SELF-ORGANIZATION IN IMMISCIBLE ALLOY SYSTEMS UNDER IRRADIATION AND SEVERE PLASTIC DEFORMATION

BY

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DISSERTATION

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ABSTRACT

There exist many practical examples of extreme environments where materials are commonly forced to operate, ranging from nuclear reactors to alloys being processed through severe plastic deformation. In each of these cases, there exists external dynamical forcing which keeps the material in non-equilibrium conditions. In the case of structural materials in a nuclear reactor environment, there are high fluxes of neutrons which can cause the alloys to become microstructurally unstable and cause their properties to change over time. In addition, nuclear reactors are kept at high temperatures in order to generate power, which can cause other deleterious effects on a material such as creep and grain coarsening. For severe plastic deformation processing of alloys, such as high energy milling, a large amount of energy is imparted in the form of stress, which causes dislocation motion and grain refinement. Temperatures can also vary depending on the process, generally ranging from room temperature to > 0.75 of the melting point. Because each of the environments listed contains an external dynamical force which is driving the materials into non-equilibrium, they are commonly referred to as driven materials.

Due to the number of external factors and the numerous practical situations involving driven materials, one may ask if there is a theoretical framework on in which it is possible to not only describe what is occurring but to also predict how the material’s microstructure will evolve over time. After gaining the understanding to be able to predict the material response to such extreme environments, it would be especially beneficial to find a class of materials which would remain stable over time. In other words, rather than determining when an alloy would fail under service, it would be best if it were possible to design an alloy which would simply never fail over its expected lifetime.
To achieve this goal, research has been conducted in material science to better understand the fundamentals of driven materials. One of the main areas of focus revolves around the idea of self-organization in nanostructured alloys. A material which self-organizes will reach a steady state microstructure and will not change as long as the environmental parameters do not change. This means that a material which self-organizes would have the same microstructure indefinitely, even in an environment as extreme as a nuclear reactor, and would not undergo the negative effects such as coarsening or phase changes.

The property of self-organization has been readily identified in moderately immiscible and highly immiscible alloy systems such as Cu-Ag or Cu-W, respectively. Furthermore, this behavior is experienced in multiple driven systems; both irradiation and severe plastic deformation (SPD) have been shown to share very similar characteristics, even though the underlying mechanisms are different. While existing models such as the “Driven System Model” and “Effective Temperature Model” can explain existing experimental results for alloys systems with low to moderate heat of mixing, there is currently a lack of understanding in how highly immiscible alloy systems can self-organize, especially at low temperatures (T < .25 T_m).

In this dissertation, several model experiments were performed to elucidate a mechanism for both irradiation and shear mixing in alloy systems with high heats of mixing. Irradiation and shear deformation experiments were performed at low temperatures (liquid nitrogen/dry ice) to understand the importance of the chemical interactions in these immiscible alloy systems. It was found that the alloys self-organized into nanoprecipitates when under irradiation or severe plastic deformation and that their microstructure was completely independent of the starting conditions.
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CHAPTER 1
INTRODUCTION

Recently, research in the material science community has focused on the production of stable nanostructured materials with novel properties. Generally, this has focused largely on 0-D structures, such as nanocubes or quantum dots, 1-D structures, such as nanotubes, and 2-D structures, such as nano-laminates [1-10]. However, these materials are mainly produced on a small scale, utilizing solution, vapor, or solid-state growth techniques. Even so, this research has been fruitful in many areas, leading to advances in fields ranging from energy storage to biological devices. However, the progress made in bulk nanostructured material has generally not received as much attention and has fallen behind, although examples do exist, such as oxide dispersion strengthened (ODS) steels and radiation resistant multilayer alloys [11-18]. However, as researchers look more at the possibilities for bulk nanostructured materials for structural applications, the same problems remain which is to ensure the stability of the material when in under operation.

As one can imagine, the ability to produce and use bulk nanostructured materials becomes even more challenging when faced with extreme conditions such as what is commonly experienced in nuclear reactors or during service wear and cyclic fatigue. These processes generally have a mixture of conditions which make stabilization of material properties difficult, such as high temperatures and large energy inputs, either in the form of radiation or mechanical attrition. Other examples of extreme nonequilibrium conditions are ion beam modification, high energy milling, vapor-phase deposition, extrusion, and severe plastic deformation processing, among others. Fig. 1.1 lists several of these systems and compares the injected power between each of the different environments [19, 20]. While these different processes each experience
different operating conditions, they are all characterized as being far from equilibrium environments which also contain external dynamical forcing. Materials that are found in these environments are referred to as driven materials. If that material happens to be a metal compound, such as ODS steel in a nuclear reactor, one can also refer to these materials as driven alloys.

As mentioned above, one of the primary goals of materials science in recent years is the ability to create materials that will retain their novel properties during service, especially in driven systems. To this end, it is of utmost importance to fully develop the theoretical framework necessary to allow for the prediction of how materials will respond under forcing conditions, how stable certain structures are, and the microstructural evolution that could take place. As an example, nuclear reactor components are exposed to many different conditions which are generally considered deleterious to material properties, such as high temperatures, high radiation

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Fig. 1.1 A comparison of the injected power in different extreme driven environments [19, 20]
fluxes, and extremely aggressive chemical environments. These environmental conditions have the ability to cause unintended consequences and to lead to microstructural changes that would not normally be predicted, such as the dissolution of precipitates and the amorphization of crystalline materials [21]. The importance of these changes occurring cannot be understated, since the material properties will vary dramatically, potentially causing the structural material to be inoperable.

To address some of these problems that occur in driven systems, Martin derived the law of corresponding states, which thermodynamically predicted the phase changes that would occur in a driven material system [21]. This law was able to help determine the mixing and demixing that occurs in driven systems by focusing on the competition between thermally activated diffusion and extrinsic ballistic mixing. The importance of these two independent parameters is that they force the material into different phases, with diffusion causing the alloy to go to equilibrium and the ballistic mixing causing complete randomization. While this law was extremely useful in predicting material changes, it did not solve the problem of creating alloys nanograin alloys which would remain stable.

In order to solve this problem, the idea occurred to use alloys which self-organize into a certain microstructure. As a result of self-organization, even though the alloy is in an extreme driven environment, the microstructure and thus the alloy properties, should remain unchanged. To better understand the theoretical framework for how self-organization arises in material systems, there has been a large amount of work done focusing on immiscible elements, and different operating conditions. While a complete review of all this work will not be given here, a brief introduction on the law of corresponding states and self-organization will be discussed.
below, so that the first-time reader can have a good theoretical background to these terms before going further into this thesis.

1.1 Law of Corresponding Temperatures

As mentioned previously, to understand and predict phase stability in driven environments, Martin developed an effective temperature model in order to describe the interesting processes that had been experimentally observed during irradiation, such as precipitate dissolution or phase disordering [21]. By keeping in mind that vacancy diffusion, which is drawing the system closer to equilibrium, is in competition with ballistic mixing, which is completely randomizing, Martin found that there existed a law of corresponding states; the equilibrium configuration of the solid under irradiation flux $\phi$ and temperature $T$ is identical to the configuration at $\phi=0$ and $T' = T(1+\Delta)$ where $\Delta$ is simply the ratio the effects from ballistic mixing to the effects of thermal diffusion. In other words, $\Delta$ can be expressed as $D_b/D$ where $D_b$ represents the contribution of ballistic mixing trying to homogenize the system, and $D$ represents thermal vacancy motion driving the alloy system to equilibrium. As a special note to any reader unfamiliar with these terms, more background information about irradiation fluxes and ballistic mixing will be given in chapter 2. Currently, it is only important to recognize the competition between equilibrating and complete randomization on the atomic scale which exists in a driven system. For a better visual understanding of this theory, Fig. 1.2 has several examples taken from Martin’s paper which shows typical alloy behavior when subjected to ballistic effects [21]. This theory has been found to be remarkably good at predicting certain alloy effects, such as increased solubility in moderately immiscible alloys. More importantly, these parameters are also what give rise to self-organization in certain alloy systems.
Fig. 1.2 Alloy behaviors that are anticipated when subjected to ballistic effects. (a) Precipitate dissolution. (b) unmixing and ultimately complete disordering in an ordered compound. (c) amorphization in a crystalline (d) T', precipitate dissolution (e) amorphization of an ordered compound [21]
While Martin was initially interested in the effects of irradiation, he also found that this phenomenon exists in other extreme driven systems, such as severe plastic deformation (SPD). More information will be given on SPD processing, but it is important to recognize here that just like irradiation, SPD also includes ballistic mixing, which in this case takes the form of sustained shearing. Because it was observed that similar alloy systems exhibit similar behavior in these seemingly different extreme conditions, a series of questions have been raised concerning what are the common control variables which ultimately causes this patterning to occur. As mentioned above, what has generally been reported is a dynamic competition between chemical forced mixing and thermally activated diffusion which then leads to compositional patterns. This is shown schematically in Fig. 1.3 [22]. Furthermore, this was also proved experimentally in the Cu-Ag system, as can be observed in Fig. 1.4 [23]. Thus, while plastic deformation and ion irradiation may have different processes at play which cause forced mixing, there are still a startling amount of similarities between the two processes, especially when it comes to patterning, which allows for many comparisons and predictions to be made. In the following

![Fig. 1.3](image)

Fig. 1.3 (a) Model prediction for the length scale of phase decomposition showing the strain rate and temperature dependencies of thermal diffusion and shear mixing as a function of length scale. Where these curves cross determines the length scale of precipitation; (b) results of KMC simulation showing the effect of strain rate on precipitate length scale at a fixed temperature [22].
sections, self-organization at elevated temperatures and low temperatures will be discussed in greater detail.

1.2 Self-organization at elevated temperatures

Self-organization of moderately immiscible alloys, such as Cu-Ag or Cu-Fe, comes from the competition between vacancy-mediated thermodynamic relaxations and forced chemical mixing. In the case of irradiation, the forced mixing comes from the ballistic mixing of incoming ions or neutrons, while for SPD, this forced mixing comes from the dislocation glide that is present. This was demonstrated using kinetic Monte Carlo computer simulations, illustrated in Fig. 1.5 and Fig. 1.6, which represent an A\textsubscript{50}B\textsubscript{50} system where the constituent atoms had a heat of mixing similar to those of the Cu-Ag system [24, 25]. Fig. 1.5 shows the different regimes immiscible alloys experience as a function R, the relocation distance of ballistic events during irradiation, and \( \gamma \), the frequency of ballistic events. While more information on these terms will be given in the next chapter, it can be observed that for moderately immiscible elements, there
exists a range of possible microstructures; a low frequency of ballistic events would cause vacancy diffusion to dominate, causing macroscopic phase separation, and a high number of events would cause complete randomization. However, in between these two extremes lie a phase patterning regime, which represents a new steady state where the alloy properties won’t change.

In Fig. 1.6, the focus has switched from irradiation to SPD processing. In this simulation, planes are shifted along the \{111\} <110> slip systems, simulating the passage of dislocations, while a single vacancy could diffuse. At high temperatures and low strain rates, Fig. 1.6(a), the A/B interface roughens, but the alloy macroscopically phase separated. When the temperature was lowered to slow vacancy diffusion or shear mixing was increased, the system undergoes phase separation, but now on a length scale that is controllable. Finally, if the temperature is further reduced or the strain rate is increased, the system then becomes homogeneous. Therefore, the key to self-organization in these systems is the competition that arises from two different
mechanisms, one which would force the system into equilibrium, and the other which induces mixing in the alloy. Furthermore, it is important to recognize that these two processes are similar in magnitude and that they operate on different length scales. As shown previously in Fig. 1.3, thermally activated diffusion dominates on the shorter length scales (nearest neighbor interactions) while shear mixing operates at a longer length scale.

1.3 Self-organization at low temperatures

As mentioned above, when thermal vacancy motion is sufficiently suppressed, there should be a complete homogenization of the alloy, which is the case for moderately immiscible alloy systems such as Cu-Ag or Cu-Fe. However, work done with highly immiscible alloys such Cu-Nb and Cu-Mo demonstrates that these alloys do not homogenize at cryogenic temperatures, even though thermally activated diffusion has been fully suppressed [26]. In fact, the solubility generally only extends a few atomic percent, raising the question why does mixing stop. This has been documented both during irradiation and during SPD. In fact, these alloys seem to select a steady-state length scale for phase decomposition just as was the case for moderately immiscible
alloys at slightly elevated temperatures. However, this behavior is found only in alloys with very large heats of mixing, larger than approximately 15 kJ mol\(^{-1}\).

While this work will give an explanation demonstrating the most likely reason that highly immiscible alloys do not completely randomize under irradiation at low temperatures, the picture remains more complicated for SPD. However, it is possible that SPD has a basis for self-organization similar to the high temperature case, but with two key differences. First, atomic transport by dislocation glide in these immiscible alloys is no longer random, but rather chemically guided. This has been shown to occur experimentally by cryo-processing Cu-Ni-Ag alloys [27]. Second, precipitate dissolution no longer relies on dislocations cutting through precipitates but rather occurs by an interfacial reaction, where solute atoms are sheared from precipitates and then transported into the matrix by dislocation glide [28]. However, even with this general outline of how these highly immiscible metal alloys evolve at both high and low temperatures, there are still other fundamental questions which have yet to be answered. These include how can thermochemically biased dislocation-mediated atomic transport result in precipitate nucleation and complex phase behavior and what are the key variables such as heat of mixing, shear modulus, interface energy, etc., that determine the precipitate size and solubility.

Hopefully, one can begin to appreciate that when studying self-organization, there are large amount of similarities that exist in all types of driven environments, ranging from irradiation to SPD. Because both environments contain competing driving forces, given the correct material system, it should be possible to not only predict the microstructure that will develop, but also to synthesize materials which can last indefinitely in harsh environments. In the next chapter, a summary of the relevant irradiation processes and severe plastic deformation mechanisms is provided to facilitate the later discussion of the experimental results. Chapter 3
offers a quick introduction of the different experimental and simulation techniques that were employed during this research. This will give the interested reader enough information and resources that they could reproduce any studies that are discussed later. In chapter 4, the evolution of highly immiscible binary alloys under ion irradiation at low temperatures will be explored. In chapter 5, the focus will switch to immiscible alloys which are subjected to severe plastic deformation at low temperatures. This will focus on the evolution binary and ternary alloys, and will explore the different mechanisms that are taking place. Finally, chapter 6 will introduce the work that has been done in ternary alloy systems, and how more complicated alloys can be used to enhance beneficial properties such as coarsening resistance in extreme environments.

1.4 References


CHAPTER 2
BACKGROUND

Because of the breadth of material that will be covered in this thesis, ranging from ion irradiation effects to severe plastic deformation, it is important to go over some of the fundamental background information which pertains to this research. However, this will in no way be exhaustive and will focus solely on the information which is important to understanding the experiments and theory developed in later chapters. For a more comprehensive introduction to these subjects, one can visit one of the many review articles and books [1-10] that have been written on these subjects, which will provide a much more robust level information.

2.1 Irradiation Damage in Metals

2.1.1 Ion Irradiation Effects

High energy charged particles slow down in a metal through a series of elastic collisions with atomic nuclei and inelastic collisions with electrons, or electronic excitation. Since electronic excitation has negligible influence on irradiation effects in metals for ion energies below several MeV, the current discussion will focus only on the elastic collisions.

The defect production process begins in a metal when a target atom is struck by the irradiation particle, through a screened Coulomb interaction, resulting in the creation of a primary knock-on atom (PKA). After this initial collision, many PKAs recoil with energies far greater than the lattice bonding energies, allowing them to leave their lattice sites. These PKAs then displace additional atoms during secondary recoil events, and they too can have very high recoil energies, leading to yet additional recoils. This cascade process continues until the energies of the recoiling atoms fall below the threshold for displacing additional atoms, ~ 25 eV. [4]. Since the cross-section for atomic collisions increases with decreasing energy, collision
cascades tend to be dense, although this depends strongly on the atomic number of the target material, owing to the screened Coulomb interaction. This so-called ballistic phase of the cascade lasts for ~0.2 ps. At longer times, as atom velocities fall below the speed of sound, the cascade energy becomes partitioned among all the atoms in this localized region establishing the conditions for a thermal spike. More detail about this phenomenon will be discussed later, but it should be noted here that the thermal spike only lasts on the order of a few picoseconds before the heat dissipates to the surrounding lattice. Nevertheless, that time frame is sufficient for additional atomic rearrangements to take place due to thermally activated motion. The resulting local supersaturation of Frenkel pairs, dislocation loops, redistribution of stresses, and mixing of atoms is referred to as the primary state of damage.

2.1.2 Binary collisions and thermal spikes

For many radiation damage problems, the binary collision approximation (BCA) can be employed to reduce the complexity of the problem. In the BCA method, it is assumed that traveling atoms/ions move only in straight trajectories between two body collisions and that due to a large number of atoms at rest compared to the number of recoiling atoms, moving atoms only collide with stationary atoms.

BCA simulations of defect production have shown that the concentration of defects produced in cascades in metals like Cu or Fe is ~0.01. Also, to produce a Frenkel pair, ~50 eV is dissipated in the lattice [4]. It is then possible to estimate an approximate energy density, \( \Theta_D \), by simply multiplying the concentration of defects by the energy stored in the lattice per defect. This suggests that cascades have an approximate energy density of .5 eV/atom by the time the ballistic phase of the cascade has ended. Because the energy density can now be readily approximated, this can also be converted into a corresponding temperature. It is well known from
statistical thermodynamics that a 3-dimensional solid will have an internal energy density corresponding to 3kT since 1/2 kT resides in the kinetic oscillations and the other 1/2 kT resides as potential energy over 3 dimensions. Therefore, since $\Theta_D = 3kT$, the corresponding temperature would be over 2000 K. Other energy densities derived from the theory of Lindhard, Scharff, and Schiott (LSS theory) have also been used to estimate the damage energy density. Using this approach, Sigmund found $\Theta_D$ to be greater than 1 eV/atom for targets with high atomic numbers, such as Au [11]. Because of this incredibly high temperature, it is reasonable to ask if the thermal spike can influence cascade dynamics.

Although the estimated energy density using various approaches shows that temperatures in the cascade can exceed the melting temperature of most materials, a thermal spike can only affect the cascade dynamics if the lifetime of the spike is long relative to the period of lattice vibrations. This thermal spike lifetime is generally characterized by time $\tau_c$. One way to estimate $\tau_c$ for a spherical cascade is to calculate the time required for the temperature of a cascade containing a calculated damage energy, $E_D$, to fall below a temperature, $T_x$, when the system can be considered static again. This then leads to the following equation to estimate the thermal spike lifetime:

$$\tau_c = \frac{r_c^2 - r_0^2}{4D}$$

where $r_c$ is given by

$$r_c = \left(\frac{E_D}{4\pi k_B T_x N_0}\right)^{2/3},$$

$r_0$ is the original radius of the cascade, and $D$ is the lattice thermal diffusivity. For typical material systems, $\tau_c$ is generally several picoseconds, which is much longer than the period of a lattice vibration. However, to answer the question if the thermal spike influences a specific
process, one must determine the characteristic energy that is involved. For example, the characteristic energy for sputtering is typically 5 eV, while desorption and liquid diffusion are on the order of tenths of an electron volt [4]. Therefore, one would expect that sputtering would not be influenced by thermal spikes in most metals, while processes such as desorption of gases or liquid diffusion would.

2.1.3 Ion-beam mixing

While the previous section summarized the dynamics of cascades, the present section outlines local rearrangements of atoms that occur in such cascades. This process is referred to as ion-beam mixing. It is a topic of practical interest since it underlies phase stability in reactor components and nonequilibrium processing of new materials. Many examples are found in the literature, for example, where mixing a thin film with its underlying substrate or mixing of a multilayered film by low-temperature irradiation can lead to metastable phases [12-16]. From an engineering perspective, it is also critical to understand ion-beam mixing as it provides a framework for quantifying the number of atoms that are relocated in a cascade and how far they relocate.

