parameter $\gamma$. For parameter set 3, i.e., $d_B^V/d_A^V > 1$, the evolution is close to that predicted by this simple approach, as patterning is extended to
high irradiation temperatures and the decomposition length scale (or precipitate size) is nearly independent of the irradiation temperature in the range 500 K – 800 K. The slight decrease of the precipitate size at 800 K is due to an increase in solute solubility at this high temperature. For parameter set 2, \( \frac{dV_B}{dV_A} = 1 \), the system also remains in the patterning regime, however, the steady-state size increases continuously with temperature. For parameter set 1, the phase separation length scale increases with temperature, with the system undergoing a transition from patterning to “large-scale” phase separation at \( \approx 700 \) K, as described below.

Direct visualization of the steady state configurations reveals important additional differences between the three alloys. Fig. 4.7 shows that at 580 K \( B \)-rich precipitates form predominantly around the sinks for parameter set 1, but away from the sinks for parameter sets 2 and 3. The different morphologies will be rationalized in the Discussion section based on the coupling between solute fluxes and defect fluxes. We note that, cherry-pit precipitate structures are also observed in this regime (see Fig. 4.5), especially in the larger precipitates. Lastly, the microstructures for parameter set 1, see Fig. 4.7 (a-d), suggest a transition to a large-scale phase separation regime between 580 K and 696 K. The characteristic length-scale of this phase separation could be either the size of the system, as in the macroscopic phase separation identified in the recombination regime in Sec. 4.3.2, or it could be determined by the separation distance between sinks. A definitive answer to this question, however, would require much larger simulation volumes so as to vary separately the simulation cell size and the sink separation distance. These simulations are beyond our present capabilities and therefore we defer additional discussion of this point to a later time.

4.4 Discussion

The main objective of work in this chapter has been to investigate the effect of the non-conservative character of point defects on irradiation-induced compositional patterning, and in particular on the range of irradiation temperatures over which patterning can be observed. We investigated the possibility of an extended stability of compositional patterning in the sink-dominated regime using atomistic simulations, so as to describe on the same footing chemical and point defect evolutions. More specifically, we employed kinetic Monte Carlo simulations relying on a kinetic model that combines finite range chemical mixing as modeled by Enrique et al. [10, 53], with the creation, recombination and sink-elimination of point defects, following the procedure proposed by Soisson [88]. This model was first validated by considering the case of a pure metal, by comparing diffusion coefficients to the values predicted from rate theory for systems with planar or spherical sinks. The agreement between the two approaches is very good, and the transition from the sink-dominated
regime at high temperature to the recombination-dominated regime at low temperature takes place when the recombination fraction reaches \( \approx 30 \% \), in agreement with rate theory.
The KMC simulations were applied to several model immiscible binary alloys, using irradiation parameters that allowed stabilization of compositional patterning at steady state [9, 10]. The domain of stability of compositional patterning was investigated as a function of irradiation temperature with sink density and efficiency such that the point defect evolution is controlled either by recombination or by elimination on sinks. In the recombination regime, the three alloys considered for the present KMC simulations showed a transition from compositional patterning at lower temperature to macroscopic phase separation at higher temperature. This transition is expected within the Enrique-Bellon model since, in the recombination regime, the forcing intensity should scale as \( \gamma \propto K_{0}^{1/2}D_{V}^{-1/2} \), and therefore increasing the irradiation temperature should lead to a continuous decrease of \( \gamma \). Eventually the system crosses the \( \gamma_1 \) boundary in Figure 1. The transition temperatures from patterning to macroscopic phase separation are similar for the three alloys, at least to within the 60 K temperature steps used in this study. This small shift, if any, is consistent with a transition temperature shift of \( \approx 30 \) K calculated from the change in diffusion coefficient values between the alloy parameter set 1 to set 3. One effect that is however not included in the Enrique-Bellon model is the composition dependence of the interdiffusion coefficient. The present study indicates that the larger the solute diffusion coefficient, as is the case with parameter set 3, the larger the steady state size of the precipitates. This is a first illustration of the important role played by alloying effects.

In the sink-elimination regime, a more intriguing situation is expected since, using rate theory for calculating atomic diffusion as function of the irradiation parameters, the forcing parameter should now scale as \( \gamma \propto (K_0)^0(D_\nu)^0 \). This scaling suggests that the forcing parameter should be independent of both the irradiation temperature and displacement rate, and result in an unlimited extension of the domain of stability of compositional patterning at higher temperatures, until equilibrium vacancies come into play.

The KMC simulations indeed indicate that in the sink-dominated regime, the phase separation length scale has a weak temperature dependence, especially for parameter sets 2 and 3, extending the compositional patterning regime to \( \sim 800 \) K. The maximum patterning temperature in the simulations is in fact limited by the increase in solute solubility at these high temperatures, which leads to a reduction in the precipitate volume fraction (for the parameters used in the simulations, thermal vacancies outnumber point defects created by irradiation at temperatures above \( \sim 700 \) K, but, for simplicity, they were not included). In the case of parameter set 1, a transition from compositional patterning to another decomposition regime, with a coarser characteristic length scale, took place between 638 K and 700 K, even though the point defect kinetics remained in the sink-elimination regime. This appears to contradict the prediction from rate theory. Visualization of the microstructures, Fig. 4.7 (a-d), suggests, however, that the scale of decomposition may be dictated by the separation between sinks, rather than the system size. The precipitation morphology for
the three alloy parameter sets is, in fact, influenced by the inverse Kirkendall effect, as detailed below.

The three alloys considered in the simulations are such that \( D_B^I < D_A^I \), and therefore the permanent interstitial fluxes to the sinks favor solute depletion near the sinks in all three cases. In contrast, vacancy fluxes and the inverse Kirkendall effect favor solute segregation on sinks in parameter set 1, is neutral for parameter set 2, and favors solute depletion for parameter set 3. Overall, it is thus expected that solute precipitation should preferentially take place on the sinks for parameter set 1, and between sinks for parameter sets 2 and 3. This is indeed observed at 580 K, as seen in Fig. 4.7. Note that owing to the formation of cherry-pit structures and to irradiation-induced kinetic roughening of interfaces the B-rich precipitates develop non-equilibrium morphologies. At higher temperatures, 700 K and above, the precipitation morphology for parameter set 1 is different from the one observed at 580 K in the sense that precipitates are only found near the sinks. This transition from a finer to a coarser decomposition scale for parameter set 1, but not for parameter sets 2 and 3, is favored by the spherical geometry of the sink. The segregation of B atoms around the sinks for parameter set 1 is indeed concentrated on a smaller volume than the one for parameter sets 2 and 3, raising the local solute concentration to much higher values, thus promoting the growth of the precipitates that formed on the sinks, at the expense of the ones that formed away from the sinks. As mentioned in Sec. 4.3.2, the exact nature of the phase separation for parameter set 1 at 700 K and above, see Fig. 4.8, cannot be unambiguously determined with the simulation volumes employed in this study. Further work will be needed to determine whether the phase separation length scale is set by the sink separation distance, or by the system size. Returning now to the compositional patterning regime, the three parameter sets produced distinct evolutions of the decomposition length scale. It is nearly independent of temperature for set 3, while it increases slightly for set 2 and significantly for set 1. These differences can be rationalized by considering the effect of alloying parameters on the forcing parameter \( \gamma \). As the ballistic jump frequency was kept constant in the simulations, the characteristic phase separation length scale should be determined by the temperature dependence of \( D_B^{\text{irr}} \) (note that the number of forced relocations per displacement, \( b \), has been adjusted so that all three parameter sets lead to a similar patterning length scale at low temperature; we also ignore the role of interstitials since they have little influence on the diffusion of B atoms). The thermal solute diffusion coefficient in alloys can be expressed as the product of the partial diffusion coefficient of B atoms via vacancies and the vacancy concentration, i.e., \( D_B = d_B^V C_V \). It is advantageous to rewrite \( D_B \) as

\[
D_B = \frac{d_B^V}{d_A^V} \cdot d_A^V C_V
\]

(4.7)

The matrix is highly diluted in B, and thus the defect regimes should be similar to those found in pure...
A. Indeed, the vacancy diffusion coefficient can be written as $D_V = d_A^V C_A + d_B^V C_B$, where $d_A^V$ and $d_B^V$ are the vacancy partial diffusion coefficient via exchanging with $A$ and $B$ atoms, respectively. Note that, $d_A^V = d_A^V$ and $d_B^V = d_B^V$, since either jump involves the exchange of a given atom-vacancy pair [81]. In the matrix where $C_B$ is small, we can thus approximate $D_V$ as $D_V \approx d_A^V$. Therefore, in the sink-elimination regime, $d_A^V C_A^{\text{irr}} = D_A^{\text{irr}}$ should be approximately constant, and $D_B^{\text{irr}}$ is mainly determined by the ratio of two partial diffusion coefficients, $\frac{d_A^V}{d_B^V}$. This ratio was calculated as a function of temperature in the dilute limit, using the standard five frequency model [64]. As shown in Fig. 4.8 (a) the partial diffusion coefficient ratio displays different temperature dependencies for the three sets of parameters. For parameter set 1, the ratio increases with temperature, resulting in a larger $D_B^{\text{irr}}$, and thus smaller $\gamma$ and larger phase separation length scale. This first effect dominates the evolution for parameter set 1. For parameter sets 2 and 3, however, this analysis alone cannot fully explain the evolutions reported in Fig. 4.6. An additional effect that contributes to these evolutions is the fact that point defects can be trapped at the chemical interfaces in a phase separated alloy, lowering the concentration of “freely migrating” point defect [95]. This trapping effect introduces another temperature dependence into $C_V$ and thus $D_B^{\text{irr}}$. To incorporate this effect, we measured in a set of separate KMC simulations the $B$ diffusion coefficient in an infinitely dilute $A$-$B$ alloy with the same sink density and sink efficiency. Also, we estimated the fraction of “freely migrating” point defects in the concentrated $A_{88}B_{12}$ alloy by measuring the fraction of time that the vacancy has less than three $B$ nearest neighbors. This analysis suggests that the fraction of “freely migrating” vacancies have slightly different temperature dependencies for parameter sets 1, 2, and 3, as shown in Fig. 4.8 (b). Finally, by combining the results from both effects, the relative partial diffusion coefficients and the trapping of vacancies at chemical interfaces, we obtain a more accurate estimation of $D_B^{\text{irr}}$ in the matrix of the concentrated alloy. Fig. 4.8 (c) shows that for parameter set 1 and 2 $D_B^{\text{irr}}$ increases monotonically with temperature, while for parameter set 3, $D_B^{\text{irr}}$ first increases, then reaches a plateau, and lastly drops slightly at the highest temperatures. These temperature dependencies for $D_B^{\text{irr}}$ thus offer a clear rationalization for the dependence of the compositional patterning length scale with temperature reported in Fig. 4.8 for the three alloy parameter sets.

