Defect-Interface Interactions

I. J. Beyerlein^{1*}, M. J. Demkowicz², A. Misra¹⁺, and B. P. Uberuaga¹

¹Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

²Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

Abstract:

Nanostructured materials contain an extremely high density of interfaces. The properties of these materials when exposed to extreme conditions of radiation dose, stress, deformation, or temperature are largely determined by defect-interface interactions. In this article, we review the present understanding of defect-interface interactions in single-phase and two-phase metal and oxide nanocomposites, emphasizing how interface structure affects interactions with point, line, and planar defects. We also review the crystallographic, chemical, and morphological stability of interfaces in different extreme environments: irradiation and mechanical deformation. Our current understanding of these topics prompts new questions that will maintain interfaces in crystalline solids at the frontier of materials research for years to come.

Keywords: nanostructures; nanocomposites; interfaces; atomic scale modeling; vacancies; interstitials; impurities; dislocations; twins; mechanisms; stability

*Corresponding author, irene@lanl.gov

+Currently at Univ. of Michigan, amitmis@umich.edu

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1. Introduction

Interfaces in solid materials are boundaries that separate crystals of the same structure and chemistry but different orientation (grain boundaries) or crystals of different structure and/or chemistry as well as orientation (interphase boundaries or heterophase interfaces). The influence of interfaces on the mechanical properties of polycrystalline materials is critical in materials design and lifetime predictions. Hirth [1] in his seminal 1972 review noted that “*if one excludes single crystal research, one could claim that the balance of the field of metallurgy relates to interfacial properties.*” These opinions are as appropriate today as in the 1970s.

Since the formative work of Chalmers [2] in 1948 illustrating the effect of grain boundaries on the plastic deformation of crystalline materials, both grain boundaries (homophase interfaces) and interphase interfaces in polycrystals have been shown to play a fundamental role in material properties, such as strength, fracture, work hardening, and damage evolution under irradiation and shock. These conditions generate defects. At a basic level, interfaces can act as: (i) sources of defects, (ii) sinks for defects via absorption and annihilation, (iii) barriers to defects, and (iv) storage sites for defects.

In nanocomposites, such elementary defect-interface interactions can have a profound effect on the behavior of the material as a whole. As the interface spacing decreases to the nanometer-scale, the total interface area per unit volume increases. As a consequence, the macroscopic properties of the solid become dominated by defect interactions at the interfaces as opposed to defect interactions in the bulk (Fig. 1.1). In other words, the role of interfaces changes from *contributing* to *dominating* the behavior of defects. Moreover, whether the defect-interface interaction is strong or weak depends largely on the properties of the interface at the sub-atomic to meso-scale. Taken together, this implies the exciting possibility that the bulk response of a nanomaterial can be tailored by controlling the properties of its interfaces, whether it is its structure, chemistry, or energetics or a combination of them.

A fundamental understanding of how the bulk properties of nanocomposites correlate with interface structure, chemistry, and energetics has not been sufficiently developed. Basic research is still needed to provide the scientific underpinning for designing materials with tailored response at extremes of irradiation dose, stress and temperature. Such knowledge is desirable for not only designing nanocomposites for high strengths but also high damage tolerance, irrespective of whether the damage is introduced via mechanical deformation, heat, or irradiation.

In this article we focus on interphase boundaries, although we will cover related work on grain boundaries as well as some concepts that could apply to grain and chemically sharp interphase boundaries alike. For recent review articles dedicated exclusively to experimental and atomistic modeling of grain boundaries in single-phase materials, we refer the reader to [3, 4]. We also do not consider compositionally-graded interfaces. Here we review the interaction of defects with these boundaries, concentrating on how these interactions relate to and depend on the properties of interfaces. The defects include vacancies, interstitials, and helium impurities (relevant to radiation damage) as well as dislocations and deformation twins (relevant to plastic deformation, including shock).

The article is organized into three primary sections. The first section reviews the unit mechanisms of point, line, and planar defect interactions with interfaces. Specifically, under

point defect interactions, we discuss the mechanisms of vacancy and interstitial emission/absorption/storage/annihilation at interfaces. Under line and planar defects, we discuss the mechanisms of glide dislocation and deformation twin nucleation and correlate these unit processes to the atomic structure of the interface. In the second section, we discuss a critical phenomenon of interest in nuclear fission and fusion applications, i.e., helium management. Here, we highlight the role of interface structures in trapping and storing helium in a stable way under irradiation conditions, and the mechanical properties of nanocomposites containing nanoscale helium bubbles at interfaces. In the final section, we present three examples of the role of interfaces in material stability at extremes of irradiation doses and mechanical strains. The first example highlights phase stability (such as amorphization of oxides) under ion irradiation and how it is affected by interfaces. The second example examines morphological stability under heavy ion bombardment. The last example discusses the formation of crystallographically stable interfaces due to severe plastic deformation. These seemingly disparate phenomena, such as helium bubble formation at interfaces, ion-irradiation-induced void formation and amorphization, and formation of crystallographically stable, low-energy interfaces due to deformation processing, are all correlated through a common theme of interface atomic structure and its influence on basic defect-interface interactions: defect nucleation, absorption, storage and annihilation.

2. Influence of interface structure on defect interactions

Supposing one could control the nature of interfaces within a material, what interfaces might be best to improve robustness in extreme radiation or mechanical conditions? Fueled by this question, there has been a surge in interest since the 1980s in correlating defect-interface interactions with interfacial structure. Because of the significant simplicity afforded by grain boundaries, much of that work has focused on grain boundaries in single-phase materials. However, because of the issues associated with grain growth and overall stability of nanocrystalline materials [5-9], recent attention has shifted towards multiphase nanocomposites and their biphasic interfaces [10].

In this section, we review the current understanding of how biphasic interfacial structure at the atomic scale determines the interaction of defects with interfaces in metals. We examine the source and sink behavior of interfaces with different types of defects relevant to metals, from zero-dimensional point defects, such as interstitials and vacancies, to one-dimensional dislocations to two-dimensional twin planes. It is possible that many concepts can also apply to non-metallic systems, such as ceramics and semiconductors, although in such cases other factors, such as electrostatics and charged defects, must also be considered.

2.1. Point defects: vacancies and interstitials

Interactions between interfaces and point defects play a central role in metal behavior such as diffusional flow [11-14], solute or impurity segregation and precipitation [15-18], microstructure stability and evolution [19, 20], and radiation response [21, 22]. It has long been appreciated that point defects behave differently within interfaces than in crystalline solids [11, 12]. However, the study of how interface structure affects interface-point defect interactions only started to gain momentum in the late 1970s and early '80s [13, 15, 23-26].

Pioneering investigations confirmed qualitatively that the response of different grain boundaries (GBs) to irradiation and impurity concentrations depends on GB crystallographic parameters [27, 28], on intrinsic interfacial defects [13, 15], and on the presence or absence of coherency [13, 25]. It was shown that many high-misorientation, non-coherent GBs are capable of exhibiting numerous atomic-level structures for a single set of crystallographic degrees of freedom [29] and that these structures can influence materials properties [30]. The structural unit model of GB behavior was developed based on this insight [31, 32] and its consequences for point defect behavior were investigated [33].

Since then, interest in how the internal structure of interfaces affects their interactions with point defects has increased greatly, in part due to the potential for engineering interfaces that exhibit tailored interactions with point defects. Such designer interfaces promise to give an enhanced degree of control over the properties of polycrystals and multiphase composites, advancing the development of new materials with improved performance [22, 34, 35].

2.1.1. Interface sink efficiency for absorbing vacancies and interstitials

The most direct form of atomic-level damage sustained by an irradiated material is the production of isolated point defects (e.g., vacancies and interstitials) and clusters thereof during

collision cascades [36]. Many deleterious effects of irradiation on material properties—e.g., void swelling [37], hardening [38], and radiation-induced segregation [17, 18]—may be traced back to these defects. In a pioneering study on austenitic stainless steels, Singh recognized that radiation-induced damage decreases with decreasing grain size because of defect trapping at GBs [21]. Similarly, nanocrystalline materials, containing a large specific area of GBs, exhibit improved irradiation tolerance compared with their coarse-grained counterparts, at least under certain conditions [39-42]. Thus, GBs, interphase boundaries, and free surfaces may reduce radiation damage by absorbing and annihilating point defects and defect clusters [21, 39-51].

The interactions of defect clusters with interfaces may differ qualitatively from the interaction of isolated vacancies and interstitials with interfaces. For example, Golubov *et al.* have connected the one-dimensional migration of glissile defect clusters [52] to enhanced void formation in a band of material adjacent to GBs in large-grained polycrystals [53, 54]. Yu *et al.* showed that coherent GBs may absorb stacking fault tetrahedra through dislocation reactions [55]. While these types of interactions are important for understanding and predicting the evolution of materials under heavy-ion or neutron irradiation, the present review will focus on discussing interface interactions with isolated vacancies and interstitials, which are the predominant type of radiation-induced defect under light-ion or electron irradiation.

A simple way to describe the interaction of just one type of radiation-induced point defect—e.g. a vacancy—with an interface is to use the following one-dimensional linear differential equation

$$\frac{\partial c_v}{\partial t} = D_v \frac{\partial^2 c_v}{\partial x^2} + K_0 - K_{sv} (c_v - c_v^{eq}). \quad (2.1.1)$$

Here x denotes the position along the direction normal to the interface plane, c_v is the vacancy concentration (in units of $\#/m^3$), c_v^{eq} is the thermal equilibrium value of c_v , D_v is the vacancy diffusivity (assumed independent of c_v), and K_0 is the rate of vacancy generation due to irradiation (assumed uniform). K_{sv} is an effective “lossiness” of the medium that describes removal of vacancies at distributed sinks, such as dislocations, voids, or other defect clusters [56]. K_{sv} may also be adjusted to model vacancy recombination with interstitials, since Eq. 2.1.1 does not account for this process explicitly.

In a semi-infinite solid with $x > 0$ and an interface at $x = 0$, the steady-state solution to Eq. 2.1.1 is

$$c_v(x) = c_v^0 + \left(c_v^{eq} - c_v^0 + \frac{K_0}{K_{sv}} \right) \left(1 - e^{-x\sqrt{K_{sv}/D_v}} \right), \quad (2.1.2)$$

where c_v^0 is the vacancy concentration immediately adjacent to the interface. If the interface maintains a thermal equilibrium vacancy concentration adjacent to itself regardless of the influx of supersaturated vacancies from neighboring solid, i.e., if $c_v^0 = c_v^{eq}$, then it is a perfect vacancy sink. Substituting $c_v^0 = c_v^{eq}$ into Eq. 2.1.2 gives the vacancy concentration in the vicinity of a perfect sink interface:

$$c_v(x) = c_v^{eq} + \frac{K_0}{K_{sv}} \left(1 - e^{-x\sqrt{K_{sv}/D_v}} \right). \quad (2.1.3)$$

However, not all interfaces are perfect vacancy sinks. For example, $\Sigma 3$ coherent twin boundaries in fcc metals are poor vacancy sinks, in part because they have a negligible binding energy for vacancies [24, 57, 58]. The vacancy “sink efficiency,” η_v , is intended to describe the ability of an interface to absorb supersaturated vacancies. It is defined as

$$\eta_v = \frac{J_v}{J_v^p}, \quad (2.1.4)$$

where J_v is the flux of vacancies to the interface of interest and J_v^p is the flux of vacancies into a perfect sink interface [59]. Thus, a sink efficiency of unity denotes a perfect sink while zero-sink efficiency describes an interface such as the $\Sigma 3$ coherent twin, which cannot absorb any vacancies. In general, interfaces may take on sink efficiency values between these two extremes.

Using the definition of η_v , the solution of Eq. 2.1.1 for an interface of arbitrary sink efficiency may be written as

$$c_v(x) = c_v^{eq} + \frac{K_0}{K_{sv}} \left(1 - \eta_v e^{-x\sqrt{K_{sv}/D_v}} \right). \quad (2.1.5)$$

An example of defect concentrations in the vicinity of an interface for a range of sink efficiencies is shown in Fig. 2.1, demonstrating that interfaces with high η_v remove more defects from their vicinity than interfaces with low η_v .

Sink *efficiency* is not to be confused with sink *strength* or *capture efficiency*. The former characterizes the ability of a single, specific interface to absorb point defects from the neighboring grains. It describes how the interface interacts with and affects local point defect concentrations in its immediate vicinity. The latter two terms are used in the mean-field theory of defect evolution in irradiated materials to describe the net effect of defect traps distributed throughout the material on average, radiation-induced defect concentrations [56]. Sink strength expressions have been developed for numerous types of sinks, including GBs [60]. These expressions are a function of GB area per unit volume in a material and describe the effect of GBs on the surrounding medium. Unlike sink efficiencies, they are not a property of the GBs themselves. Capture efficiency describes the relative ability of one type of sink, such as GBs, to capture different kinds of point defects, e.g., vacancies vs. interstitials, or the relative ability of different kinds of sinks, e.g., GBs vs. voids, to capture one type of defect [61]. Similar to sink strength, capture efficiency is related to the mean-field theory of average, radiation-induced defect concentrations, rather than to the effect of individual sinks on their immediate neighborhood.

Early investigations tended to treat most GBs as perfect point defect sinks [56, 62]. However, it has been increasingly recognized that GBs or interfaces of differing crystallography or composition possess markedly different structures and, hence, are likely to have distinct sink

efficiencies. The most frequently reported evidence of differing sink efficiencies for different interfaces is obtained from studies of defect precipitation. In such experiments, a vacancy supersaturation is introduced by electron [25], ion [22, 26, 63, 64], or neutron [65] irradiation or by quenching from elevated temperature [24]. Far from interfaces and free surfaces, the supersaturated vacancies are observed to precipitate into voids [22, 64, 65] or other types of defect clusters [24-26, 63].

The density of these precipitates is in general reduced in the vicinity of interfaces. Using Transmission Electron Microscopy (TEM), these studies have observed the formation of zones depleted of defect clusters near interfaces. When the defects formed are voids, these zones have been referred to as “void denuded zones” (VDZs) [22, 64, 65]. An example of a VDZ adjacent to a GB in Cu is shown in Fig. 2.2. The width of a VDZ, λ_{VDZ} , or that of any defect depleted zone, may be quantified by finding the density of defect clusters as a function of distance from the interface. Using this procedure, several groups have shown that different interfaces (including GBs of differing crystallography) have different defect depleted zone widths [22, 24, 64]. For example, Fig. 2.3 shows variations of VDZ widths with misorientation angles of Cu GBs.