Ion beam mixing arises from two distinct processes, ballistic mixing and thermal spike mixing. Ballistic mixing arises from energetic recoil events which relocate atoms in the matrix, while thermal spike mixing is due to thermal diffusion in the thermal spike and is generally assumed to be liquid-like diffusion. To illustrate these two processes, mixing was simulated using molecular dynamics in both copper and nickel after the initiation of a 5 keV cascade. Since copper and nickel have similar atomic numbers (they are next to each other on the periodic table), and have similar displacement energies, the amount of ballistic mixing should be the same. Copper, however, has a melting temperature of 1085 °C, while nickel has a melting point
of 1455 °C. This suggests that the contribution of thermal-spike diffusion should differ for the two metals. In fact, it was observed that copper had three times the amount of mixing due to the thermal spike [17]. The effect of thermal spike mixing was further studied by looking at the mixing in the copper system at different ambient temperatures. This study showed that the total amount of mixing increases with increasing lattice temperature. Specifically, ion beam mixing was found to be a factor of 4 larger at 700 K than at 0 K [18]. This result is explained by the higher temperature in the thermal spike and its larger volume and longer lifetime at higher temperatures. Although thermal spike mixing is often associated with liquid diffusion, most of the mixing takes place in the early phases of the thermal spike while the cascade volume is rapidly expanding, suggesting that this liquid diffusion description is very approximate and that the dynamics are more complex.

To supplement the information gathered from the simulations that were done on ion-beam mixing, tracer diffusion experiments were also conducted on both metals and semiconductors to measure how impurities would be mixed in the system. It was reported for metal systems that ion beam mixing is not sensitive to the type of tracer impurity, which is indeed similar to liquid diffusion; however, in semiconductors this not the case. The main conclusions from these experiments can be summarized as follows: the magnitude of the mixing parameter is greater than what is predicted by the models of ballistic mixing, the mixing parameter in metal matrices increases with atomic number and decreasing melting temperature, the mixing rates appear to be correlated with thermal diffusion coefficients, and mixing is greater in amorphous alloys.
2.2 Severe plastic deformation

To produce nanograin alloys, severe plastic deformation (SPD) is generally employed which includes but is not limited techniques such as high energy ball milling (BM), accumulative roll bonding (ARB), equal channel angular pressing (ECAP), wire drawing, or high-pressure torsion (HPT). However, severe plastic deformation can also lead to many other interesting phenomena in addition to refining the grain structure, such as homogeneous precipitate dispersion in a matrix, amorphous phase formation, solid solubility extension in immiscible systems, and many others [19-23]. Metals processed by severe plastic deformation also exhibit excellent properties such as high strength, especially when compared with the conventional materials which generally have a grain size of over several tens of micrometers. It should be noted that while each of the processing techniques mentioned above has been found to have slightly different microstructural evolutions, properties and steady states, the basic principles at work remain the same. However, the primary methods for studying severe plastic deformation in this work were ball milling and high-pressure torsion. More detailed information on these processing techniques will be given in the next chapter on experimental techniques.

2.2.1 Structural Refinement

While the knowledge about SPD processing is still growing since it is an active area of research, there exists a large body of work which deals with the mechanical properties of alloys and how a material responds when deforming plastically. While this information may not exactly describe the processes occurring at extremely high strains and is over-simplistic, it is still instructive and can help one begin to form a picture of how the alloy microstructure is evolving.
In the simplest case, when the stress applied to a ductile material exceeds the yield strength, dislocation motion is activated which causes permanent deformation of the material. To the reader unfamiliar with this concept of dislocation motion, there are numerous mechanical behavior of material textbooks which go into detail on this subject. However, Fig. 2.1 has also been included to give the reader a basic understanding of dislocation motion under shear stress $\tau$ [24]. Moving from 2.1(a) to 2.1(b), one can see the perfect crystal lattice breaks, and the resulting crystal misalignment results in a dislocation. As the shear stress continues to be applied, the dislocation progresses across the crystal until finally, the entire crystal has shifted. It is important to take note that as a result of this motion, every atom above the slip plane has shifted, and the atoms located on the slip plane now have new atomic neighbors. The atoms below the slip plane are indicated in red as soon as they have changed nearest neighbors.

Fig. 2.1 Cartoon schematic of dislocation motion occurring in a crystal. Atoms that fall below the slip plane which gain new neighbors are indicated in red. [24]

As higher stresses are introduced to the material, the production of dislocations occurs from various sources such as surfaces, grain boundaries, and Frank-read sources. This concept has been measured experimentally using resistivity in pure Cu, shown in Fig. 2.2, which shows
how the density of dislocations changes depending on the amount of stress that is applied [25]. This behavior ultimately leads to the phenomenon known as work hardening, where the amount of dislocations in a material increases to the point where they start interacting with each other, forming tangles which act as knots to reduce further material flow. This basic understanding of dislocation motion however only applies to very small strains ($\varepsilon$), on the order of $\varepsilon = 0.1$, where $\varepsilon = \frac{\Delta l}{l_0}$, where $l_0$ refers to the original sample length and $\Delta l$ is the change in length. During severe plastic deformation using techniques such as ball milling or high-pressure torsion, strains on the order of hundreds or thousands are generally applied to a material. However, during the initial stages of SPD, the mechanisms that were mentioned above occur as well. As strain is applied, dislocations are produced, increasing the amount present in the material by orders of magnitude. In certain cases of severe plastic deformation, plastic deformation is localized to shear bands.
which eventually spread out over the entire material [26]. As more strain is applied, these dislocations not only form tangles, but also rearrange to form subgrains which begin to refine the microstructure, and are characterized by having low-angle boundaries with respect to one another. An illustration of this effect is shown in Fig. 2.3 [27].

![Subgrain boundary formation from a uniform distribution of dislocations after the application of stress][27]

As the strain continues to increase in the material, the dislocation density saturates, along with the refinement process, so that a minimum grain size is achieved. Further straining also replaces the small angle boundaries with high angle boundaries, which implies that grain rotation is occurring once the microstructure has ceased refining. The minimum grain size which is achieved is determined by comparing the plastic deformation/dislocation motion which is occurring to the recovery and recrystallization behavior of the material. For low temperature SPD processes, it has been proposed that the limiting factor for grain size is grain boundary motion, with more mobile grain boundaries showing larger steady state grain sizes [28]. It has also been found for pure elements that FCC materials have the smallest grain size while HCP materials have larger sizes. However, the steady state grain size can be affected by other independent variables such as temperature and alloying elements. Ultimately though, there is always a steady state size reached during SPD that generally leads to a grain size on the order of nanometers, but which still allows for plastic deformation and dislocation motion.
Previous simulations on nanocrystals have shown that depending on the grain size, deformation in a material can occur primarily either from grain boundary sliding or dislocation glide. Schiotz and Jacobsen concluded through MD simulations that the inverse Hall-Petch behavior resulted from the material switching from dislocation glide to grain boundary sliding as the primary mechanism for plastic deformation [29]. However, Schiotz and Jacobsen did not give quantitative results indicating the percentage of dislocation glide vs. grain boundary sliding as a function of grain size. This was accomplished by Vo et al. using MD simulations, who found that for a grain size of 20 nm, the amount of plastic deformation that resulted from grain boundary sliding was only 10% when using a strain rate of $10^{10}$ s$^{-1}$ [30]. If a more realistic commercial strain rate of $10^2$ s$^{-1}$ was used instead, it would be found that almost all the plastic deformation occurred as a result of dislocation glide, since large strain rates were found to increase the occurrence of grain boundary sliding [30, 31]. Li et al. also experimentally found that while grain boundary sliding is important during the early stages of plastic deformation in nanomaterials (a strain < 2.2%), dislocation glide is the predominant form of plastic deformation at higher strains [32].

### 2.2.2 Superdiffusive Mixing during Shear

While the previous section describes the microstructural evolution occurring because of plastic deformation, it is important not to overlook the fact that dislocation motion causes atomic mixing and rearrangement. In addition to the atoms being rearranged directly on the slip plane, the atoms further above the slip plane are also in motion relative to the atoms below the slip plane. This leads to the concept of superdiffusive mixing, meaning that the relative mean square displacements between pairs of atoms increases more rapidly than linearly in time, and cannot be considered the same as Fickian or random walk diffusion. In other words, for any two given
atoms in a crystal, the likelihood of a dislocation passing between them increases the farther apart they are. Furthermore, it can be verified by simple geometry that the atoms that are farther away from the slip plane are moving farther relative to atoms on the slip plane, although the overall change in position is smaller the farther away from the slip plane one looks. While this may initially seem like an insignificant point, the implications of how an alloy will mix and evolve during SPD are quite important. An example is shown in Fig. 2.4, where the evolution of a layer due to superdiffusive mixing vs Fickian diffusion is shown [33]. It is observed that while an initially flat interface remains flat during Fickian diffusion, but becomes diffuse, the same interface remains relatively sharp for superdiffusive mixing, but becomes wavy. Furthermore, it was observed that while the number of A-B bonds increases linearly with the interface width for diffusive mixing, it increases as the square of the interface width for superdiffusive mixing, indicating that random walk diffusion is incapable of describing the mixing occurring by shear, and also explaining why there are problems predicting the behavior of alloys during SPD.

Fig 2.4 The comparison between the evolution of an A-B alloy through superdiffusive mixing (top) and Fickian diffusion (bottom) [33]
2.3 Copper Alloys

While the fundamentals involving ion irradiation damage, severe plastic deformation, and self-organization have been briefly discussed, all the experimental work that will be demonstrated involves the use of copper as the main alloy constituent. Since the typical structural metals used in industry are primarily steel, aluminum, and in some cases titanium, a reasonable question would be why are copper alloys the primary choice. Self-organization is generally observed in alloys whose constituents are immiscible in each other, so it is important to make sure that any material system that is studied has this characteristic, as outlined by Enrique and Bellon [34, 35]. Furthermore, to fully understand the fundamental physics that are taking place, secondary effects should be eliminated. This includes compound/intermetallic forming elements, effectively removing aluminum and iron from consideration. Oxides, while industrially relevant, are also excluded because of the effects that can occur as a result of charge and covalency. It is also important to keep the number of alloying constituents low, in order to isolate the effects that each alloying element causes. This makes copper an ideal candidate to study these effects experimentally since there are many available elements on the periodic table which are immiscible and do not form compounds. This is shown below in Fig 2.5 [36]. Furthermore, there exists a trove of thermodynamic and kinetic data on copper alloys.
Fig. 2.5 Periodic table showing how different interact with Cu. Immiscible, non-compound forming elements are shown in dark blue [36].

2.4 References


CHAPTER 3
EXPERIMENTAL METHODS

This chapter will cover all the sample synthesis, processing, and characterization methods. While there is a lot of overlap between the analysis techniques employed for the irradiation studies and severe plastic deformation studies, especially when it comes to sample synthesis and material characterization, there were also significant differences. This chapter will give a detailed understanding of the different methods that were employed.

3.1 Thin Film Deposition

For most of the studies that were conducted, the samples were synthesized using physical vapor deposition (PVD) which, depending on the requirements, was conducted in two different sputtering chambers. Detailed information on PVD and the different variables that can cause changes during the process can be found in [1-3].

Both chambers where baked to achieve high vacuum and had a base pressure in the 10^{-8} Torr range before sputtering. 99.999% pure argon gas was used to sputter the metallic targets. Furthermore, every chamber that was used for sputtering had a load lock attached to it, so that oxygen, water vapor, and other contaminants could be minimized during sputtering. The targets that were used during deposition ranged from 4N to 6N purity and were used to grow sample ranging from 200 nm to 15 μm, generally through co-deposition of targets. RBS and XRF techniques were used to calibrate the composition and thickness of the grown films routinely. More information on these characterization techniques will be given in later sections of this chapter.

For irradiation experiments, samples were grown on a Si (100) substrate with a 1 μm amorphous SiO₂ surface layer. This allowed for the growth of a 200-300 nm films with nano-
sized grains and nearly random in-plane orientations. Furthermore, the SiO$_2$ layer made sure that no reaction would take place between the substrate and the alloy during ion irradiation or annealing. If a pure silicon substrate was used instead, this would lead to interface interactions and diffusion during ion implantation and irradiation, since Si is soluble in Cu and is also capable of forming compounds. For severe plastic deformation experiments, a single crystal 3” Si wafer with no surface oxide was used to grow 10-15 μm thick films. Interface reactions were no longer a consideration since the film was delaminated from the Si wafer substrate. Furthermore, a very thin Ag layer was deposited on the top and bottom of the film, which helped prevent any oxidation and minimized any interaction with the substrate.

Before loading the samples into the deposition chamber, the substrates were ultrasonically cleaned with acetone, then isopropanol, and finally methanol for 10 min each, and then blown dry with compressed air. To load the substrates into the chamber, they would generally be attached to a transfer puck either by being held down using a mounting screw and washer or by applying silver paint to the substrate and then bonding it to the puck. If silver paste was used, it was generally left outside of the vacuum chamber for a day in order to cure and make sure that no organic solvents contaminated the vacuum system.

3.2 Sample Processing Techniques

3.2.1 Ion Irradiation

Irradiations were performed using a 3.0 MeV Van de Graaff accelerator to accelerate inert gas ions towards the samples, although in principle most elements on the periodic table could be used. The ion beam is electrostatically rastered using deflectors to ensure uniform irradiation over the entire sample surface, and limit variations in the sample.
For the following experiments that were conducted, the thin films were irradiated with 1.8 MeV Kr+ ions. At this energy, the expected implantation damage profile over ~300 nm of Cu is uniform and there is a negligible amount of residual Kr to be found in the sample after the experiment is concluded. A Cu-plate stage was used for mounting the samples inside the irradiation chamber. The stage could be heated up to 600 °C using an enclosed halogen bulb, and K-type thermocouples were utilized to monitor the temperature. Samples were generally bonded to the Cu plate with the use of Ag paint, to not only make sure there were no obstructions to block the ion beam path, but also to minimize heat loss between the sample and Cu stage.

The samples were placed perpendicular to the incident beam at a vacuum level in the 10^{-8} Torr range. For experiments that were conducted at higher temperatures, the vacuum generally degraded to 5x10^{-7} Torr, as the amount of outgassing increased. To ensure that a good vacuum was maintained throughout the implantation process, a liquid nitrogen cold finger was also used, which would preferentially gather any contaminants in the chamber. To control the dose that the sample received, the ion beam passed through an aperture of selected size before entering the irradiation chamber and was also monitored by using a Faraday cup. This would be moved in front of the sample and would measure the total current that would irradiate the sample. Generally, currents ranging from 100 to 200 nA were used for an hour in order to get an irradiation dose of \( \sim 3.0 \times 10^{16} \) ions, which is equivalent to \( \sim 65 \) dpa. A laser was also pre-aligned with the beam so that the user could align the sample with the beam before irradiation started.

3.2.2 Ball Milling

For some severe plastic deformation experiments, ball milling was used to observe how certain alloys mix and undergo microstructural changes while under shear. In this case, it was necessary to start with commercially pure powders, rather than growing samples through
physical vapor deposition. Cu powder which was less than 200 μm in size and 99.8 at. % pure, Nb powder which was approximately 74 μm in size and 99.85 at% pure, and Si powder which was on the same size scale as Nb and 99.999 at. % pure was purchased from Sigma-Aldrich (now Millipore-Sigma). While the purities were not as high as what was used during PVD, oxygen contamination is routinely found to be on the order of several atomic percent and is a larger impurity than other trace elements. Fe contamination from the ball milling process is also usually present. As a result, higher purity powders were not needed.

The powders were then measured, mixed together and placed in a stainless-steel vial with three stainless-steel balls which would act as grinding media. A SPEX 8000D mill was used to process 10 g powder batches at a time. During milling, the vial is secured in a clamp and swung in a figure 8 motion ~ 1000 times a minute. With each motion, balls impact the powder and the vial, mixing and milling the sample, as shown in Fig. 3.1 [4]. This generally leads to a ball velocity of 5 m/s which is generally enough kinetic energy to induce mixing or chemical reactions even in immiscible alloys [4,5]. Although some researchers use process control agents (PCA) to reduce cold welding, no other chemical besides the metallic powder and stainless-steel balls was added to reduce contamination. However, approximately 6 at% silver was added to each powder batch to prevent cold welding. Previous studies have shown that silver does not affect the kinetics or microstructural development of the alloys of interest here in a significant way [6]. Furthermore, all ball milling experiments were done in an argon atmosphere glovebox, in order to reduce the formation of oxides and nitrides. However, as stated previously, due to the presence of surface oxide on the powder, some oxygen contamination is present, usually on the order of several atomic percent. Furthermore, the high energetic collisions also lead to the
powder sample mixing with the vial and grinding balls themselves, which leads to several atomic percent of Fe and Cr contamination, depending on the system. Contamination during milling is, in fact, one of the main drawbacks of high-energy ball milling. To address this problem, high pressure torsion, which is described in detail below, was also used for severe plastic deformation experiments.

3.2.3 High Pressure Torsion

In order to apply severe plastic deformation to the sample while also reducing the contamination problems which are common in ball milling, high pressure torsion (HPT) was
used. For this processing method, a sample is placed between two anvils and pressed under a large pressure, and then sheared through surface friction forces by one of the anvils rotating. Furthermore, HPT can be carried out in a variety of sample geometries, generally either fully constrained, quasi-constrained, or completely unconstrained. All the HPT experiments conducted used the unconstrained geometry. For better illustrative purposes, a cross-sectional view of the HPT process is shown Fig. 3.2 [7]. During HPT, the main volume of the material is strained in conditions of quasi-hydrostatic compression, allowing for large strain values and deformation, but leaving the sample intact [8]. In order to create and process the alloys using HPT, the alloys were grown using PVD to about 15μm and then stacked on top of each other to reach the required thickness for HPT. This is generally a value between 100 to 200 μm. The HPT processing could then be performed at different temperatures, but generally ~ −78 °C for most experiments, for a series of cycles, where a cycle represents rotating the anvils back and forth by 90°. An applied pressure of 4.5 GPa and a rotation speed of ~1.0 rpm was used for these experiments. To calculate the shear strain applied to the sample, the following equation is generally employed:

\[ \gamma = n \pi r / t \]

![Fig 3.2 Cross-section illustrations of different HPT processing geometries. The sample being strained is represented in black, while anvils are represented as grey [7].](image-url)
where $n$ is the number of cycles, $r$ is the radial position on the sample, and $t$ is the sample thickness. This equation relies on an assumption that the sample is strained homogeneously. In this case, as the strains increase (linearly) with the radius, it allows for microstructural characterization as a function of strain by simply taking different samples radially.

3.3 Characterization Techniques

The following is a description of the various characterization techniques that were employed to determine composition and microstructural developments of the immiscible alloys before and after processing.

3.3.1 Rutherford Backscattering Spectroscopy (RBS)

Rutherford backscattering spectrometry (RBS) was utilized to determine deposition rates, thin film depth profiles and alloy compositions after co-sputtering from multiple targets and was performed using the same Van de Graaff accelerator as mentioned previously for ion implantation processing. A good overview of RBS spectroscopy and other ion-beam techniques can be found in [9]. He$^+$ ions with energies of 2.0 MeV were used after passing through a circular aperture with a 1-mm diameter. The RBS chamber was held at a base pressure of $1 \times 10^{-6}$ Torr. To collect data, the sample was aligned with the incident beam at 22.5° relative to sample plane normal. The solid-state detector that collected the backscattered He$^+$ ions was placed 30° from the incident beam, but in the opposite direction from the sample normal, leading to a scattering angle of 150°.

The RBS spectra were analyzed using a fitting software called SIMNRA. During this fitting process, the spectra were normalized based on substrate peaks, which was normally the Si and O peaks from the SiO$_2$ oxide layer. RBS was able to determine film thickness information within ±10% and composition information within ±0.5 at.%.
3.3.2 X-Ray Fluorescence (XRF)

For bulk samples, X-Ray Fluorescence (XRF) instead of RBS was employed to help determine composition and, in some instances, thickness. The general principles behind XRF are similar to electron dispersive spectroscopy. More background information can be found in [9]. In these experiments, a Shimadzu EDX-7000 X-ray Fluorescence Spectrometer was used for analyzing both ball milled powder samples and HPT samples before and after SPD processing. No special sample processing had to be performed in order to gather XRF measurements. As shown in Fig. 3.3, which can be found on the Shimadzu website, the current model was able to detect all elements of interest for concentrations as low as .1 to 10 ppm. The x-ray source was a Rh target, using an energy of 50 kV. Generally, a collimator of 5 mm was used to collect sample information, although the instrument had a choice of collimator ranging from 1 to 10 mm. Most measurements were also collected under a He atmosphere. After several calibration

![Periodic Table](image)

Fig 3.3 The periodic table color-coded to show the lower limits of detected elements. As the elements get heavier, sensitivity generally increases. As shown here, the XRF is capable of observing all the elements of interest to the ppm range (from Shimadzu online brochure).
measurements, it was found that the XRF supplied compositional information within ±0.5 at. %, and was comparable to RBS data.