The present KMC simulations relied on several, often used, simplifications [10, 96], however they deserve some comment. The assumption of a rigid lattice makes it possible to reach steady state for fairly large simulated volumes, and while stress effects can influence point-defect and atomic diffusion, it is expected that the key conclusions regarding the sink effects on compositional patterning would remain valid. Another simplification was ignoring the collective nature of atomic motion in displacement cascades [52]. Past modeling [9, 10, 97, 11, 14] and experimental works [11, 4, 13] indicate, however, that for modeling compositional patterning in moderately immiscible alloy systems such as Cu-Ag, Cu-Co or Cu-Fe the prevailing feature
Figure 4.8: (a) $B$ tracer diffusion coefficients for three sets of parameters, measured by KMC in a dilute limit (b) “freely migrating” vacancy fraction for three sets of parameters, measured by KMC in the $A_{88}B_{12}$ alloy (c) estimation of $B$ diffusion coefficients for three sets of parameters in the $A_{88}B_{12}$ alloy after considering the “freely migrating” vacancy fraction.
of cascades is the finite-range of ballistic relocation distances. Following the detailed atomic modeling for Cu$_{50}$Ag$_{50}$ [97, 53] this finite range mixing was modeled here as an exponential distribution with a decay length $R$. Another simplification of the present work is the neglect of defect clustering, either directly in displacement cascades or through the diffusion and reaction of point defects. These defect clusters should act as sinks and therefore they favor the stabilization of compositional patterning under irradiation. In addition, the sinks are modeled as geometrical sites and have no thermodynamic or strain interactions with solute atoms. In actual alloy systems, if present, these interactions could modify the sink efficiency of the nanoparticles and the stability of solute precipitates. This effect could be particularly important when solute precipitates form at the sinks, as observed for instance with parameter set 1, see Fig. 4.7 (a, b). One more point is that the B-rich precipitates themselves, if semi-coherent or incoherent with the A-rich matrix, will provide sites for point defect elimination, promoting even further the stabilization of compositional patterning. Finally, we had assumed that the sink structure is stable for the whole range of irradiation temperatures investigated. In the case where nanoparticles serve as defect sinks, these nanoparticles could coarsen at high irradiation temperatures, and this would affect the sink strength. In particular, coarsening would result in a decreased nanoparticle number density and possibly a transition of the nanoparticle/matrix interfaces from semi-coherent to incoherent. The former effect would reduce the sink strength, while the latter could increase the sink efficiency of the interfaces. As a result, the characteristic length scale of the compositional patterns could change over large-dose irradiations. It will therefore be important to test experimentally the present simulation results and predictions. We note that progress in developing new nano-composite alloys, offers a means to introduce a high density of stable small spherical sink particles in a matrix, either by severe plastic deformation and annealing, as in nano-ODS steels [84], or by intra-cascade precipitation during low temperature irradiation, as demonstrated in Cu-W and Cu-Mo alloys [4, 12, 98].

4.5 Conclusion

In this chapter we investigate the effect of point defect regimes under irradiation on compositional patterning in model binary alloys. For that purpose, we extended existing KMC codes to allow for point defect production, recombination, and elimination on sinks, as well as irradiation-induced chemical mixing. The irradiation of pure metals is first used to validate and calibrate the KMC simulations using standard predictions from rate theory for the case of microstructures with planar and spherical sinks. This comparison provides a simple yet robust criterion, based on the fraction of point defects annihilated by recombination, to distinguish the steady-state point defect regimes of recombination and sink elimination. In the case of
a model immiscible $A$-$B$ alloy, the effect of point defect regimes on the temperature range of stability of irradiation-induced compositional patterning is then investigated using spherical sinks with various densities and defect absorption efficiency. In the recombination regime, increasing irradiation temperatures leads to a continuous increase in steady-state $B$-rich precipitate sizes, and eventually to a transition to macroscopic phase separation, as expected from the Enrique-Bellon model. In the sink-elimination regime, however, compositional patterning can be extended to much higher temperatures, in particular when the relative diffusivities of $A$ and $B$ atoms favor the depletion of $B$ atoms at sinks via inverse Kirkendall effect. This stabilization of the compositional patterning regime to high temperature is rationalized by the weak temperature dependence of the forcing parameter in the sink-dominated regime.
Chapter 5

EXPERIMENTAL STUDY OF PRECIPITATE STABILITY OF A CU-AG-W MODEL ALLOY

5.1 Introduction

In Chapter 4 the KMC modeling predicts that for alloys under irradiation, the maximum temperature for compositional patterning can be increased, if a high density of point defect sinks is introduced. This provides a promising way of stabilizing nanostructured materials, which have long been recognized for their excellent mechanical behavior for applications requiring high strength and hardness [99, 100, 101, 102]. Recent attention in these materials has focused largely on controlling their stability at high temperatures, as they are inherently unstable to coarsening. A number of approaches have been taken to mitigate this problem, including grain boundary (GB) stabilization using GB doping [103, 104] or Zener pinning [105, 106, 107].

For multiphase alloys, different approaches are employed. These strategies typically rely on the general observation that in a dilute binary alloy the coarsening rate \( \frac{dR}{dt} \) of a precipitate of radius \( R \) scales with the solute diffusion coefficient, \( D_S \), the solubility limit of the alloying element, \( X_{\text{sat}} \), the precipitate matrix interface energy, \( \gamma \), and the size distribution of the precipitates, i.e., \( \frac{dR}{dt} = \frac{2D_S\gamma^{\frac{2}{3}}X_{\text{sat}}}{kTR} \left( \frac{1}{\langle R \rangle} - \frac{1}{R} \right) \).

Oxide-dispersion strengthened (ODS) alloys [108, 84, 109] and core/shell-structured precipitate strengthened Al alloys illustrate this approach [48, 50, 49, 110, 98]. Alloys under irradiation present an even more challenging problem, since irradiation can greatly enhance both \( D_S \) and \( X_{\text{sat}} \); moreover the above expression for \( \frac{dR}{dt} \) may not even apply to this situation, as irradiation can drive materials away from equilibrium states [45].

Apart from the method discussed in Chapter 4, a second possible approach for suppressing precipitate coarsening involves a Zener-like pinning mechanism. This possibility has been considered in soft materials and in computer simulations studies (of quenched disorder) [111, 112, 113], but not previously in an irradiation environment. In this chapter we examine the effectiveness of these mechanisms for stabilizing nanostructured metal alloys under elevated-temperature irradiation.

Previous work on Cu-based immiscible alloys has demonstrated that one method for decreasing RED
is to use solutes with relatively small diffusion coefficients in Cu, relative to self-diffusion. Thus, $T_{\text{max}}$ in systems like Cu-Mo and Cu-Nb is very high in comparison to systems like Cu-Ag and Cu-Fe [4]. Another possible means to suppress RED and thereby increase $T_{\text{max}}$ is to introduce a high density of unsaturable sinks into the alloy microstructure to reduce the supersaturation of point defects, as recently illustrated using kinetic Monte Carlo (KMC) simulations [16], discussed in Chapter 4. This work suggests, in fact, that for sink densities above a critical concentration, $T_{\text{max}}$ increases to the temperature at which equilibrium vacancies begin to dominate the kinetics.

The second possibility for stabilizing precipitate sizes, Zener pinning, is commonly employed for controlling grain sizes or magnetic domain sizes, but we are unaware of comparable work on controlling precipitate sizes during thermal aging or during irradiation. We point out that the use of Zener pinning for controlling precipitate size is intrinsically different from traditional Zener pinning, since the composition field is a conserved order parameter for the former, but grain orientation and magnetization are non-conserved order parameters for the latter. This point will be revisited in the discussion section. While the control of precipitate size during irradiation through compositional patterning and Zener-like pinning both rely on additions of stable nanoparticles we emphasize that these two mechanisms result in distinctly different kinetic behaviors. The first relies on a dynamical competition between IM and RED, which leads to a microstructural steady state, whereas the second simply adds a kinetic barrier to coarsening.

The experimental procedure employed here for creating a nanoparticle-stabilized alloy begins with first forming a solid solution of $\text{Cu}_{83.5}\text{Ag}_{15}\text{W}_{1.5}$ using physical vapor deposition. By irradiating the alloy with energetic particles at room temperature, the alloy undergoes selective precipitation whereby the W atoms come out of solution to form nano-sized precipitates, while Ag atoms remain in solution. As described in Chapter 2, this process is a consequence of the extreme immiscibility of W in Cu, whereas Ag is only moderately immiscible in Cu. Thus W precipitates out in the thermal spike phase of energetic displacement cascades, whereas Ag does not. The W precipitates, moreover, are particularly effective for the present experiments as they are themselves highly stable against coarsening in Cu at temperatures below $\approx 0.8 T_m$ ($T_m =$ melting temperature) [12]. The Cu-Ag-W system was selected for this study since the heats of mixing of the binary alloy systems obey $\Delta H_{\text{Ag-W}}^m > \Delta H_{\text{Cu-W}}^m > \Delta H_{\text{Cu-Ag}}^m > 0$, and therefore the Ag precipitates should not wet the W precipitates at elevated temperatures, but rather nucleate between them. The heats of mixing for these binary systems are provided in Table 5.1. In the results section we show that with the irradiation-induced 1-3 nm sized W precipitates, $T_{\text{max}}$ for compositional patterning can be increased during MeV Kr ion irradiation from 175 $^\circ\text{C}$, which is found for the Cu-Ag binary alloy [4], to over 300 $^\circ\text{C}$ in the ternary alloy. Above 300 $^\circ\text{C}$ the Ag precipitates grow to a size at which direct interaction of Ag precipitates
and W nanoprecipitates is possible, and the pinning effect of the W nanoprecipitates then becomes relevant.