The notion of interface sink efficiency may be used to explain variations of VDZ width between different interface types. Following Zinkle [63], assuming voids only form above a critical vacancy supersaturation $\Delta c_v^* = (c_v - c_v^{eq})$, then using Eq. 2.1.5 the following relation between VDZ width and η_v is obtained:

$$\lambda_{VDZ} \sqrt{\frac{K_{sv}}{D_v}} = \ln \eta_v - \ln \left(1 - \Delta c_v^* \frac{K_{sv}}{K_0} \right). \quad (2.1.6)$$

Thus, λ_{VDZ} and η_v are monotonically related and variations in VDZ width are evidence of corresponding variations in interface sink efficiency. The wide scatter in the data in Fig. 2.3 shows that η_v depends not just on GB misorientation but on other GB-related parameters as well [64]. Similar scatter may be seen in the work of Siegel *et al.* [24]. Variations in VDZ widths have also been examined at Cu-Nb interfaces, confirming that crystallographic character also affects the sink efficiency of heterophase interfaces [22]. As will be discussed in section 2.1.2, the microscopic interface state is also likely to affect η_v .

Zones depleted of defect clusters provide compelling visual evidence that solid-state interfaces exhibit a wide range of sink efficiencies. However, they do not offer a straightforward way of determining the numerical value of η_v . For example, to compute η_v using Eq. 2.1.6, both Δc_v^* and K_{sv} must be known. In practice, these quantities are difficult to obtain. Moreover, the simple model that led to Eq. 2.1.6 ignores the fact that defect clusters are themselves discrete vacancy sinks and, as such, give rise to a non-uniform perturbation in the vacancy concentration near the interface.

To date, there has only been one experiment that provided a quantitative measurement of η_v [66]. This experiment was based on determining the effect of interfaces on radiation-enhanced diffusion (RED), rather than on observing the distribution of radiation-induced defect clusters. The authors used physical vapor deposition (PVD) to synthesize samples containing layers of Cu separated by layers of another metal, X. Three different types of samples were made, each with a

different metal separating successive Cu layers: one with $X = \text{Nb}$, another with $X = \text{V}$, and finally one with $X = \text{Ni}$. Thus, each of these three samples contained a different kind of Cu-X interface, providing the opportunity to compare their sink efficiencies.

Each sample contained several layers of Cu with thicknesses ranging from ~ 10 to ~ 100 nm. In the middle of each Cu layer, the authors deposited a layer doped with 10% Au. This Au concentration is high enough to be easily detectable using energy-dispersive spectroscopy (EDS) in a TEM, but small enough so that the doped layer remains coherent with the neighboring pure Cu. The Au in this layer undergoes vacancy-mediated diffusion throughout the Cu layer, causing the initially sharp Au concentration profile to broaden out. The rate of broadening of the profile in thermal equilibrium at the temperatures used in the experiment (300°C and 350°C) is too low to detect. By contrast, the rate of broadening under irradiation is much more rapid because the high vacancy supersaturation generated by inter-nuclear collisions leads to RED.

The authors of Ref. [66] measured the radiation-enhanced diffusivity from the rate of broadening of the Au concentration and used these values to compute the vacancy concentration in the center of each Cu layer. This process was repeated for several different layer thicknesses. The variation of vacancy concentration in the middle of layer with layer thickness depends on the sink efficiency of the adjoining Cu-X interfaces. Thus, by comparing the experimentally measured vacancy concentrations with ones predicted numerically for different layer thicknesses and η_v values [67], the authors were able to determine η_v for all three Cu-X interfaces investigated. They found that $\eta_v \approx 0.95\text{--}0.99$ for Cu-Nb interfaces, $\eta_v \approx 0.9$ for Cu-V, and $\eta_v < 0.5$ for Cu-Ni.

Thus, as expected [22, 48], Cu-Nb interfaces have high sink efficiency, but are not perfect sinks. The difference in sink efficiency between Cu-Nb and Cu-V interfaces may be due to the distinct, inhomogeneous distributions of vacancy trapping sites in them. Previous studies have identified misfit dislocation intersections (MDIs) as preferential vacancy trapping locations at several heterophase interfaces [48, 68, 69]. The Cu-V interface contains a smaller density of MDIs than Cu-Nb, indicating that the lower sink efficiency of Cu-V may indeed be related to the distribution of vacancy trapping sites [70].

The fact that the Cu-Ni interface exhibited a significantly lower value of η_v than Cu-Nb and Cu-V suggests—in agreement with studies on void denuded zones [64]—that sink efficiency is highly sensitive to interface crystallography. Cu-Nb and Cu-V interfaces synthesized by PVD both have identical crystallographic character: a Kurdjumov-Sachs orientation relation and closest-packed crystallographic planes along the interface [71, 72]. By contrast, Cu-Ni interfaces formed by PVD typically have a crystallography distinct from Cu-Nb and Cu-V, e.g. cube-on-cube orientation relation with $\{100\}$ interface planes [73]. The relatively low (2.5%) lattice mismatch between Cu and Ni may also give rise to larger regions of coherency in Cu-Ni interfaces and, hence, fewer MDIs to trap vacancies. Thermodynamic considerations may also play a role: while Cu/Nb and Cu/V have extremely low solubility, Cu and Ni are fully miscible.

A quantitative model of the dependence of interface sink efficiency on crystallography, internal structure, and defect behavior is currently unavailable. Indeed, even the mechanisms that govern interface sink efficiency are not yet fully understood. An early attempt by Ashby to model sink efficiency assumed that defect trapping at interfaces is reaction controlled [12]. According to this view, the energy barrier for a defect to migrate into an interface is larger than the energy barrier for diffusion in the crystal. However, atomistic simulations have since shown that, in pure metals

[46, 74] and in multiphase metal composites [75, 76], the energy barriers for defect migration are lower near interfaces than in the bulk. Indeed, upon approaching close enough to an interface, defects are often seen to undergo barrier-less diffusion into the interface. These simulations, therefore, militate against the view that sink efficiencies arise from reaction-controlled defect absorption.

An alternative view was proposed by Balluffi and Granato [77]. They hypothesized that defect fluxes to GBs are diffusion controlled and that GB sink efficiencies are due to the balance of vacancy influx from the adjacent crystal and vacancy emission from the GB back in the crystal. Using low-angle tilt GBs as a model, they derived an expression for η_v assuming that point defects are trapped at jogs on the edge misfit dislocations intrinsic to these boundaries:

$$\eta_v = \frac{1}{1 + \ln(cd_s) \frac{d_s}{d_d}}. \quad (2.1.7)$$

Here, d_s is the average distance between point defect trapping sites within the boundary, d_d is the characteristic defect diffusion distance to the boundary, and c is a constant. The dislocation bias for interstitial absorption in such boundaries has also been calculated [78]. Recently, Jiang *et al.* extended the analysis of Granato and Balluffi to compute sink efficiencies of interstitials at low-angle tilt GBs [79].

While it appears to be more realistic than the Ashby model [12], the expression proposed by Granato and Balluffi [77] predicts that η_v is generally close to unity, except for high d_s , characteristic of subgrain boundaries. Such boundaries, however, are likely to constitute a minority of the GBs in real polycrystals [80]. Tschopp *et al.* investigated vacancy and interstitial formation energies in a wide range of GBs in α -Fe with a view toward identifying properties that govern sink efficiency in general GBs [74]. Many of the non-coherent GBs they investigated contained sites with vanishing or even negative vacancy formation energies, suggesting that all these boundaries should behave as perfect sinks. Similar conclusions have been drawn in the case of several heterophase interfaces [48, 68, 75, 81, 82]. Therefore, available analytical models and atomistic simulations cannot yet account for the variety of sink efficiencies indicated by experimental measurements of VDZ widths, especially for general GBs and incoherent heterophase interfaces, whose structure in most cases cannot be described using misfit dislocation models.

2.1.2. Dynamic interactions of interfaces with vacancies and interstitials

One factor that seems to influence the sink efficiency of interfaces is the kinetic properties of defects within those interfaces, which in turn affects the emission rates of vacancies from GBs back into the crystal. The kinetic processes associated with point defect-interface interactions were examined, using Cu GBs [46, 83-85] and Cu-Nb interfaces [76, 81, 86, 87] as model systems. Molecular dynamics (MD) simulation was used to determine the influence of interfaces on defect production during collision cascades. Temperature accelerated dynamics (TAD) [88] and adaptive kinetic Monte Carlo (AKMC) [89] were used to study the kinetics of defects both as they approach GBs as well as within the GB plane, and object kinetic Monte Carlo (OKMC)

simulations were used to gain insight into how in-boundary defect mobility influences sink efficiency.

During collision cascades, if the cascade overlaps with a GB or interface, the interface can dramatically influence the morphology of the final defect state. In particular, because of their higher mobility and higher binding energies to interfaces, interstitials can be preferentially absorbed by interfaces, leading to a defect state that is vacancy rich in the interior of the material [46, 83, 90]. In fact, because of the interstitial absorption, the number of vacancies that are created during collision cascades can be significantly higher than if the interface were not present. This is because the recombination mechanism is suppressed as the number of interstitials in the system is reduced. Such behavior is not only seen near single-phase GBs [46, 83, 90] but similar conclusions have been drawn from simulations on Cu-Nb heterophase interfaces [76].

As a consequence, at low temperatures where the defect structure created in collision cascades is effectively frozen in place, GBs and heterophase interfaces can exacerbate damage accumulation, as observed in low-temperature experiments on nanocrystalline Au [41]. Importantly, the way that a GB modifies the damage production during collision cascades depends on the boundary structure. For example, highly symmetric tilt GBs only modestly modify the damage production while even simple twist GBs have a much greater impact [90]. At Cu-Nb interfaces, interstitials are preferentially absorbed on the Cu side of the interface, but not on the Nb side [76]. Further, this preferential absorption of interstitials by GBs is not unique in Cu, and has been observed in MD simulations of various materials [83].

The collision cascade simulations show that GBs and heterophase interfaces preferentially absorb interstitials, leaving behind a vacancy-rich defect structure in the grain interior. This phenomenon has two important ramifications. First, the structure of the interface is modified by the presence of the interstitials. Essentially, the properties of a damaged interface are not the same as a pristine interface [90]. In particular, how defects within the grain interior interact with a damaged boundary is significantly different than with a pristine interface. For example, the segregation energy of vacancies is typically much higher near damaged grain boundaries than pristine ones [90]. In some cases, the segregation energy is larger in magnitude than the formation energy of the vacancy itself, which means that some positions for the vacancy within the boundary are unstable. This leads to longer-range interactions of the vacancy with the boundary. A so-called “interstitial emission” process, schematically illustrated in Fig. 2.4, was identified in which a vacancy near the grain boundary and an interstitial within the boundary plane could annihilate over several atomic distances via the vacancy effectively pulling the interstitial out of the boundary [46]. This phenomenon was also seen in simulations of Cu-Nb interfaces [76] and of GBs in oxides [91]. It provides a mechanism for healing damage in the material that would not be present if the interface were an ideal sink that perfectly annihilated the interstitials. Further, these interstitial emission mechanisms have lower barriers for activation than vacancy diffusion, suggesting they would happen at intermediate temperatures and, indeed, enhance defect recovery is seen in nanocrystalline Au, as compared to large-grained Au, at temperatures at which vacancy mobility would be expected to be non-existent [41]. Frolov et al. have shown that the introduction of defects within GBs changes their structure and have identified particularly stable “damaged” boundaries that have significantly different properties than the initial structures [92, 93]. Von Alfthan and coworkers have also shown how the stability of GBs depends on effective defect content [94].

Second, the typical interstitial structure at the grain boundary plane after a cascade consists of clusters of interstitials rather than isolated point defects. It is often assumed that defect mobility at GBs is much higher than in the bulk material. However, this depends on both the character of the boundary and the size of the defect cluster. Using AKMC and TAD simulations, the mobility of interstitial clusters as a function of size for several different GB structures was characterized [85]. Two key results were that (a) the mobility of the cluster tended to decrease with cluster size such that by sizes of 3-5 interstitials, the mobility of the cluster within the GB was slower than that of mono-interstitials in bulk Cu and (b) only in tilt GBs were mono-interstitials faster than in the bulk. In boundaries with twist components, mono-interstitials were slower in the GB plane than in bulk Cu. These results suggest that recombination mechanisms within the GB plane will be a function of the GB character and the types of defect clusters formed in the boundary. Further, for highly damaged boundaries in which the actual structure of the boundary has changed, defect mobilities will change even more dramatically.

In contrast, simulations on Cu-Nb interfaces revealed that point defect clusters at these interfaces are thermodynamically unstable with respect to decomposition into isolated defects [86]. This finding has important consequences for the stability of these interfaces under irradiation, since the inability of vacancies or interstitials to cluster reduces the likelihood of nucleating deleterious defect agglomerates, such as voids. On the other hand, lack of clustering may also elevate the concentration of supersaturated interfacial point defects under irradiation, increasing the likelihood of their re-emission in the adjacent crystalline material and reducing the sink efficiency of the interface. It is interesting to note that a more general twist plus asymmetric tilt boundary exhibits similar behavior regarding defect clustering and may have similar responses to radiation damage [85].

Isolated point defects at Cu-Nb interfaces migrate by a complex, multi-stage mechanism, which is closely related to the arrangement of misfit dislocations in this interface [86, 87]. Both vacancies and interstitials trapped at this interface tend to migrate along misfit dislocations of nearly perfect screw character through a collective process that causes these defects to displace between adjacent misfit dislocation intersections (MDIs). Migration events perpendicular to these dislocations are extremely rare, giving rise to a highly anisotropic, nearly one-dimensional diffusivity. Because the arrangement of misfit dislocations at heterophase interfaces depends on the lattice parameters of the neighboring crystals, interfaces composed of different pairs of elements are expected to exhibit vastly differing diffusivities [81].