3.3.3 X-ray Diffraction (XRD)

X-ray diffraction was employed to explore the crystallinity and composition of samples before and after processing. It was generally of interest to gather information on the average grain size, the solubility of an element in a phase, and the number of different crystalline phases present. XRD was not only useful for gathering this information but since the grain size was on the order of nanometers, the volume which was sampled was statistically significant. Solubility was obtained by measuring the shift in the Bragg reflections with respect to the pure phase. This data was analyzed in conjunction with experimental or simulation data which relates the composition to lattice parameters. However, all simulation data was confirmed through extensive experimentation as well. Examples of experimental tables which were used are Linde’s table for Cu-Ag and example for simulations are the molecular statics gathered for Cu-Nb in previous studies [10, 11]. XRD was also useful in collecting data to allow for quick evaluation of the microstructure evolution, and to judge whether to further explore the material system or modify the experimental design for very little cost.

In this thesis, two types of XRD measurements were performed: data was collected using a Philips X’Pert Diffractometer system and data was also collected at the Advanced Photon Source (APS) at Argonne National Lab. For the Philips X’Pert Diffractometer, Cu-Kα x-ray emission was employed. The optical configuration was a Point- Parallel Plate geometry, which is very similar to Bragg-Brentano and is illustrated in Fig 3.4. General 2θ-ω scans were performed,
which allowed for the same data collection as 2θ-θ except with the ability to optimize the scan to increase the intensity of the diffracted beam. For thin film samples that were grown on a single crystal Si substrate, any misalignment that occurred during sample mounting, such as not being at the correct specimen height, was corrected using the Si (004) peak as a reference. For HPT specimen disks, micro x-ray diffraction was used to analyze small sample volumes, by limiting the incident x-ray beam to a diameter of 100 μm. This was essential to gathering accurate data from the HPT sample as the shear strain changes dramatically as one progresses radially outward.

Because of the low volume fraction, size, and atomic number of some of the phases that formed, ball milled powder samples and some HPT disks were also analyzed at APS, as mentioned above. High-resolution synchrotron diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory using an average
wavelength of 0.414580 Å. Discrete detectors covering an angular range from -6 to 16 ° 2 theta are scanned over a 34° 2 theta range, with data points collected every 0.001° 2 theta and a scan speed of 0.1°/s. Measurements were collected from the samples using a transmission geometry over a 2mm square area. Because the transmission geometry was used, no shifts due to sample height or sample preparation had to be corrected. The high intensity was also able to resolve phases that were not previously visible on the benchtop XRD systems. The peak profiles for all XRD collected data were analyzed using GSAS software.

### 3.3.4 Focused Ion Beam/Scanning Electron Microscopy (FIB/SEM)

To get cross-sectional SEM images without oxygen contamination, and to prepare cross-sectional TEM specimens and APT specimens, an FEI Helios 600I dual beam SEM/FIB was used. For all imaging and sample preparation, the vacuum was generally maintained at 8x10⁻⁶ Torr, although the vacuum improved as more time elapsed. Plasma cleaning was also performed each time before sample preparation to reduce carbon contamination and to keep the sample clean throughout the process. The Helios also has a sub-nanometer SEM resolution at high beam energies and remains very good, ~1.4 nm, even when the accelerating voltage is lowered to 1 kV. The ion beam column is oriented 52° from the electron column to allow dual milling and imaging.

In order to produce cross-sectional images, the specimen was tilted to 52° so that the sample was perpendicular to the ion column. A platinum layer of approximately 2 μm was then deposited to reduce surface damage from the ions and to ensure uniform milling. Cross-sectional cuts were then made with Ga ions at 30 kV, starting with a current of approximately 9 nA, and then making subsequent cuts at lower currents, until ending at 0.23 nA. By systematically reducing the current of the ion beam, this action allows for exposure of the metal alloy while also
making sure to reduce the surface damage caused by the milling action. A final low voltage polishing step was then applied to ensure that all ion damage is removed. This was generally performed at 5 kV with a current of 41 pA. An accurate image of the cross-sectional microstructure can then be obtained using the electron beam. All image processing was accomplished using the open source software ImageJ. More information about this will be given in the section on transmission electron microscopy.

To produce APT samples, a platinum layer was deposited on the area of interest, just as with the cross-section viewing. In this case, however, a rectangular cut 4μm deep was made at a tilt of 22°, not 52°, on the edge of the platinum layer. The sample was then rotated 180° and another rectangular cut was made on the opposite side of the area of interest. This created a wedge cut, which would then be welded to the Omniprobe and transferred over to the APT silicon coupon. The wedge would be welded to the silicon coupon and polished to a fine tip of approximately 60 nm diameter. A low 5 kV ion polish was then used at a very low current to polish the tip and remove Ga and any ion damage from the surface. An example of a completed APT tip is shown in Fig. 3.5.

For the production of TEM cross-sectional samples with the use of the FIB, the procedure was very similar to the cross-sectional imaging method, except carried out on both sides. This allowed then for the Omniprobe to be welded to a rectangular specimen, which would then be lifted out and attached to a copper post. Generally, after the FIB lift out was welded to the post, the sample is still approximately 1 μm thick, which is too thick to be electron transparent. To be used in the TEM, the thickness generally needed to be between 50-70 nm. To get to this level,
cleaning cross-sectional cuts were made at low ion currents to further thin the sample. When the sample was approximately 100 nm thick, a low kV polish was used to remove the amorphous damage layer that was created when thinning the sample and to further reduce the thickness of the sample. An example of a finished TEM sample is shown in Fig. 3.6.
(Scanning) Transmission Electron Microscopy ((S)TEM)

(Scanning) Transmission electron microscopy ((S)TEM) was also employed to examine the microstructure after processing. The electron microscopes used were a JEOL 2010 LaB6 TEM, a JEOL 2010F EF-FEG TEM/STEM and a JEOL 2200FS STEM, each of which operated at 200 kV. Furthermore, the JEOL 2200FS STEM was aberration corrected, which improved the high-angle-annular-dark-field (HAADF) resolution to 0.1 nm. These tools were used to gather bright-field (BF) TEM images, diffraction patterns (DP), dark-field (DF) TEM images and HAADF STEM images on almost every sample that was produced to provide comprehensive

Fig 3.6 An example of a finished TEM cross-section sample produced using an FEI Helios 600I dual beam FIB. This sample is also commonly referred to as “flag” and is attached to a post located on the left, currently out of view. The holes were already present in the sample, and are not a result of the thinning process.
information about the grain size, precipitate density and precipitate size. All the samples that were investigated were polycrystalline with grain sizes ranging from 20-200 nm.

While both plane-view and cross-section samples were analyzed for thin film specimens, only cross-sectional samples were prepared for the bulk HPT specimens. For the thin film samples, plain view and cross-section TEM foils were prepared using mechanical polishing, which involved hand-polishing the samples down to about 30 μm by using diamond lapping films from 15 μm to 1 μm. Samples were then ion-milled using a Gatan Precision-Ion-Polishing-System (PIPS). Ion energies of 4-5 keV at an angle of about 6° from the sample surface were used initially until the formation of a hole was observed. This was observed by turning on a light located below the sample which would illuminate any hole that was created. The ion energy was then reduced to below 1 keV at an angle of 2° from the sample surface to remove ion-damaged layers and minimize surface roughness. Liquid nitrogen cooling was always used to minimize beam heating effects which could affect the microstructure. HPT cross-sectional foils were produced using the FIB, and the process for creating those samples was outlined above.

In addition to the imaging techniques mentioned, chemical analysis was also performed to gather more information on the microstructure and the composition of the different phases/precipitates before and after processing. Since the elements used were all relatively heavy, EDS was the ideal technique to gather compositional information and was used for most of the samples produced. TEM/STEM images were also helpful in gathering accurate information on precipitate size. Furthermore, because of their small size, hundreds of precipitates were counted, which allowed for a statistically significant sampling. Just as with FIB/SEM images, ImageJ was used to analyze the different images collected from the TEM. For determining precipitate size, two methods were generally employed. One method was to circle
out the individual precipitates, measure the area of projection, and to treat each precipitate as spherical to get the radius. The other method involved using a cutoff threshold to determine the precipitate sizes. Since SEM images and HAADF STEM images give large contrasts depending on the elements present, this method was possible. Finally, ImageJ was also used to gather the average grain size using the mean intercept length,

\[ \bar{L} = \frac{L}{N} \]

where L is the total length of the line drawn and N is the total number of the grain boundary intercepts [12]. The average grain size can be related to \( \bar{L} \) by a proportionality constant \( K \), which is dependent on the grain geometry. For spherical grains, \( K \) is taken to be 1.39 [12].

3.3.6 Atom Probe Tomography (APT)

Atom Probe Tomography (APT) was conducted with the aid of a collaborator at Karlsruhe Institute of Technology (KIT) in Germany using an Imago LEAP 3000. Measurements were performed using a pulsed laser in an ultra-high vacuum environment, greater than \( 10^{-10} \) Torr, while the APT tip was cooled to 65K. Under laser pulsing, atoms are evaporated from the surface, by a field effect and projected onto a Position Sensitive Detector (PSD) with a very high detection efficiency. Generally, the number of atoms collected from each tip was about 50 million atoms. The APT data was analyzed using the open source software 3Depict, which allowed for tip reconstruction using the atom position file and the range file which contains the mass spectrometry data.

Cluster analysis could be conducted in 3Depict by determining a clustering radius around each atom. This method involves choosing a characteristic distance \( d_{\text{max}} \) as well as a minimum number of solute atoms required to be considered a cluster. The main function of the
characteristic length is to draw a radius around a given Nb atom and see if any other Nb atoms are located within the distance $d_{\text{max}}$, which would indicate a cluster. If the minimum number of atoms is not satisfied, these atoms are considered in solution. More about cluster analysis can be found in [13].

3.4 Kinetic Monte Carlo Simulations (KMC)

Simple Kinetic Monte Carlo (KMC) simulations were also employed in order to better understand and isolate the important physics that was occurring. The KMC simulations for modeling both irradiation and SPD involved simple cubic lattices, so each atom had only 6 nearest neighbors, was performed in a 128 x 128 x 128 cubic cell. The simulations were restricted to the case of binary alloys, so generically referred to as an A-B alloy, where A atoms were the majority and comprised the matrix, while B atoms represented the solute. Furthermore, it was assumed that these atoms were highly immiscible in each other. Therefore, if any B atoms encountered each other, the overall free energy will decrease if they precipitate. However, after this point, the similarities between the irradiation KMC simulation and the SPD simulation end.

For the KMC simulation of the irradiation case, the primary focus was on the collision cascade and resulting thermal spike event which occurs. More detailed background information on this process will be presented in the next chapter. However, by limiting the simulation to this process, the solute atoms were able to undergo two different processes: either nearest neighbor diffusion, which could allow for growth, or ballistic relocation, which would also allow for movement throughout the lattice at longer length scales. However, ballistic relocation had the added effect of causing larger precipitates to shrink by allowing for single solute atoms to go back into solution. These two mechanisms, therefore, set up competing dynamics of the model alloy system.
For the KMC simulation during severe plastic deformation, shearing was simulated by moving all atoms along a randomly selected slip plane by a single Burgers vector. Because the simulation cell was simple cubic, a Burgers vector corresponds to a single lattice parameter. However, no vacancy motion was included, so all movement occurred due to the dislocation motion, not random diffusion. Because of the simplicity of the simulation, the details of particle coagulation were not considered, and instead, it was assumed that spherical precipitates are formed. Furthermore, in order to better simulate areas of disorder where nucleation events occur such as grain boundaries, a probability function was used to determine if two solute atoms stick. This function was also dependent on the size of the precipitate, which means that as precipitate nucleation started to occur, and the precipitates began to grow, the probability of continued growth increased, until ultimately the particle was large enough that it automatically stuck to any other solute atoms it encountered. While this model was simplistic, it most likely accurately modeled the underlying phenomenon which was occurring during precipitation under shearing. However, the fact that dislocations do not interact further with the precipitates except as a mechanism to move them around the lattice means that there are other terms which are missing which would need to be included to have a fuller understanding.

3.5 References


4.1 Introduction

The current US nuclear energy program is at cross roads, unclear whether it will continue by stretching out the lifetimes of existing reactors, or if it will be regenerated by the introduction of a new fleet of advanced reactors that operate more safely and efficiently. The second alternative would lead to building of new Generation IV reactors, which would come online around mid-century [1]. The new reactors are currently planned to operate at very high temperatures, up to 1000 °C, to achieve efficiency, while being resistant to degradation up to doses of ~200 dpa, which is three to four times higher than in previous reactor models, as shown in Fig. 4.1 [1]. It is clear from this plot that operating environment for the next generation of

![Fig 4.1 Temperature and dose requirements for structural materials for the operation of proposed Generation IV advanced reactor concepts. The dimensions of the colored rectangles represent the temperature and displacement damage ranges for each reactor. Generation II and III reactor conditions are also included for comparison in the opaque green rectangle [1].](image)

* This work was done in conjunction with Dr. Xuan Zhang, and was published in Acta Materialia 120 (2016)
nuclear power will be far more extreme than present, and that new advanced materials will be required to meet these conditions.

The choice of structural materials for Gen IV presently focus on ODS (oxide dispersion strengthened) steels and refractory alloys due to their outstanding high temperature properties, as shown in Fig 4.2 [2]. Nano-ODS alloys appear particularly promising owing to their high strength and resistance to irradiation damage [3-6]. Their high density of small inclusions, for example, serve as obstacles for dislocation motion, suppressing creep, while providing sinks for irradiation induced point defects. Coarsening is also reduced since the precipitates can slow down the motion of grain boundaries by exerting a pressure, which is commonly referred to as Zener pinning [7]. In nuclear reactor materials, while aging is often accelerated due to the damage produced by energetic projectiles, the particle/matrix interfaces can act as internal sinks and traps for irradiation-induced defects, resulting in a significant extension of the material’s lifetime in service. Therefore, a large density of precipitates would also mean that more surface area exists to trap point defects. This is illustrated in Fig 4.3 where a collision cascade near a

![Functional temperature ranges for structural materials in nuclear power systems](image)

Fig. 4.2 Functional temperature ranges for structural materials in nuclear power systems (SNRPS stands for Space Nuclear Reactor Power System) [2]
grain boundary reveals strong interaction with the cascade, preferentially absorbing interstitials [8]. In many cases, so many interstitials are absorbed that in-cascade vacancy annihilation reduces. Furthermore, the excess interstitials at the grain boundaries/precipitate interface interact strongly with nearby vacancies, leading to enhanced recovery.

Despite these benefits, one of the difficulties in using nanostructured materials for engineering applications in general, and nuclear applications, arises from their tendency to coarsen in extreme environments such as high temperatures and prolonged irradiation. While research focused on stabilizing the microstructure of nanomaterials at high temperatures has greatly improved, far less progress has been made for non-equilibrium, irradiation conditions [9-13]. For example, it is known that nanocrystalline metals undergo extensive grain growth during irradiation, even at low temperatures [14, 15]. In addition, nanocrystalline metals also experience phase instability during irradiation. For example, typical structural metals such as Fe or Ni have irradiation-induced diffusion rates at low temperatures, i.e., ion beam mixing, that are ~1 nm²-dpa⁻¹ [16]. Recall, dpa is a measure of irradiation dose signifying the probability of creating a vacancy on a lattice site per incident ion (or neutron) times the total number of ions impinging on the specimen during the irradiation. Therefore, in Fe or Ni, ion beam mixing has caused atoms to
diffuse a few nanometers after an ion irradiation dose of 1 dpa. Since nuclear materials can be subjected to irradiation fluences over 100 dpa during their service lifetime, the stability of small nanoparticles becomes questionable. Also, at elevated temperatures, radiation-enhanced diffusion can increase the rates of interdiffusion by orders of magnitude, possibly leading to extensive coarsening [17, 18].

Attempts to overcome the incompatibility of nanostructured materials with nuclear environments have focused on strong phase-separating systems, including highly immiscible alloys or compound forming precipitates, such as nano-oxide dispersive strengthened (ODS) steels [3, 13, 19-23] noted above. Nano-ODS steels, however, are quite complex, involving many different constituent components, which makes elucidating the basic mechanisms controlling the stability of nanoprecipitates under irradiation difficult. Therefore, the research in this thesis focuses on the phase evolution during irradiation at low temperatures of the far simpler binary alloy, Cu-W.

The Cu-W phase diagram is shown in Fig. 4.4 [24]. As can be observed, the solubility of copper in tungsten, and vice versa, are negligibly small. While Cu-W is highly immiscible, and does not form compounds, the alloy shares similarities with the industrially important nano-ODS steels and can be considered as a model alloy when operating at high temperatures. The interest in strongly phase-separating systems for nuclear applications stems largely from past work that showed that alloys which have high heats of solution tend to be resistant to intermixing (i.e., phase dissolution) during irradiation [19, 25-27]. This finding is rationalized, at least qualitatively, on the basis that mixing within energetic displacement cascade occurs predominantly within the thermal spike phase of a cascade by thermally activated diffusion in a liquid-like zone. Since these systems are highly immiscible, even in the liquid phase, they tend to
phase separate, i.e., de-mix, under irradiation [28]. At high temperatures, radiation-enhanced diffusion can further enhance the de-mixing of the alloy as vacancy motion becomes more important.

Despite the large body of work on ion beam mixing and radiation enhanced diffusion in immiscible alloys, predicting how these systems evolve under prolonged irradiation remains elusive. Examples of fundamental questions of interest in this work include: Will nanoprecipitates shrink and dissolve or grow? Will multilayered materials convert to three dimensional morphologies? What determines the solubility of the two-phase alloys during low-temperature irradiation? What is the length scales of the two-phase alloy if it forms a three-dimensional morphology? Do these systems have a unique steady state? To answer these questions, a series of experiments using in-situ electrical resistivity measurements during ion irradiation are employed to follow the kinetics of the phase evolution in systems having very different initial states and morphologies. This is followed by characterization of the
microstructures using transmission electron microscopy. These experimental results are then analyzed with the help of using Monte Carlo simulations.

4.2 Experimental Methods: In-Situ Electrical Resistivity Measurements

The experimental methods employed in this thesis were discussed previously in chapter 2, including electrical resistivity. The details for performing in-situ resistivity measurements during ion implantation, however, were not provided, and therefore the remainder of this section is devoted to this topic.

The in-situ electrical resistance of thin films was measured using a four-point probe method. The samples, requiring the same temperature and irradiation conditions, were deposited onto a single substrate, which was generally 1cm². A beam line aperture was selected so that all of the samples could be irradiated simultaneously. In order to deposit the samples and lead pads, two sets of masks were fabricated. The mask for depositing the lead pads is shown in Fig. 4.5 (a), which are approximately 0.8 mm². The lead pads consisted of a layered structure, Ti-15nm/Cu-500nm/Au-200nm. The Ti, which was in contact with the SiO₂ substrate, provided good adhesion, while the Au facilitated wire bonding. The mask for depositing samples is shown in Fig. 4.5 (b). Up to four different samples could be grown on each substrate, in addition to a reference sample. Each sample segment had the dimensions of 0.4 mm × 2 mm. By overlapping the two mask patterns, the complete pattern is obtained, as shown in Fig. 4.5 (c). The patterned substrate was then glued to a leaded chip carrier using Ag paint. Au ball bonding was used to connect the lead pads of the pattern to the lead pads of the carrier. For in-situ resistance measurements, the carrier was mounted on a specially designed sample stage which allowed for sample heating and had an electrical feedthrough so that chip leads could be connected to an external power supply using thin Cu wires. Fig.4.6 (a) shows a photo of the carrier attached to
the sample stage. Using the labeling shown in Fig. 4.5 (c), current entered through pad 1, and passed through samples 4, 3, 2, 5 until ending at pad 2. The current then went to sample 1 through pad 14, and finally exited through pad 11. This is shown in Fig. 4.6 (b). The remaining pads were used to measure the voltage across the samples. The area marked by the grey lines in Fig. 4.6 indicates the size of the beam after passing through the aperture, which was 4.5 mm x

Fig. 4.5 Mask patterns for the deposition of lead pads (a) and samples (b). The complete pattern is obtained by overlapping (a) and (b). The sizes given in the diagram are in mm.