## 5.2 Experimental methods

Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ thin film alloys were grown on oxidized Si wafers at room temperature using three independent DC magnetron sputtering sources. The base pressure in the sputtering system was $\sim 3 \times 10^{-8}$ torr, and the operation pressure during growth was $\sim 2.1 \times 10^{-3}$ torr Ar. The film thickness was chosen to be $\approx 300$ nm, with a 2-3 nm W capping layer deposited at the top surface of the film to prevent preferential sputtering of the alloying elements and Ag segregation to the surface at elevated temperatures. The samples were subjected to various irradiation treatments at different temperatures. The irradiations were performed using 1.8 MeV Kr ions, as this irradiation condition leads to reasonably uniform defect production across the thickness of the film, with the maximum variation across the film being less than 30% [32]. The dpa rate was $1.77 \times 10^{-2}$ dpa/s for the room-temperature (RT) irradiations and $1.33 \times 10^{-2}$ dpa/s for the irradiations at elevated-temperature; these conditions limit the beam heating to less than 10 °C. The sample thicknesses and compositions were obtained using Rutherford backscattering spectrometry (RBS). All samples were studied using X-ray diffraction (XRD) to obtain information about phase evolution and solubility. Transmission electron microscopy (TEM) was used to obtain complete size distributions of the Ag precipitates, the average size of the W nanoprecipitates, and the grain sizes of the Cu matrix. The average precipitate sizes in this work represent volumetric averages. The statistical analysis of precipitate sizes includes measurements on hundreds of precipitates obtained from multiple TEM/STEM images. The open-source software ImageJ was used to outline the individual precipitates and measure their areal projections. The effective diameters of the precipitates were then calculated by treating the precipitates as spheres.

Scanning electron microscopy (SEM) was used to examine the surface condition of the samples after the different treatments to ensure that the internal structure of the samples had not changed due to any surface related processes. Selected samples were examined by TEM using a JEOL 2010 LaB$_6$ microscope for general bright field (BF), selected area diffraction (SAD) and dark field (DF) imaging. Additional characterization was performed using a JEOL 2200FS Cs-corrected Scanning TEM (STEM) with a high-angle annular dark-field (HAADF) detector for Z-contrast imaging. All TEM observations were performed at a voltage of 200 kV.
Table 5.2: Solubilities and Ag precipitate sizes from XRD and TEM measurement of Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ after various treatments. The Ag solubility in copper matrix is calculated based on the Linde table [118]. W has been assumed to precipitate out of the matrix without interfering with the Ag phase, and has little effect in the peak analysis here.

<table>
<thead>
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<th></th>
<th>RT</th>
<th>RT + 200 °C</th>
<th>RT + 300 °C</th>
<th>RT + 400 °C</th>
<th>RT + 500 °C</th>
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</thead>
<tbody>
<tr>
<td>Ag solubility in Cu (at.%)</td>
<td>15</td>
<td>5.9</td>
<td>1.2</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Cu solubility in Ag (at.%)</td>
<td>6.4</td>
<td>4.6</td>
<td>1.9</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Ag precipitate size from XRD (nm)</td>
<td>3.6 (±0.5)</td>
<td>8.7 (±0.2)</td>
<td>21.2 (±0.3)</td>
<td>33.8 (±0.5)</td>
<td></td>
</tr>
<tr>
<td>Ag precipitate size from TEM (nm)</td>
<td>1.8 (±0.5)</td>
<td>9.3 (±0.5)</td>
<td>13.8 (±0.6)</td>
<td>32.7 (±0.9)</td>
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5.3 Experimental results

5.3.1 Effect of W nanoparticles on Ag precipitate evolution under irradiation

In this section we report the evolution of Ag precipitates at elevated temperatures, for RT pre-irradiated samples. Part of the results were reported previously in Ref. [116], but we briefly review them for completeness.

Fig. 5.1 shows XRD $\theta$-2$\theta$ scans on the as-grown sample and on samples following various thermal/irradiation treatments. The scan on the as-grown sample shows only the Cu (111) peak, which is shifted from that of pure Cu due to the Ag and W in solution, and broadened by the small grain size. After room-temperature irradiation, there is a slight shift of Cu (111) peak to higher angle due to W precipitation, but since the Ag remains in solution, the shift is small. The precipitation of W is not observed directly in the XRD profiles, but this is due to the low concentration and small sizes of the W nanoprecipitates. It is also observed that the Cu peak narrows; this arises from an increase in the Cu grain size during irradiation. Upon further irradiation at elevated temperatures, Ag precipitation is clearly evidenced by the emerging (111) peak of the Ag-rich phase and the additional shift of Cu-rich phase. Both peaks shift closer to (111) positions of the corresponding pure phases as the irradiation temperature is increased. For the higher temperature irradiated samples, a small overshift of the Cu (111) peak to an angle higher than that of pure Cu is seen; this is a consequence of residual strain developed in the Cu film during cooling, as the thermal expansion coefficient of Cu is larger than that of the Si substrate. When calculating the solubility listed in Table 5.2, the peak positions are adjusted according to the calculated residual strain [117]. The Ag precipitate sizes and the Cu grain sizes can also be determined from the XRD data using the Scherrer equation, however, since the XRD results reflect mainly the heavily twinned structure of the film in the growth direction, this measure of the grain size is inaccurate. Plane view TEM shows that the average Cu grain size normal to the growth direction after room-temperature irradiation is $\sim$ 200 nm, and thus comparable to the film thickness. Ag precipitate sizes were obtained using both XRD and TEM; these results are reported in Table 5.2.
Figure 5.1: XRD scans for Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ in the as-grown state as well as subjected to various treatments. The ion dose for RT irradiation is $2.7 \times 10^{16}$ cm$^{-2}$ and for irradiation at elevated temperatures is $2.0 \times 10^{16}$ cm$^{-2}$.

Fig. 5.3 (a) is a micrograph showing the precipitates in the Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ samples after RT irradiation. Only W atoms precipitated while Ag atoms remained in solution. The diameters of these W precipitates are on average $\sim 1$ nm. High-resolution TEM analysis (see Fig. 5.2) shows the orientation relationship between the precipitates and the matrix being Bain type, the same as reported previously for other Cu-based alloy systems containing small W precipitates [98, 119]. The precipitate concentration (in atomic fraction) $C_p$ is $\sim 3 \times 10^{-4}$, however, this will be discussed in more detail below.

Following the RT irradiation, the samples were irradiated a second time at elevated temperatures. In this case Ag begins to precipitate, and owing to the extremely high heat of mixing between Ag and W, the Ag precipitates nucleate between the W precipitates. Fig. 5.3 (b) and (c) show the microstructures of samples after irradiation to a dose of $2.0 \times 10^{16}$ cm$^{-2}$ at 200 $^\circ$C and 250 $^\circ$C, respectively (denoted in the following as the 200 $^\circ$C and the 250 $^\circ$C samples). The presence of Ag precipitates is confirmed by the Moiré fringes in the BF TEM micrographs, as shown in Fig. 5.3 (b)-inset and (c). The Moiré fringe spacing measured in these figures is $\sim 1.6$ nm, which corresponds to Ag \{200\}\|Cu \{200\}, indicating a cube on cube orientation relationship. No combination of W and Cu planes yields a beat frequency corresponding to this value. An accurate determination of the Ag precipitate size in the 200 $^\circ$C sample is difficult due to the problem of distinguishing the W and Ag precipitates, as both types of precipitate are quite small; however an upper limit of 1.8 nm can be placed on the average Ag precipitate size. Since smaller precipitates are harder to
distinguish, they are more likely to be undercounted, and so the true average size is less than 1.8 nm. For the 250 °C sample, the average Ag precipitate size is ≈ 6.7 nm. The size distribution of these Ag precipitates will be discussed in more detail below (see Fig. 5.11), where it is compared with results for irradiations at higher temperatures.

Figure 5.3: Micrographs showing the precipitates in the Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ samples after various irradiation treatments: (a) RT irradiation only; (b) RT irradiation followed by 200 °C irradiation; (c) RT irradiation followed by 250 °C irradiation. (a) and (b) Main are high-resolution Z-contrast STEM images and (b) inset and (c) are BFTEM images. Coexistence of W (small) and Ag (large) precipitates is observed in (b) and (c). Moiré fringes are used to identify the Ag phase, as illustrated in (b) inset and (c). The ion dose for RT irradiation is $2.7 \times 10^{16}$ cm$^{-2}$ and for irradiation at elevated temperatures is $2.0 \times 10^{16}$ cm$^{-2}$.