The simulations described above reveal that during irradiation, interfaces become damaged, with some retained defect content, and that these defects may cluster, leading to very different mobilities than found for single interstitials. To understand how these factors might influence the sink efficiency of the boundary, an OKMC model was constructed to determine sink efficiency as a function of the defect energetics at the GB plane [85]. Consistent with Eq. 2.1.3, sink efficiency is defined as the flux of vacancies to the boundary compared to a case in which the boundary is an ideal sink. As a consequence of the contrasting mobilities of isolated point defects and defect clusters within the GBs, two limiting cases can be considered.

In the first case, it was assumed that as interstitials diffuse, there is some chance that they escape the system, effectively reaching a triple junction or free surface that serves as ideal sinks. Essentially, the system is open, with a possibility of interstitials leaving the local region considered explicitly in the simulation cell. However, this probability is a function of the

interstitial mobility – as their mobility decreases, so does the probability that they escape the system. In this scenario, the sink efficiency of the boundary decreases as the probability of interstitials escaping increases, as shown in Fig. 2.5b. That is, as interstitials are removed from the system, the annihilation mechanisms at the boundary between interstitials and vacancies are eliminated and the vacancy concentrations increase. The probability of vacancies emitting back into the grain interior thus increases and the sink efficiency consequently decreases. This scenario corresponds to a situation in which there is some bias to eliminate interstitials. In this model, the bias occurs because of fast diffusion of interstitials along the grain boundary, which provides a pathway for the interstitials to escape the local vicinity. However, any bias would lead to a similar consequence: as interstitials are eliminated from the material, vacancy-interstitial recombination is reduced and vacancy accumulation at the boundaries increases. This leads to higher rates of vacancy emission from the boundaries and thus a lower sink efficiency.

In the second scenario, there is no assumed external sink for defects; the system is closed. All defects, once created, remain in the system until they annihilate with another defect. In this model, a limit was assumed in which interstitials have clustered at the boundary so that, within the boundary, their mobility is zero. This is consistent with the atomistic results described above that show that, as interstitials cluster within a grain boundary, the mobility of the cluster decreases. In this case, which is illustrated in Fig. 2.5d, the sink efficiency is a function of the vacancy mobility, rather than the interstitial mobility. As the vacancy mobility in the boundary decreases, so too does the sink efficiency. If the vacancy mobility is too low, the vacancies return to the grain interior at a rate faster than their migration in the boundary, reducing the overall flux of vacancies to the boundary and thus the sink efficiency. Again, this is a consequence of reduced vacancy-interstitial recombination within the grain boundary, although the origin is different from the first scenario. Here, the reduced recombination occurs because vacancies can leave the boundary faster than they can diffuse within the boundary and thus emission is faster than annihilation.

Together, these scenarios indicate that if vacancy-interstitial recombination within a grain boundary is reduced for any reason, the sink efficiency of the boundary will be lowered. This is true whether recombination is reduced because of a bias, as in the first scenario, or because of slow kinetics as in the second scenario. Further, whether this reduction occurs depends on the relative rate of recombination – dictated by the mobility of vacancies and interstitials within the grain boundary plane – and the rate of emission from the grain boundary, which is controlled by the binding energy of vacancies to the boundary. Both factors, in turn, depend on grain boundary character. Sink efficiency is reduced when the rate of recombination is slower than the rate of emission, as shown in Figs. 2.5b and d.

While most of the results discussed in this section were obtained studying GBs in single-phase materials, the results on Cu-Nb interfaces demonstrate that the same concepts will hold in multi-phase materials [68, 75, 76]. Taken together, these results indicate that

- (a) interface structures are not static and evolve with radiation dose,
- (b) the interaction of defects with interfaces depends on the damaged interfacial structure,
- (c) the mobility of defects within interfaces depends on the interface character and structure, and
- (d) the sink efficiency of interfaces depends on the mobility of defects within the boundary plane which dictate in-boundary recombination rates of vacancies and interstitials.

These findings imply that sink efficiency is not a static quantity that depends only on the pristine interface character. It depends on the damaged atomic structure of each particular interface, which evolves with time, as well as the distribution of different types of interfaces. Moreover, the fluxes to one interface will depend on the damaged structure of nearby interfaces and thus the entire system must be considered as a whole to make predictions of defect evolution under irradiation.

Thus, the response of any given interface to radiation-induced defects may be very sensitive to the irradiation conditions, as schematically illustrated in Fig. 2.5a and c. In the case of electron or light-ion irradiation, isolated point defects are created. If the irradiation flux is small, these defects will remain isolated as they arrive at grain boundaries. At tilt boundaries, where isolated interstitials can diffuse very quickly along the tilt axis, these defects will quickly diffuse away, leaving behind vacancies that are unable to recombine, and thus accumulate. However, in more general boundaries, interstitials do not diffuse so quickly and they will remain in the vicinity to annihilate vacancies. Thus, the sink efficiency will be low for tilt boundaries and higher for general boundaries under such irradiation conditions. However, in the case of heavy-ion irradiation, where defects cluster within the tilt boundaries, the mobility of interstitial clusters is lower at tilt boundaries than at random boundaries, where clustering tendencies are weaker. Thus, the opposite scenario occurs, with the tilt boundaries having a higher sink efficiency than the general boundaries. This demonstrates that the overall response of the microstructure will be dependant on the irradiation conditions, with different boundaries responding differently to varying irradiation conditions.

2.1.3. Outstanding Questions

While the results presented here provide some insight into the nature of point defect interactions with interfaces and the relationship between sink efficiency and interfacial structure, many unresolved questions remain to be addressed before quantitative predictions of interface sink efficiency and radiation damage evolution in nanocrystalline materials are possible.

The understanding of the mechanisms of point defect accommodation at interfaces remains embryonic. Since experiments cannot directly observe these mechanisms, atomistic simulations have been crucial in elucidating them. Large numbers of such studies of GB interactions with point defects have been performed [95-99]. Most of them have focused on characterizing the properties of static defects or on short-range migration of isolated defects [100, 101]. Molecular dynamics (MD) may be used to simulate small numbers of thermally activated migration events at elevated temperatures [81, 102-104]. However, the simulation times required for direct MD to model the long-term flux balance that determines interface sink efficiency are prohibitively long, especially at low homologous temperatures. In some cases, vacancy diffusion to and within interfaces may be modeled using kinetic Monte Carlo (kMC) methods [105-107] or combinations of molecular statics (MS) and rate theory [108]. These methods work best for interfaces with relatively regular, ordered structures and are therefore of limited utility for non-coherent interfaces that may contain disordered regions.

Section 2.1.1 discussed interface sink efficiency in the presence of just one type of defect diffusing to the interface (vacancies). However, under realistic irradiation conditions, both vacancies and interstitials are absorbed at interfaces, altering the response of interfaces to irradiation [67]. Moreover, some defect clusters may also be mobile and interface sink

efficiencies for such clusters may also be defined. Both vacancies and interstitials as well as clusters thereof may interact with impurities and alloying elements, present either at interfaces or in the neighboring crystalline solid. The influence of different defect types and their interactions with impurities on sink efficiencies have yet to be studied.

The results discussed in section 2.1.2 indicate both that defect mobility depends strongly on interfacial character and that interfacial character evolves with radiation dose and together these determine in-boundary defect annihilation rates. Coupling these two is a significant challenge as it requires knowing the interfacial character as a function of time and then determining the mobility of defects within that interface. However, predicting the interfacial character at time t_0 requires knowing the defect mobilities within the interface for all $t < t_0$. Thus, a great deal of characterization is necessary for making quantitative predictions. Further, these interfaces do not exist in isolation and their evolution depends on the surrounding microstructure and the interaction of defects with those other microstructure features. This means that an integrated simulation is needed that accounts for all of these competing processes at the same time. This is particularly true of a nanocrystalline material in which distances between various microstructural features are small.

Related to this, it is unclear at this time whether quantities such as sink efficiency can be determined *a priori* for predicting the defect evolution in an irradiated nanocrystalline material. It is also unknown whether sink efficiencies can only be ‘co-determined’ in such a simulation because of the potentially complex dependencies of sink efficiency on factors such as temperature, dose, dose rate, defect content, etc. For instance, are sink efficiencies a more fundamental quantity than e.g., void denuded zones? If not, is there another quantity or set of quantities that are intrinsic to the interface character that can be used to quantify the influence of interfaces on defects?

2.2. Linear defects: dislocation nucleation

2.2.1. Background on dislocation nucleation from interfaces

Internal interfaces play an important role in supplying mobile dislocations during the mechanical deformation of metals [1, 109-111]. In this section, we begin with a brief summary of the reported mechanisms of dislocation nucleation from GBs and interfaces.

One of the earliest observations via TEM of dislocation nucleation was emission of extrinsic GB dislocations via cross-slip onto a glide plane intersecting the boundary [112, 113]. This mechanism requires the presence of dislocations in the boundary plane with Burgers vectors that are common to both the boundary plane and the intersecting glide plane on which the emission occurs. Typically plastic pre-straining is required to initiate the glide of lattice dislocations that are trapped in the boundary. Hence this mechanism can only be operative during plastic straining and not at the onset of plastic yielding.

In a variation of the above, Baro et al. [114] presented a mechanism for the generation of multiple dislocations on two glide planes from the same source in a flat grain boundary. This mechanism necessitates that two lattice glide planes have a common line of intersection in the boundary plane, which is also the line direction of a GB dislocation source. This mechanism is

also an emission rather than a nucleation mechanism since it assumes that the dislocations, which can emit as glide dislocations onto an intersecting slip plane under an applied stress, are already present in the boundary.

In addition to pre-existing dislocations, ledges or steps at interfaces are known to serve as sites for dislocation nucleation due to local stress concentration [115-118]. A ledge can be viewed as an array of extra half planes such that the ledge height (H) is $n\mathbf{b}$, where $\mathbf{b}$ is the Burgers vector and n is the number of dislocations in the ledge. Under applied stress, the extra half planes in the ledge can be punched out sequentially to supply a total of n dislocations to the crystal into which the ledge extends [119, 120]. This mechanism can only produce a finite number of dislocations since the ledge gets consumed in the dislocation nucleation process. Price and Hirth [121] proposed a mechanism for the generation of an infinite number of screw dislocations from a GB ledge oriented along a slip plane and parallel to the Burgers vector for one set of screw dislocations in the slip plane. The mechanism requires shearing the ledge one Burgers unit along the slip plane. As the dislocation is generated and moves away from the ledge, continued shearing of the ledge can cause additional dislocation generation by the same mechanism while still preserving the ledge. Several TEM investigations have revealed nucleation of dislocations from ledges at interfaces [120, 122-124] and from piled-up dislocations at the boundary [125-127]. The nucleation of partial dislocations from GB ledges has also been simulated numerically [128].

Finally, mechanisms have been proposed for dislocation nucleation from surfaces. Orlov [129] proposed a mechanism for dislocation nucleation via removal of a surface ledge. In a finite size crystal, the nucleated dislocation would glide across and create a step on the parallel surface. The new surface step could act as a source for another dislocation on a cross-slip plane, thereby creating a zig-zag pattern of slip lines linked with surface ledges that act as sources. Dregia and Hirth [130] extended this idea of a “rebound mechanism” to internal interfaces. For the specific case of fcc crystals, a Shockley partial dislocation nucleated from a surface after rebounding from an internal $\{100\}$ interface as a different Shockley partial would leave behind a Lomer dislocation at the interface. This mechanism of dislocation nucleation from surfaces is particularly relevant to the formation of misfit dislocations that relieve coherency strains in epitaxial thin films on substrates.

The mechanisms reviewed above are general in nature and point to different unit mechanisms that could nucleate dislocations from surfaces and internal interfaces. Recent work reviewed below attempts to understand dislocation nucleation in terms of the atomic structure of bimetal interfaces. This understanding will lead to a prediction of the dislocation type and nucleation site for different interfaces and the capability to compare interfaces in terms of their ability to act as efficient dislocation sources.

2.2.2. Dislocation nucleation from bimetal interfaces

Bimetal interfaces have an atomic structure that is distinct from the two crystals that they join. When they are strained, bimetal interfaces can supply mobile dislocations into the adjoining crystals. The dislocations nucleated can be classified as either interfacial dislocations that propagate within the interface or lattice dislocations that are emitted into the adjoining crystals [68, 131, 132]. Both are mechanisms of strain accommodation; the former supports interfacial sliding, whereas the latter enables plastic crystallographic slip [132-134].

The study of dislocation nucleation from bimetal interfaces is particularly relevant in nanocomposites. As crystallographic dimensions shrink to the nanoscale, lattice dislocations are more likely to originate from the interfaces than the fine nanocrystalline interior. Regardless of deformation history, nanocrystals contain minimal to no dislocation structures whereas bimetal interfaces contain the dislocations needed for producing mobile lattice dislocations. In this way, interfaces can determine the deformation behavior of nanomaterials.

Bimetal interfaces can be structurally pristine or defective. Pristine bimetal interfaces contain a network of misfit dislocations in the plane of the interface to accommodate the misfit in lattice parameter and crystal structure across the interface plane [110, 135]. The characteristics of this network depend sensitively on the interface character (orientation relationship and interface plane) and chemical composition [136, 137]. Because of their inherent defect structure, when strained, even pristine interfaces are seen to emit dislocations into the adjoining crystals [138-140]. Defective interfaces contain additional (extrinsic) defects, such as steps or ledges, which can arise as a result of processing or multiple dislocation interactions. They vary statistically in size and location and are not an inherent part of the structure of the interface. As is the case for GBs, these (random) structural defects in bimetal interfaces can easily act as sources for dislocations [141] [142, 143].

The emission of lattice dislocations from bimetal interfaces has been studied experimentally and numerically via molecular dynamics (MD) simulations [131, 138, 140, 141, 144-148] [68]. Via in-situ TEM or post-mortem high resolution (HR) TEM, experimental studies have provided evidence of partial dislocation emission or twin nucleation directly from interfaces [144, 146, 149]. In the MD simulations cited, lattice dislocation emission was observed during nano-indentation, spall conditions, shock compression, and interface-parallel shearing. In these cases, the model interfaces were initially pristine, in which case there can be no dislocation emission from extrinsic defects.