Fig. 4.6 A fully assembled sample, bonded to the carrier and on the sample stage with the leads connected to other parts of the circuit by Cu wires shown in (a). A schematic drawing showing the connection between the sample pattern and the pads using Au ball bonding is shown in (b). The grey area represents the samples which are irradiated simultaneously.
4.5 mm. A 50 Ω standard resistor was installed in series with the samples, to ensure that there was a constant current. The current used was generally tens of microamperes.

**4.3 Experimental results**

**4.3.1 Electrical resistivity**

The electrical resistivity was first measured on a series of as-grown Cu-W samples to calibrate the dependence of resistivity on alloy concentration. These results are shown in Fig. 4.7, where a linear increase in resistivity is observed with increasing W concentration for solute concentrations up to 4.6 at.%. \( X_w \) represents the molar fraction of W in units of atomic percent. The measured resistivity for \( X_w = 0 \) agrees well with that of pure, bulk Cu at room temperature. It is safe to assume that the resistivity of sputtered, pure Cu is negligible compared to the alloy samples, and that electron scattering from imperfections in the lattice can be neglected. The good linearity of resistivity with alloy concentration indicates that deviations from Matthiessen’s rule are small and that Nordheim’s rule applies. Fitting the data thus gives

\[
\rho = 1.87 + 11.8X_w \ \mu\Omega \cdot \text{cm}
\]  

Fig. 4.7 Electrical resistivity at RT as a function of W concentration for the as-grown samples (square symbols) and the samples irradiated to steady state (circular symbols).
For verification, the value at 4.4 at. % W is found to be in good agreement with that reported by Vüllers and Spolenak [29].

The change in the resistivity as a function of dpa for different alloy compositions is shown in Fig. 4.8. These films were irradiated at room temperature with an average dose rate of ~1.6 x 10^{-2} dpa-s^{-1}. The resistivity of the alloy films initially experienced a rapid decrease with dose, but then saturate. Steady state values for the resistivity is shown in Fig. 4.7. The change in the resistivity of pure Cu is quite small, although a rapid increase in resistivity of ~0.18 μΩ cm at the beginning of irradiation is observed, and is followed by a slow, steady increase of ~2x10^{-3} μΩ cm/dpa. The initial increase in resistivity is consistent with a steady state concentration of point defects of ~1x 10^{-3} [30], which is reasonable for copper at room temperature [31]. The slow increase at higher doses can be explained by sputter erosion of the sample. For all the alloy samples, it is assumed that only W atoms in solution contribute to the impurity scattering. This means that incoherent W precipitates have little influence. This approximation is justified by noting that the electron mean free path in these W-saturated Cu alloys is λ ~3 nm (see [32]), which is smaller than the W precipitate spacing after irradiation (see below). The changes in X_w

Fig 4.8 Resistivity as a function of irradiation dose (at RT) for solid solution samples with different initial W concentration. The CuW1.6-ann sample is the reference sample that was not irradiated. The inset plots the derivative of the resistivity curve up to 1 dpa, showing the rate of resistivity change at the early stage of the irradiation experiment.
due to irradiation using this assumption are presented in Table 3.1. While the solubility of W in Cu decreased significantly during irradiation, it remained orders of magnitude greater than the equilibrium solubility at room temperature [33]. The rates of change of the resistivity with dose, i.e., d\rho/d\phi are shown as inset in Fig. 4.8. Given that the maxima of d\rho/d\phi scales with the square of the as-grown value of X_W, it is possible second order kinetics are involved, i.e.,

\[ dC_W/d\phi = kC_W^2. \]

<table>
<thead>
<tr>
<th>X_W-as grown (at. %)</th>
<th>1.1</th>
<th>1.6</th>
<th>3.1</th>
<th>4.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>X_W-irradiation (at. %)</td>
<td>0.76</td>
<td>0.84</td>
<td>1.32</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Table 4.1 List of W concentrations in as-grown solid solutions and the steady-state W concentrations in RT irradiation.

Next, it was shown that the steady state values of the W solubility observed in Fig. 4.8 represent true steady states characteristic of irradiated, dilute Cu-W alloys, or whether there exists a dependence on the initial microstructure. Using the sample Cu-1.6 at. % W as a test, the alloy was first irradiated at room temperature, similar to the samples in Fig. 4.8, but then annealed at 600 °C for 1 h. As shown in Fig. 4.9, the resistivity decreased significantly after this annealing treatment, by -60% from 12.7 \( \mu \Omega \) cm to 5 \( \mu \Omega \) cm. The sample was then re-irradiated at room temperature under the same beam conditions as before. The resistivity is observed in Fig. 4.9 to increase, returning to within ~1% of its value following the initial room temperature irradiation. Also shown in Fig. 4.9 are the derivatives d\rho/d\phi, showing the time scale for the annealed alloy to relax during irradiation. Starting from the solid solution case, the time constant is ~0.2 dpa, which is like those found in Fig. 4.8.
Electrical resistivity measurements on irradiated Cu-W multilayered samples, also helped elucidate the kinetics of the dissolution process. The W layers in these samples were kept at a constant thickness of 10 nm, while the thickness of the Cu layers in the different samples, varied from 10 nm to 100 nm. All films were approximately 200 nm thick in total. By measuring the dose dependence of resistivity in these samples, the irradiation-induced diffusion rates could be obtained since the change in resistance is due to W going into solution in the Cu layers. The time required for the W to homogenize in the Cu layers, therefore depends on the W diffusion constant and the thickness of the Cu layers. Fig. 4.10 plots the electrical resistivity of the irradiated sample versus dose. As can be observed, \( \rho \) increases more slowly as the thickness of the Cu layers increases. This illustrates that the change in Cu resistivity is not an interface effect but rather reflective of the transport of W into the Cu layers. When very thin Cu layers were used, the resistivity nearly saturated, indicating that W has homogenized across the Cu layers.

The small but continued increase in resistivity at high doses is attributed to significant interface roughening and a change in the layer morphology, which will be discussed later. For the samples with 50 nm or 100 nm Cu layers, the resistivity increased nearly linearly with dose, illustrating
that the W has not yet diffused throughout the Cu layer. In addition to these experiments at room temperature, multilayered samples were also irradiated at 600 °C. As shown in Fig. 4.11, there is a significant difference between the increase in resistivity at room temperature and that at 600 °C, with the latter exhibiting a lower overall change. This difference illustrates can be rationalized by use of the effective temperature model. As the temperature increases, vacancy motion becomes more important and lowers the effective temperature, driving the system to

Fig. 4.10 Resistivity as a function of irradiation dose (at RT) for multilayer samples with different Cu layer thicknesses, as specified in the legend (W layer thickness is constant at 10 nm).

Fig. 4.11 Resistivity as a function of irradiation dose at both RT and 600 °C, for both the 10-100 layer case (a) and the 10-25 layer case (b).
phase separate. It can also be observed from Fig. 4.11 that the change in resistivity starts to plateau. As mentioned above, this indicates that W has homogenized across the layer.

4.3.2 Transmission electron microscopy

The effect of irradiation on the microstructure in the Cu-W alloys was also examined using TEM. Shown in Fig. 4.12 are Z-contrast images of the initially solid solution Cu-W alloys after room temperature irradiation. Included as part of Fig. 4.12 (right side) are size distributions for the W precipitates. The fundamental result is that the density of the nano-precipitates increases dramatically with alloy concentration, but that the size distributions are stable, with the volume-averaged diameter of ~2 nm. The images also reveal that in the more concentrated alloys, the W nanoparticles begin to impinge on one another. Additional irradiation experiments were carried out at much lower temperatures to verify that the results obtained at room temperature were influenced by thermally activated diffusion processes, and that a similar steady state W precipitate size developed. For this experiment, Cu-3 at. % W alloy was irradiated at liquid nitrogen temperature. W precipitates were again observed, as shown in Fig. 4.13, although their average size was somewhat smaller, ~1.5 nm. This smaller size was expected due to the competition that occurs in the system under irradiation. While the ballistic mixing is not affected by the decrease in temperature, the diffusivity of W during irradiation is reduced at lower temperatures, leading to smaller precipitates.
Fig. 4.12 (Left column) STEM-HAADF images showing irradiation-induced precipitate structure and (right column) precipitate (volume-averaged) size histograms in Cu-W alloys with different initial W solute concentration.
Experiments were also performed to see if the system truly self-organizes, i.e. if the size distributions of the W precipitates are independent of the initial alloy structure. For this experiment, the 3 at. % W alloy was annealed for 1 hour at 700 °C and then irradiated at room temperature to ~55 dpa. Micrographs showing the final precipitate sizes after annealing and subsequent room temperature irradiation are presented in Fig. 4.14 (a) and (b), respectively; the corresponding volume-averaged size distributions are plotted in Fig. 4.14 (c). Fig. 4.14 shows that (i) annealing at 700 °C leads to W particles that are significantly larger than those observed following room temperature irradiation of as-prepared samples, and (ii) that re-irradiation of these annealed samples reduces the size of the W precipitates. While a clear shift in the size distribution of precipitates in the annealed samples toward that for irradiated as-prepared
samples, the two distributions do not yet overlap fully, suggesting that steady state has not yet been attained. Nevertheless, the resistivity experiments and TEM images demonstrates that the microstructure approach a unique steady state during the irradiation Cu-W alloy.

The Cu-W multilayer samples were also examined by TEM. Shown in Fig. 4.15 are bright field images of sample with 10 nm-W/100 nm-Cu: (a) as prepared; (b) irradiated at room temperature to a dose of ~60 dpa; (c) irradiated at room temperature and subsequently annealed at 600 °C for 1 h. While irradiation at room temperature reveals small W precipitates close to the Cu/W interface, subsequent annealing of this sample at 600 °C, leads to significantly more precipitation, with the precipitates appearing farther from the interface. Because of the low mobility of W in copper at 600 °C, it can be assumed that precipitation occurs locally, and is due to the supersaturation of W created during ion beam mixing. It is also observed that after a dose of 60 dpa the W layers roughen, but remain continuous. Fig. 4.16, on the other hand, shows that the interface of the W layers in the 10 nm- Cu/10 nm-W multilayer film is strongly affected by high dose irradiation. This indicates that the structure of this sample may be transforming to a three-dimensional morphology. TEM images were also collected on the Cu-W 100-10 sample

![Fig. 4.14 STEM-HAADF images showing: (a) W precipitates in 700 °C annealed 3 at.% Walloy; (b) W precipitates of the alloy in (a) after being irradiated to ~55 dpa. Precipitate size histograms for the alloy after different treatments are shown in (c).](image-url)
Fig. 4.15. Bright field TEM images showing W layer morphology in the 100 nm-Cu/10 nm-W multilayer sample: (a) in the as-grown state; (b) after RT irradiation to ~60 dpa; (c) after post-irradiation annealing at 600 °C.

Fig. 4.16 Bright field (a) and STEM-HAADF (b) images showing the W layer morphology in the 10 nm-Cu/10 nm-W multilayer sample: (a) in the as-grown state; (b) after RT irradiation to ~60 dpa.

Fig. 4.17 STEM-HAADF images of 10-100 multilayer sample after irradiation to ~55 dpa at 600 °C. A closer look at precipitates nucleating on Kr voids (b).
irradiated at high temperatures. As can be seen in Fig 4.17, the W layers are completely absent. This intuitively makes sense since the increased mobility of the W allows for the layers to break apart and for the Cu-W system to reduce the overall energy by reducing the total Cu-W interface.

4.4 Discussion

4.4.1 Radiation Enhanced Diffusion in Cu-W layers

We first examine the tracer-impurity diffusion coefficient of W atoms in Cu during room temperature irradiation. Previous work on ion beam mixing in metal alloys typically employed Rutherford backscattering [25]; however, this method is not suitable for Cu-W, owing to the very low concentrations of W soluble in irradiated Cu. Alternatively, electrical resistivity and X-ray diffraction measurements had been previously employed to probe ion beam mixing in Cu-W under irradiation, but these studies focused primarily on chemical interdiffusion under irradiation, not tracer diffusivity [34]. The analysis of the present experiments using electrical resistivity measurements on multilayer Cu-W samples makes the following assumptions (i) the Cu/W interfaces remain sharp during irradiation, at least relative to the thickness of the Cu layers; (ii) the W concentration in the Cu phase at the Cu/W interface is fixed at the saturation concentration of W in irradiated Cu; (iii) the resistivity of the W layers are not much affected; (iv) the resistivity can be defined locally as a function of position since, as noted above, the electron mean free path is small in the Cu-W alloy. With these assumptions the diffusion equation for a layered structured is solved numerically for this geometry as a function of dose (or time), with the diffusion coefficient left as a parameter. The resistivity of the irradiated samples at each dose was then found by using the calculated diffusion profiles, and adding the contribution of depth of the sample to the total conductivity. The calculated resistivity as a function of dose were then compared with the experimental curves to obtain the diffusion
The four experimental resistivity curves are shown in Fig. 4.18, in this case represented by a solid line. It is important to note that in this case only the resistivity of the Cu layers is shown, instead of the entire sample. A resistivity of 50 μΩ-cm was assumed for the W layers, which acted as resistors in parallel with the Cu layers [35]. Furthermore, it was assumed the resistivity of the W layer did not change with time. Except for the 10 nm-Cu/10 nm-W alloy, the experimental data fit quite well with the calculated values using an irradiation-induced diffusivity of $D_{W}^{irr} = 2.1 \text{ nm}^2\text{-dpa}^{-1}$ and a solute resistivity of 12 μΩ-cm/at. % W as given by equation 1. The 10 nm-Cu/10 nm-W was not used in the fitting since the approximations employed in the model break down at high dose, since as shown in Fig. 4.16 the layer structure becomes unstable at high doses. However, the initial portion of the resistivity curve for the 10 nm-Cu/10 nm-W does fit the model quite well. It is interesting to compare the value found for the tracer diffusion coefficient of W in irradiated Cu with that of self-diffusion in irradiated Cu, which was measured using secondary ion mass spectrometry (SIMS) after irradiation at 6 K. The
value for $D_{Cu}^{irr}$ is ~3.5 nm$^2$-dpa$^{-1}$ [25] and thus only somewhat greater than the value of $D_W^{irr}$ found here. We note that while $D_{Cu}^{irr}$ was measured at 6 K and $D_W^{irr}$ measured at room temperature, past measurements on tracer diffusion of Au markers in Cu under similar irradiation conditions showed that $D_{Au}^{irr}$ varies by only ~50% between these two temperatures [36]. Therefore, it is very likely that the diffusivities are identical, since a ~50% variation makes 2.1 nm$^2$-dpa$^{-1}$ match 3.5 nm$^2$-dpa$^{-1}$.

4.4.2 KMC Simulation of W Precipitation Kinetics

We can use the value of $D_W$ just obtained to explore the precipitation kinetics in the solid solution samples. If the assumption is made that W diffuses primarily in the thermal spike and that the precipitation occurs by an agglomeration-coagulation process, then the concentration of W precipitates per unit volume (N) can be obtained using the Smoluchowski model [37], i.e.,

$$\frac{1}{N(t)} - \frac{1}{N(0)} = \frac{4kT}{3\mu} \cdot t$$

(2)

The effective viscosity, $\mu$, in this thermal spike model can be estimated using the new value of $D_W^{irr}$ W using Stoke's Law, $\mu = \frac{kT}{6\pi D_W^{irr} r}$. Figs. 4.8 and 4.9 show that the change in the resistivity saturates after a dose $\tau_R \sim 0.2$-0.5 dpa. Using this dose (or time) in Eq. (2) yields $N \sim 0.2$-0.4 nm$^{-3}$, and each W precipitate contains ~5-10 atoms. The spacing between precipitates is correspondingly ~1.4-1.8 nm, and thus comparable to the electron free path in W-saturated Cu, i.e., once the W precipitates are separated by a distance comparable to the electron mean free path, the resistivity no longer changes. This approximate analysis thus adds support for the stated precipitation process, which will be discussed in more detail below with the help of kinetic Monte Carlo modeling.
The radiation-induced W precipitates in the initially solid solution samples appear to adopt a characteristic size, ~2 nm, after prolonged irradiation. Also, only the density of W precipitates increases significantly with increasing W concentration, not the precipitate size. Therefore, it is likely that a size selection, one that is independent of the initial precipitate size, represents a self-organizing process. This behavior would be similar to the patterning that has been reported for high-temperature irradiation of moderately immiscible alloys, such as Cu-Ag, Cu-Fe, and Cu-Co [22, 38]. Self-selection of precipitate size in those systems has been explained in terms of a dynamical competition between ordering and disordered reactions [39-42]. Disordering is affected by ballistic events in energetic displacement events. For the moderately immiscible alloys noted above, these ballistic events occur predominantly in the thermal spike phase of the cascade, but some also occur by recoil events involving energetic two-body collisions. At high-temperatures, ordering is achieved through thermally-activated diffusion processes, such as radiation-enhanced diffusion. Theory and modeling have shown that patterning occurs when these two processes are of comparable strength, but the basic diffusion steps operate over different length scales. In the case of modeling the thermal spike during low temperature irradiation, the ballistic relocation transports atoms by two atomic distances, which was also approximated by SRIM, whereas thermally activated diffusion moves atoms one atomic distance at a time, i.e. to its nearest neighbor.

In the present situation, the alloy components, Cu and W, are immiscible in the liquid and the thermal-spike interdiffusion is small near interfaces, as demonstrated in previous experiments. W is nevertheless mobile in the thermal spikes, and migrates freely while in dilute liquid Cu solutions. It can be assumed then that ballistic transport of W occurs entirely by energetic recoil events (and not thermal spikes), and that thermally activated diffusion occurs by
liquid diffusion in the thermal spike (eq. (2)) and not by traditional point defect mediated radiation-enhanced diffusion. The diffusion coefficient in the thermal spike is known from the experiments described above, and the recoil mixing is readily calculated by Monte Carlo methods, such as SRIM [43]. A model can be implemented to examine the competition between recoil mixing and thermal spike diffusion using a simplified kinetic Monte Carlo procedure, as follows. First, a simple cubic lattice is created with x at. % B atoms and the rest A atoms (referred to hereafter as W and Cu atoms, respectively). All W atoms, regardless of their location, can undergo recoil events, with the recoils occurring in random directions. The number of recoils is determined by assuming a recoil probability, per atom, of 0.1 per dpa over a fixed distance of 2 lattice parameters. This value was obtained using SRIM calculations. At the same time, all single W atoms and small W precipitates diffuse according to the Stokes-Einstein Law [44] (i.e., inversely proportional to their radius) using the above measured value $D_W$ for determining the mobility of a single W atom. W clusters larger than a thermal spike event, ~5 nm, are assumed immobile since they are not completely immersed in liquid Cu. If during a recoil or diffusive jump, W atoms or precipitates become nearest neighbors, the two bodies coalesce. All precipitates are assumed spherical. While the model is simple, it includes the essential physical processes.

The results for the steady state sizes of precipitates are presented in Fig. 4.19 (a)-(c) for three W concentrations, 1, 3, and 5 at. % W. Each simulation also uses two starting conditions, either a complete solid solution or a two-phase alloy containing W precipitates with a diameter of 5.94 nm. These figures show that, like the experimental findings, the initial state of an alloy has little effect on the steady state size distribution of W precipitates. The average sizes of the steady-state precipitates, moreover, are comparable to experimental values. Plotted in Fig. 4.19
Fig. 4.19 (a): Steady-state precipitate size distribution (weighted by precipitate volume) from the KMC simulation for the Cu-1 at.%W alloy with two different initial structures: solid solution or having one 5.94 nm W precipitate; (b): the same as (a), but for the Cu-3 at.%W alloy; (c): the same as (a), but for the Cu-5 at.%W alloy; (d): the rate of resistivity change with dose for the solid solutions during irradiation.