Fig. 5.4 shows BF images of samples irradiated at RT, followed by 300 °C irradiation (denoted as the 300 °C sample hereafter) to a dose of (a) $2.0 \times 10^{16}$ cm$^{-2}$ and (b) $4.0 \times 10^{16}$ cm$^{-2}$. Again the coexistence of
Ag and W precipitates is observed; the Ag precipitates are easily identified by the Moiré fringes. Note that the images in Fig. 5.4 (a) and (b) are remarkably similar, despite the factor of two difference in irradiation dose. This suggests that the microstructure may have reached a steady state (i.e. patterning) by a dose of $2.0 \times 10^{16} \text{ cm}^{-2}$. The average size of the Ag precipitates in these samples is now 9.3 nm; additional details will be provided below in Fig. 5.11. Unlike the 200 °C and 250 °C samples, the Ag precipitates in the 300 °C sample are now running into the W precipitates and becoming encaged by them. An example is shown in Fig. 5.4 (a)-inset where a Ag precipitate, indicated by the Moiré fringes, is surrounded by the much smaller W precipitates. We point out that even though the average precipitate size of the Ag precipitates increases somewhat with temperature between 200 °C and 300 °C, the systems appear to be approaching steady state at each temperature. This conclusion, which is in agreement with theoretical predictions [9], was further confirmed by a second set of experiments. In these experiments, the RT pre-irradiated samples were first irradiated at some high temperature and then again at a somewhat lower temperature. Two such irradiation sequences were performed: RT + 300 °C + 200 °C and RT + 400 °C + 300 °C. It was observed that the final, lower-temperature, irradiation always tended to bring the microstructure to a state with smaller Ag precipitates, similar to the size reached if the sample had been directly irradiated at this low temperature. Results from these experiments can be found in Fig. 5.5 and Fig. 5.6.

![Figure 5.4: BF TEM images showing the precipitates in the Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ samples after RT irradiation followed by 300 °C irradiation to a dose of (a) $2.0 \times 10^{16} \text{ cm}^{-2}$ and (b) $4.0 \times 10^{16} \text{ cm}^{-2}$. Ag precipitates are identified by the Moiré fringes. The inset in (a) is a high-resolution TEM image showing the caging of a Ag precipitate by W precipitates.](image)

Returning attention to the two-step irradiations, i.e., RT + high-temperature, we next raised the 2nd-step irradiation temperatures to 400 °C and 500 °C, each with two doses, $2.0 \times 10^{16}$ cm$^{-2}$ and $4.0 \times 10^{16}$ cm$^{-2}$. Fig. 5.9 shows micrographs for the sample irradiated at 400 °C to the lower dose: (a) shows a Z-contrast STEM image, and (b) a BF TEM image. Notably the grain boundaries do not appear to be preferred sites for Ag precipitation, in contrast to the small W precipitates. The average size of the Ag precipitates after
the lower dose irradiation is 13.8 nm. A closer examination of the precipitates reveals that similar to the 300 °C sample, the Ag precipitates are surrounded by small W precipitates, as shown in Fig. 5.9 (b). TEM characterization of the higher-dose sample (see Fig. 5.7 (a) and Fig. 5.8) shows that the Ag precipitates are now coarsening, with a volume averaged diameter increasing to 28.0 nm.

Fig. 5.10 shows two Z-contrast images of a pre-irradiated sample irradiated at 500 °C to $2.0 \times 10^{16}$ cm$^{-2}$. The average Ag precipitate size has increased to 32.7 nm. In Fig. 5.10 (b), a string of W precipitates clearly marks the Cu grain boundary. Similar to the other specimens, the grain boundaries do not appear to be
Figure 5.7: Micrographs showing the precipitates in the Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ sample after RT irradiation followed by (a) 400 °C and (b) 500 °C irradiation to a dose of $4.0 \times 10^{16}$ cm$^{-2}$. The volume averaged Ag precipitate diameter are 28.8 nm and 50.7 nm, respectively. The round dark regions found in Ag precipitates are Kr bubbles from irradiation, confirmed by Fresnel contrast in bright field TEM. The W precipitates have rod shapes.

Figure 5.8: Statistical information on precipitates of samples irradiated to a dose of $4.0 \times 10^{16}$ cm$^{-2}$ at various temperatures: (a) histograms of Ag precipitates; (b) average Ag precipitate size vs. irradiation temperature for Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ after RT irradiation and for Cu$_{85}$Ag$_{15}$ [4].

preferred precipitation sites for Ag, and in the grain interior Ag precipitates are always surrounded by W precipitates. The higher-dose sample was also characterized by TEM (see Fig. 5.7 (b) and Fig. 5.8), which yielded an average Ag precipitate size of 48.7 nm.

Fig. 5.11 summarizes the results for the sizes of both Ag and W precipitates in samples irradiated at different temperatures to the dose of $2.0 \times 10^{16}$ cm$^{-2}$. Corresponding information for the samples irradiated to the dose of $4.0 \times 10^{16}$ cm$^{-2}$ can be found in Fig. 5.8. Fig. 5.11 (a) shows the size distributions of the Ag
Figure 5.9: Micrographs showing the precipitates in the Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ sample after RT irradiation followed by 400 °C irradiation to a dose of $2.0 \times 10^{16}$ cm$^{-2}$: (a) a Z-contrast STEM image showing the precipitation in several grains with the arrows pointing to grain boundaries (the few very dark features are analyzed as Kr-stabilized voids); (b) a BF TEM image showing the coexistence of the Ag precipitates (large) and W precipitates (small) and the caging of Ag precipitates by W precipitates.

Figure 5.10: Z-contrast micrographs showing the precipitates in the Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ sample after RT irradiation followed by 500 °C irradiation to a dose of $2.0 \times 10^{16}$ cm$^{-2}$: (a) showing precipitation across an entire grain; (b) showing a Ag precipitate being caged by W precipitates near a grain boundary triple junction.

precipitates; as discussed above, the peak in the distribution shifts to larger sizes as the 2nd-step irradiation temperature increases, and the width broadens. Fig. 5.11 (b) plots the average diameter of the W precipitates and their corresponding interspacing, also as a function of the 2nd-step irradiation temperature. The W precipitate interspacing, which will be important for analyzing the caging effect, was calculated from average size of the W precipitates (TEM data in Table 5.2), assuming negligible W solubility in the matrix after irradiation (this assumption can result in a small underestimation in the spacing, $\sim 25\%$, which we neglect.
here [120]. Notice that the W precipitate size (and interspacing) increases with irradiation temperature; this slow coarsening of W precipitates had been observed previously in a Cu$_{90}$W$_{10}$ binary alloy [12]. If the W precipitates were to form a simple cubic lattice, for example, the largest Ag precipitate that could be contained without enveloping any W precipitates is $\sqrt{3} \times \text{interspacing}$; this dimension thus defines a “caging limit”.

Figure 5.11: Statistical information on precipitates of samples being RT irradiated and then irradiated at various temperatures for a dose of $2.0 \times 10^{16}$ cm$^{-2}$: (a) histograms of Ag precipitates; (b) average W precipitate sizes and W precipitate interspacing vs. the highest irradiation temperature; (c) average Ag precipitate size vs. irradiation temperature for Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ and Cu$_{85}$Ag$_{15}$ [4], as well as the “caging limit” (for definition see text) vs. temperature.

The volume-averaged sizes of the Ag precipitates after irradiation to the dose of $2.0 \times 10^{16}$ cm$^{-2}$ are plotted as a function of the 2nd-step irradiation temperature in Fig. 5.11 (c) (solid line). The dotted line in this figure represents the caging limit; it crosses the line for the average Ag precipitate size at $\sim 350$ °C. Below 300 °C, the Ag precipitates are smaller than the W precipitate interspacing and consequently they do not interact significantly with the W precipitates, while above 400 °C the Ag precipitates impinge on
the W precipitates, as was illustrated in Fig. 5.9 (b) and Fig. 5.10 (b). For comparison, data from Ref. [4] for the average Ag precipitate sizes in irradiated Cu$_{85}$Ag$_{15}$ binary alloys, irradiated to a dose of $4.0 \times 10^{16}$ cm$^{-2}$, are also included in Fig. 5.11 (c). The compositional patterning regime and the macroscopic phase separation (coarsening) regime for this binary alloy are labeled in the plot, showing clearly the much higher maximum temperature for compositional patterning in the ternary alloy system.

5.3.2 Effect of W nanoparticles on Ag precipitate evolution during annealing

The thermal coarsening of W precipitates in binary Cu$_{98.5}$W$_{1.5}$ alloys is insignificant below $\sim 600 \, ^\circ C$ [12], while that for Ag in Cu$_{85}$Ag$_{15}$ is already significant at $\sim 200 \, ^\circ C$ [4]. We thus expect that on annealing RT pre-irradiated Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ samples at 400 $^\circ$C or 500 $^\circ$C, W precipitates will not change significantly in size, but that Ag precipitates will nucleate and grow. Fig. 5.12 shows XRD scans from samples in the as-grown state, after RT irradiation, and again after RT pre-irradiation and annealing at either 400 $^\circ$C or 500 $^\circ$C. After annealing the pre-irradiated sample at 400 $^\circ$C or 500 $^\circ$C, the presence of Ag precipitates is clearly observed, as evidenced by the presence of the Ag (111) peak and the shift of the Cu (111) peak to higher angles. The Ag precipitate sizes, estimated using the Scherrer equation, are 8.9 nm, 11.5 nm and 12.5 nm in diameter for the samples annealed at 400 $^\circ$C for 1 h, 5 h and 10 h, respectively, and 17.7 nm, 22.4 nm and 25.4 nm for the samples annealed at 500 $^\circ$C for 1 h, 5 h and 10 h, respectively.

As noted above, the heats of mixing between alloying elements have the relationship $\Delta H^m_{Ag-W} >$
\[ \Delta H_{m}^{Cu-W} > \Delta H_{m}^{Cu-Ag} \] and for this reason the Ag precipitates are expected to nucleate between the W precipitates rather than nucleating on them and forming core-shell structures, as reported for Cu-Nb-W alloys [98]. Thus during annealing, the size of coarsening Ag precipitates would inevitably reach the interspacing of W particles and interact with them. Fig. 5.13 shows the microstructure of the sample after RT irradiation followed by annealing at 400 °C for 1 h and 10 h. Two sets of precipitates are observable: smaller and brighter W precipitates and larger and irregular shaped Ag precipitates. It is observed from the micrographs that the size of Ag precipitates in the grain interior are of similar size for both the 1-h and 10-h samples. For the 10 h annealed sample, the average size of the Ag precipitate in the grain interior is 11.1 nm. Ag precipitates are found both on the grain boundaries and in the grain interiors. For the 1-h case, the grain boundary Ag precipitates are mostly isolated, decorating the grain boundary. While for the 10-h case, it appears that the grain boundary Ag precipitates begin to impinge each other and form an interconnect strips of Ag phase.