2.2.3. Relationship with bimetal interface structure

The most detailed work on dislocation nucleation is theoretical or numerical. Dislocation nucleation is tremendously challenging to capture as it happens in experiment. To understand how the interface structure affects dislocation nucleation, a series of theoretical and numerical studies were performed on model pristine interfaces. To simplify the analysis further, these investigations focused on pristine interface structures that can be described by a misfit dislocation network comprised of intersecting arrays of discrete and distinct misfit dislocations, each with a well-defined line orientation and Burgers vector [48, 68, 150-152]. The details of the misfit network depend on the crystallographic character of the interface, the five-parameter description that defines the plane and orientation relationship of the interface.

The first atomic-scale study on such interfaces attempted to elucidate the sequence of events leading to nucleation of a single loop from a pristine Cu-Nb interface [139]. In MD simulation, a strain was applied to a Cu-Nb bicrystal containing a single interface to promote dislocation nucleation into the Cu crystal. (The preference is a consequence of the Cu Shockley partials having a smaller Burgers vector and self-energy than dislocations in Nb.) It was found that the nucleation sites were not random, but highly correlated with the misfit dislocation lines (Fig. 2.6a,b). Disregistry analysis of the strained interface revealed that intense in-plane shear concentrations tended to develop along these misfit dislocations prior to nucleation (Fig. 2.6c).

The observed dislocation loops had nucleated onto slip planes that intersected the interface along these highly strained misfit lines.

This observation of nucleation along misfit dislocation lines suggested a direct relationship between the dislocation network lying in the plane of the interface and lattice dislocation nucleation. Thus, two interfaces with different misfit dislocation networks may not nucleate the same dislocation under the same stress state. This further implies that interfaces can be designed to govern crystal plasticity by controlling the number, type, and rate of mobile dislocations emitted from the interface.

Results from a recent shock compression simulation of Cu-Nb 5 nm multilayers demonstrated clearly that interface structure can drive plasticity [138]. Two models were constructed differing in the interface character, one with a $\{112\}\langle 111\rangle\text{Cu}||\{112\}\langle 110\rangle\text{Nb}$ interface and the other with a $\{111\}\langle 110\rangle\text{Cu}||\{110\}\langle 111\rangle\text{Nb}$ Kurdjumov-Sachs (KS) interface. The shock caused the dislocations to first nucleate into the Cu phase from the pristine interfaces. Again, these dislocations nucleated along the misfit dislocation lines intrinsic to these interfaces. However, both the critical stress for dislocation nucleation and the number of dislocation slip systems activated (on which mobile dislocations nucleate) were significantly different between the two interfaces (Fig. 2.7). Clearly interface structure played a role; however, the crystallographic orientations of the Cu and Nb crystals with respect to the shock direction were also different. Crystal orientation is well known to affect both the elastic and plastic responses of Cu and Nb crystals [153-157]. Thus, in this shock study, the effect of interface structure could not be completely separated from that of crystallographic orientation.

Later, a small-scale study was carried out in an attempt to isolate the effect of interface structure on dislocation nucleation. The two interfaces generated were the KS and Nishiyama-Wasserman (NW) interfaces, which have nearly the same formation energy ($\sim 576\text{-}586\text{ mJ/m}^2$) [48, 152]. They are only misoriented by 5° , and hence under the stress state, differences in the Schmid factors of all slip systems are negligible. As desired, the main difference between these two interfaces was their atomic structure, as shown in Fig. 2.8. Interface defect analysis was carried out to describe their structure in terms of a discrete misfit dislocation network [151]. These calculations found that characteristics of their networks differ significantly, both in the number of misfit dislocation arrays and in the line orientation and Burgers vectors of these arrays.

As anticipated, the structural differences between these two interfaces were observed to profoundly affect nucleation behavior. Under a tensile loading along the $[11\bar{2}]_{fcc}$ direction, the KS interface nucleates Shockley partial dislocations only on one of these glide systems in Cu (Fig. 2.9a), whereas the NW interface nucleates partials on two distinct systems (Fig. 2.9b). In both cases, the emitted dislocations were associated with slip systems with a positive Schmid factor and with crystallographic slip planes that intersected the interface plane along a misfit dislocation line. Another important observation was that there were other equally stressed slip systems and other misfit lines within the same interface that did not produce dislocation loops. Evidently, not all misfit dislocation lines are sites for dislocations and not all stress-driven slip systems can be activated from an interface. Clearly the interface structure strongly biased where and which dislocations nucleated.

To understand the bias, we first recall why dislocations are emitted from interfaces. From a pristine interface, emission of mobile dislocations occurs as a consequence of an applied stress.

Without an applied stress, dislocation emission is not favored, since the misfit dislocations intrinsic to the pristine interface were generated to remove the coherency stress. An applied stress, however, disturbs the perfect interface structure and increases its energy. It is expected that dislocation nucleation can potentially relieve these stress concentrations, do plastic work in the adjoining crystals, and lower the energy of the strained interface. However, as was seen in simulation, not all mechanically driven slip systems that can do work in the crystal are emitted from the interface. Furthermore, not all misfits that generate stress concentrations in the interface result in dislocation emission. Thus, we turn to the last form of relief, which is related to how nucleation alters the interface structure. This leads to the hypothesis that only those dislocations that lead to a reduction in the local interface energy after their emission are preferred.

Because of the misfit dislocation network, the stress field generated within a strained interface is non-uniform. The heterogeneous strain field of a strained interface is not assessable analytically but a few basic trends have been obtained via calculation. Disregistry analysis has shown that localized strains tend to develop along the interfacial (misfit) dislocation (ID) lines and at their intersections (MDIs), and the coherent regions in-between experience considerably less strain [139]. Further, the strain concentrations along the misfit dislocations tend to act along their lines $\xi^{(i)}$ and have magnitudes that scale with the value of their Burgers vector $\mathbf{b}_l^{(i)}$. This last relationship, albeit qualitative, has proven useful in understanding where and which dislocations nucleate from an interface, as will be described next.

2.2.4. Geometric relationships between the interface and adjoining crystals

In this section, we discuss dislocation nucleation from pristine interfaces that can be well described by a discrete misfit dislocation network. For such an interface under an applied stress state, three types of geometric relationships can be defined. The first one is the orientation relationship between the loading state and the ensemble of two crystals joined at a common interface. This one provides some guidance as to which dislocations in the crystals could be driven to nucleate from the interface in either one or both crystals. The remaining two are related to the interface (crystallographic) character, defined, at minimum, by the interface plane and orientation relationship. (The interface plane is associated with a particular crystallographic plane in each crystal and the interface orientation relationship defines which crystallographic axes of each crystal are parallel.) The interface character not only determines the characteristics of the misfit dislocation network but also the relationships between a) the slip systems on which dislocations can nucleate on either side of the interface and b) the misfit dislocation network, which are of interest for nucleation. The second type of geometric relationship consists of the orientation relationships between the Burgers vectors of the misfit dislocations in the interface $\mathbf{b}_l^{(i)}$ and the lattice dislocations $\mathbf{b}_p^{(j)}$ that are emitted from the interface. The third type consists of the orientation relationships made by the intersection lines $\eta^{(i)}$ between the slip planes in the crystals and the interface plane and the dislocation line orientations $\xi^{(i)}$ in the network in the interface. (Note the symbol for the vectors for the intersection lines $\eta^{(i)}$ is not to be confused with the symbol for sink efficiency in Section 2.1.) The above three types of geometric relationships will be used in tandem in the nucleation model below.

In a pristine interface with a well-defined dislocation network, there are three potential nucleation sites ($k = 0, 1, 2$): the misfit dislocation lines ($k = 1$), the misfit dislocation

intersections ($k = 2$, where a junction line forms), and the coherent regions in-between ($k = 0$). For the first two sites ($k = 1, 2$), a Burgers vector $\mathbf{b}_l^{(i)}$ and line orientation $\xi^{(i)}$ can be determined.

We reduce the set of slip systems to *candidate slip systems* on which lattice dislocations (LDs) will potentially nucleate. These are slip systems that do work in the crystal when activated. These can be identified by considering the orientation relationship between the deformation state and the crystallographic orientation. For an fcc crystal, for instance, Shockley partials $\{111\}\langle 112 \rangle$ are the first to be emitted. Among these, the candidate systems for nucleation are those that:

- 1) Form intrinsic faults in the crystal when they are emitted from the interface.
- 2) Have resolved shear stresses that can drive them away from the interface (2.2.1)

Now suppose that a lattice dislocation LD (j) with Burgers vector $\mathbf{b}_p^{(j)}$ nucleates at an interface site k that has a net Burgers vector of $\mathbf{BX}^{(k)}$ (whether a misfit line $k = 1$ or junction $k = 2$). Conservation of the Burgers vector dictates that

$$\mathbf{BX}^{(k)} = \mathbf{b}^{r(ij)} + \mathbf{b}_p^{(j)} \quad (2.2.2)$$

where $\mathbf{b}^{r(ij)}$ is the residual defect remaining at this interfacial site after nucleation of LD (j) and $\mathbf{BX}^{(1)} = \mathbf{b}_l^{(j)}$ for a misfit line or $\mathbf{BX}^{(2)} = \mathbf{b}_l^{(i)} + \mathbf{b}_l^{(l)}$ for a junction line. The residual $\mathbf{b}^{r(ij)}$ locally changes the interface structure.

The corresponding energy expression associated with the nucleation event is

$$\Delta E^{(ij)} = E_{core}^{(ij)} + E_{if}^{(ij)} + W_{int}^{(ij)} \quad (2.2.3)$$

where $E_{core}^{(ij)}$ is the core energy of the Shockley partial in the crystal, which scales with the value of $\mathbf{b}_p^{(j)}$ [135], $E_{if}^{(ij)}$ is the change in the interface energy at the nucleation site, and $W_{int}^{(ij)}$ represents the interaction energies between $\mathbf{b}^{r(ij)}$ and $\mathbf{b}_p^{(j)}$. Among the candidate slip systems, those that lead to a reduction in $\Delta E^{(ij)}$ are likely to nucleate.

Of the three terms in Eq. 2.2.3, the one that is the most sensitive to changes in interface structure due to nucleation is $E_{if}^{(ij)}$. Lowering $E_{if}^{(ij)}$ requires that the residual dislocation left after the nucleation event can reduce the strain energy of the interface. Calculating $E_{if}^{(ij)}$ can be done via MD simulation. However, to attain a general understanding of the role of dislocation structure on nucleation, we aim to identify a few simple geometric relationships between the lattice dislocations being emitted and the misfit dislocations in the interface that would lower $E_{if}^{(ij)}$. These will later be tested against MD simulations of dislocation nucleation from interfaces.

In a strained interface, misfit lines generate strain concentrations and thus reducing $E_{if}^{(ij)}$ by the greatest amount would correspond to nucleation events that lead to a smaller $\mathbf{b}^{r(ij)}$ along the misfit lines. On this basis, whether LD (j) can nucleate along ID (i) is based on two geometric criteria:

1) The Burgers vector $\mathbf{b}_p^{(j)}$ of LD (j) acts in the same direction as the Burgers vector $\mathbf{b}_l^{(i)}$ of misfit dislocation ID (i), i.e.,

$$\mathbf{b}_p^{(j)} \cdot \mathbf{b}_l^{(i)} > 0 \quad (2.2.4)$$

2) The interface segment of LD (j) deposited along $\boldsymbol{\eta}^{(i)}$ after nucleation lies (nearly) parallel to the ID line $\boldsymbol{\xi}^{(i)}$. In other words, the minimum angle $\theta^{(ij)}$ between the line orientation $\boldsymbol{\xi}^{(i)}$ of an ID (i) and trace $\boldsymbol{\eta}^{(i)}$ of the LD (j), is nearly zero; that is,

$$\theta^{(ij)} = \cos^{-1}(\boldsymbol{\xi}^{(i)} \cdot \boldsymbol{\eta}^{(j)}) \leq \theta_c \quad (2.2.5)$$

is no greater than a small tolerance θ_c , at most 10° . If these criteria are met, then nucleation of LD (j) from the interface along misfit dislocation ID (i) is preferred. The favorability arises because this event reduces $E_{if}^{(ij)}$. These criteria were tested against the interfaces investigated via MD simulation in Figs. 2.7 to 2.9. They successfully explained why two slip systems with the same Schmid factor did not have the same propensity to nucleate. They predicted, in agreement with MD simulation, the particular slip systems that were seen to emanate from the interface.

The situation could arise where none of the candidate slip systems (Eq. 2.2.1) satisfy criteria Eqs. 2.2.4 and 2.2.5 with any of the misfit dislocation lines in the network. However they could satisfy these criteria with one of the junction lines formed at the intersection of two non-planar misfit dislocation arrays. If so, dislocation loops can nucleate at these junctions.

Figure 2.10 shows an example of junction-nucleation from a $\{112\}<111>\text{Cu}||\{112\}<110>\text{Nb}$ interface. This interface contains two parallel misfit arrays and a third array that is oriented 90° from the first two [131, 158]. In Fig. 2.10, this interface has been strained in a direction such that none of the candidate slip systems (Eq. 2.2.1) satisfy both criteria (Eqs. 2.2.4 and 2.2.5) with any of the three misfit dislocation arrays. However, the junctions formed at misfit dislocation intersections between two of these arrays do satisfy the criteria. As predicted, dislocation loops are seen to nucleate only from these junctions and not along misfit lines (Fig. 2.10).

The three possible nucleation sites are not equal in their propensity for nucleating a dislocation. Within the same interface and loading state, misfit-line nucleation would be easier than junction-nucleation. MD simulations find that dislocation loops formed via misfit-line nucleation tend to expand along the misfit line, relieving an increasing region of the interface with increasing loop size [139, 159]. Comparatively, loops emitted from junctions in the interface are limited in the distance they can expand within the interface plane (Fig. 2.10) [160]. Last, nucleating a dislocation within the coherent regions of an interface between dislocation lines is the least favorable nucleation mode since it would destroy the coherent structure.

2.2.5. Mapping nucleation site of a given slip system

The above joint theoretical and numerical study provides for and validates a geometric-based argument for *which* dislocations nucleate and *where* they prefer to nucleate from a pristine interface. Two geometric criteria were presented. These were based on the notion that the drive to reduce the local interface energy $E_{if}^{(ij)}$ by the greatest amount favors nucleation of certain

dislocations. To generalize this insight to other interfaces, some simple expressions representing criteria 1) and 2) were devised.