(d), in addition, is the dose dependence of the solubility of W in solution, in terms of resistivity.

For this plot, we have again used eq. (1) to convert solubility to resistivity, assuming W atoms in clusters containing less than or equal to 5 atoms contribute to the resistivity, i.e., are in solution.

The time constant obtained for the radiation-induced precipitation is notably quite similar to the experiments. The steady-state solubility found in this model are comparable to, but somewhat smaller than, those deduced from the resistivity experiments, as seen when comparing the value
in Table 4.2 (0.61 at. %) to the value in Table 4.1 for the Cu-3.1 at. % W alloy (1.32 at.%).

Despite some small differences, these simulation results are in good overall agreement with the experiments, both in terms of the qualitative trends and the quantitative values. Regarding the quantitative agreement, we checked the sensitivity of the precipitate size and solubility on our measured value of $D^{irr}_W$. As we reported above, the precipitate size was reduced from ~1.9 nm to ~1.5 nm when the irradiation temperature was lowered from room temperature to 80 K, and we speculated that this was due to a somewhat reduce value of $D^{irr}_W$. The results shown in Table 4.2 indeed show that a factor of two smaller diffusivity results in a reduction in precipitate size comparable to that found on irradiating at lower temperature. As expected, the solubility also increases with decreasing $D^{irr}_W$.

<table>
<thead>
<tr>
<th>$D^{irr}_W$</th>
<th>1.05 nm$^2$/dpa</th>
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<th>4.2 nm$^2$/dpa</th>
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<tr>
<td>Diameter</td>
<td>2.1 nm</td>
<td>2.7 nm</td>
<td>3.0 nm</td>
</tr>
<tr>
<td>Solubility</td>
<td>0.93 at. %</td>
<td>0.61 at. %</td>
<td>0.35 at. %</td>
</tr>
</tbody>
</table>

Table 4.2 Average precipitate sizes and steady-state solubilities under irradiation for a Cu-3 at.%W alloy, when different $D^{irr}_W$ values are used in the simulation.

Finally, to gain further insight about the low-temperature self-organization process proposed here, we examined the significance of our assumption that W precipitates larger than the size of the melt zone are immobile. We emphasize that the model just described does not impose a limit on the maximum size of the W precipitates, but only on the mobility of large precipitates; i.e., precipitates can grow larger by the addition of mobile W atoms and small precipitates to the larger immobile precipitates. We thus recalculated the size distribution for the 3-at. % W alloy, but with condition limiting precipitate mobility extended to either 8 nm or even to an indefinite size. In the case that precipitates up to 8 nm are mobile, the average steady state
size of the W precipitates approximately doubles, from 2.7 nm to 5 nm, while for the unrestricted case, the final size of the precipitate becomes limited only by the size of the computational cell. Therefore, the size of the thermal spike is critical in limiting the precipitate size. Also, the high temperature model of compositional patterning also allows for precipitate mobility, at least as implemented by KMC, but in that case diffusion of large precipitates has negligible effect on the patterning, due to the rapid decrease in cluster diffusivity with size. Therefore, these two behaviors derive from the different dependencies of the precipitate mobility on precipitate size: in the solid state (i.e., under radiation-enhanced diffusion), the diffusivity of large precipitates varies as $1/d^4$ (or even more strongly with precipitate diameter, d) whereas in the (thermal spike) liquid, it varies as $1/d$. Thus, diffusion of large particles can play a far stronger role in the liquid thermal spike than in the solid.

4.5 Conclusion

This work has clarified several of the issues regarding the response of strongly immiscible alloys to energetic particle irradiation. Using the dilute Cu-W system as a model alloy for such systems, it was shown that prolonged irradiation at low temperatures causes the microstructures to reach a self-organized, two-phase steady state whereby the size and density of W precipitates and the W solubility obtain fixed values. These values are governed by the specific thermochemical properties of the system and the irradiation particle, but they are independent of the initial microstructure of the system and depend only weakly on alloy concentration. The solubility of W in Cu matrix is raised many orders of magnitude above its equilibrium value at room temperature and even orders of magnitude larger than its solubility in the liquid at the melting temperature of Cu. The precipitate sizes remain about 2 nm. It is found that in irradiation of multilayered samples, the W layers remain continuous up to doses of ~60
dpa when the Cu layer thickness is 100 nm, but they appear to become unstable at this dose when the Cu layer is less than \(~10\) nm. This suggests that thin multilayer structures of Cu-W will eventually transform to 3-dimensional structures. These observations can be rationalized by a model that includes a competition between ballistic recoil events and thermal spike diffusion. In this model, the finite length scale of the local thermal spikes is an essential requirement to reproduce the stabilization of finite size precipitates at steady state under irradiation.

The key parameter found here controlling how nominally two- or multi-phase systems behave under low temperature irradiation is the chemical interdiffusion coefficient in the thermal spike, i.e., a combination of heat of mixing and tracer diffusivity, as ballistic recoil events do not vary significantly between different alloys when normalized by dpa. In the next chapter, it will be explored if the behavior observed here for irradiation of Cu-W alloys extends to types of driving forces; specifically, it examines the behavior of strongly immiscible alloys subjected to severe plastic deformation at low temperatures.

4.6 References


143.

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CHAPTER 5

SELF-ORGANIZATION IN HIGHLY IMMISCIBLE ALLOYS DURING SEVERE PLASTIC DEFORMATION

5.1 Introduction

The processing of metal alloys by SPD has attracted much attention over the past several years as a “top-down” procedure to fabricate nanocrystalline materials, mainly by grain refinement [1]. The shear of atomic planes, however, does more than just create high densities of dislocations, and domain walls; it also shifts atoms just above the shear planes relative to atoms just below them, thereby causing atomic mixing. This was described in chapter 2 but is also illustrated in Fig 5.1. In this figure, every time an atom below the slip plane acquires a new nearest neighbor, it becomes red, showing how eventually every atom on the slip plane changes a nearest neighbor. Two additional atoms are highlighted, one in yellow and one in blue, to demonstrate how other atoms are affected by shearing. It can easily be seen that all atoms above the slip plane are moving relative to atoms below the slip plane. This forced chemical mixing.

Fig. 5.1 Illustration of shear in a crystal lattice. Every time an atom below the slip plane gets a new nearest neighbor, it becomes red. Two atoms are highlighted above the slip plane.

† This work was done with the help of Dr. Miao Wang and was published in Acta Materialia 140 (2017)
process was reported by J.S. Benjamin, who referred to it as mechanical alloying [2]. Similar to ion irradiation, moreover, chemical mixing has been observed in immiscible alloys, such as Cu-Ag, Cu-Fe, and many others, illustrating that the external driving forces are sufficient to drive systems far from equilibrium [3–5]. Various explanations have been suggested for this behavior, based on thermodynamics, pipe and grain boundary diffusion, dislocation glide, or some combination of the previously mentioned mechanisms [6-10]. What has been much less discussed and is still not properly understood is why highly immiscible alloys, such as Cu-Ta, Cu-Nb, Cu-Mo, Cu-Cr, Fe-Ag, and Ni-Ag, fail to homogenize during SPD [11-15]. Shown below in Fig. 5.2, for example, is the phase diagram for Cu-Nb [16]. While it shows more liquid-phase solubility of Nb in Cu than, for example, Cu-W, which was discussed in Chapter 4, the solubility of Nb in copper and vice versa is nevertheless extremely limited, clearly indicating a high heat of mixing. Shear mixing thus appears to behave very similarly to ion beam mixing.

Fig. 5.2 Phase diagram of the Cu-Nb binary alloy system. White regions represent two phases present, while blue regions represent single phases. Very little solubility exists between Cu and Nb, even after the Cu has melted [16].
Two important observations regarding the shear mixing of these highly immiscible alloy systems are that while they do not homogenize, the length scales of the phase separation dramatically reduces to some tens of nanometers [12, 17, 18]. In a recent study, in fact, it was shown for dilute Cu-Nb alloys, Cu$_{85}$Ag$_{10}$Nb$_5$ and Cu$_{80}$Ag$_{10}$Nb$_{10}$, the initial Nb precipitates, independent of their size, preferred a given size after extended SPD, $\sim$10 nm in radius [19]. It was hypothesized that the Nb precipitate size in Cu-Nb alloys is controlled by a dynamical competition between two processes [18]. The first concerned the shear removal of atoms from large Nb precipitates by dislocations. This mechanism has been observed in MD simulations, which showed that random shearing of a Cu matrix containing Nb or V precipitates leads to the emission of precipitate atoms from the Cu/Nb and Cu/V interface [20, 21]. Although these simulations were limited to relatively small sized particles, $\sim$5 nm in radius (all precipitate sizes herein will refer to radius), this process could explain, at least qualitatively, how large precipitates could shrink in size during SPD. These simulations are also consistent with past experiments using wire drawing, ball milling, or HPT which show that the solubility of Nb in Cu increases during processing [12, 18, 22, 23]. However, while computer molecular dynamics and molecular statics simulations have shown that shear mixing can lead to some short range chemical ordering in binary alloys with large heats of mixing, they have yet to reveal precipitation at low temperatures [10, 24].

Alternative mechanisms to explain the size selection of initially large Nb precipitates in Cu concern co-deformation and subsequent fracture of the precipitate particles and atomic shuffling [25-27]. The co-deformation of two-phase alloys is well documented in the literature for a number of binary systems [25, 26]. This mechanism is further supported for the Cu-Nb system by the observation that Cu/Nb laminate structures co-deform during accumulative roll
bonding (ARB) [28]. When these co-deformed structures are deformed additionally to much higher strains, the interfaces roughen and eventually convert to a three-dimensional structure containing small Nb precipitates [23]. The details of this conversion, however, are not yet clear. The shuffling mechanism for refining the precipitate size in strongly immiscible alloys like Cu-Nb assumes that small precipitates are “cut out” from the large parent precipitate by the successive passage of dislocations across the interface on the same slip system and at the same locality, i.e., by shear banding [27]. While these mechanisms possibly explain how large precipitates shrink in size, they are incomplete since they do not consider how these systems come into a dynamic steady state with extended solid solutions in the matrix and specific precipitate size. However, the model involving a dynamic competition suggests that the steady size is independent of the initial state of the alloy.

Fundamental to understanding the mechanisms of severe plastic deformation in these strongly immiscible alloys, therefore, is whether alloy components can precipitate out of solution and grow during low temperature SPD and whether the steady state is indeed independent of the initial state. In the present work, new experiments using HPT of oxygen free alloy films demonstrated that shear mixing of Cu-Nb solid solutions leads directly to the nucleation and growth of Nb precipitates and that the growth saturates. In addition, it is shown that this size is very close to that obtained if the alloy initially contains large Nb precipitates >50 nm, and virtually no Nb in solution. A simple model for the growth of precipitates is presented and implemented by Monte Carlo simulations. The experimental details of this work have been explained previously in chapter 3, and the interested reader is referred there for details regarding HPT sample processing and sample characterization.
5.2 Results

The concentration of Nb remaining in solution is first reported as a function of initial supersaturation and strain. This was accomplished by measuring the lattice parameter using “micro” X-ray diffraction along the radius of the circular-disk specimens and employing a Rietveld analysis. The Nb solubility was subsequently deduced assuming that the atomic volume of Nb in Cu is a factor of 2.1 larger than the host atomic volume, i.e., $\Omega_{\text{Nb(Cu)}} = 2.1 \Omega_{\text{Cu(Cu)}}$ [20]. Good agreement for the Nb concentrations in the as-prepared alloys is found by comparing x-ray diffraction results using the above value of $\Omega_{\text{Nb(Cu)}}$ with x-ray fluorescence analysis, shown in Table 5.1. The solubility results for the various samples during HPT are plotted in Fig. 5.3. A reduction in the solubility is clearly observed with increasing strain for the three alloys containing more than 2 at. % Nb. The sample containing less than 1 at. %, in contrast, shows no decomposition; in fact, a small increase in the lattice parameter is observed. This increase, however, can be accounted for by shear-induced mixing of the thin Ag protection layers into the Cu matrix, using the lattice parameter data for Cu-Ag alloys from Linde’s previously published

<table>
<thead>
<tr>
<th>Nominal Concentration (at.%)</th>
<th>XRF Measurement (at.%)</th>
<th>XRD Measurement (at.%)</th>
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<tbody>
<tr>
<td>1</td>
<td>1.467</td>
<td>.65</td>
</tr>
<tr>
<td>2.5</td>
<td>2.584</td>
<td>2.32</td>
</tr>
<tr>
<td>5.0</td>
<td>5.689</td>
<td>5.47</td>
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<tr>
<td>10.0</td>
<td>10.369</td>
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Table 5.1 Concentrations of as grown samples determined by x-ray fluorescence (XRF) and x-ray diffraction (XRD).
Fig. 5.3 Solubility of Nb in Cu versus strain. Solid symbols indicate HPT of as-deposited samples; open circles HPT of pre-annealed samples.

work [29]. While steady state has not been quite achieved in these samples, even after a strain of ∼2,500, the data are consistent with a steady state Nb concentration of ∼1–3 at. % Nb, increasing somewhat with increasing average concentration of Nb in the sample. For comparison, the concentrations of Nb found in a sample that was first annealed at 700 °C prior to HPT are also plotted in Fig. 5.3. Annealing at 700 °C results in precipitation of Nb, leaving negligible amounts of Nb in solution. During HPT of this pre-annealed sample, the solubility increases with strain and approaches the same steady state values obtained for the unannealed samples. We note that steady state solubility measured here are somewhat larger than those reported after HPT of Cu₈₅Ag₁₀Nb₅ and Cu₈₀Ag₁₀Nb₁₀ [19] and Cu₅₀Nb₅₀ [23], however, these latter experiments were performed at higher temperatures, possibly explaining the difference. Furthermore, oxide contamination could also have played a much larger role in the previous studies. However, these possibilities will be discussed later. The first main conclusions that can be drawn are that the steady state solubility of Nb in Cu under prolonged low-temperature SPD is
highly supersaturated, \( \sim 2\text{–}3 \text{ at. \%} \), weakly dependent on average alloy concentration, and independent of the initial microstructure of the alloy.

The microstructures of as-deposited samples and pre-annealed samples, both before and after low-temperature HPT for 20 cycles were examined using the FEI Helios Nanolab 600i FIB/SEM. As shown in Fig. 5.4, no precipitates are observed in the as-prepared specimens, (a), while large, \( \sim 75 \text{ nm} \), Nb precipitates are observed in the sample following pre-annealing at 700 °C, (b). Fig. 5.4 (c) shows the precipitate structure after HPT of the as-prepared sample; Nb precipitates nucleate and grow, reaching an average volume-averaged radius of \( \sim 10 \text{ nm} \), while Fig. 5.4(d) shows the precipitate structure after HPT of the pre-annealed sample. The large Nb precipitates, in this case, shrink to about that same steady-state size as that observed in the

Fig. 5.4 SEM images of (a) as-prepared Cu-10 at.\% Nb; (b) after annealing of sample in (a) at 700 °C; (c) after HPT of sample in (a); (d) after HPT of sample in (b).
sheared, as-prepared, sample. The complete size distributions of the Nb precipitates and volume-weighted radii for the various samples are shown in Fig. 5.5. This was determined from SEM images using a threshold analysis function discussed in chapter 3. The outstanding features of Fig. 5.5(a) are that (i) Nb indeed precipitates out of solution during low-temperature shearing, and (ii) the average size of the precipitates is approximately the same as that found after low-temperature HPT of well-annealed samples, where the alloys initially contained large Nb precipitates, greater than 75 nm in size. Fig. 5.5(b) shows in addition that the total volume-weighted size distribution of the precipitates of size r, is not strongly sensitive to the alloy concentration. The weighted-average precipitate size for the Cu-2.5 at. % Nb sample, for example, is nearly the same as that for the 10 at. % Nb sample; only the density of precipitates is different. The sample containing 1 at. % Nb showed no evidence of Nb precipitation during low-temperature HPT, as expected from the solubility results, which showed no reduction in solubility of this sample during HPT. Energy dispersive analysis confirmed that the particles were indeed Nb rich, while electron diffraction and x-ray diffraction confirmed that they had a

Fig. 5.5 (a) Normalized size distribution of precipitates comparing the as-grown and pre-annealed samples following HPT in 10 at% case; (b) volume-weighted size (in units of atomic volume, U0) (i.e., # precipitates x number of atoms in precipitates of size r) as a function of size after low-temperature HPT showing the effect of alloy concentration. Average volume-weighted radii (radius$_{avg}$) are shown in the text box.
BCC structure matching pure Nb. An electron diffraction pattern showing the (110) ring of Nb precipitates is shown in Fig. 5.6 (a) for the 10 at% Nb solid solution case after shearing at dry ice temperatures for a strain of ~2000. Fig 5.6 (b) and (c) show the corresponding BF and DF TEM
of the sheared 10at% sample, which helps illuminate the Nb precipitates. The DF image was collected from the area outlined in red in the electron diffraction image.

The smallest precipitates that could be clearly identified by SEM had a radius of \(\sim 3\) nm. We thus prepared APT tips using the same focused ion beam processing unit discussed previously to examine whether large populations of smaller precipitates were also present. The Cu-2.5 at. % Nb sample was used for the APT analysis since this sample was considered most likely to contain smaller precipitates. Shown in Fig. 5.7 is a reconstruction of the atom probe tip taken from a region of high strain, \(\varepsilon \sim 1500\). Only Nb clusters containing more than 6 Nb atoms are shown, which roughly corresponds to an isosurface concentration of 15 at%. These clusters contain \(\sim 2\%\) of the Nb, while most of the Nb is observed as monomers (\(\sim 50\%\)). Here, we have used procedures outlined in Ref. [30] to determine cluster size; these procedures are discussed briefly in chapter 3.

![Fig. 5.7 Atom probe tomography reconstruction of the Cu-2.5 at.% Nb sample following low-temperature HPT to a strain of 1500. Sample dimensions are 70 nm x 70 nm x 500 nm. (i.e., # precipitates x number of atoms in precipitates of size \(r\) as a function of size after low-temperature HPT showing the effect of alloy concentration. Average volume-weighted radii \((\text{radius}_{\text{avg}})\) are shown in the text box.](image)

Comparison of the APT results with those from x-ray diffraction and SEM imaging show good agreement. The density of Nb precipitates observed in the SEM images with radii greater \(\sim 3\) nm is \(\sim 1 \times 10^{-6} \text{ nm}^{-3}\). Since the volume of the APT examined is \(\sim 2.5 \times 10^6 \text{ nm}^3\) \((70 \times 70 \times 500 \text{ nm}^3)\), we expect \(\sim 3\) such precipitates to be located in the reconstruction; we observe four using our cluster analysis. Similarly, the average Nb concentration in this
reconstructed volume is \(\sim 1.5\) at. %, which agrees well with the lattice parameter measurements, considering that the volume sampled is small and the \textit{ad-hoc} assumption concerning the cut-off in precipitate size where they are no longer considered in solution.