Figure 5.13: Z-contrast micrographs showing the precipitates in the Cu_{83.5}Ag_{15}W_{1.5} sample after RT irradiation followed by 400 °C annealing: (a) 1 h; (b) 10 h

Fig. 5.14 (a) and (b) are HAADF images showing microstructures in the grain interior of Cu_{83.5}Ag_{15}W_{1.5} samples after a 2nd step annealing at 500 °C for 1 h and 10 h. It is remarkable that the two microstructures look very similar with the second sample being annealed 10 times longer. Similar to the 400 °C case, both the Ag and W precipitates are presenting. The shape of many of the Ag precipitates deviates significantly from a sphere, indicating the direct interaction between Ag and W precipitates. The Ag precipitate size distribution is plotted in Fig. 5.14 (c). From the histogram we see that compared to the 1-hour sample, the peak position for the 10-hour sample shifts slightly to larger diameters, while the average size only changes by 0.1 nm, within the error of determining the average. Since the average is volume averaged, the average value is affected more by the larger precipitates. Thus we can conclude that the extra 9 hour of annealing
caused some coarsening of smaller Ag precipitates, but the larger Ag precipitates did not coarsen.

Figure 5.14: Z-contrast micrographs showing the precipitates in the Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ sample after RT irradiation followed by 400 °C annealing: (a) 1 h; (b) 10 h; and (c) the Ag precipitate size distribution for the two cases.

Interestingly, examining samples annealed at 400 °C and 500 °C reveals that continuous grain boundary wetting layers gradually develop as the annealing temperature and time increase. The morphology of the grain boundary Ag phase in the ternary alloy is compared with microstructures in binary Cu$_{85}$Ag$_{15}$ in Fig. 5.15, with binary alloy in Figs. 5.15 (a-c) and ternary alloy in Figs. 5.15 (d-f). Dramatic differences in the microstructures are indeed observed. As shown in Fig. 5.15 (a), the binary alloy undergoes predominantly homogeneous nucleation of Ag precipitates following low temperature annealing at 300 °C for 30 minutes, possibly by spinodal decomposition (the alloy lies within the coherent spinodal [121]). Some coarsening
of these precipitates at the grain boundaries is evident. As the annealing time is increased to 2 hours, the growth of the GB precipitates begins to dominate the microstructural development, accompanied by precipitate depletion in the surrounding regions. At higher annealing temperature, 500 °C, eventually these GB precipitates grow to a size comparable to that of the Cu grains, leaving few Ag precipitates within the Cu grains, see Fig. 5.15 (c). For the ternary alloy, small Ag precipitates are also observed nucleating both within the Cu grain interiors and at the Cu grain boundaries after annealing at 400 °C for 1 hour, shown in Fig. 5.15 (d). As the annealing time is increased, the GB precipitates do not grow in this case, but rather they begin to form a continuous Ag layer within the GB, as shown in Fig. 5.15 (e) and (f) for the specimen annealed at 400 °C and 500 °C, respectively. Notice that small Ag precipitates remain homogeneously distributed within Cu grain interiors, but with a denuded zone near the GBs. At still higher temperatures, 600 °C, the Ag wetting layer thickens until reaching a critical thickness, at which point some of the layers transform from a 2-dimensional to 3-dimensional morphology.

Figure 5.15: HAADF TEM micrographs showing microstructural evolution during annealing following pre-irradiation at room temperature in binary Cu85Ag15 (a-c) and ternary Cu83.5Ag15W1.5 (d-f): (a) 300 °C for 30 min; (b) 300 °C for 2h; (c) 500 °C for 10h; (d) 400 °C for 1h; (e) 400 °C for 10h; (f) 500 °C for 10h.

Fig. 5.16 shows a closer look at the evolution of the grain-boundary Ag phase in the ternary alloy. For the sample annealed at 400 °C for 1h, see Fig. 5.16 (a), the grain-boundary Ag precipitates are still
isolated, apparently slightly larger than those inside the grain. In Fig. 5.16 (b), we see the formation of a grain-boundary Ag layer of thickness $\sim 20$ nm. In addition, the wetting layer is seen to envelop the W nanoparticles as it thickens. Eventually, i.e., at 600 °C, the Ag layer reaches a critical thickness and converts to 3-D precipitates, which coexist with thick Ag layers, see Fig. 5.16 (c). Thus the wetting layer is a transient state imposed on the system by a high density of W nanoparticles.

Figure 5.16: HAADF TEM micrographs showing morphology evolution of grain boundary Ag phase during annealing following pre-irradiation at room temperature in ternary Cu$_{83.5}$Ag$_{15}$W$_{1.5}$ (a) 400 °C for 1h; (b) 500 °C for 10h; (c) 600 °C for 10h.

5.4 Discussion

We have shown that the existence of high density of nm-sized W precipitates can strongly suppress the coarsening of Ag precipitates, and develop non-equilibrium microstructures, either under irradiation or annealing. For the high-temperature irradiated alloy, the W precipitates play different roles depending on the irradiation temperature. Below 300 °C the W precipitates serve primarily as sinks for point defects, and this leads to an extension of the compositional patterning regime in the Cu-Ag system. Above this temperature, the Ag precipitates grow to a size comparable to the interspacing between W precipitates, and direct interaction between the two kinds of precipitates is expected. In this case, Ag precipitates are pinned by the more immobile W precipitates and coarsening is largely suppressed. Differently, for the annealed alloy, only the pinning mechanism is effective. Next we will discuss the involving mechanisms.

First we evaluate the role of W precipitates for the elevated-temperature irradiated case, under the framework of the compositional patterning theory [9], taking advantage of some of the results discussed in Chapter 4.

The first step in evaluating the role of W precipitates on compositional patterning is determining the radiation-enhanced diffusion coefficient of Ag in Cu as a function of temperature [85]. As discussed in
the Introduction, compositional patterning results from a competition between RED, causing precipitate coarsening, and IM, leading to precipitate dissolution. The important variable for patterning is the ratio of the radiation-enhanced diffusion coefficient, $D_{Ag}^{RED}$, to the rate of relocating atoms in ballistic events. Since the latter is nearly independent of temperature, we consider the effect of the W precipitates on $D_{Ag}^{RED}$. For relatively dilute Cu-Ag alloys, we are specifically interested in the quantity $D_{Ag}^{RED} = d_{v}^{Ag} C_{v}$, where $d_{v}^{Ag}$ refers to the partial diffusivity of Ag in Cu by a vacancy mechanism [81] and $C_{v}$ is the vacancy concentration during irradiation. Since Ag is oversized in Cu, we neglect Ag mobility by an interstitial mechanism. Following Refs. [3, 85] we write the rate equation for the vacancy concentration as:

$$\frac{\partial C_{v}}{\partial t} = \xi_{FM} K_{NRT} - \frac{4\pi r_{iv}}{\Omega} (D_{i} + D_{v}) C_{i} C_{v} - \frac{4\pi r_{p}}{\Omega} \xi_{p} D_{v} C_{p} C_{v} - \frac{3\pi^{2}}{L^{2}} \xi_{gb} D_{v} C_{v},$$  (5.1)

where $K_{NRT}$ is the production rate of point defects in terms of displacements per atom per second, dpa/s (calculated within the NRT model [29] using SRIM [32]; $\Omega$ is the atomic volume; $D_{i}$ is the interstitial diffusivity; $D_{v}$ is the vacancy diffusivity; $C_{i}$ is the interstitial concentration; $C_{p}$ is the precipitate density; $r_{iv}$ is the recombination distance for a vacancy and an interstitial; $r_{p}$ is the capture radius of the precipitates for defects; $L$ is the average grain size; $\xi_{FM}$ is the fraction of freely migrating defects; $\xi_{p}$ is the sink efficiency of the precipitate/matrix interface; $\xi_{gb}$ is the sink efficiency of the grain boundaries. All concentrations refer to atomic fractions. Note that the concentration of equilibrium vacancies is small for $T < 300 \^\circ C (C_{v}^{\text{thermal}} = 8.5 \times 10^{-12}$ at $300 \^\circ C$) and thus ignored in this temperature regime. Before determining whether recombination or annihilation at sinks is more important, we assess the ratio $R$ of defects annihilating at precipitate/matrix interfaces versus at grain boundaries, which is the ratio of third and fourth term in Eq. (5.4). Using the values, $K_{NRT} = 1.33 \times 10^{-2}$ dpa/s, $\xi_{FM} = 0.01$ [15], $L = 200$ nm, $\Omega = 1.2 \times 10^{-23}$ cm$^{3}$, $C_{p} = 3 \times 10^{-4}$, $r_{iv} = 0.6$ nm [122], $r_{p} = 0.5$ nm, $E_{mig}^{i} = 0.12$ eV, $E_{mig}^{v} = 0.72$ eV [123], we obtain $R \approx 200 \frac{\xi_{p}}{\xi_{gb}}$. Assuming that the sink efficiency of W precipitate/matrix interfaces is comparable to that of grain boundaries, we expect that most of the defects will annihilate at the W precipitates. Note that the Ag precipitate/matrix interfaces may also serve as sinks once the Ag precipitates form, but since they grow quickly, their number density soon becomes far smaller than that of the W precipitates, and therefore their contribution is neglected. The relative strength of the second term (recombination) compared with the third term (sink elimination) in right-hand-side of Eq. (5.4) thus determines whether the system is in the recombination or sink-limited regime.