For the first criterion, a factor $A^{(ij)}$ is introduced to measure the degree of alignment between the Burgers vector of the misfit (i) $\mathbf{b}_I^{(i)}$ and slip system (j) $\mathbf{b}_P^{(j)}$ in question (Eq. 2.2.4).

$$A^{(ij)} = p\langle \mathbf{b}_{le}^{(i)} \cdot \mathbf{b}_P^{(j)} \rangle + (1-p)\langle \mathbf{b}_{ls}^{(i)} \cdot \mathbf{b}_P^{(j)} \rangle + \langle \mathbf{b}_{IN}^{(i)} \cdot \mathbf{b}_P^{(j)} \rangle. \quad (2.2.6)$$

Reading from left to right, the three terms correspond to the contribution of the in-plane edge, in-plane screw, and out-of-plane (edge) component of $\mathbf{b}_I^{(i)}$. The parameter p , which ranges from 0 to $\frac{1}{2}$, further biases the relative contributions of the edge and screw parts of the in-plane Burgers vector component of $\mathbf{b}_I^{(i)}$. For demonstration, we use $p = \frac{1}{2}$, so that screw and edge components have equal weight; however, it may be the case that screw components, which could place the interface in a greater degree of in-plane shear, would have a greater influence on dislocation emission.

For the second criterion, the following factor $S^{(ij)}$ is introduced to quantify alignment in line orientation (Eq. 2.2.5):

$$S^{(ij)} = \text{sech} \left(\frac{\theta^{(ij)}}{\theta_c} \right), \quad (2.2.7)$$

which varies from 0 to 1. When $\theta^{(ij)} = 0$, $S^{(ij)}$ equals 1. When $\theta^{(ij)}$ exceeds θ_c , $S^{(ij)}$ drops below ~ 0.5 .

Plotting these two measures, Eqs. 2.2.6 and 2.2.7, creates the map in Fig. 2.11 that identifies the type of nucleation site expected for a given lattice dislocation from a given interface structure. Slip systems that satisfy both criteria (Eqs. 2.2.4 and 2.2.5) will land in the upper right-hand corner of the map, will form along a misfit line, and are easiest to nucleate. Other slip systems that lie in other parts of the map, such as the central part corresponding to junction nucleation, or the lower left-hand corner, for nucleation within a coherent region, represent relatively harder modes of nucleation from the interface. For instance, straining the KS or NW interfaces in different uniaxial directions finds that at least one candidate slip system will nucleate along a misfit line [159]. Straining the same $\{112\}\langle 111 \rangle \text{Cull}\{112\}\langle 110 \rangle \text{Nb}$ interface in one direction, the map can predict misfit-line nucleation for at least one candidate slip system, whereas in another direction (Fig. 2.10), it predicts junction nucleation [160].

2.2.6. Outstanding questions

This review of recent progress in dislocation nucleation at interfaces has demonstrated that bimetal interface structure profoundly affects dislocation nucleation. Yet these advances only serve to open up still more questions concerning the possible ways in which interface structure can impact dislocation nucleation. First, for bimetal interfaces, changes in mismatch between the two dissimilar metals can change misfit array spacing and the density of misfit dislocation junctions. The associated changes in mesh length will alter the critical stresses to nucleate and expand the loop into the crystal. Second, most of the above MD studies were carried out at very low homologous temperatures in order to isolate the effect of structure on nucleation behavior.

As a consequence, the critical nucleation stresses were relatively large and do not incorporate significant aid by thermal activation. Furthermore, in the Cu-Nb system, nucleation was preferred in the fcc Cu phase. Nucleation of dislocations into bcc crystals and the effects of temperature on the energetics of nucleation from bimetal interfaces have yet to be explored. Third, there are other classes of interfaces, such as grain boundaries or phase boundaries between other crystal structures (bcc/bcc, hcp/bcc), exhibiting structural order. These metals deform on many more slip systems and modes than fcc and it would be interesting to see if the interface can alter the predominance of one slip mode over another differently than observed in the bulk crystal. Last, the theory described above applies to pristine interfaces that can be modeled by a network of distinct and discrete dislocations. Many pristine interfaces, however, possess ordered atomic structures that cannot be described by such a network. Furthermore, after exposure to extreme environments, pristine interfaces can accumulate defects, losing their original regular structure. Only recently has attention been paid to whether the mechanisms for dislocation nucleation in such irregularly structured interfaces change from those operating in interfaces possessing discrete dislocation networks [161]. The results suggest that the above a critical concentration of vacancies in the interface, nucleation behavior can be significantly altered, a finding that clearly indicates that further exploration is needed.

2.3. Planar defects: deformation twin nucleation

The plastic deformation of a metallic grain is accommodated primarily by the motion of dislocations. For some metals under certain conditions of temperature and strain rate, a second mechanism for accommodating grain deformation, deformation twinning, can operate in addition to dislocation slip. Unlike dislocation slip, deformation twins suddenly reorient the crystallographic lattice of the grain and create a coherent boundary between the twinned orientation and the original parent orientation [162, 163]. Both the reorientation and boundaries introduced by twins can significantly change the way the grain responds to strain. The reoriented twin domains can be more (or less) favorable for slip compared to the original grain orientation and the twin boundaries can act as obstacles to slip. This interplay of slip and twinning within the crystal has been known to greatly affect the flow stress, strain hardening, and elastic and plastic anisotropy of the polycrystal [164-167]. For this reason, for several decades understanding when and where twinning occurs in metallic crystals has been a subject of intense research. For the most part, coarse-grained single- and poly-crystalline metals have been studied. In these systems, it has been observed that the propensity to twin depends on crystal orientation and alloy composition and tends to increase with increases in strain rate, decreases in temperature, decreases in stacking fault energy, and increases in grain size [162, 163, 168]. Throughout these years, several mechanisms for twin nucleation and growth have also been proposed. Most of these ideas presume that twins are triggered by pre-existing defects, dislocations in the grains and grain boundaries.

For nanocrystalline metals with grains of fine dimensions (e.g., < 100 nm), twins originate from the grain boundaries and interfaces [169-171]. Consequently, some of the trends seen in coarse-grained metals may not apply to nanostructured metals. Numerous experimental studies have shown that some fcc metals, such as Ni, Al, and Cu, that do not twin easily as coarse-grained structures twin much more easily as nano-grained structures [172-175]. Consequently, over the past few decades, several studies have been devoted to identifying the mechanisms for twinning

from grain boundaries and free surfaces in single-phase nanostructured metals [156, 172, 174, 176, 177].

Compared to twinning in single-phase fcc nanocrystals, there are far fewer investigations of twins in two-phase nanocomposites. As in single-phase metals, twins are often seen connected to or emanating from the bimetal interfaces in such materials [144, 146, 178]. Bimetal interfaces can take on special atomic structures distinct from those seen in ordinary grain boundaries (see Sects. 1 and 2.2). Possible correlations between the propensity for twinning and the structure of the bimetal interfaces have not been as thoroughly studied and hence deserve particular attention.

2.3.1. Evidence of twinning in fcc metals from bimetal interfaces

Studies on twin formation from bimetal interfaces have largely focused on twinning in the fcc phase of the composite, perhaps to build upon the large body of work on single-phase fcc metals. The dislocation responsible for twinning in fcc metals is a Shockley partial dislocation $\mathbf{b}_s$, which glides on the $\{111\}$ plane in the $\langle 112 \rangle$ direction [135]. There are four independently oriented $\{111\}$ planes and three different partials on each, giving 12 twinning systems with distinct Burgers vector. As these partials glide, they leave behind an intrinsic stacking fault with formation energy γ . Fcc deformation twins form by the glide of Shockley partial dislocations on adjacent planes [135]. These partials may have similar or unlike Burgers vectors belonging to the $\{111\}\langle 112 \rangle$ twinning family. Theoretical considerations and numerical calculations have suggested that a minimum of two adjacent fault layers can form a nascent, stable fcc twin [179, 180]. Much like grain boundaries, the bimetal interfaces can serve as a source for the Shockley partial dislocations needed to form a twin in the fcc phase.

Two fcc-based composite systems are examined below, both containing pure Cu, a material that alone does not twin so easily due to its intermediate value of γ . One material system is Ag-Cu and the other Cu-Nb. The former combines Cu with Ag, a material that alone twins easily at room temperature due to its low intrinsic stacking fault energy γ . The latter one, however, joins Cu with Nb, a material that is even harder to deformation twin than Cu.

In a few studies, in room temperature and quasi-static conditions, twins have been observed to form from Ag-Cu interfaces in Ag-Cu nanocomposites. In such deformation conditions, twinning is expected in coarse-grained Ag but not in coarse-grained Cu. In cold-wire-drawn Ag-Cu filaments, twins in both Ag and Cu were seen emanating from Ag-Cu interfaces [181, 182]. In rolled cast eutectic Ag-Cu composites, profuse deformation twinning occurred in the Cu phase after 75% rolling reduction (1.6 strain) [144]. X-ray analysis of the deformation texture of the Cu phase suggested that the twin volume fraction was at least 30% (Fig. 2.12).

In the case of rolling, the mechanisms of deformation twinning were studied in detail [144]. In the as-cast composite, the Ag and Cu crystals are joined at their mutual $\{111\}$ planes and for a majority of these Ag-Cu interfaces, the interface orientation relationship is cube-on-cube¹. TEM analyses of the microstructure before and after rolling indicated that the Ag-Cu interfaces had transformed from their initial $\{111\}$ interface plane to a $\{001\}$ interface plane (Fig. 2.13). The connection between this change and deformation twinning was later demonstrated by MD

¹ Cube-on-cube refers to a special orientation relationship between two cubic crystals in which all crystallographic axes of the two crystals are parallel.

simulation. An MD model showed that with sufficient stress, twinning partials in Ag are able to cross Ag-Cu interfaces with a cube-on-cube orientation relationship and result in the $\{111\}$ -to- $\{001\}$ transformation of the interface plane [143]. Figure 2.14 shows a snapshot from this MD simulation where a set of Ag twinning partials have impinged on the $\{111\}$ interface, entered it, and re-emitted as twinning partials in Cu. As shown, the transmission event leaves a $\{001\}$ step in the interface. Evidently during deformation, the twinning partials needed for twins in Cu originated from Ag. Twins generated in Ag were able to cross the Ag-Cu interfaces and re-emit as twins in Cu.

Based on the above insight, it can be envisioned that building a twin domain in Cu would require sequential interface transmissions of twinning partials from Ag to Cu. Each event must leave a residual dislocation that remains in the interface. Consequently, expansion of the Cu twin would lead to the accumulation of many residuals within the interface and increases in interface energy. In order to reduce the interface energy, it was proposed that the smaller residuals rearranged into larger steps, which then dissociated into very fine twins or stacking fault layers into the adjoining crystals on either side of the interface [143]. Fig. 2.15a illustrates the proposed sequence of events from the rearrangement of the residuals to subsequent twin emission. Notably, this phenomenon explained the observation of very fine twins emanating from the $\{001\}$ interface into both the Cu and Ag crystals (Fig. 2.15b).

The other nanocomposite system in which deformation twinning has been studied is Cu-Nb [146, 178, 181, 183]. Deformation twins have been observed in the Cu phase of wire-drawn, nanostructured Cu-Nb filaments in the vicinity of the Cu-Nb interfaces [181]. It was presumed that these twins formed to relieve stress concentrations generated at the bimetal interfaces. Twins have also been reported in the Cu phase of accumulative roll bonded (ARB) nanolayered Cu-Nb composites [146, 184]. For this material, Figure 2.16 shows the progression of twinning in the Cu phase with increasing rolling strain (the rolling direction is horizontal in the figure). As the Cu layer thickness h is reduced from 135 nm to 10 nm, the frequency of twinning in Cu increased from $< 5\%$ to $\sim 30\%$ [146, 178].

In order to gain some understanding of the types of dislocations within the twin and the possible sequence of dislocation emissions from the bimetal interface that constructed the twin, TEM analyses were performed in the vicinity of the twin/interface area. Figure 2.17a shows a HRTEM image of a twin emanating from the $\{112\}<110>\text{fcc}||\{112\}<111>\text{bcc}$ interface [146, 185]. Since the Cu grain has twinned and the Nb grain has not, the original $\{112\}<110>\text{fcc}||\{112\}<111>\text{bcc}$ Cu-Nb interface has changed its orientation relationship within the twinned domain. As shown in the HRTEM image, the interface has reoriented to a $\{552\}<110>\text{fcc}||\{112\}<111>\text{bcc}$ orientation relationship.

Further, we note that this twinned Cu/Nb interface is morphologically flat, which many believe provides information on how the twin formed. Two opposing reasons have been given for this flat configuration. In one case, the flat interface after twinning may have resulted from the emission of twinning partials with different Burgers vectors. This mechanism is the same as the random activation partial (RAP) emission mechanism or the zero-strain twin mechanisms that have been proposed for twinning in nanocrystalline fcc metals [172]. Fig. 2.17b shows some evidence of zero-strain twinning via emission of a group of partials from the Cu-Nb interface with an incoherent $\Sigma 3$ twin front that is vertical, which indicates a zero-strain twin. Alternatively,

the flat interface could have formed from emission of like twinning dislocations, which is analogous to the multiple activation partials (MAP) mechanism proposed for grain boundaries [176]. Expanding the twin via sequential emission of partials of like sign and like Burgers vector would be expected to leave the interface kinked rather than flat. However, TEM analysis of twin formation from a Cu-Nb interface suggests that after twinning, the residuals left in the interface could have rearranged to a lower energy configuration corresponding to a morphologically flat interface [184, 186] (Fig. 2.18).

As another way to examine the kinetics of twin growth from bimetal interfaces, an in-situ nanoindentation study was carried out on a Cu-Nb nanocomposite fabricated by ARB (with $h = 20$ nm layers) [146]. The authors observed that twin formation began by the nucleation of two fine twins separated by ~ 10 nm within the same crystalline layer. Subsequently, more fine (two-layer) twins from the opposing interfaces on either side of this crystalline layer were emitted into the crystal just within the 10 nm region in-between the first two fine twins. This process of twin emission from both opposing interfaces continued until the 10 nm region twinned entirely. The observed alternate-emission process [146] revealed another way in which the flat interface observed in Fig. 2.19 could have been produced.