5.3 \textit{Discussion}

5.3.1 \textit{Precipitation Mechanisms in Highly Immiscible Alloys During SPD}

The experiments demonstrate that SPD can lead to phase decomposition in highly supersaturated immiscible alloys, even when performed at temperatures far too low for significant thermally-activated vacancy or Nb diffusion. They also show that the steady state solubility and precipitate size are independent of the initial state of the alloy. Before discussing the significance of these results in detail, it is helpful to first review previous work on the decomposition of immiscible alloys during SPD. These past studies, however, considered “moderately” immiscible alloys, where solubility at the melting temperature are at least several percent, and processing temperatures are typically \(\sim 300\) K. Decomposition under these conditions is reasonably explained by thermally activated diffusion and falls within the effective temperature model of Martin [31]. Klassen et al. for example showed that Cu-Ag alloys completely homogenize during ball milling at liquid nitrogen temperature, but begin to decompose as milling temperature is increased, with significant decomposition by \(\approx 43\) °C (the homologous temperature \(T_H \sim 0.23\)) [32]. Straumal et al. showed similar behavior in Al-Zn and Al-Mg (\(T_H \sim 0.32\)) and a series of dilute Cu-based alloys [10, 33] at room temperature. For the current study using HPT of Cu at \(-78\) °C (\(T_H \sim 0.14\)), the vacancy hopping rate is negligible [34], and thus the effective temperature within the Martin model approaches infinity and Cu-Nb alloys should not decompose.
While we can exclude thermally-activated vacancy diffusion from the discussion of the precipitation results, the underlying mechanisms controlling atomic motion and precipitation during low-temperature SPD, remain unclear. Previous MD simulations [35], however, have revealed that the relative motion of atoms during shear deformation can occur athermally by dislocation glide, as atoms above and below the slip plane switch neighbors. Such an atomic transport process is “superdiffusive,” as the relative motion of two atoms in a lattice requires the passage of a dislocation between them, and hence this relative motion increases linearly with their distance apart. In this way, Nb atoms can relocate during deformation, and since Nb is strongly immiscible in Cu, Nb atoms will attract and possibly agglomerate. If the Nb atoms are on lattice sites, however, we would expect that subsequent gliding dislocations to later separate these Nb atoms. MD simulations indeed illustrate that two neighboring Nb atoms in solution in Cu or even a small semi-coherent BCC Nb nanoparticles in Cu are cut by dislocation glide [36]. In amorphous alloys, on the other hand, deformation does not require dislocation motion. Malandro and Lacks showed using MD simulation that atomic motion and deformation in amorphous materials can occur at very low temperatures by athermal, local relaxations, as the potential energy landscape contains many low energy barriers that can be overcome by shearing stresses, as illustrated in 5.8 [37]. The interaction between two Nb atoms can be expected to bias such athermal rearrangements and lead to clustering. Lund and Schuh [34] showed using molecular statics simulations that, indeed, short range chemical ordering occurs athermally in 2D immiscible amorphous alloys during shear deformation. We propose, therefore, that the nucleation of Nb precipitates occurs at locations with similar topological disorder, e.g., grain boundaries and dislocation intersections. Since the grain size of our Cu-Nb samples during low-temperature HPT is \(~40\) nm, we expect that Nb precipitates nucleate in the grain boundaries.
These Nb clusters can then grow as dislocation glide processes deliver additional Nb solute to these sites by the superdiffusive mass transport process described above. In this regard, Vo et al. showed using MD simulation that over 90% of the deformation in nanocrystalline Cu occurs by dislocation glide processes when grain sizes exceed 20 nm [38].

This athermal relaxation mechanism for precipitate nucleation and growth may also have some bearing on the temperature dependence of shear-induced decomposition. Since there is a wide distribution of energy barriers for atomic relaxations/mixing in amorphous materials, shear mixing may lower many of them, perhaps not to the point of instability, as shown in Fig. 5.8 (b), but to within kT of this limit, as shown in 5.8 (c), thus enabling thermally assisted local relaxation during shear. This latter possibility was proposed by Vo et al. to explain their MD simulation results on high temperature shear mixing [10]. Whether this local relaxation mechanism contributes significantly to the alloy decomposition reported in Cu alloys during shear deformation near room temperature, however, is unclear since as discussed above,

![Fig. 5.8 Schematic representation of shear-induced diffusion](image)

(a) $\sigma = 0$

(b) $\sigma = \sigma_c$

(c) $\sigma < \sigma_c$

$\pm kT$
vacancies are mobile in Cu at room temperature, and thermal diffusion mediated by shear-induced vacancies may be the more dominant mechanism.

5.3.2 KMC Simulations of Precipitation and Growth During SPD

We explored the feasibility of the above model for alloy decomposition using Monte Carlo computer simulation, eschewing analytic attempts to describe this mechanism owing to the complexities of superdiffusive motion of atoms during shear [39]. The simulation model tracks the displacements of solute atoms on a simple cubic lattice containing $(128)^3$ atoms as the lattice is sheared along randomly selected slip planes, one Burgers vector at a time, in the spirit of the model proposed by Bellon and Averback [8]. Unlike that model, however, vacancies are not included, since at low temperature they are immobile. Also unlike Ref. [8], when two solute (Nb) particles meet, they are joined into a single larger, spherical particle, and located at the lattice site closest to their center of mass. The simulation model does not consider the details of particle coagulation, but the observation that Nb precipitates are mostly equiaxed suggests that coagulation occurs rather quickly. Since it is unlikely, as noted above, that two Nb atoms will bind during shearing unless they are in a grain boundary or other region of topological disorder, we assume that when two particles meet, i.e., they are separated by a distance less than or equal to the sum of their radii, they have a probability, $p = 1 - \exp(-ar^n)$ to form an agglomerated larger particle, where $r$ is the root mean square (rms) radius of the two particles. For the present simulations we choose $n = 4$ and $a = 0.05$, which yields a “characteristic” rms radius for agglomeration of $\sim 2$ Burgers vectors, i.e., particles with larger radii have a nearly unity probability to agglomerate. Particles that do not agglomerate are separated by one lattice parameter in a random direction before the next shearing event.
The results of the model for solubility and precipitate size are shown in Fig. 5.9 as a function of strain. In Fig. 5.9(a) the calculated solubility is shown for both the 5 and 10 at. % alloys, along with the experimental data. Only monomer Nb atoms are considered to be in solution, since within our physical model small clusters, dimers etc., are assumed to be in grain boundaries and would not change the lattice parameter of the Cu matrix. The agreement is very good over the entire range of strain, and for both alloys. There are, of course, two fitting

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Fig. 5.9 Model calculations of solubility and precipitate size as a function of strain: (a) experimental and simulation results for solubility for the 5 and 10 at.% alloys; (b) volume-averaged precipitate size at high strain; (c) largest precipitate size; (d) largest precipitate size for the 5 at.% alloy versus strain assuming 10 slip steps on same slip plane before changing the slip plane (see text).
parameters to achieve this fit, but the important point is that the model provides good agreement with the experiment using physically reasonable values for these parameters. The model was also applied to the 1 at. % alloy; naturally, it yields some precipitation since unlike the experiment no competing dissolution process has been activated in the simulation model. It is nevertheless interesting that after a strain of 3000 the solubility has been reduced by only \( \sim 15\% \), providing some insight about the dynamical competition between dissolution and decomposition processes, e.g., for alloys containing less than 1 at. % Nb in solution, the agglomeration process is extremely slow, setting a low required dissolution rate of small clusters.

The volume-averaged size distribution of the Nb clusters and precipitates after a strain of 3000 is plotted in Fig. 5.9(b), for the 5 and 10 at. % alloys. Here it is seen that the distributions are bi-modal, with one broad peak near to the largest sized precipitates and the other corresponding to monomers and dimers. We believe this distribution, which is weighted to large precipitate sizes, for example in comparison to a log-normal distribution, derives from the fact that the relative diffusion coefficient of large precipitates during dislocation glide has the same magnitude as it does for monomers, while their cross-section for capturing other precipitates scales with their radii. A possible indication of this process is illustrated in 5.10(a), which is an SEM images similar to those shown in 4.7. Shown in the inset is what appears to be two large Nb precipitates merging into a single larger particle.

Since the distribution of precipitates is weighted toward large size, we also calculated the largest-sized precipitate in the distribution as a function of strain for the 5 and 10 at. % alloys. The jumps in these curves illustrate that growth after the initial nucleation period occurs predominantly by collisions between larger particles. In this case the largest precipitate for the 10 and 5 at. % alloys are \( 19a_0 \) (7060 atoms) and \( 15a_0 \), (3600 atoms) respectively (\( a_0 = \) lattice
parameter) (about a factor of 3–4 smaller than the steady state experimental values). This agreement, however, is reasonable given the simplicity of the model. For example, assuming that the precipitates are spheres minimizes their capture radius for other particles. More significantly, perhaps, is our assumption that the shearing occurs randomly on slip planes, one Burgers vector at a time. For HPT and ball milling, the strain can be extensive in one direction before switching to another direction, for example in a single collision event between two milling balls and a powder particle. Bachmaier et al. [13], for example, illustrated the importance of strain path for alloy homogenization during HPT. We thus repeated these simulations but now introducing 10 successive slip steps on a particular slip plane before selecting another. The results are shown in 5.9(d) for the 5 at. % alloy. It is seen that the effect is significant, with the precipitate size increasing a factor of ~4 in comparison to straining one Burgers vector at a time. While the agreement with experiments is improved using this new strain path, we emphasize that our goal is not to achieve quantitative agreement with experiments, but rather to check if the model predictions can reasonably explain the experiments, and to gain a better understanding of the effect of different kinetic processes.

5.3.3 Self-Organization During SPD

Our second major conclusion, that the steady-state microstructure is independent of the initial state of the alloy, requires a second mechanism that dissolves precipitates faster than they can grow, once their radius increases above ~10 nm. One possibility, as noted above, is that Nb precipitates larger than 10 nm co-deform with the Cu, elongate, and eventually fracture. While this mechanism has been reported in the literature for large precipitates [26], we see little evidence of this mechanism for Nb precipitates with radii less than ~ 20 nm, see e.g., Figs. 5.4
We therefore examined the specimen that was initially annealed to 700 °C at low strain; this specimen initially contained precipitates larger than 75 nm. The results are shown in Fig. 5.10(b). While co-deformation is clearly observed, it is not seen in precipitates smaller than 30 nm or in any of the precipitates in 5.10(a), nor is there evidence of fracture or shuffling in 5.10(b) or in several similar images. We suggest, therefore, that the refinement of large precipitates begins by their co-deformation with Cu and subsequent fracture until their size is reduced to some smaller value, perhaps ~50–100 nm, after which the emission of Nb monomers becomes more dominant. This emission process, moreover, is likely enhanced at interface regions that have high curvature, explaining why the small precipitates are equiaxed during steady state shearing. As a final comment we note the results of recent MD simulations of a BCC Nb particle, 5 nm in radius, embedded in a Cu matrix and subjected to shear deformation (see Refs. [19, 20] for details). After a strain of 100, the volume of the BCC Nb particle was reduced by ~20%, illustrating that the emission process appears to be the right order of magnitude [41].
5.4 Conclusions

It has been shown that dilute, strongly immiscible alloys, exemplified here by Cu-Nb, self-select a steady state microstructure when subjected to severe plastic deformation at very low temperatures, and that this microstructure is independent of the initial state of the alloy. Alloys prepared by vapor deposition with high supersaturations of Nb in Cu, ranging from 2.5 at. % to 10 at. %, were observed to decompose during HPT at −78 °C to form small Nb precipitates, ∼10 nm in radius; this size was insensitive to the initial alloy concentration. Alloys pre-annealed to form large Nb precipitates were found to acquire nearly the same microstructure during similar low-temperature HPT processing. The very low temperature during shearing precludes any significant Nb diffusion mediated by a vacancy mechanism, illustrating that the effective temperature model of Martin [31] cannot explain these results. In lieu of such effective temperature models, a heuristic kinetic model was proposed that suggests the steady state microstructure is controlled by a dynamical competition between precipitate growth and dissolution processes. In this model, nucleation of Nb precipitation occurs by chemically biased, athermal relaxations in grain boundaries and they grow by a superdiffusive transport process mediated by dislocation glide. The shrinkage of precipitates is controlled the emission of Nb monomers at the Cu-Nb interfaces, as observed in MD simulation.

Because a steady-state precipitate size is selected regardless of the initial starting conditions, this driven alloy system is considered to self-organize, which was also found for the highly immiscible alloys during ion irradiation, suggesting that the basic mechanisms are likely to be similar. Differences between irradiation and SPD, however, are clearly evident. While irradiation causes the formation of a thermal spike, which allows for nucleation at any point a cascade event occurs, severe plastic deformation appears to require a local region with large
topological disorder, such as a grain boundary. Growth of the precipitates in both cases require forced atomic motion; for irradiation, this entails thermal spike diffusion, while for SPD it is superdiffusive mixing through dislocation glide. The consequences of these differences are presently not understood. Nevertheless, it appears that the underlying feature that in both cases the dissolution and precipitation processes operate on different length scales is sufficient to drive self-organization.

In the present chapter phase separation was driven the underlying immiscibility of the two binary alloy components. In the next chapter, additional complexity is introduced by adding a third constituent to the alloy, one that is strongly reactive with the dilute components of the binary system, allowing for possible compound formation. This work will largely focus on Cu-Mo-Si during irradiation, and Cu-Nb-Si during SPD, with the expressed goal of using Si to create Mo or Nb silicides. While adding another constituent element to the alloy which is not inert complicates the ability to understand the fundamentals which are occurring, it also allows for the opportunity to understand more practical systems such as ODS steels. There is also the added benefit that it may become possible tune alloy properties as more degrees of freedom are added. It is believed that having thoroughly studied the highly immiscible binary alloy systems, it should be possible to use this new understanding to interpret the results found in more complicated systems.

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CHAPTER 6
ION IRRADIATION AND SEVERE PLASTIC DEFORMATION EFFECTS IN TERNARY ALLOYS

6.1 Introduction

In Chapters 4 and 5, the self-organizational behavior of binary alloys was investigated during both irradiation and severe plastic deformation (SPD), two classic examples of driven systems. This work provided a deeper understanding of the fundamental mechanisms that underlie phase separation even at low temperatures. With this foundation, it becomes possible to shift focus to ternary alloy systems. These alloys provide more flexibility to tune alloy properties and thus greater potential for applications; however, they are vastly more complicated than binary alloys owing to the increased number of degrees of freedom. Like chapters 4 and 5, the work in this chapter on ternary alloys compares and contrasts the behaviors in irradiated and plastically deformed system, treating first irradiation of ternary alloys and then switching to severe plastic deformation.

6.2 Ternary Alloy Systems Under Irradiation

While previous studies have shown such benefits as phase stability and radiation resistance when using binary immiscible alloy systems during irradiation, additional benefits can be anticipated in systems that form compounds. In particular, one can envision compound formation in a ternary system if the two solutes present are mutually reactive. More importantly, the precipitation of a compound with a large heat of formation, such as the Mo silicide compounds in Cu, could provide additional resistance to thermal coarsening [1, 2]. However,

‡ Ion irradiation work was accomplished in conjunction with Dr. Jaeyel Lee and was published in Acta Materialia 132 (2017)
whether irradiation can cause the direct formation of precipitates, what precipitates would form, and how these precipitates would respond to high temperatures, remains unclear. As an example of the difficulty in predicting the evolution of ternary systems under irradiation, a previous study reported that room temperature irradiation of Cu-TiB\(_2\) caused the precipitation TiB nanoprecipitates, instead of the TiB\(_2\) equilibrium compound [3]. To address these questions, experiments were conducted on the Cu-Mo-Si ternary system, given the understanding that had been achieved from previous work on the effects of irradiation on the Cu-Mo binary system [4-6]. Cu-Mo also has the added benefit of having a phase diagram that is similar to Cu-W, and therefore the previous kinetic studies should also be helpful here as well. Furthermore, since Si has both the ability to react with Mo while staying soluble in Cu, adding Si has the potential to lower the overall free energy of the system through the precipitation of Mo-Si silicides. The experimentally determined phase diagrams for the Cu-Si system and the Cu-Mo-Si system at 700 °C are shown in Fig. 6.1 [7, 8]. The significant points are that Si has a large solubility in Cu, ~7 at. % Si, and that Mo has little solubility in Si, but rather form intermetallics.

The results gathered for the Cu-Mo-Si ternary system are instructive for understanding similar effects which are observed during SPD processing of ternary systems. Therefore, a summary of the results will be given before continuing. Two solid solution compositions were grown of the ternary alloy, one with a composition of Cu\(_{98}\)Mo\(_{1}\)Si\(_{3}\) and the other Cu\(_{90}\)Mo\(_{3.5}\)Si\(_{6.5}\), to assess the effect of the nominal composition on phase evolution. These compositions were also selected so that the ratio of Mo:Si was close to that of the MoSi\(_2\) silicide, which has been found to have beneficial wear and high temperature properties [9]. Previous work on the irradiation of Cu-Mo had shown effects identical to Cu-W, so there was a conceptual framework to compare
Fig. 6.1 Binary phase diagrams of Cu-Si (top) and Cu-Mo-Si (bottom). There is very little solubility of Si in Mo [7, 8].
the ternary results to the simpler binary case [10].

6.3 Irradiation Results

6.3.1 Nanoprecipitation in Cu-Mo-Si During Room Temperature Irradiation

XRD analysis was performed on the samples after room temperature irradiation to determine what, if any, precipitation was occurring. In the case of the Cu₉₀Mo₃.₅Si₆.₅ samples, the observed shift in the Cu (111) peak towards higher scattering angles in Fig. 6.2 (a) strongly suggested that some of the Mo had precipitated out of solution. The peak shift, although small, is consistent with the positive size mismatch of Mo in Cu. The Si mismatch is negligibly small, on the order of $10^{-4}$ per at. % of Si and can, therefore, be neglected when looking at larger shifts [11]. By measuring the change in the lattice constant from the XRD peaks, a rough estimate of residual solute concentration could be obtained which found that ~2 at. % of Mo was still in solution after irradiation. This suggesting that the remaining 1.5 at% of Mo precipitated out.

Electron diffraction, TEM BF and DF imaging and HAADF-STEM imaging were also performed and confirmed that room temperature irradiation led to the formation of nanoscale precipitates, 2 to 3 nm in diameter, shown in Fig. 6.2 (b). While some precipitation occurred at the grain boundaries, the majority of the precipitates were intragranular, accounting for a volume fraction of ~.7. Electron diffraction indicated that the precipitates were a Si-rich crystalline phase. Therefore, it was determined that the precipitates were most likely MoSi₂ or Si-rich Mo₅Si₃ precipitates with nonstoichiometric compositions since a range is possible as indicated by the phase diagram in Fig. 6.1. Although not shown here, the more dilute alloy Cu₉₆Mo₄Si₃ also indicated signs of precipitation. In this case, the precipitates were found to be smaller than ~1
nm. Precipitation in Cu₉₆Mo₁Si₃ was also found to be dominated by intragranular precipitates, similarly accounting for a volume fraction of ~.7 as well. In addition to precipitation, radiation-induced grain growth was also observed, coarsening the initial grain size from 28nm to ~52 nm for Cu₉₀Mo₃.₅Si₆.₅ and to ~ 62 nm for Cu₉₀Mo₁Si₃, which is consistent with what was previously recorded [12-14].

6.3.2 Evolution of Nanoprecipitates in Cu-Mo-Si at High Temperatures

After room temperature irradiation, the coarsening resistance of the precipitates and microstructure was determined for the Cu₉₀Mo₃.₅Si₆.₅ and Cu₉₆Mo₁Si₃ alloys. This was accomplished by annealing the samples at temperatures ranging from 650 °C to 750 °C for 1 hour. A Mo capping layer was grown on top of the samples before annealing to suppress Cu evaporation, which in a vacuum occurs at ~ 650 °C. To compare the effects of nucleating precipitates at room temperature on high temperature stability, as-grown samples of the same composition were directly annealed, i.e., without prior room temperature irradiation. The results
on the room temperature-irradiated and annealed samples are presented, followed by the samples processed through direct annealing.

During the post-irradiation annealing, the average in-plane grain size of the room temperature-irradiated Cu$_{90}$Mo$_1$Si$_3$ increased slightly, from 62 nm to 74 nm after annealing at 650 °C, while the grain size for Cu$_{90}$Mo$_{3.5}$Si$_{6.5}$ remained essentially unchanged at ~50 nm. BF-TEM imaging also verified that most of the precipitates remained intragranular after annealing, and did not segregate to the grain boundaries. The volume averaged diameters after annealing was found to be 2.9 ±0.6 nm and 3.0 ± 0.5 nm, for Cu$_{90}$Mo$_1$Si$_3$ and Cu$_{90}$Mo$_{3.5}$Si$_{6.5}$, respectively and did not depend on the annealing temperature. The major difference that could be observed was that the alloy with the higher solute concentration had a higher density of precipitates.