Rate theory predicts that at the cross-over between recombination and sink elimination regime, the point defect recombination fraction is roughly 1/3 (see Chapter 4 for details). With this criterion and assuming that the W precipitate/matrix interface is an ideal sink, i.e., $\xi_{p} = 1.0$, we find that when the irradiation...
temperature is greater than \( \approx 50 \, ^\circ \text{C} \), the system enters the sink elimination regime at steady state. In contrast, if we consider a system without the W precipitates, the transition temperature is \( \approx 200 \, ^\circ \text{C} \). Recall that the maximum temperature of compositional patterning for the Cu\(_{85}\)Ag\(_{15}\) binary alloy under Kr irradiation is \(175 \, ^\circ \text{C} \) [4]. Therefore, for the binary system, the transition from patterning to macroscopic phase separation occurs at a temperature lower than that for the transition from the recombination-limited to sink-limited regimes. This is significant since, as we will now show, when the transition temperature from recombination-limited to sink-limited kinetics is lower than the transition temperature from patterning to macroscopic phase separation, the patterning regime will persist up to the temperature at which equilibrium vacancies dominate the kinetics.

For dilute Cu-Ag alloys, \(D_{\text{RED}}^\text{Ag}\) can be written as

\[
D_{\text{RED}}^\text{Ag} = d_{\text{Ag}}^v C_{\text{Cu}} = \frac{d_{\text{Ag}}^v}{d_{\text{Cu}}^v} d_{\text{Cu}}^v C_{\text{Cu}},
\]  

(5.2)

where \(d_{\text{Ag}}^v\) and \(d_{\text{Cu}}^v\) are the partial diffusion coefficients of Ag and Cu in the Cu matrix, both via a vacancy mechanism [81]. In the sink-elimination regime, the steady state vacancy concentration is

\[
C_v = \frac{\xi_{\text{FM}} K_0 \Omega}{4 \pi r_p \xi_p C_p D_v} \propto D_v^{-1},
\]  

(5.3)

As pointed out in Ref. [16], \(D_v \approx d_{\text{Cu}}^v C_{\text{Cu}}\), since the Ag concentration in the matrix is low. Taking advantage of the relationship \(d_{\text{Cu}}^v = d_{\text{Cu}}^v\) [81], the Ag diffusivity becomes \(D_{\text{RED}}^\text{Ag} \propto \frac{d_{\text{Ag}}^v}{d_{\text{Cu}}^v}\). Fig. 5.17 (a) shows the temperature dependence of the ratio \(\frac{d_{\text{Ag}}^v}{d_{\text{Cu}}^v}\) obtained by taking the ratio of the tracer diffusion coefficients of Ag and Cu in a Cu matrix [124]. For the temperature range of interest (below 300 \( ^\circ \text{C} \)), \(D_{\text{Ag}}\) is only weakly dependent on temperature. Accordingly, the steady-state precipitate size remains nearly constant as the irradiation temperature increases, in agreement with Fig. 5.11 (c). We note that the experiments in fact show that the precipitate size increases slowly with increasing temperature in the patterning regime, in contrast to the slow decrease in \(D_{\text{Ag}}\) calculated in Fig. 5.17 (b). This difference, however, is very small and can be caused by a number of possibilities. For example, we have assumed that \(\xi_{\text{FM}}\) (the fraction of freely migrating defects) is independent of temperature, but past work has shown that \(\xi_{\text{FM}}\) increases slowly with temperature [125]. Such details are beyond the scope of this work.

For samples irradiated at high temperatures (higher than 400 \( ^\circ \text{C} \)) as well as annealed at high temperatures, the interactions between the Ag precipitates and the W nanoprecipitates become significant, as indicated in Fig. 5.11 (c) by the line for the caging limit crossing the line representing Ag precipitate size. At 400 \( ^\circ \text{C} \), with \(C_p = 2.9 \times 10^{-5}\) and \(r_p = 1.1\) nm, the irradiation-induced and equilibrium vacancy con-
centrations are becoming comparable [126, 127]. This indicates that the role of W precipitates as defect sinks is becoming less important. Our experiments reveal, however, that coarsening is slow in comparison to binary Cu$_{85}$Ag$_{15}$ at both 400 °C and 500 °C, as shown from Fig. 5.11 and Fig. 5.8 for those temperatures. In addition, TEM images, as pointed out above, show a direct interaction between W precipitates and Ag precipitates, evidenced by formation of Ag precipitates of irregular shape. These observations suggest that the W precipitates can now serve as pinning sites.

We have estimated the energy barrier for de-pinning using KMC simulations; by de-pinning we mean the Ag precipitates overgrow the W precipitates. Details regarding the KMC algorithm can be found in Ref. [128]. In this set of simulations, a ternary A-B-C system was constructed to mimic the Cu-Ag-W system (A-Cu, B-Ag, C-W): the pair-wise ordering energies were set to be $\omega_{AB} = 0.0553$ eV, $\omega_{AC} = 2\omega_{AB} = 0.1106$ eV and $\omega_{BC} = 3\omega_{AB} = 0.1659$ eV, so as to reproduce $\Delta H_{Ag,W}^m > \Delta H_{Cu,W}^m > \Delta H_{Cu,Ag}^m > 0$; the vacancy migration energies were set as $\Delta E_{VA} = \Delta E_{VB} = 0.8$ eV and $\Delta E_{VC} = 1.8$ eV, which leads to much slower diffusion of C in A, compared to that of A and B, again similar to the Cu-Ag-W system. The tracer diffusivity of W in Cu is not well known, but we assume it is similar to that of other refractory elements in Cu, which is very small (for example, for Ir $D \sim 2 \times 10^{-18}$ cm$^2$/s at 500 °C in Cu, whereas for Ag in Cu $D \sim 4 \times 10^{-14}$ cm$^2$/s [129]). The simulation cell is of size $128 \times 128 \times 128$. In the cell contains 512 C particles, which are of size $\sim 1$ nm, forming a “fcc lattice”, serving as pinning sites. With the current kinetic parameters, The diffusion of C particles and the solubility of C in A are negligible. A single B precipitate is placed inside the cell. The size of the B precipitate is small enough so that it does not touch any of the C particles. The system is then annealed at $T = 0.055$ eV (365 °C). During the simulation, the size of the B precipitate and the solubility of the B species are obtained using a cluster analysis algorithm. If the B
solubility is maintained at a level which provides slight supersaturation, so that $B$ atoms in solution will continuously condense onto the larger $B$ precipitate, and overgrow the $B$ precipitate at some situations. The pumping is stopped once the total nominal $B$ concentration reaches a pre-set value. Then the system is being annealed for some longer time so that equilibrium is reached. Running a series of such simulations will give the equilibrium $B$ solubility as a function of the size of the $B$ precipitate.

![Figure 5.18: (a) Solubility of $B$ measured for the system with 512 $C$ pinning particles (black squares). The line is the fitting using Gibbs-Thomson equation for the system with no $C$ pinning particles. Inset (a) is the KMC-measured solubility subtracted by the Gibbs-Thomson fitting, showing solely the effect of $C$ pinning on the $B$ solubility. (b) A slice of the microstructure at the end of the simulation of the system at the highest point in the solubility bump, showing a pinned $B$ precipitate developing positive and negative curvatures. (c) A slice of the microstructure at the end of the simulation of the system with a relatively large $B$ precipitate.](image)

Fig. 5.18 (a) shows the results of these simulations, here plotting the solubility of $B$ as a function of the precipitate size. Shown in inset Fig. 5.18 (a) is the effect of $C$ pinning sites on solubility of $B$, obtained by subtracting the Gibbs-Thomson effect from the KMC measured solubility. In (b) and (c) we show two
slices of the simulation cell showing the shape of B precipitate being affected by the existence of C particles, with both positive and negative curvatures presenting. From Fig. 5.18 (a) we see that for the system with C pinning sites, although the B solubility generally follows the Gibbs-Thomson relationship, we can see several bumps along the curve, which is illustrated in inset Fig. 5.18 (a) in a clearer way. Since the chemical potential $\mu_B = RT \ln C_B$, Fig. 5.18 (a) is essentially a plot of chemical potential versus precipitate size for a given density of C precipitates. At small B precipitate size, the chemical potential of B atoms decreases rapidly; this is the usual Gibbs-Thomson effect, which is indicated by the solid red curve; the solid curve was obtained by simulations for the A-B binary alloy. When the B precipitate size approaches the inter C-particle spacing the chemical potential increases with B size; this gives rise to the Zener-like pinning. The barrier energy for a single B precipitated caged by C particles is very high, on the order of 10 eV to 100 eV. This prevents coarsening by the usual evaporation-condensation mechanism. On the other hand, at very large B size in this plot is increased only slightly by the C nanoparticles, and the barriers are relatively small.

B atoms in the small caged precipitates, therefore, will flow to GB wetting layer, enabling layers to overrun the W nanoparticle obstacles and thicken. Fig. 5.16 (b), indeed, clearly illustrates that the region close to the wetting layer is being depleted of Ag precipitates. Eventually this wetting layer becomes sufficiently thick that it is unstable to transformation to a 3-D morphology, with dimensions on the order of the Cu grain size, similar to the binary case. The formation of these large Ag precipitates in the ternary alloy, however, has been delayed by several hundred degrees, and it develops by a completely different mechanism.