Based on the above, the partials that constructed the twins from bimetal interfaces could have possessed like or dissimilar Burgers vectors; neither possibility can be discounted. Layers in which twins had formed had thinned under deformation, indicating that the twins contributed to strain accommodation. Further, a high-resolution EBSD study recently showed that twinning in the Cu layers was strongly dependent on crystallographic orientation [156]. Because twins accommodate strain and exhibit strong orientation effects, we suspect that a majority of these twins involved emissions of partials with the same Burgers vectors from the interfaces.

Comparing results from recent experimental studies on Cu-Nb nanocomposites points to the interface structure as another possible factor influencing the propensity to twin. As seen in Fig. 2.16, when ARB Cu-Nb nanolayered materials are rolled to layer thicknesses below 60 nm, deformation twins in Cu began to form from the interface [156, 185]. However, when the layers of Cu-Nb nanocomposites fabricated by physical vapor deposition (PVD) were rolled below 60 nm under similar conditions, no twinning was observed [183, 187]. In fact, there is little or no evidence of twinning in the PVD nanocomposites when they are deformed via in-plane tension over a range of temperatures [188-190], micropillar compression normal to the interfaces [191], and in shear applied parallel to the layers [148, 192]. It has also been observed that twinning is suppressed in the ARB nanocomposite system when the rolling direction was altered 90° to reduce the layers below 60 nm [10, 193]. Although these three Cu-Nb layered composites did not vary appreciably in material details or nanolayer thickness and were rolled under similar conditions (room temperature and low rates), twins appeared in the first but not the second and third. In each case, the Cu crystals were oriented differently, a factor that can possibly explain their different tendencies for twinning. Another outstanding difference is the crystallographic character of their interfaces. The PVD Cu-Nb nanocomposites contain predominantly $\{111\}<110>\text{Cu}||\{110\}<111>\text{Nb}$ interfaces [194, 195], the ARB nanocomposites mainly $\{112\}<111>\text{fcc}||\{112\}<110>\text{bcc}$ interfaces [194, 196], and the ARB nanocomposites after the orthogonal strain path change, a prevailing $\{110\}<111>\text{fcc}||\{001\}<110>\text{bcc}$ interface [10]. As twins would have formed from the bimetal interfaces, it may be inferred that in addition to

crystal orientation, the interface character and its corresponding defect structure could also influence whether twinning occurs.

2.3.2. Model for twinning from a bimetal interface

The above observations motivate two key questions: how are twins emitted from the bimetal interface into the crystal and what is the role of interface structure in the emission process? As an attempt to address these questions, below we review a model that considers deformation twin formation from pristine interfaces. These are interfaces that contain only misfit dislocations intrinsic to its structure and no extrinsic dislocations. The misfit dislocation structure can be generally described as a network of n intersecting dislocations arrays, $i = 1, \dots, n$, where all dislocations belonging to the same array (i) have the same Burgers vector $\mathbf{B}^{(i)}$ and line orientation $\xi^{(i)}$. The model accounts for two possible ways in which this interface, when stressed, can produce twinning dislocations. Both ways have been proposed previously based on calculations via dislocation theory or MD simulation [141, 178, 186]. In the first, one or more of the sets of misfit dislocations can dissociate into Shockley partials. These partials glide into the adjoining fcc crystal, leaving stacking faults behind. Consequently, an array of regularly separated stacking faults is produced. Further straining emits Shockley partials on planes adjacent to these stacking faults, forming a twin. The second way involves dislocations gliding within the adjoining crystal. Under stress, lattice dislocations in one crystal intersect the interface, cross it, and emit a Shockley partial in the other (fcc) crystal. As this interface transmission process continues, a twin or twins can form.

2.3.3. Twinning via nucleation directly from the interface

We begin by modeling the first mechanism, in which Shockley partial dislocations nucleate directly from the interface and form twins. Fig. 2.20 illustrates a possible sequence of events according to this mechanism. In the first step, one set of intrinsic interfacial dislocations have dissociated into Shockley partials. As the Shockley partials are emitted, they produce stacking faults, which we call the first faults (see sf1 and sf2 in Fig. 2.20a). The regular spacing of these first faults equals that of the interfacial dislocations that have dissociated. Generally the spacing is more than one atomic plane.

Whether an interface dislocation can dissociate to emit this Shockley partial depends on the characteristics of the interface dislocation. A favorable dissociation would leave a smaller residual dislocation at the interface and hence lower its energy. Thus, interface dislocations with similar characteristics as the Shockley partial, i.e., with a large non-planar interface component and directed in a similar sense, are more prone to producing it. To quantify the degree to which the dissociation reaction could occur, we consider cases when B_N , the magnitude of the out-of-plane Burgers vector component of the interface dislocation, is larger than b_s , the value of the Burgers vector of the partial. Accordingly, an interface dislocation array (i) with spacing $s^{(i)}$ is prone to dissociating into an fcc partial with Burgers vector b_s , when this ratio exceeds unity, i.e.,

$$\frac{B_N^{(i)}}{b_s} > 1 \quad (2.3.1)$$

For several model interfaces, Table 2.1 lists the largest value of $B_N^{(i)}$ among the interfacial dislocations in a given interface [178]. These were calculated using methods described in [131,

158]. Note that for some interfaces, such as KS and NW, all the interfacial dislocations have only in-plane components and thus $B_N^{(i)}$ is null for these interfaces.

To form a twin, a second step is required. The regular array of first stacking faults are not twins but they can act as precursors to the formation of a twin. A twin is constructed of partials lying on adjacent planes. In the region between the first faults, a second set of partial dislocations could nucleate from the interface and glide on planes adjacent to the first faults (Fig. 2.20b). This action would cause the region s between two adjacent first faults to transform into a twin.

The driving forces for the second step are strain energy and elimination of the fault boundaries in between. Opposing these, however, is the barrier to create the additional partial dislocations. Physically, this competition means that, in order for the second step to occur, the spacing between the first faults s would have to be sufficiently small, such that the number of Shockley partials that need to be subsequently nucleated would be small. Or vice versa, when the first faults are well separated, twinning would not be favored as it is energetically difficult to nucleate a large number of partials.

Suppose the first faults are a distance s apart. The number k of unfaulted planes spanning s is equal to the number of partials that need to be subsequently formed. The relationship between k and the spacing s is

$$s = (k+1)d/\sin\theta, \quad (2.3.2)$$

where d is the interplanar spacing for the twin plane and θ is the angle between twin and interface planes. We define a critical k^* above which nucleation of fresh partial dislocations becomes unfavorable. Accordingly, twinning is favored when $s < s^*$ or equivalently $k < k^*$. This leads to the following criterion for the second step toward twinning [178]:

$$\frac{d(k^*+1)}{s^{(i)} \sin \theta} > 1 \quad (2.3.3)$$

The critical k^* , above which twinning is not possible, can be estimated via the following energetic expression for the change in energy due to the nucleation of k twinning dislocations [178]:

$$\Delta E = kE^{self} + \frac{(k+1)}{\sin\theta} \Delta E^{int} - E^{sf} - W^{int}(k) - kW^{strain} < 0 \quad (2.3.4)$$

where l_x is the distance traveled by the k TDs (Fig. 2.20b). The first term is the self-energy of the k TDs. The second term ΔE^{int} is the change in the interface energy per length, which includes the change in formation energy and compatibility with the adjoining crystal on the other side of the interface. The third term is the reduction in energy due to the removal of the two interior stacking faults. The fourth is the interaction energy between the partials, particularly involving the interaction between the oppositely signed k TDs created upon nucleation. The last term is the work term, the strain energy supplied by the glide k TDs. In the case of nanolayered Cu ($h < 100$ nm), k^* is estimated to be 2 [178]. This means that when there are more than two atomic planes between the first faults, twins cannot form easily via the mechanism of direct dissociation.

Achieving both steps, which are determined by Eqs. 2.3.1 and 2.3.3, is essential for twin formation. Accordingly, the product of these two expressions can measure the likelihood that twinning occurs. As both measures are related to the structure of the interface, one to the Burgers vector of the misfit array (i) and the other to the dislocation spacing, we denote their product as S and use it to assess whether twin formation is possible directly from the interface at interfacial dislocation array (i):

$$S^{(i)} = \left(\frac{B_N^{(i)}}{b_s} \right) \frac{d(k+1)}{s^{(i)} \sin \theta}$$

For an interface containing more than one array of interfacial dislocations, its twinning propensity can be measured by whether the array (i) with the largest $S^{(i)}$, is greater than unity, that is:

$$S_{\max} = \max_i S^{(i)} > 1 \quad (2.3.5)$$

2.3.4. Twinning via slip transmission across the interface

Next we consider modeling the second interface-driven mechanism for twinning. This one relies on the transmission of dislocations from one crystal across the interface to the other. Various called glide transmission, slip transmission, or dislocation transmission, this interfacial phenomenon involves a sequence of events, beginning with a lattice dislocation from the adjoining crystal running into their common interface, entering the interface, and eventually emitting into the fcc crystal as a twinning dislocation. When a dislocation fully traverses the interface, a residual dislocation is then left behind in the interface.

Whether the dislocation can transmit across the interface depends on many factors. Below we identify three variables that depend on interface structure and can affect the propensity for a dislocation to cross. One variable is related to the resistance of an interface to shear along the interface plane, another to the interface crystallography, and the last one to mechanical stress. In doing so, it is assumed that the interface remains intact during the transmission event and accommodates the residual dislocation that has been left behind.

The first one concerns the structure of the lattice dislocation after it has run into the interface and entered it. The core of the dislocation can spread in plane to a certain extent w [159, 197-199]. Transmission across the interface is easier when the core remains compact with minimal additional spreading. When the absorbed dislocation core becomes too wide, transmission becomes difficult. In this case, the dislocation remains trapped in the interface and does not pass into the other crystal.

The degree of spreading has been related to various measures of interfacial shear strength τ_{ISS} [197-199]. The value of τ_{ISS} is related to the structure of the interface at an atomic level. Generally when the interface plane corresponds to the glide plane in the crystal, such as the $\{111\}$ plane in an fcc crystal or $\{110\}$ plane in a bcc crystal, interface core spreading is promoted and the interfacial shear strength is low. Smaller amounts of core spreading and higher τ_{ISS} are associated with interface planes that are not glide planes (i.e., not atomically dense).

The second factor considered, interface crystallography, is associated with the orientation relationship of the incoming and outgoing slip/twin systems across the interface. Let α represent the incoming slip system and β the outgoing twinning system. Transmission is favored when the slip direction and slip plane of α and β are well aligned across the interface. As a measure of this alignment the following factor was adopted:

$$\left\langle \cos\left(\frac{\pi \Psi^{\alpha\beta}}{2 \Psi_c}\right) \right\rangle \left\langle \cos\left(\frac{\pi \theta^{\alpha\beta}}{2 \theta_c}\right) \right\rangle \quad (2.3.6)$$

which was first introduced by Werner and Prandl [200]. In Eq. 2.3.6, $\Psi^{\alpha\beta}$ is the angle between the Burgers vectors and $\theta^{\alpha\beta}$ is the angle between the glide plane and interface intersection lines of α and β . We use the brackets $\langle \rangle$ to signify that $\langle x \rangle$ equals x when $x > 0$ but $\langle x \rangle$ equals zero otherwise. Accordingly, when either $\Psi^{\alpha\beta}$ or $\theta^{\alpha\beta}$ exceeds their assigned limit Ψ_c or θ_c , respectively, the quantity in Eq. 2.3.6 is zero. Physically, this criterion reflects that the better aligned the incoming and outgoing slip systems, the smaller the size of the residual Burgers vector left behind at the interface. Thus, the interface incurs a smaller increase in its energy, which can favor the transmission event [201, 202].

Last, considering mechanical driving forces, transmission is favored when the crystals are oriented with respect to the loading, such that dislocations on α are stress-driven toward the interface and those on β are stress-driven to propagate away from it. As a simple, geometry-based alternative to calculating the resolved shear stresses on α and β , we use their corresponding Schmid factors m_α and m_β . For slip transmission, the m_α for the incoming glide dislocation must be positive when directed into the interface and the m_β for the outgoing TD must be positive when directed away from the interface. In this way, the orientations of the crystal on both sides of the interface also play a role in the transmission process. In selecting the dislocations for calculating these Schmid factors, one must take care that the dislocations being transmitted from α to β must have the same line sense ξ .

The influence of the last two factors, interface crystallography and stress state, on the propensity for slip transmission can be reflected in one geometric measure g , given by

$$g = \left\langle \cos\left(\frac{\pi \Psi^{\alpha\beta}}{2 \Psi_c}\right) \right\rangle \left\langle \cos\left(\frac{\pi \theta^{\alpha\beta}}{2 \theta_c}\right) \right\rangle [m_\alpha]_\xi [m_\beta]_\xi \quad (2.3.7)$$

where the $[\]_\xi$ brackets are used to account for the shared line sense of α and β .

The geometric factor g can vary from 0 to $0.25 = g_{\max}$ or as a normalized quantity, $G = g/g_{\max}$ from 0 to 1. A favorable pathway can then be arbitrarily defined as those with G exceeding a threshold value, G_c . For instance, when efficient pathways are indicated by say, $G > 0.8 = G_c$, one quickly finds that most interfaces (of the immense space of interfaces) under a given stress state do not have many efficient pathways [203].

A few special interface characters, however, have been identified as offering multiple pathways, such as the $\{110\}\langle 001\rangle\text{Cu}\parallel\{112\}\langle 110\rangle\text{Nb}$ interface [203]. To use G as a means of relating transmissibility and twinnability, we further need to consider the number N of α - β distinct

pathways across an interface satisfying $G > G_C$. Multiple pathways tend to promote multiple slip and orientational stability and hence not twinning. To capture the twin-suppressing effect of multiple slip, we consider normalizing G by N ($G_T = G/N$), where maximizing the value of G_T implies a high likelihood for twinning.