In order to determine the chemical makeup of the precipitates after annealing, HAADF-STEM imaging and electron dispersive spectroscopy (EDS) was used. The precipitates were found to still be dark, and thus silicon-rich. EDS spot analysis was then focused on the precipitates in order to get a qualitative description of the chemical makeup. It was determined not only that the precipitates were enriched in Mo and Si, but that the ratio of Mo:Si was found to be 1.1.

Having observed how precipitates formed during room temperature irradiation behave at high temperatures, it is now possible to compare these results with alloys that are directly annealed without any prior irradiation. For direct annealing of the solid solution alloys, Cu$_{96}$Mo$_1$Si$_3$ and Cu$_{90}$Mo$_{3.5}$Si$_{6.5}$ were annealed at 650 °C and 750 °C for 1 hour without any other processing. While the grains in Cu$_{90}$Mo$_{3.5}$Si$_{6.5}$ experienced some growth at 650 °C, increasing from 28 nm to 37 nm, Cu$_{96}$Mo$_1$Si$_3$ was found to have a grain size increase to 74 nm. Furthermore, it was observed that the density of intragranular precipitates which were formed
from direct annealing was much less than what was caused by room temperature irradiation, although they were still present. The precipitates were also a larger size when the alloys were directly annealed. TEM analysis indicated that both the inter- and intragranular precipitates which were formed were Mo$_5$Si$_3$, as shown in Fig. 6.3.

![Fig. 6.3 An electron diffraction pattern and the BF-TEM image of the 750 °C annealed Cu$_{90}$Mo$_{3.5}$Si$_{6.5}$ sample used to collect the diffracted pattern. A corresponding DF-TEM image of Mo$_5$Si$_3$ precipitates is shown to the right, using the (202) peak.](image)

6.4 Discussion of Cu-Mo-Si

One of the primary findings of this study on Cu-Mo-Si ternary alloys is that room temperature irradiation of dilute Cu-Mo-Si alloys results in the formation of Mo-Si-rich
precipitates which are extremely resistant to thermal coarsening, even more so than the Cu-Mo binary alloy. The most likely explanation is the thermodynamic stability of Mo silicides. This has the effect of reducing the Mo solubility in the Cu-rich matrix by making it necessary to break apart the Mo silicide bond before going into the Cu matrix. However, a more detailed discussion on the reasons behind the thermal stability of the Mo silicide precipitates in Cu will be given.

The general expression for the coarsening rate of the average precipitate radius with time in an N-component alloy can be described by

\[ r(t)^3 - r(0)^3 = k t \]  

The coarsening constant, \( k \), is defined as

\[ k = \frac{8V_m^\beta \gamma}{9RT \sum_{i=2}^{N} \left( \bar{C}_i^\beta - \bar{C}_i^\alpha \right)^2 / D_i \bar{C}_i^\beta} \]  

where \( \alpha \) and \( \beta \) refer to the matrix phase and the precipitate phase, respectively; \( V_m^\beta \) is the molar volume of the \( \beta \) phase; \( \gamma \) is the precipitate/matrix interface energy; the index \( i = 2 \), \( N \) labels all the elements, except the host element, which in this case is Cu; \( \bar{C}_i^\alpha \) and \( \bar{C}_i^\beta \) are the equilibrium concentrations of the \( i \)-species in the \( \alpha \) and \( \beta \) phases; and \( D_i \) is the diffusion coefficient of the \( i \)-species in the matrix [15, 16]. In this case, since the system is a dilute alloy and since Mo is a much slower diffuser in Cu than Si, the expression for the rate constant can be simplified [17].

The coarsening rate constant can now be expressed as

\[ k = \frac{8V_m^\beta V_{Mo} \bar{C}_Mo^\alpha}{9RT \left( \bar{C}_Mo^\beta - \bar{C}_Mo^\alpha \right)^2} \]  

As seen in the Eq. (3), there are four distinct factors that can contribute to the differences between the coarsening rates of Mo precipitates and Mo-Si-rich nanoprecipitates in a copper matrix. The factor in the denominator, which accounts for the Mo concentration difference in the
precipitate vs the matrix can range from 1 for pure Mo precipitates in Cu, as is the case for Cu-Mo, to ~0.11 for MoSi₂ precipitates in Cu-Mo-Si. This factor, which would initially indicate that the silicide should coarsen more quickly, can be offset by the terms in the numerator in Eq. (3), namely the solubility. By employing CALPHAD data, it was found that the formation of Si-rich silicides reduces the Mo solubility by more than 2 orders of magnitude at 750 °C more than the binary Cu-Mo system. This effect is therefore very large and accounts for a large part of the reported coarsening resistance.

Si may also have affected the coarsening rate constant by modifying the precipitate/matrix interface energy, and by modifying Mo diffusivity in the matrix. Although no data is currently available to quantify these effects, it is likely that Si can reduce the interfacial energy in the system by segregating to the Cu/Mo interfaces, which are extremely high in their chemical interfacial energy. This is further supported by detailed atom probe tomography (APT) studies which have shown Si segregation can be significant at Fe/Cu, Fe/carbides, and Al/Cu interfaces [18-21]. However, since this effect cannot be quantified, this is more speculative in nature.

Another important contribution to reducing the coarsening of the Mo silicides was the large fraction of intragranular precipitates that were produced. Because precipitation had already taken place before annealing, reducing the amount of molybdenum that was in solution, the amount of solute left that could contribute to growth was reduced. Furthermore, since numerous precipitates had formed, there were plenty of sites for the solute to diffuse to, instead of all collecting quickly at the grain boundary. It may also be tempting to include the fact that since the precipitates were intragranular, they had an increased resistance to coarsening since there were no fast pathways for diffusion such as grain boundaries. However, given that the sample was
annealed at temperatures of 750 °C, any enhanced diffusion pathways such as grain boundaries would be insignificant.

The large density of stable nanoprecipitates during annealing is also likely the reason grain growth is suppressed since they are able to stabilize the microstructure through Zener pinning. Since room temperature irradiation of Cu-Mo-Si alloys caused the formation of nanoprecipitates with radii ~1.5 nm and volume fractions, f, ranging from ~1% to 3%, the maximum grain diameters for pinned grains, using the expression $4r/(3f)$, ranges from 70 nm to 200 nm depending on the precipitate density [22]. Since the higher concentrations of Mo and Si led to a higher concentration of precipitates and significantly reduced grain coarsening during annealing, it is likely that Zener pinning contributed to stabilizing the grain size.

6.5 Ternary Alloys Under Severe Plastic Deformation

As mentioned at the beginning of this chapter, the ability to form compounds in a matrix provides control over the alloy properties and accordingly the capability to tune alloys to fit a wide variety of applications. In the case of forming Mo silicides, it was shown that by precipitating out Mo-Si in thermal spikes during low-temperature irradiation, the precipitate structure could be stabilized against subsequent coarsening at high temperatures, even more stable than the binary, Cu-Mo. Although the experiments were not conducted to see if a unique steady state was achieved, one can infer from the Cu-W studies conducted that since the mechanism of precipitate formation occurs in the thermal spike, it is most likely the case that the Cu-Mo-Si ternary system would also undergo a similar microstructure evolution. New experiments, however, would be interesting.

Despite its achievement in advancing our understanding of systems under irradiation and coarsening in general, the previous study has several drawbacks. One is that ion beams are
mostly limited to modifying surface properties, owing to the small penetration depths. Therefore, while ions are useful for simulating radiation damage quickly, they are not practical for processing bulk materials. Furthermore, since the previous experiments focused on ion irradiation, thin films were employed to understand the mechanisms taking place. Unfortunately, this places a constraint on the maximum grain size possible during annealing, since the grains generally do not become larger than the film thickness, which is typically ~ 200 nm. To avoid these problems, severe plastic deformation was used to gather information on coarsening kinetics in bulk materials. This study was also of interest to further our understanding of the similarities in alloy response to different driving conditions.

In order make an informed comparison between immiscible ternary alloys in driven systems, the Cu-Nb-Si system was chosen to draw on the previous wealth of information available on the SPD processing of the binary Cu-Nb system. Cu-Nb, moreover, reacts exothermically with Si to form stable compounds, similar to Cu-Mo-Si. However, similar questions remain such as whether ball milling leads to compound formation during low-temperature processing, what structures will form, if the precipitates will stabilize a preferred size, and how they might respond to extreme environments. Previous research has shown that metal matrix composites could be created using mechanical alloying by either milling the constituent elemental powders together or by using exothermic processing of compounds [24-26]. For example, Marques et al. had explored the possibility of producing crystalline Nb carbides in a copper matrix by using mechanical alloying [24]. While they were successful in their production of nanocrystalline carbides, no in-depth explanation was given for how this occurred, the evolution of the precipitates with milling time was not explored, or why the composition NbC was preferred over the many other possible carbides that are found in the Nb-C
phase diagram. This study was also complicated by the fact that C is not soluble in Cu and the x-ray measurements were unable to determine how C interacts with Cu, if at all, after ball milling and if the shearing mechanism played any part besides adding energy to the system. The Cu-Nb-Si system, therefore, provides a better model system understanding the fundamental questions that are the focus of this thesis. An experimentally determined Cu-Nb-Si phase diagram is shown in Fig. 6.4 [26]. While there are some small differences between the Cu-Nb-Si and the Cu-Mo-Si

![Phase diagram of Cu-Nb-Si system at 700 °C](image)

Fig. 6.4 An experimentally determined phase diagram of the Cu-Nb-Si system at 700 °C. There is very little solubility of Si in Nb and vice versa, although several intermetallic phases exist [27].
phase diagram, comparison of Fig 6.1 with Fig. 6.4 illustrates that they both are capable of forming the same intermetallic compounds.

In order to carry out the SPD processing of Cu-Nb-Si alloys, ball milling and HPT were employed. For ball milling, pure elemental powders were charged into a stainless-steel vial with steel balls and milled for at least 10 hours to thoroughly mix and shear the powders. Some powders were sheared for as long as 40 hours. It was found however that the longer time did not significantly refine the microstructure nor cause any additional mixing/reactions. For HPT processing, clean oxygen free films were grown, compacted, and then subsequently sheared. The main ternary alloy composition under consideration is Cu_{85}Nb_{5}Si_{10}. The relatively high alloy content was selected for this study in order to reduce the influence of oxygen contamination that is normally present during ball milling. As mentioned in chapter 3, ~ 6 at. % Ag powder was also added to the ball milling powder to reduce cold welding, yielding an overall composition of Cu_{79}Nb_{5}Si_{10}Ag_{6}. The Nb:Si ratio was kept at 1:2 in an attempt to stabilize the NbSi_{2} compound, just as had been accomplished during irradiation. Details of sample preparation and characterization techniques are found in chapter 3.

6.6 SPD Results

6.6.1 Nanoprecipitation in Cu-Nb-Si During Low Temperature SPD

Ball milling and HPT were performed on Cu_{85}Nb_{5}Si_{10} to examine if precipitation of nanocrystalline silicides was possible inside a metal matrix, in this case, Cu. For comparisons purposes, ball milling and HPT were also carried out on the binary Cu-Nb system and ball milling was performed on Cu-Si. The compositions for these “pseudo”-binary cases were Cu_{89}Nb_{5}Ag_{6} and Cu_{84}Si_{10}Ag_{6}. i.e., since Ag fully dissolves in Cu under SPD at these low concentrations and does not interact with Nb or Si, its addition has limited influence on the alloy
properties and can be considered inert. In order to determine the extent of precipitation, FIB/SEM and TEM imaging, along with XRD measurements were performed on the prepared samples. XRF analysis was also performed, in this case, to verify that the composition remained the same during processing, and to check for possible sample contamination during processing.

After ball milling the binary Cu-Nb and Cu-Si powders at room temperature, XRD analysis indicated that roughly half the niobium went into solution, while the remainder formed pure niobium nanoprecipitates as is discussed below. The Si powder mixed more completely with the Cu matrix, ~7.6 at. % going into solution. However, when Cu_{79}Nb_{5}Si_{10}Ag_{6} was ball milled, there was no obvious diffraction from any phase other than the FCC Cu matrix. This is shown by the θ-2θ scans in Fig. 6.5 for binary Cu-Si and Cu-Nb and the ternary Cu-Nb-Si alloys. One will also notice that additional peaks are present in the Cu-Nb binary, which are consistent with Fe and Nb peaks. Fe contamination is a common contamination after ball milling for long periods of time; XRF measurements indicated that the Fe concentration was ~ 7 at% from. Using the experimental Nb value of the atomic volume of Nb in Cu found in chapter 4, the Cu-Ag lattice shift reported by Linde, and using the lattice shift attributed to Si as $6.67 \times 10^{-4}$ per at. %, the amount of niobium in solution as a result of shearing was estimated to be ~.5 at% [11, 27]. This compares to ~ 2 at. % for the Cu-Nb binary powder. The absence of Nb diffraction peaks and the large reduction in Nb in solution in the Cu matrix, strongly suggest that Nb reacted with Si and precipitated out of solution.
In addition to the XRD measurements, SEM imaging was employed to determine if precipitates could be identified and their approximate size measured. Shown below in Fig. 6.6 are the SEM images collected from $\text{Cu}_{84}\text{Si}_{10}\text{Ag}_{6}$, $\text{Cu}_{89}\text{Nb}_{5}\text{Ag}_{6}$, and $\text{Cu}_{79}\text{Nb}_{5}\text{Si}_{10}\text{Ag}_{6}$ after ball milling. As can be observed in Fig. 6.6(a), Si does not fully dissolve in pure Cu, as remnants of the Si powder, up to $\sim 250$ nm in size, are clearly visible. A closer inspection of the matrix using EDS indicated that the total amount of Si in solution with Cu was $\sim 8$ at%. Possibly additional ball milling would lead to full homogenization of the Cu-Si alloy, but this was not pursued. One

Fig. 6.5 XRD data collected at APS using a wavelength of 0.414216 angstroms. Ball milled powders of $\text{Cu}_{90}\text{Si}_{10}$, $\text{Cu}_{90}\text{Nb}_{5}$, and $\text{Cu}_{90}\text{Nb}_{5}\text{Si}_{10}$ are shown. Niobium (110) peak is located at 10.2°. Fe contamination can also be observed in $\text{Cu}_{90}\text{Nb}_{5}$ sample.

In addition to the XRD measurements, SEM imaging was employed to determine if precipitates could be identified and their approximate size measured. Shown below in Fig. 6.6 are the SEM images collected from $\text{Cu}_{84}\text{Si}_{10}\text{Ag}_{6}$, $\text{Cu}_{89}\text{Nb}_{5}\text{Ag}_{6}$, and $\text{Cu}_{79}\text{Nb}_{5}\text{Si}_{10}\text{Ag}_{6}$ after ball milling. As can be observed in Fig. 6.6(a), Si does not fully dissolve in pure Cu, as remnants of the Si powder, up to $\sim 250$ nm in size, are clearly visible. A closer inspection of the matrix using EDS indicated that the total amount of Si in solution with Cu was $\sim 8$ at%. Possibly additional ball milling would lead to full homogenization of the Cu-Si alloy, but this was not pursued. One
Fig. 6.6 SEM images of (a) Cu$_{84}$Si$_{10}$Ag$_6$, (b) Cu$_{89}$Nb$_5$Ag$_6$, and (c) Cu$_{79}$Nb$_5$Si$_{10}$Ag$_6$ after ball milling for 40 hours. Cu matrix is grey, while Nb or Si precipitates appear darker.
can observe in Fig. 6.6(b), in contrast, a high density of Nb nanoparticles in the Cu-Nb binary case shown, in agreement with the incomplete dissolution of Nb reported by the XRD measurements. The average radius of the precipitates is \( \sim 13\text{nm} \), in agreement with past work [28]. For the Cu-Nb-Si alloy, Fig. 6.6(c), there is a bimodal distribution of nanoparticle sizes, with the larger particles on the order of 50 nm, which were identified as Si, while the smaller particles have an average radius of 11 nm.

Additional characterization of the ternary alloy was performed using TEM imaging, electron diffraction, STEM-HAADF, and EDS. As can be observed in the Z-contrasts shown in Fig. 6.7, the precipitates that are present after ball milling Cu\textsubscript{79}Nb\textsubscript{5}Si\textsubscript{10}Ag\textsubscript{6} are dark, suggesting that they are silicon rich. EDS analysis was able to confirm that some precipitates were rich in

![Fig. 6.7 HAADF-STEM image of Cu\textsubscript{79}Nb\textsubscript{5}Si\textsubscript{10}Ag\textsubscript{6} after low temperature ball milling. The dark precipitates were found to be enriched in both Si and Nb.](image)
Nb and Si, and some just Si. For the Nb-Si clusters, the Nb:Si ratio was approximately 1.3, although a wide range of compositions was found. Electron diffraction failed to show diffraction rings from these precipitates, suggesting that the precipitates were an amorphous Nb silicide. This observation contrasts with results on ball-milled Nb-C and irradiated Cu-Mo-Si which formed nanocrystalline precipitates during low-temperature processing. For the ball milled Cu-Si, Cu-Nb, and Cu-Nb-Si alloys, the initial grain size was found to be similar regardless of the composition. The average grain size was found to be ~ 40 nm. This was verified through TEM images and peak broadening in the XRD measurements.

To reduce the contamination associated with ball milling experiments, HPT of solid solution Cu$_{90}$Nb$_5$Si$_{10}$ was also performed, in this case at dry ice temperatures (-78 °C); this low temperature was employed to suppress thermally activated diffusion. Starting from a solid solution, moreover, had the added purpose of testing whether the alloy system behaved ergodically under SPD processing, i.e., was the steady state independent of the initial conditions. This test thus explores self-organization in this ternary alloy. XRD measurements, shown in Fig. 6.8 XRD pattern of Cu$_{85}$Nb$_5$Si$_{10}$ processed at dry ice temperatures (-78 °C) to a strain ~ 2000.
6.8, reveal only Cu diffraction peaks and that the Nb solubility in Cu was ~0.3 at%. HAADF-STEM imaging revealed a much richer microstructure with many fine precipitates present. Fig. 6.9 illustrates this microstructure after low temperature HPT processing to a strain of ~2000. In this case, the average precipitate radius is ~5 nm. Also, the large Si pieces observed after ball milling are no longer present, indicating that their presence was most likely an artifact of the ball milling process. Unfortunately, the large residual strain in these HPT’ed samples prevented a precise determination of a grain size, but the TEM BF images indicate that the grain size dropped from 40 nm observed after ball milling at room temperature to ~17 nm.

6.6.2 Evolution of Nanoprecipitates in Cu-Nb-Si at High Temperatures

Fig. 6.9 HAADF-STEM image of Cu$_{85}$Nb$_{5}$Si$_{10}$ collected on the JEOL 2010F that was initially a solid solution and then sheared using HPT. The strain is ~2000 in this image. Precipitates are indicated by dark spots while the bright and grey areas are the Cu matrix.
Evolution of the microstructure formed during SPD-processed of Cu-Nb-Si was followed during annealing at high temperatures. For comparison, as grown solid solutions of Cu$_{95}$Nb$_5$ and Cu$_{85}$Nb$_5$Si$_{10}$ were similarly studied. Annealing was performed at 700 °C for 12 hours. In addition, HPT processing of Cu$_{85}$Nb$_5$Si$_{10}$ was performed at high temperatures, 200 °C and 400 °C to explore possible effects of these two very different kinetic pathways, i.e., low temperature shearing at low temperature plus annealing versus shearing at high temperature, albeit a lower temperature.

For the ball milled samples, the powders were sealed in a glass tube that had been backfilled with argon and then annealed at 700 °C for 12 hours. Fig. 6.10 shows SEM images of the different ball milled powders before and after annealing. The Cu-Si binary alloy shows very poor coarsening resistance. For this case, the grain size increases from an average size of 38 nm to 600 ± 60 nm (neglecting twin grain boundaries). The Cu-Nb binary alloy is found to have better coarsening resistance, its grain size increasing to 228 ± 28 nm. The ternary alloy shows similar grain growth as the Cu-Nb binary, although with a somewhat smaller average grain size, 186 ± 20 nm. While the resistance to grain size coarsening was only moderately improved by the addition of Si, its effect on the resistance to precipitate coarsening is quite notable. While the average radius of Nb precipitates increased from ~11 nm to 56 ± 28 nm, the Nb silicide precipitates remained stable, with their average radius increasing only to 13 ± 3 nm.