5.5 Conclusion

In this study we demonstrated a remarkable stability of Ag precipitates in the Cu-Ag-W system under high-temperature ion irradiation as well as under high-temperature annealing, owing to the presence of a high density of 1-3 nm W precipitates formed under room-temperature irradiation. The role of the W precipitates is different for different regimes: in moderate temperature regime (≤ 300 °C), they serve as defect sinks which lead to an extension of the compositional patterning regime under irradiation to higher temperatures compared to binary Cu-Ag system, as predicted in Chapter 4. During irradiation at high temperatures (≥ 400 °C), W nanoparticles serve primarily as pinning sites to stop the growth of Ag precipitates. Rate theory reveals that the W clusters as sinks lower the temperature for the defect kinetics to enter the sink elimination regime from 200 °C to 65 °C, which extends the patterning regime to much higher temperatures. In addition, we showed that an unusual grain-boundary wetting layer can form during high temperature annealing of the pre-irradiated Cu-Ag-W sample. KMC simulations of the pinning phenomenon show that the energy
barrier for de-pinning is extremely high so the microstructure is stabilized at nano-scale, and that the pinning mechanism is less effective for large $B$ precipitates. The results from this study add feasibility in engineering materials for advanced nuclear reactor applications.
Chapter 6

CONCLUSIONS

In this dissertation we employ analytical modeling, computer simulation and experimental methods to study the stability of precipitates in binary and ternary alloys, under elevated-temperature irradiation or annealing.

We first focus on the effect of competing dynamics, namely the thermally activated and irradiation-enhanced diffusion, and the irradiation-induced ballistic mixing, on the stabilization of a complex, non-equilibrium microstructure: the cherry-pit structure. By performing kinetic Monte Carlo simulations on an A-B model binary alloy, we systematically investigate the influence of a broad range of thermodynamic and kinetic parameters on the stability of cherry-pit structures. It is found that the cherry-pit structures are dynamical structures, which periodically evolve during the irradiation. Stronger ballistic mixing, larger relocation distance, faster solute impurity diffusion and higher solute solubility relative to matrix species will favor the stabilization of cherry-pit structures. We then extend the Frost-Russell model to inside the B precipitate, revealing that the dynamical stabilization of the cherry-pit structures is a special case of compositional patterning. For the B precipitates in the A matrix, once the system enters the compositional patterning regime, inverse coarsening happens. In this regime, smaller precipitate grows at the expense of the larger precipitates, i.e., precipitates with smaller curvature will feed precipitates with larger curvature. For the cherry-pit structure, instead of treating B as a precipitate, B is the “matrix” for the A pits. Here, an A pit can exchange atoms with other pits, as well as the A matrix, outside the B precipitate. Thus the A matrix can also be viewed as an A “precipitate”, which has negative curvature. Thus, since the curvature of the matrix “precipitate” is always smaller than that of the A pits, the matrix will always feed the pits, until the B shell between the pits and the matrix become thin and unstable.

Then, we explore the possibility of extending the compositional patterning to higher temperatures by introducing point-defect sinks, both by KMC methods, and experimentally with a model Cu-Ag-W alloy. The original KMC model is extended to capture the non-conserved nature of point defects, which enables us to investigate the effect of point-defect sinks on compositional patterning. Different sink structures (spher-
ical or planar) and sink densities are considered. The simulations predict that with certain solutes, upon increasing temperature, the compositional patterning regime can be maintained to much higher temperatures if the transition from recombination regime to sink-elimination regime happens before the transition from compositional patterning to macroscopic phase separation regime. This prediction is then tested with a model Cu-Ag-W alloy. Taking advantage of the selective precipitation phenomenon, room temperature irradiation is used to induce 1-2 nm sized W nanoparticles, which serve as point-defect sinks. The system is then irradiated at elevated temperatures, and the size evolution of the Ag precipitates is measured. It is shown that, with the W nanoparticles induced by RT irradiation, the system enters the compositional patterning regime at about 65 °C, compared to 200 °C in the binary Cu-Ag system. Thus the maximum temperature for compositional patterning is increased to at least 300 °C, compared to 175 °C for the binary system.

During the experimental study of the Cu-Ag-W, we find that some Ag precipitates are caged by the W nanoparticles. We investigated the effectiveness of the caging effect on Ag precipitates, either in grain interior or at grain boundaries. We show that the RT irradiation induced W nanoparticles dramatically alters the kinetic pathway followed by the ternary system during annealing, compared to the binary Cu-Ag alloy. The Ag precipitates become encaged by the nanoparticles as they grow, and this suppresses their growth, which in turn drives the formation and growth of a non-equilibrium Ag grain boundary wetting layer. This finding suggests a promising scheme for synthesizing novel high-strength nanostructured alloys, as highly immiscible nanoparticles can be incorporated into alloys not only by ion beam irradiation but also by severe plastic deformation.

The work in this dissertation has illustrated the rich complexity of driven materials, and contributed to a better understanding of how compositional patterning can be optimized and integrated into the design of alloys that are radiation resistant at elevated temperatures. Also, the investigation of the effect of W nanoparticles on compositional patterning has led to the discovery of a novel effect of refractory nanoparticles on the stabilization of non-equilibrium grain boundary wetting phase, which illustrates a new approach of controlling microstructures in hard matter.

For future work, it would be interesting to focus on the following points. For the KMC model with non-conserved point defects, taking into account the size dependence of the absorption probability of a sink structure would be beneficial, since the precipitate/matrix interface structure often changes as the precipitate grows in size, leading to different sink efficiency. Also, the current model considers the sinks as geometrical sites, which does not include the chemical interaction between sink structures and the matrix. This limitation can be overcome by treating some of the chemical interfaces as sinks. For the pinning effect
of W on coarsening of Ag precipitates, the role of irradiation is not yet clear. Experimental observations show that high-temperature irradiation can “depin” the Ag precipitates, i.e., helping them to grow larger. The mechanism behind this observation is to be determined: whether the irradiation (cascades) helps the Ag interface to overrun the W nanoparticles, or the W nanoparticles move during irradiation. Modeling these processes is challenging, as it involves very different timescales, from the timescale of a cascade to that of long range diffusion of solutes.
Appendix A

DETAILS OF THE KMC MODEL WITH NON-CONSERVED POINT DEFECTS

Irradiation induced Frenkel pairs are generated by first choosing two atoms, X and Y, separated by a distance $r_{xy}$. A vacancy is then created on the lattice site initially occupied by atom X, by moving X to form a dumbbell with Y. The distance $r_{xy}$ could be chosen to reproduce physical distributions, but here $r_{xy}$ is chosen as a random distance within the simulation cell, i.e., point defects are created uniformly in the cell. This choice is made so that the production rates are equivalent to those used in rate theory modeling. Recombination occurs when a vacancy and an interstitial come closer than a critical distance, $d_{rec} = 3a_{nn}$, which corresponds to a recombination volume of 160 $\Omega$ ($\Omega$ is the atomic volume), similar to values reported for Cu and other fcc metals [3]. During a recombination event, one atom of the interstitial dumbbell is randomly chosen and moved into the vacancy site, the other atom of the dumbbell remaining at the original dumbbell site. Following Soisson [88], we introduce a “reservoir” of A and B atoms, which ensures the numerical stability of the program, and the chemical composition of the overall system “simulation cell + reservoir” is conserved. When a dumbbell interstitial is absorbed at a sink site, one atom of the dumbbell is randomly chosen and moved to the reservoir. When a vacancy is absorbed at a sink site, an atom is randomly chosen from the reservoir to replace the vacancy. In practice, the reservoir size (0.1% of the total number of atoms in the simulation cell) is very small compared to the size of the simulation cell and it has no significant effect on the results.

As reviewed by Dederichs et al. [130] the dominant mechanism of dumbbell interstitial diffusion in fcc alloys is by isotropic diffusion of $\langle 100 \rangle$ dumbbells in three dimensions. We model these interstitial dumbbells by placing two atoms on one fcc lattice site and allowing either atom of the pair to jump to any of the 12 nearest neighbor sites. This corresponds to the case of a high rotation frequency of the interstitial dumbbells, for which the directionality of the dumbbells can be ignored [130]. With such approximation, during the exchange of an atom and a mixed dumbbell, two types of exchange occur with equal probabilities: $AB + A \rightarrow A + AB$ and $AB + A \rightarrow B + AA$. 

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Table A.1: Thermo-kinetic parameters used in the KMC simulations. See text for definition of variables.

<table>
<thead>
<tr>
<th>$E_{A,coh}$</th>
<th>$E_{B,coh}$</th>
<th>$E_{f,AV}$, $E_{f,BV}$</th>
<th>$E_{f,A,AA}$, $E_{f,B,AA}$, $E_{f,B,BB}$</th>
<th>$E_{f,A,AB}$, $E_{f,A,BB}$, $E_{f,B,AB}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-4.34 eV</td>
<td>-4.34 eV</td>
<td>1.28 eV</td>
<td>3.24 eV</td>
<td>5.90 eV</td>
</tr>
<tr>
<td>Parameter set</td>
<td>$E_{AV}$</td>
<td>$E_{BV}$</td>
<td>$E_{A,AA}$</td>
<td>$E_{X,I}$</td>
</tr>
<tr>
<td>1</td>
<td>-9.83 eV</td>
<td>-9.93 eV</td>
<td>-8.69 eV</td>
<td>-8.26 eV</td>
</tr>
<tr>
<td>2</td>
<td>-10.22 eV</td>
<td>-9.88 eV</td>
<td>-9.96 eV</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The parameters of the kinetic model are related to physical quantities through the following relationships:

- homo-atomic pairwise interactions are related to cohesive energies for A and B metals through $E_{A,coh}^A = \frac{Z}{2}\varepsilon_{AA}$ and $E_{B,coh}^B = \frac{Z}{2}\varepsilon_{BB}$, where $Z$ is the nearest-neighbor site coordination number ($Z = 12$ for fcc structure).

- hetero-atomic interactions are defined through the ordering energy, defined as $\omega_{AB} = 2\varepsilon_{AB} - \varepsilon_{AA} - \varepsilon_{BB}$, and a positive value of $\omega_{AB}$ results in an immiscible alloy at low enough temperatures, which will be the case in all alloys considered in this study.

- atom-defect effective interaction energies are used to reproduce realistic values of defect formation energies, which are defined as $E_{f,XV}^X = Z\varepsilon_{XV} - \frac{Z}{2}\varepsilon_{XX}$ and $E_{f,XI}^X = Z\varepsilon_{XI} - \frac{Z}{2}\varepsilon_{XX}$ ($X = A,B; I = AA, AB, BB$) for vacancies and various interstitials, respectively, following the procedure introduced by Doyama and Koehler [58].