For successful transmission, all three factors need to be satisfied. Physically, this translates to both minimal spreading (high τ_{ISS}) and high geometric efficiency G_T . Capturing the combination motivates use of their product, $T = \tau_{ISS} G_T$, as a measure for transmission-induced twinning. To test for transmissibility of an interface, we plot different interfaces on a map of τ_{ISS} / τ_{theo} vs. G_T (Fig. 2.21), where the τ_{ISS} is normalized by its upper limit, the theoretical shear strength τ_{theo} . Interfaces ready for transmission-induced twinning would in principle lie in the top right hand corner of this map, where both G and τ_{ISS} / τ_{theo} are high.

In the transmission map Fig. 2.21 the following interfaces are plotted: $\{112\}\langle110\rangle\text{Cull}\{112\}\langle111\rangle\text{Nb}$, $\{338\}\langle443\rangle\text{Cull}\{112\}\langle110\rangle\text{Nb}$, $\{110\}\langle111\rangle\text{Cull}\{001\}\langle110\rangle\text{Nb}$, $\{110\}\langle112\rangle\text{Cull}\{112\}\langle111\rangle\text{Nb}$, $\{551\}\langle110\rangle\text{Cull}\{112\}\langle111\rangle\text{Nb}$, $\{110\}\langle001\rangle\text{Cull}\{112\}\langle110\rangle\text{Nb}$, KS, and NW. The latter two interfaces are seen to lie at the origin, implying that transmission-induced twinning is not likely. In agreement, atomic-scale studies have shown that this interface requires large stresses for transmission, due to their relatively low interfacial shear strength [131, 197]. Another interface forecasted to be poor at twinning is the $\{110\}\langle001\rangle\text{Cull}\{112\}\langle110\rangle\text{Nb}$ interface. Crystal plasticity simulations have found that this interface is orientationally stable in deformation due to a symmetric slip geometry enabled by slip transmission [204]. The remaining interfaces collect in the upper right-hand region, where both G_T and τ_{ISS} / τ_{theo} are high, indicating that both the geometrical and material aspects needed for transmission twinning are satisfied. Atomistic simulation studies on the $\{110\}\langle001\rangle\text{Cull}\{112\}\langle110\rangle\text{Nb}$ interface have indicated that transmission across this interface requires lower stress than the KS interface [138, 186]. Although more validation is required, it appears that the product, $T = \tau_{ISS} G_T$, provides a reasonable indicator for transmission-induced twinning.

2.3.5. Mapping twinning from a bimetal interface

The model described above suggests that the propensity for these two mechanisms, direct dissociation-induced twinning and transmission-induced twinning, to operate depends on interface structure. Further, it proposes that these mechanisms have a different dependency on interface structure. To forecast which interface structures are suitable for twinning by either mechanism, we construct a map in Fig. 2.22, which plots T and S (Eq. 2.3.5) on each axis [178]. As indicated, the region near the origin corresponds to interface structures less able to twin and those farther away from the origin to interface structures more able to twin.

According to the map, both mechanisms for twinning are easy from the $\{112\}\langle111\rangle\text{fcc}\{112\}\langle110\rangle\text{bcc}$ interface, which is the predominant interface character in the bulk ARB composites (see Sect. 4.3 and Fig. 2.16). This interface has a large S factor since it contains intrinsic interface dislocations with non-planar, large-valued Burgers vectors that can dissociate into twinning dislocations (Table 2.1). Likewise, this particular interface also has a large T factor since it is resistant to interfacial sliding [131]. Thus, an impinging Nb dislocation is unlikely to be trapped in the interface plane via core spreading and can be easily emitted into

the Cu side, possibly as a twinning dislocation, leaving a residual dislocation behind at the interface. In contrast, the characteristic interfaces in the physical-vapor-deposited (PVD) Cu-Nb foils, the Kurdjumov-Sachs interface $\{111\}<110>\text{fcc}||\{110\}<111>\text{bcc}$ or the Nishiyama-Wasserman interface [194, 195], are anticipated to not twin so easily. These interfaces have a limited ability to act as a source for twins since they possess interface (misfit) dislocations with only in-plane Burgers vectors and a low shear resistance [151, 197]. In agreement, twins are not seen in these Cu-Nb deposited thin films under all deformation modes and conditions. Also the map indicates that the $\{110\}<111>\text{fcc}||\{001\}<110>\text{bcc}$ and $\{110\}<001>\text{fcc}||\{112\}<110>\text{bcc}$ interfaces are not suitable for twinning, which is also consistent with experimental observation [10, 185].

The idea behind this map is to predict the propensity for interface-driven twinning based solely on interface structure. The important implication is that the twinnability of a composite material can be tuned by changing the geometric properties of the interface, such as interface character and defect structure. From this aspect alone, we find that nucleation of deformation twins from interfaces is easier for interfaces that meet the following two criteria:

- (i) They contain interfacial dislocations with non-planar Burgers vectors that can dissociate into twinning dislocations, and
- (ii) They are resistant to interfacial sliding, and hence favor glide dislocation to twin dislocation transmission across interfaces as opposed to shear via core spreading along interfaces.

2.3.6. Outstanding questions

The foregoing works imply that twinning at interfaces can be controlled by redesigning the structure of the interface. These findings inspire many more questions that could be addressed in the future. For instance, twinning in fcc metals has been the focus of most nanoscale research, as we have reviewed above. Many low symmetry crystal structures, such as hexagonal close packed and monoclinic structures including Mg, Ti, Zr, and U, have been observed to deform readily by both slip and deformation twinning. Thus, in light of the present studies on fcc metals, it becomes interesting to ask: can bimetal interfaces comprised of these crystal structures alter the propensity for twinning in these phases? As another example, we note that most of the first studies on twinning from bimetal interfaces aptly focused on high-purity (model-like) metals, yet most materials of technological relevance contain alloying elements. These elements can greatly alter the structure and energy of the bimetal interfaces and therefore potentially impact the propensity for twin nucleation and growth.

3. Helium storage at interfaces

Implanted Helium (He) is a major concern for the reliability of structural materials, cladding, and fuels in future fusion and fast fission reactors [205, 206]. Alpha particles generated during nuclear reactions are in fact He nuclei. Once these particles come to rest in a material, they begin to interact with its microstructure, binding strongly with vacancies and thereby stabilizing void nuclei, leading to accelerated swelling [207-209]. Helium enhanced void growth at grain boundaries promotes high-temperature embrittlement [210, 211]. At higher He concentrations, neighboring voids may coalesce and produce a nanoporous solid [212].

Several decades of research have led to a remarkably complex picture of He behavior in metals, spanning multiple length- and time-scales and leaving many open questions [213]. A key advancement made during these years is the theory for “bubble-to-void” transition [214, 215] that predicts two characteristic sizes for helium-filled cavities. Above a critical diameter of ~10 nm, helium-filled cavities grow without bound by vacancy capture to form “voids.” This critical diameter is a function of temperature, vacancy and interstitial supersaturation, and number of He atoms per cavity. Its exact value therefore depends on the detailed irradiation conditions. Below this critical diameter, helium-filled cavities remain stable as spherical bubbles with diameter close to 1-2 nm. Voids are particularly deleterious in causing swelling and high temperature embrittlement while bubbles below the critical size for “bubble-to-void” transition can be relatively benign [216].

Based on understanding of bubble-to-void transition, the following two approaches are employed to extend the life of He bubbles and delay their transformation into voids under irradiation:

- 1) Maximize the critical diameter at which bubbles transform into voids, for example, by reducing the concentration of radiation-induced vacancies.
- 2) Increase the number of stable bubbles by maximizing the number of nucleation sites. This reduces the He flux to individual bubbles for any given He implantation rate, decreasing the number of He atoms per cavity at a given total dose.

Examples of materials where these approaches are used are nanoferritic alloys (NFAs), such as oxide dispersion-strengthened (ODS) steels. NFAs contain a high concentration of nanoscale oxide precipitates that serve as nucleation sites for a high density of nanoscale He bubbles [217-219].

The majority of investigations focus on He precipitation within the interiors of the grains. In contrast, in this article, we will focus on the role of the atomic structure of interfaces in controlling the formation of helium nanoclusters and stable bubbles. Given the vast range of possible interface structures, a fundamental understanding of the correlation between interface structure and stable helium storage is crucial for predicting He-induced degradation of interfaces as well as for designing interfaces that trap He in stable bubbles and resist embrittlement.

3.1. Influence of interface structure on helium storage

Grain or interphase boundaries with differing crystallography or compositions may have vastly differing atomic-level structures [59]. Studies of He behavior at interfaces must take this structure into account. In their investigation of He at grain boundaries (GBs) in austenitic steels, Lane and Goodhew found that He bubble densities were greatest at GBs containing misfit dislocations and that these dislocations were in fact preferred bubble nucleation sites [15]. Singh and co-workers confirmed the importance of misfit dislocations, but further elaborated that, in aluminum, the preferred bubble nucleation sites are dislocation intersections, both within and outside of the GBs [220]. A dramatic example of He precipitation on misfit dislocation intersections at low-angle twist GBs in Au, shown in Fig. 3.1, was observed by Di *et al.* [221]. These findings were also confirmed using atomistic simulations in Cu and α -Fe [222, 223].

In all of these studies, bubble sizes varied from boundary to boundary, but were always larger than in the crystal. This trend was investigated further via high-temperature He implantations in Cu, which showed a correlation between GB energy and He bubble size [224, 225]. The scatter of bubble sizes within a given GB type, however, was large—more than 50% in some cases—suggesting that other factors besides average interface energy also influence GB-He interactions. Atomistic modeling of He trapping [226, 227], migration [228, 229], and clustering [227, 228] point to the importance of GB structure.

Similar to nanoprecipitates in NFAs, some interfaces may be excellent sites for trapping He in stable bubbles. Many interfaces also impart mechanical strength and recombine radiation-induced point defects [21, 46, 48, 230]. Mechanistic connections between interface structure and interface-He interactions have been obtained through quantitative investigations of semicoherent fcc-bcc heterophase interfaces as model systems. Semicoherent interfaces may be described using misfit dislocation models [59]. Experimental investigations of these interfaces have centered on multilayered thin films synthesized via physical vapor deposition (PVD) techniques, such as magnetron sputtering, because these materials have a high ratio of interface area to total volume. By controlling the thickness of individual layers, this ratio can be varied systematically, allowing the influence of interfaces on composite properties to be deduced. Moreover, in magnetron sputtered composites, the interfaces between successive layers are all identical, making it easy to connect experiments with atomistic modeling. We focus our review on composites of immiscible metals and refer the reader to [49, 231] for investigations on the He-response of miscible metal multilayers.

He has negligible solubility in crystalline metals [232] and, if introduced in any measurable quantity, rapidly precipitates out in the form of bubbles. It is, therefore, surprising that no He bubbles were detected via TEM in sputtered Cu-Nb multilayer thin films that were He-implanted to concentrations of more than 5 at% [233]. Since He-implanted pure Cu and Nb both contain copious bubbles [234, 235], it was inferred that the Cu-Nb interfaces trap He in the form of small clusters too small to be resolved via through-focus imaging in TEM [234]. At sufficiently high He concentrations, bubbles are eventually resolved, as shown in Fig. 3.2, suggesting that there is a critical He concentration for visible bubbles to form at these interfaces.

The interface-He interactions responsible for this surprising behavior were investigated through an integrated modeling/experimental study. A method for measuring the critical concentrations for observing He bubbles at interfaces in TEM was developed and demonstrated on the case of Cu-Nb [236]. In this approach, several multilayers with differing layer thicknesses are synthesized and implanted with He^3 . The samples are not annealed, either before or after implantation. The He^3 concentration is then measured as a function of depth by nuclear reaction analysis (NRA), which detects high-energy α particles generated when an implanted He^3 atom fuses with a particle from an incident deuterium beam. NRA measurements accurately reflect the true He^3 depth profile, including the effect of any post-implantation redistribution, and so are favored over using SRIM (Stopping and Range of Ions in Matter, <http://www.srim.org>) [237] calculations alone.

He^3 depth profiles are then compared with bubble distributions found from underfocus bright field TEM images, where bubbles 1-2 nm in diameter appear as white dots [235, 236]. In all samples studied, there was a critical He concentration below which bubbles were not observed.

In Fig. 3.2, no bubbles are detected in the layers close to the surface and layers below ~200 nm, despite the 1-2 atom/nm³ He concentration found at this depth. By overlaying the calculated concentration profile of implanted helium on the TEM image, the critical He concentration at which bubbles are detected can be measured. This concentration scales with interface area per unit volume, as expected when He is preferentially trapped at interfaces. When converted to the number of He atoms per unit of interface area (rather than sample volume), the critical concentration at which bubbles are observed is the same for all layer thicknesses and equals ~8.5 atoms/nm² for Cu-Nb [236]. Analogous studies found that the critical interface He concentration is ~1.9 atoms/nm² in Cu-V multilayers [238] and ~3.0 atoms/nm² in Cu-Mo multilayers [239].

All interfaces in Cu-Nb, Cu-V, and Cu-Mo magnetron sputtered multilayers form along close packed planes of the neighboring crystals, $\{111\}_{\text{fcc}}\parallel\{110\}_{\text{bcc}}$, in the Kurdjumov-Sachs orientation relation, where $\langle 110 \rangle_{\text{fcc}}\parallel\langle 111 \rangle_{\text{bcc}}$ [71]. Atomic interface models that reproduce this experimentally determined crystallography were constructed [70, 240] and their structure and properties were studied using specially constructed Embedded-Atom-Method (EAM) potentials to describe interatomic interactions [241, 242]. Atomistic modeling revealed that $\{111\}_{\text{fcc}}\parallel\{110\}_{\text{bcc}}$ interfaces contain two sets of parallel misfit dislocations and the intersections between these dislocations form a quasi-periodic pattern within the plane of each interface.

Misfit dislocation intersections (MDIs) are the preferred sites for He trapping. Helium interstitial energies at MDIs in Cu-Nb are nearly 2 eV lower than in Cu and 1 eV lower than in Nb [243]. He substitutional energies are about 0.5 eV lower at Cu-Nb MDIs than in Cu and 1 eV lower than in Nb. These results suggest that, up to the critical concentration needed to form bubbles, the He trapped at fcc/bcc interfaces is stored at MDIs and that the difference in critical He concentrations at Cu-Nb, Cu-V, and Cu-Mo arises from differing areal densities of MDIs at these interfaces. The areal density of MDIs in any semicoherent interface may be computed directly using O-lattice theory [244, 245], allowing the above hypothesis to be tested. Moreover, based on these calculations, mechanistically informed predictions for the relative He trapping efficiency at general semicoherent interfaces may be made.