Additional characterization of the ternary alloy was performed using electron diffraction and HAADF-STEM imaging. As shown below in Fig. 6.11 (a), the electron diffraction pattern displays many diffraction rings in addition to those of the Cu matrix. Indexing of the diffraction
As prepared  

Annealing

**Cu-10 at% Si**

![SE images of Cu-10 at% Si before and after annealing](image)

**Cu-5 at% Nb**

![SE images of Cu-5 at% Nb before and after annealing](image)

**Cu-5 at% Nb-10 at% Si**

![SE images of Cu-5 at% Nb-10 at% Si before and after annealing](image)

Fig. 6.10 SEM images of the ball milled powder before and after annealing for 12 hours at 700 °C. Cu$_{85}$Nb$_5$Si$_{10}$ displayed the best coarsening resistance, both in terms of grain size and precipitate size, while Cu$_{90}$Si$_{10}$ performed the worst.

Pattern show d-spacings consistent with Cu$_{83}$Si$_{17}$ and Nb$_5$Si$_3$. STEM-HAADF, shown in Fig. 6.11 (b) and EDS were also employed to resolve if there were any differences between the two new precipitates which had formed. Interestingly, one can notice two different sizes of precipitates: larger precipitates which have an average radius of 15 nm, and the other an average radius of 4-6 nm. The larger clusters are primarily Cu$_{83}$Si$_{17}$ intermetallics, while the much smaller precipitates are Nb$_5$Si$_3$ clusters, indicating that the Nb silicides are indeed stable.
Solid solutions of Cu$_{95}$Nb$_{5}$ and Cu$_{95}$Nb$_{5}$Si$_{10}$ were also annealed at 700 °C for 12 hours.

Fig. 6.11 (a) Electron diffraction pattern showing diffraction rings from Cu, Nb$_5$Si$_3$, and Cu$_{87}$Si$_{13}$. (b) HAADF-STEM image of Cu$_{79}$Nb$_5$Si$_{10}$Ag$_6$ that was initially ball milled and then annealed for 12 hours at 700 °C. The very small precipitates (examples are outlined in red) are Nb$_5$Si$_3$, while the larger precipitates (examples outlined by a dotted line) tend to be Cu-Si intermetallics. The bright grains are Ag which has precipitated out of solution.
Solid solutions of Cu$_{95}$Nb$_5$ and Cu$_{95}$Nb$_5$Si$_{10}$ were also annealed at 700 ºC for 12 hours. Fig 6.12 shows a direct comparison of the two alloys after annealing. As observed the presence of Si significantly improves the coarsening resistance of precipitates. The average radius is 60 ± 20 nm for the binary Cu-Nb alloy, while for the ternary Cu-Nb-Si alloy, the average precipitate radius is 20 ± 7 nm. The average grain size for the two alloys, on the other hand, is the same at 207 ± 18 nm. Therefore, while low-temperature shearing does cause precipitate formation and grain refinement, it results in only a slight improvement in grain size and precipitate stability.

Fig 6.12 Initially solid solutions of Cu$_{85}$Nb$_5$Si$_{10}$ and Cu$_{95}$Nb$_5$ that have been annealed for 12 hours at 700 ºC. While there is a dramatic difference in the precipitate size, the grain size remains the same.

Finally, HPT specimens were processed at 200 ºC and 400 ºC, to determine the stability of this system in a driven environment where vacancy motion is no longer suppressed and possibly contributes to the alloy development. As seen in Fig. 6.13, the precipitates stay roughly the same size as during room temperature ball milling for a processing temperature of 200 ºC, and the precipitates remain amorphous. There is, however, a noticeable difference between 200 ºC and dry ice processing of the solid solution alloy, with the low-temperature processed alloy characterized by smaller precipitates and large amounts of strain. On increasing the processing
temperature to 400 °C, significant differences are observed. Crystalline Cu silicides and Nb silicides now begin to appear. The grain size, however, was not much affected by the processing temperature, as they both were ~ 50 ± 1 nm at a strain of ~2000. nm after a strain of ~2000. The average precipitate radius, moreover, was also unchanged, ~8 nm. Finally, the high temperature HPT processed samples were annealed at 700 °C for 12 hours. As seen in Fig. 6.14, no significant is observed in the differently processed alloys.

6.7 Discussion of Cu-Nb-Si

6.7.1 Reduced Coarsening in Cu-Nb-Si
The main findings of this study were that it is indeed possible to form nanoscale Nb disks processed at (a) 400 °C, (b) 200 °C, and (c) dry ice to a strain of ~2000 and then annealed at 700 °C for 12 hours.

Fig. 6.14 HPT disks processed at (a) 400 °C, (b) 200 °C, and (c) dry ice to a strain of ~2000 and then annealed at 700 °C for 12 hours.
The main findings of this study were that it is indeed possible to form nanoscale Nb-silicides in a copper matrix during low temperature SPD, and that precipitates were resistant to coarsening to at very high temperatures, 700 °C, or over 70% of the melting temperature of Cu. The ternary alloy thus shows much greater stability than Cu-Si or Cu-Nb binary alloys. The reasons for this enhanced stability were discussed in section 6.4, and will not be discussed in as much detail here. However, it is well known that forming stable compounds is a very reliable way to reduce the solubility of an element. Common examples in industry include the addition of carbide forming elements. In fact, by using a similar thermodynamic analysis performed for the Mo-Si case, it is found that the solubility of Nb silicides decreases by three orders of magnitude at 750 °C, which is an even larger effect than for Mo silicides. In addition to lowering the Nb solubility in Cu, Si may also change the interfacial energy between the precipitates and the matrix, either because the intermetallic has a lower interface energy with Cu than pure Nb, or possibly due to Si segregation to the precipitate-matrix interface. For example, Si has been found to preferentially segregate to the Cu boundary in previous work [29].

6.7.2 Shear Induced Precipitation and Self-Organization

While this work demonstrated the coarsening resistance that can be gained in compound forming systems, it was also observed that this ternary system seemed to reach a steady-state regardless of the initial starting conditions. Furthermore, while previous research conducted on the mechanical alloying of niobium silicides has produced mixed results, and has formed both crystalline and amorphous precipitates, amorphous precipitates appear to have formed here during low temperature SPD processing. This finding differs from results gathered on Al-Mg-Si or Cu-Nb-C, where crystalline phases were produced after room temperature ball milling. Furthermore, even though the ratio of Nb:Si was kept at 1:2, the preferential silicide which
formed was Nb₅Si₃. This suggests that there is a need to improve our understandings of driven ternary systems, to allow for more informed choices and predictions regarding these and more complicated systems.

When transformation occurs in a chemical system, a driving force is always required, which generally derives from lowering Gibb’s free energy. In driven systems, however, there is an additional energy input that must be considered. In the case of solid state amorphization in driven systems, there are two theories that have been adopted. If starting from a pure metal mixture, amorphization is generally thought to occur because of the amorphous phase acting as an intermediate metastable stage during transformation to an equilibrium crystalline state. This requires the condition that there is a negative heat of mixing, and that the amorphous phase forms faster than the crystalline intermetallic compound. While this idea has been invoked to explain amorphization in Ni-Nb and Ti alloys undergoing mechanical alloying, it fails to explain why some intermetallics amorphize during SPD, [30, 31].

To help explain this phenomenon, the generalized Lindemann criterion for melting becomes instructive. In this model, the free energy of the system can be raised when defect structures such as antisite defects or dislocations are present. Therefore, if we look at Fig. 6.15, which shows the free energy curves of an ideal pure mixture, an amorphous phase and an intermetallic phase for an arbitrary AB component system, one can imagine that raising the free energy could cause crystalline intermetallics to change and become amorphous [30]. A more rigorous treatment of this theory can be found in ref. [32]. However, as can also be observed from Fig 6.15, the free energy of the intermetallic is very steep and cannot deviate too much from the stoichiometric composition. However, in the Cu-Nb-Si study conducted, any given Nb atom is most likely surrounded by a non-stoichiometric amount of Si. Therefore, if an
intermetallic were to precipitate, it’s free energy would be much higher than the amorphous phase. Therefore, because of the composition of the compounds and the high disorder that is present in a driven system, there exists a driving force for amorphous precipitation to occur.

In the Cu-Nb-Si study that was described above, two initial conditions were tested, one in which elemental powders were mixed together through ball milling, and the other in which there was initially a solid solution. This work has demonstrated that the production of niobium silicides through mechanical alloying can lead to the production of crystalline intermetallics and amorphous phases, depending on the processing temperature. At high temperatures, the crystalline phase \( \text{Nb}_5\text{Si}_3 \) was observed, while at lower temperatures, only the amorphous phase was observed. Therefore, it seems likely that if the temperature is too low, defect motion will not allow for atomic rearrangements necessary to form a stoichiometric intermetallic. However, by processing at 400 °C, defect motion increases which allow for the crystalline phase to appear.

Fig. 6.15 A graph showing the free energy \( F \) vs the dislocation density \( \bar{\rho}_d \), for various temperatures [33].
While this may be a convenient explanation of why the precipitates are amorphous, one could ask why the silicide would form an amorphous compound while the Cu-Nb binary system formed crystalline Nb precipitates, as discussed in the previous chapter. Generally, examples of amorphization of pure elemental powders by ball milling are rare, except in certain circumstances such as Si or Ge, and has not been demonstrated in pure metals. Unfortunately, this fails to address how precipitates form, why the system seems to reach a steady-state precipitate size, and why the Nb₅Si₃ phase precipitates out when the system has a Nb to Si ratio of 1:2.

The occurrence of Nb₅Si₃, as opposed to the desired NbSi₂ precipitates, can most likely be explained by the large solubility of Si in Cu. Since there is ~7 at% Si still in solution with Cu, which is also thermodynamically stable, this leaves roughly 3 at% of Si left to react with Nb, which was conveniently added at about 5 at%. Therefore, Nb₅Si₃ precipitated out because of the stability of Si in Cu. While an obvious solution to this problem would be to add less Nb if NbSi₂ was desired, the problem still exists that the Nb silicide which will initially precipitate out will be amorphous and non-stoichiometric. Therefore, while reducing the Nb content would certainly increase the chances of forming a disilicide compound, it is not guaranteed since the heat of formation of Nb₅Si₃ is ~ -60 kJ/mol, while the heat of formation of NbSi₂ is ~ -46 kJ/mol [34]. Therefore, given that the exact composition of the amorphous precipitate cannot be controlled, it possible that Nb₅Si₃ would still preferentially precipitate, or that a mixture of the two compositions would form. More work would have to be done to verify this.

To explain how the precipitates form, it should be possible to draw on the conclusions found in the Cu-Nb binary. For this case, Nb precipitation occurred by Nb atoms diffusing through the Cu matrix until they reach an area of topological disorder, such as a grain boundary.
At this point, they were able to cluster and grow, until they reached a certain size, at which point the shrinking mechanism of shaving off atoms took over. It is very likely that the microstructural evolution of Cu-Nb-Si occurs in a very similar way. In this case, Nb atoms are traveling in the same way until they reach an area of disorder. While Si atoms are present in the Cu matrix, in the absence of any area of topological disorder such as grain boundaries, it is unlikely that any reaction occurs between the Nb and Si atoms. This is due to the fact that the atoms can be sheared apart in the matrix and are unlikely to precipitate out inside the grain, just as was the case for the Cu-Nb binary. Therefore, once the Nb atoms are located on a grain boundary or dislocation tangle, they can interact with other Nb and Si atoms to start precipitating. Furthermore, since there is a supersaturation of Si in the system, there is no shortage of Si atoms to react with, forming a Nb-Si cluster.

However, in most cases where an intermetallic becomes amorphous with mechanical alloying, usually the crystalline phase forms first, and then over time becomes amorphous, as is the case in the Nb-Sn system, where the crystalline A15 structure was first formed, and then after further milling became amorphous [35]. This did not happen in the ternary system and instead, only the amorphous phase was observed. Therefore, it is very likely that given the description of precipitation above, occurring in areas of high disorder with off-stoichiometric ratios, the precipitates which form are more stable in the amorphous phase.

While the system was not primarily chosen to study self-organization, the system did evolve in such a way that there existed a steady-state size distribution in the precipitates regardless of the starting conditions. Furthermore, this precipitate size was found to be very small, on the order of several nanometers. Other work on the ball milling of oxides has shown that not all precipitates reach a small steady-state size of several nanometers but instead can
grow to be hundreds of nanometers or microns after low temperature shearing. Therefore, it is possible that the system self-organizes in a similar fashion as the binary case. Also, since the precipitates are amorphous, it is conceivable that the shrinkage mechanism could be the same as described by Askenazy et al., who showed that during shearing of the amorphous Cu-Ta system, dislocations are able to shear off the atoms that are on the precipitate surface, and cause them to go back into solution until they precipitate somewhere else [36]. However, a more carefully controlled experiment involving Nb silicides would have to be conducted to verify this point.

6.8 Conclusions

After studying the compound forming ternary systems of Cu-Mo-Si and Cu-Nb-Si, it was found that there is both a large increase in coarsening resistance, as well as self-organization which has been observed in other highly immiscible driven alloy systems. However, there are still some differences between irradiation and SPD that can be observed in these two cases. The irradiation of Cu-Mo-Si is a rather straightforward system, whose evolution can be conveniently explained by the ballistic mixing and thermal spike model laid out in Chapter 4. Because the precipitation of the Mo silicide takes place in the thermal spike, which is at an extremely high temperature, the crystalline phase precipitates out. Furthermore, the thermal spike acts as a nucleation site which can appear anywhere, including inside the grain boundary. In the case of SPD, it does not seem possible to precipitate out the crystalline intermetallic phase in the Cu-Nb-Si ternary alloy at low temperatures. However, both irradiation and SPD do maintain the same basic precipitation mechanisms as the binary systems, which means that they also undergo self-organizational patterning at low temperatures.

Another question that can be raised is if there exists any benefit to ball milling the Cu-Nb-Si at low temperatures to initially precipitate out amorphous silicides before applying high
temperatures. As can be seen comparing the annealed ball milled case to the annealed as grown Cu-Nb-Si solution, the average precipitate size increases from ~13 nm to ~20 nm. Furthermore, closer inspection in using HAADF-STEM found the true Nb silicide size to be closer to 6 nm. Therefore, by precipitating the niobium out of solution beforehand, the total amount of niobium which could diffuse to the grain boundaries was already greatly reduced, which helped with coarsening resistance. Ball milling also has the benefit of being a very cheap and rapid way of processing alloys, as opposed to ion irradiation which can only affect the surface. Therefore, to produce these alloys, ball milling is currently the only practical method.

6.9 References


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CHAPTER 7

CONCLUSIONS

The purpose of this thesis research was to explore the microstructural evolution of materials in driven environments, specifically focusing on self-organization behavior in highly immiscible alloy systems. While Martin had focused on developing an effective temperature model to understand driven systems, Frost and Russell, and later Enrique and Bellon showed that the length scales over which the driving force act also play an important role in determining the steady state microstructure. These models, however, break down at very low temperatures, when thermally activated diffusion is suppressed. For example, while oxides particles in ODS steels completely dissolve under irradiation at low temperatures, as predicted by the above models, W precipitates in Cu-W alloys do not. Similar exceptions to these models are also observed during SPD of highly immiscible alloys. Therefore, since this low temperature behavior in driven systems cannot be explained using the existing models, it was the purpose of this work to develop a broader base of data for this surprising behavior and to explore possible explanations for it.

In the case of self-organization at low temperatures, it was clearly shown that for ion irradiation the creation of thermal spikes is critical for the self-organization that is observed in binary or ternary alloy systems. Because ODS steels have an iron matrix, i.e., relatively low atomic number and high melting temperature, thermal spikes are not intense and the amount of thermally stimulated atomic motion is small compared to metals like Cu or Au. Consequently, most of the atomic mixing during irradiation at low temperatures results from random ballistic mixing. In the case of copper based alloys, the thermal spike is stronger and allows for sufficient atomic rearrangement to take place in a localized liquid melt in which clustering of solute and
patterning can occur. This was highlighted in both chapters 4 and 6. While these studies were able to show the importance of miscibility on predicting alloy phase evolution during low temperature irradiation, they were quite limited and failed to fully isolate and quantify the effects of heat of mixing, and energy density in cascades. Since the most thorough understanding of these effects came from an in-depth analysis of the binary Cu-W, there was no further way to address how important the specific heat of mixing is to low temperature patterning.

To address this problem, irradiation studies of ternary Cu-Ni-X systems, where X could be W, Mo, Nb, etc. would be a very easy way to potentially measure the importance of heat of mixing in driven systems. The main logic behind this approach is that while Cu and element X are highly immiscible, X and Ni are completely miscible, along with Cu and Ni. Therefore, the Ni should allow for more of the immiscible element to go into solution during low temperature irradiation since the heat of mixing is decreased, eventually lowering the effective heat of mixing to that of Ag in Cu, which has been shown to be completely miscible in driven systems at low temperatures. This would then allow for one to quantify the effects of heat of mixing. While Ni is nearly an ideal choice because of its similarities to Cu, it also has a much smaller thermal spike due to the difference in melting temperature. Therefore, there might be a change in the thermal spike as more Ni is added to the Cu which should be considered. However, this effect should be quantifiable since Ni and Cu form nearly ideal solid solutions. Therefore, this alloys system a direct test of the role heat of mixing in self-organization at low temperatures. Also, given the similarities that can be observed in extreme environments, it would offer a comparison to work conducted on alloys during SPD, with the added benefit that irradiation experiments are much easier to control and understand.
This thesis also investigated self-organization that occurs during SPD of highly immiscible systems at low temperatures. However, while experimental observations determined that regardless of starting conditions, steady-state precipitation of fixed size will always ensue, the experiments failed to elucidate an exact mechanism taking place and simulations were required. Reasons for the difficulty in isolating the underlying mechanisms include the many complexities of the problem which includes alloy hardness, dislocation motion on specific slip planes, the possibility of forming metastable phases, and multiphase deformation. Therefore, much work remains to be done for fully understanding SPD processing, such as how hardness effects the steady state precipitate size and mixing. In fact, it is quite possible that hardness can be considered the SPD analog of the thermal spike during irradiation. Also, can it be experimentally determined if shearing causes atoms to be sheared from the precipitate/matrix interface into solution. It would also be interesting to determine the extent to which heat of mixing is important during SPD. While it clearly does have an important role, since Nb did precipitate out of solution, Nb is also a different phase than Cu, and therefore must interact with dislocations differently. In fact, it was shown using simulations that Nb does not precipitate out of solution in the Cu matrix, but must aggregate in a region where they would not initially be sheared apart.

It would then be interesting to use an extremely immiscible FCC phase material to determine how important the heat of mixing is versus the kinetics surrounding the growth and dissolution rate. To carry out this experiment, the only material that the author can think of is Cu-Pb. Unfortunately, Pb is toxic (and therefore cannot be sputtered), a low temperature material (melts at 327 °C) and is much more oversized in Cu than other materials such as Ag. However, it is highly immiscible and precipitates out in the FCC phase. Therefore, dislocation glide should
be unimpeded, although it will be more difficult due to the interface strain. If this experiment were to be carried out, all SPD would need to take place at liquid nitrogen temperatures, as this would be below \( \frac{1}{4} T_M \) of Pb and therefore constitute a low temperature. Also, if a solid solution would be desired, electroplating would most likely have to be accomplished as opposed to sputtering. If this experiment is done, it is possible that Pb would completely dissolve, since the kinetics for dissolution could become faster than growth now that it’s not only single atoms that are shaved off the precipitate surface. However, whether it is safe and practical to go through these experiments remain to be seen.

In conclusion, this thesis demonstrated the importance of the heat of mixing in patterning at low temperatures in extreme environments. However, not all variables were completely controlled and there is certainly more work that could be done in irradiation and especially SPD processing to further determine the important parameters that are needed when designing alloys and predicting their behavior.