The thermo-kinetic parameters used in the KMC simulations are listed in Table A.1. The pre-exponential factor for all thermal jumps is set to be $10^{14}s^{-1}$. The $A-V$ saddle point energy was set so that the vacancy migration energy in the matrix is 0.8 eV, slightly higher than its value in Cu [89]. Three distinct parameter sets are considered, see in Table A.1, with different relative diffusivity of solute and solvent atoms, by varying the $B-V$ saddle point energy. For saddle point energies involving interstitials, the $A-AA$ saddle point energy is set to result in an interstitial migration energy of 0.37 eV, which is lower than that of the vacancy, as found in Cu and other pure metals [131]. Although the particular value of the interstitial migration energy we use in this study does not exactly match the experimental value for Cu system, we note that since the interstitial migration energy is still significantly lower than that of the vacancy, it has little effect on the main results. Other saddle point energies involving interstitial jumps are set equal for simplicity, but higher than that for the $A-AA$ exchange. These settings capture the diffusion characteristics of binary alloys with oversized solute atoms, i.e., where solute atoms are mainly transported via vacancy mechanism.
Appendix B

SINK ABSORPTION PROBABILITY AND SINK EFFICIENCY

For the case of planar sinks, we study here the relationship between the sink absorption probability $p$ and the sink efficiency $\eta$, as defined by Eq. (4.2.2). Simulations were run at the same temperature and displacement rate used in Sec. 4.3.1, but for system sizes of $200 \times 200 \times L_3$, with $L_3 = 12$ to 256. The resulting steady-state vacancy concentration is plotted as a function of the layer thickness, assuming different absorption probabilities, see Fig. B.1. For a perfect sink with absorption probability $p = 1$, the vacancy concentration varies as the square of the layer thickness when the thickness is small, as sink elimination dominates over recombination. For a poor sinks, i.e., with small $p$ values, the vacancy concentration does not depend much on the layer thickness, as recombination always dominates.

For comparison, we also calculated using rate theory the vacancy concentration as a function of film thickness with constant sink efficiency $\eta$, see Fig. B.2. One notices that the shape of the constant $p$ curves in Fig. B.1 and the constant $\eta$ curves in Fig. B.2 are different. Although for perfect sinks, i.e., $p = 1$ or $\eta = 1$ or completely ineffective sinks, i.e., $p = 0$ or $\eta = 0$, the two descriptions are equivalent, for intermediate sink efficiencies, the two descriptions are very different. The description relying on the defect absorption probability $p$ provides an intrinsic characteristic of that sink. On the contrary, the sink efficiency defined through Eq. (4.2.2) is affected by the distance between sinks, and the possible presence of other type of sinks.

The difference between the two descriptions is more directly seen by plotting the sink efficiency, measured during the KMC simulations, versus the sink absorption probability $p$, for various layer thicknesses, see Fig. B.3. The relationship between $\eta$ and $p$ can be highly non-linear. For $p$ values below $\approx 1\%$, the $\eta$ values obtained for different layer thicknesses deviate significantly from each other. For large thicknesses, near the center of the layer, recombination is the dominating mechanism for defect annihilation, and the values reflect fairly accurately the quality of the sink. For small layer thicknesses, however, the two boundaries of the layer can no longer be considered as isolated sinks, and point defect annihilation on one sink is affected by the
Figure B.1: KMC simulation measured average vacancy concentration in the layer with constant absorption probability $p$. Irradiation temperature is 406 K.

Figure B.2: Rate theory calculated average vacancy concentration in the layer with constant sink efficiency $\eta$. 
presence of nearby sinks (here the periodic image of the first sink). Therefore, the absorption probability $p$ is a more physical parameter for describing the quality of the sink. We note also that the present description is equivalent to using a reaction rate that would characterize the reaction and elimination of the point defects with the sink structure.
Figure B.3: $\eta$ as a function of $p$ for different layer thicknesses.
Appendix C

DEFECT ANNIHILATION
REGIMES FOR SPHERICAL SINKS

We present here simulations evaluating the transition from recombination to sink elimination for the case of spherical sinks, thus extending the results and analysis given in Sec. 4.3.1. Such sinks are for instance found in microstructures containing semi-coherent or incoherent spherical precipitates. In order to test the effect of different sink densities on sink efficiency, two sets of simulations were carried out with 1 or 8 spherical sinks, uniformly embedded in a $64 \times 64 \times 64$ simulation cell, keeping the volume fraction of sink sites fixed at $\sim 0.1\%$, and the absorption probability at $p = 1$. The corresponding sink densities, $3.2 \times 10^{23} m^{-3}$ and $2.6 \times 10^{24} m^{-3}$, are comparable to experimental observations for some nano-ODS steels developed for nuclear applications [132, 133]. The transition temperature from recombination to sink elimination is lower for the higher sink density, and, the diffusion coefficient in the sink regime is decreased by a factor 4, see Fig. C.1. This is in agreement with rate theory, since, for a fixed fraction of sink sites, the sink strength scales as $(N_p)^{2/3}$, $N_p$ being the number of sink particles in the simulation cell. Again, the recombination fractions at the transition point from recombination to sink elimination, 29.9% and 27.9% for the low and high sink number densities, respectively, agree well with the $\approx 30.9\%$ value predicted by rate theory.
Figure C.1: Atomic diffusion coefficients as a function of temperature for two sink densities, measured by KMC and calculated using rate theory.
Appendix D

IRRADIATION-INDUCED NANO-RODS IN CU-W ALLOY

In Chapter 5, we have shown that the enormous effect of the RT irradiation-induced W nanoparticles on the evolution of Ag precipitates, both under irradiation and during annealing. In most cases, the size and morphology of the embedded W nanoparticles remain stable. However, in several samples irradiated at higher temperatures with higher dose, W nanoparticles coarsen, and deviate from spheres. In Fig. 5.10, we see many W particles evolve from the original spherical shape and form rod-like precipitates. These W rods are found both along grain boundaries and in the grain interior. While it is not surprising that W precipitates elongate along grain boundaries, the formation of the rod-like precipitates in the grain interior is worth investigating. We present here preliminary results documenting this morphological transition.

To make the system simpler, instead of the Cu-Ag-W ternary alloy, a Cu$_{98.5}$W$_{1.5}$ binary alloy was used. The Cu$_{98.5}$W$_{1.5}$ thin films were grown on oxidized Si wafers to a thickness of $\approx 300$ nm. Details of the deposition method were described previously in Chapter 5. Each of the thin film samples was first irradiated at room temperature to a dose of $2.7 \times 10^{16}$ ions/cm$^2$, in order to induce 1-2 nm sized W precipitates. Then the samples were irradiated at elevated temperatures. For elevated-temperature irradiation, the dose rate was $2.0 \times 10^{16}$ ions/cm$^2$ per hour.

Fig. D.1 shows the microstructural evolution of a Cu$_{98.5}$W$_{1.5}$ sample first irradiated at RT, then irradiated at 500 °C for different times. W rods are observed in all three samples. However, the percentage of W precipitates taking the rod shape increases as irradiation time increases, suggesting that the W rods grow at the expense of the spherical W precipitates. Also, the length of the rods increases as irradiation dose increases. At higher dose, many of the W rods have aspect ratios larger than 10. In all three micrographs, a W denoted zone on the order of 10-20 nm is observed near the grain boundaries. Thus, some long range W diffusion should be present. Whether the W rods have preferred orientation in a given grain is not clear, since the lack of statistics and the fact that we only have the 2D projection of the 3D structure.

Fig. D.2 shows the microstructural evolution of a Cu$_{98.5}$W$_{1.5}$ sample first irradiated at RT, then irradiated
Figure D.1: HAADF TEM micrographs showing microstructural evolution of the pre-irradiated Cu\textsubscript{98.5}W\textsubscript{1.5} sample irradiated at 500 °C for (a) 1h (b) 2h; (c) 3.5h.

Figure D.2: HAADF TEM micrographs showing microstructural evolution of the pre-irradiated Cu\textsubscript{98.5}W\textsubscript{1.5} sample irradiated at 600 °C for (a) 20min (b) 1h; (c) 2h.

at 600 °C for different times. Very different from the sample irradiated at 500 °C, the majority of W precipitates in the 600 °C sample adopt the spherical shape. Clearly, as irradiation time increases, the W precipitates coarsen. At higher dose, some elongated W precipitates form, but the aspect ratio is much smaller than that of the 500 °C sample.

In order to determine whether the W rods observed at 500 °C are at steady state, for one pre-irradiated sample, a special 2-step irradiation process was performed: 600 °C to a dose of 2.0 × 10\textsuperscript{16} ions/cm\textsuperscript{2}, and back to 500 °C for another dose of 4.0 × 10\textsuperscript{16} ions/cm\textsuperscript{2}. The results are shown in Fig. D.3.

Comparing the morphology of W precipitates in Fig. D.3 (a) and (b), we see that, after the second step at 500 °C, the W rods again form. Therefore, the rod-like W precipitate is a stable form at 500 °C, and not a transient state. Measurements show that the width of the rod is positively correlated to the size of the size of the spherical W nanoparticles, suggesting that W rods are directly generated from the spherical W nanoparticles at the beginning stage of their formation.
The mechanism of the stabilization and growth of the W rods is under investigation. One possible mechanism could be that a W rod formation could begin by the coagulation of two spherical W nanoparticles. Then, due to the recoil mixing imposed by irradiation, unlike in the thermal system, the solute concentration field around the middle of the W rod, where the curvature is smaller, can be higher than that around the two tips of the rods. Thus the W rods can continue to grow one dimensionally, forming the structures observed in the experiment. Analytical modeling and computer simulations are to be used to determine whether the proposed mechanism is valid.
REFERENCES