Figure 3.3 plots the MDI density as a function of the bcc/fcc lattice parameter ratio. The simulated interface structures of Cu-Nb and Cu-V are shown as insets. MDI density varies non-linearly and non-monotonically with lattice parameter ratio. Figure 3.3 also shows the critical concentration of He needed to observe bubbles at a given interface in TEM. The dependence of these critical concentrations on lattice parameter ratio closely matches that of the MDI density. Indeed, for Cu-Nb, Cu-V, and Cu-Mo interfaces, the critical concentration and the MDI density are found to be proportional to each other, with a proportionality factor of ~25 atoms/MDI [16]. This result supports the hypothesis of He trapping at MDIs and suggests that 25 atoms may be trapped at each MDI before a bubble, which would be visible in TEM, is formed.

Further evidence for trapping of implanted He at MDIs was found using neutron reflectometry (NR), which is sensitive to He through its effect on local density [246, 247]. Unlike ion beam analysis techniques, neutron reflectometry has Å-level depth resolution, allowing detection of He at individual interfaces. This technique was therefore able to demonstrate that regions of high He concentration are localized at Cu-Nb interfaces while bulk Cu and Nb layers remained intact and free of He [246]. These results have been further validated using x-ray reflectometry [248]. Moreover, it was found that, at each interface, there is no detectable change in interface density up to a characteristic critical He dose [247]. Above this characteristic He dose, there was clearly

a detectable drop in interface density, suggesting He bubble formation. Figure 3.3 plots these critical doses for Cu-Nb, Cu-V, and Cu-Mo interfaces. The variation of these critical doses is again closely correlated to the MDI density and to the critical He concentration required to see bubbles in the TEM, providing further evidence for stable He storage at MDIs.

These measurements and calculations were extended to other interfaces, such as coherent $\Sigma 3$ twins in Cu [58] and magnetron sputtered Ag-V multilayers [249]. Because coherent $\Sigma 3$ {111} twin boundaries have a completely uniform internal structure, He bubbles form on them much as they would in pure Cu. Thus, coherent $\Sigma 3$ twins cannot store He, as fcc/bcc interfaces do. By contrast, the critical He concentration to observe bubbles in Ag-V multilayers is comparable to that in Cu-Nb, even though in the Kurdjumov-Sachs orientation relation, interfaces along close-packed planes of Ag and V are predicted to have an exceptionally low MDI density: $\sim 1.3 \cdot 10^{-4}/\text{\AA}^2$. Unlike the other fcc/bcc systems, however, magnetron sputtered Ag-V multilayers do not contain just one type of interface. Rather, a variety of orientation relations, including Kurdjumov-Sachs, Nishiyama-Wasserman, Bain, Pitsch, and intermediate ones were identified [249]. A range of interface plane orientations were also observed, many of them non-close-packed. Some interfaces were wavy and seemed to contain disconnections [250]. The critical He concentration per unit area in Ag-V therefore represents a weighted average of all observed interface types and does not follow the trend in Fig. 3.3. Its value is comparable to that of Cu-Nb [16], suggesting a predominance of interfaces with high MDI density.

The data in Fig. 3.3 indicate that 25 He atoms may be stored at each MDI without forming a bubble. Recent atomistic modeling work has explained how so much He may be stored at a single MDI in terms of an unexpected new kind of morphological transformation: the “platelet-to-bubble” transition [247, 251]. Much like the well-known bubble-to-void transition, platelet-to-bubble transitions are driven by a competition between three kinds of pressure acting on interfacial He-filled cavities: the mechanical pressure P_{He} of the trapped He gas, the osmotic pressure P_V due to the flux of radiation-induced vacancies within the crystal to the cavity, and the capillary pressure P_c arising from the surface energy of the cavity. P_{He} and P_V tend to expand the cavity while P_c tends to shrink it. When these three pressures balance, i.e.,

$$P_{\text{He}} + P_V = P_c, \quad (3.1)$$

then the cavity is in equilibrium; that is, it neither expands nor contracts.

Inside crystalline metals, there is only one stable equilibrium configuration for He-filled cavities: an approximately spherical bubble of ~ 2 nm diameter [252]. At certain interfaces, however, there is another stable state: platelet-shaped He-filled cavities. The origin of stable interfacial He platelets may be traced back to interface energy. Semicohherent fcc-bcc interfaces have a characteristic location-dependent, internal structure consisting of misfit dislocations. Associated with this structure is a non-uniform, location-dependent interface energy. In particular, the local interface energy at MDIs is so high that there is a thermodynamic driving force for He precipitates to wet these regions, much like water wets a glass pane. Along such “heliophilic” interface regions, He precipitates into relatively flat platelets, rather than spherical bubbles.

Owing to their higher surface-to-volume ratios, platelets have higher capillary pressures than spherical bubbles. This higher capillary pressure balances the mechanical and osmotic pressures that tend to expand the platelet, stabilizing it against growth into a spherical bubble. However, if

a platelet should grow larger than the “heliophilic” interface region on which it nucleated and expand into the surrounding lower-energy, “heliophobic” regions, the capillary pressure drops precipitously. This drop may de-stabilize the He platelet, causing it to expand rapidly into a more equiaxed precipitate, as illustrated in Fig. 3.4. Such precipitates are easier to detect in TEM, explaining the appearance of interfacial He bubbles at a critical He concentration in TEM micrographs.

These insights suggest a pathway toward understanding and predicting the behavior of He on any interface, including those that do not contain misfit dislocations. Using atomistic modeling, the location-dependent energy of the interface may be determined and used to calculate wetting coefficients for different parts of the interface. The distribution of wetting and non-wetting regions defines the maximum size and areal density of interfacial He platelets. It may also be used to determine the number of He atoms that can be stably stored in interfacial platelets without forming bubbles. Such predictions are invaluable in calculating the expected lifetime of interface-dominated engineering materials when exposed to long-term He implantation.

At semicoherent interfaces, He behavior may be predicted even more straightforwardly. Assuming that the MDIs are wettable by He and the remainder of the interface is not, the critical concentration of He needed to form bubbles at the interface is simply the product of the MDI density and the number of atoms that may be stored per MDI. The former may be calculated analytically using O-lattice theory [244, 245]. The latter requires some atomistic modeling input, namely the diameter of the wettable patches on MDIs and their wetting coefficients. A similar procedure to that used for Cu-Nb interfaces may be applied to obtain these parameters for other semicoherent interfaces [251].

3.2. Effects of stored helium at interfaces on hardening

If interfaces are to be used to stably store He, it is crucial to understand the impact that trapped He platelets or bubbles may have on material strength and deformability. A convenient way to study hardening due to He at interfaces is to use model systems of fixed geometry such as the multilayered thin films. In these multilayers, interface structures and spacings may be independently varied, via choice of constituent layers and deposition parameters, respectively, and known He concentrations introduced via ion implantation.

Through appropriate choice of implantation conditions, a uniform distribution of He bubbles (~2 nm in diameter) can be produced over 1 μm or higher depth [253], making it possible to probe hardness using nanoindentation. Additionally, micropillar compression samples can be machined via focused ion beam milling from the implanted region to perform compression tests and measure stress-strain curves [44, 253, 254].

The resolved shear stress needed to move a dislocation past two penetrable obstacles a distance l apart is

$$\tau = \frac{\mu b}{2\pi l} \ln\left(\frac{l}{r}\right) \sqrt{\cos \phi_c} \quad (3.2)$$

where ϕ_c is half of the critical bow-out angle between dislocation lines cutting through the

obstacle, b is the value of the Burgers vector, μ the shear modulus, and r is the obstacle radius [255-258]. When $\phi_c = 0$, Eq. 3.2 reduces to the Orowan formula. Recently, Osetsky and Bacon [259] used molecular dynamics to compute ϕ_c for the case of dislocation interactions with voids, thereby making it possible to compute their hardening effect.

In multilayers where the interphase boundary is a strong barrier to slip transmission, in addition to a distribution of bubbles with radius r and average spacing l , there is also the interphase boundary spacing (i.e. layer thickness), h . Thus, both bubbles and layer thickness contribute to hardness (Fig. 3.5a). However, the flow strength of multilayer materials (in the absence of bubbles) depends on h via different unit mechanisms [230, 260-263]: the dislocation pile-up-based Hall-Petch model at larger length scales and single-dislocation-based confined layer slip (CLS) model at nanoscales.

The CLS stress scales directly with $h^{-1} \ln(h/b)$ [230]. When the CLS stress is added to the bubble hardening stress estimated from Eq. 3.2, the calculated strength matches well with experimental measurements in a number of multilayers such as Cu-Nb and V-Ag [44, 45, 254] for h greater than approximately 10 nm. To apply Eq. 3.2, bubble spacings and radii are obtained from TEM measurements on implanted samples and the critical bow-out angle is taken from the simulations reported in Ref. [259]. The exact relationship between the He/vacancy ratio in a bubble and the critical bow-out angle for bubbles at interfaces remains to be determined via atomistic modeling.

As the layer thickness is reduced from a few hundred nanometers to below 10 nm, the hardening increment due to bubbles, ΔH , decreases. The dependence of ΔH on h is found to fit the following phenomenological form: $\Delta H = H_i(1 - l/h)$, $l \leq h$. Here, l is an empirical length constant found to be on the order of the bubble spacing in a number of multilayer systems [44] and H_i is a measure of bubble hardening at very large layer thickness or in the limit of single crystal metals. The physical interpretation of this dependence is that when the average bubble spacing is equal to or larger than the layer thickness, bubble hardening is negligible compared to the CLS hardening.

For h below approximately 5 nm, however, the unit dislocation mechanism of strengthening changes from CLS to interface crossing in multilayers (Fig. 3.5b). Here, the effect of He bubbles decorating MDIs at the interfaces on the interface barrier stress to slip transmission cannot be neglected. If the bubble hardening is estimated from Eq. 3.2, assuming a CLS unit mechanism, it leads to an erroneous estimate of multilayer flow strength [254]. Atomistic modeling of dislocation transmission across interfaces is then required to compute the hardening.

Experimental measurements indicate significant suppression of bubble hardening [44, 253, 254] at h below approximately 5 nm. In the absence of dislocation pileup-induced stress concentrations, slip transmission is extremely difficult at fcc/bcc interfaces, even in the absence of bubbles [264] and the relative contribution from nanoscale He bubbles at interfaces is expected to be small.

Finally, the total He concentration also has an effect on hardening. For h greater than approximately 10 nm, decreasing the implanted He concentration from 7 at% to 1 at% leads to a significant decrease in hardening due to a reduction in bubble number density (thereby increasing bubble spacing in Eq. 3.2). For h below approximately 5 nm, however, no significant change in hardening was found for He concentrations of 1 at% compared to 7 at%. This is

particularly interesting since 1 at% He in 5 nm layer thickness Cu-Nb is below the critical concentration of He to detect bubbles, as discussed in the previous section. This implies that interface He platelets too small to be detected in TEM interact equally effectively with glide dislocations as the relatively larger interface bubbles, but interface helium platelets and bubbles result in only a modest hardening increment in nanocomposites as compared to bubbles in bulk crystals. The interaction of glide dislocations with helium bubbles and platelets at misfit dislocation intersections remains an active area of future research.

3.3. Outstanding questions

The insights into He behavior at interfaces described above prompt several new scientific questions. It is now understood that the location-dependent interface energy governs the initial stages of He precipitation [251]. These location-dependent energies may be found for any interface using atomistic modeling. Moreover, for semicoherent interfaces, the location-dependent energy correlates with the misfit dislocation pattern. Since interfacial misfit dislocation configurations may be calculated analytically [137], additional atomistic simulations are not required to predict He precipitation behavior at such interfaces. However, it is not yet possible to analytically predict location-dependent energies at interfaces whose structure cannot be described by misfit dislocations, such as incoherent interfaces and general GBs. Predicting the internal structure of these interfaces is a long-standing challenge that has yet to be conclusively resolved.

The influence of additional physical factors (besides misfit), on location-dependent interface energies has also yet to be investigated. Such factors may include interfacial charges in ionic solids, segregants in alloys, or extrinsic defects deposited in the interfaces due to plasticity in the neighboring grains. Furthermore, while interfacial platelet-to-bubble transitions have been modeled [251], the effect of interface structure on He bubble-to-void transition has yet to be fully understood. Such modeling should yield insight into the critical radius for bubbles nucleated at MDIs to transition into voids, as a function of irradiation conditions and interface dislocation structure. Recent work by Caro *et al.* has investigated such transitions for bubbles formed at low-angle twist grain boundaries in α -Fe and Cu [222, 223, 265].

Another open question concerns the stability of bubbles at interfaces under heavy-ion irradiation at elevated temperatures. Due to trapping at high-interface energy regions, such as MDIs, nano-scale interfacial platelets or bubbles may be impeded from coarsening or coalescing into larger precipitates. However, high-energy collision cascades may re-solutionize He precipitates, accelerating coarsening. Meanwhile, high temperatures may impart elevated mobility to interfacial bubbles, as seen in perfect crystals [266], hastening their coalescence.

Finally, investigations of the effect of He precipitates on interface mechanical properties are at a nascent stage. In particular, the effect of He precipitates on interfacial fracture remains poorly understood. Although it is well recognized that He impurities reduce interface cohesive energies [267, 268], the fracture mechanisms of He-charged interfaces have yet to be investigated in detail. In particular, it is not clear whether plasticity plays a role in fracture or how He precipitates may interact with advancing intergranular cracks.

4. Stability of Interfaces

The previous two sections examined how defect interactions with interfaces depend on the structure of those interfaces, with a focus on interfaces as sinks or sources for various types of defects (point defects, dislocations, and twins). Sections 2 and 3 examined how interfaces influenced defect evolution both under irradiation and deformation. However, defects also influence interfacial structure, and to a great extent, the stability of the composite itself. In this Section 4, we examine interface stability under several extreme conditions.

Stability is a broad concept and can take many different meanings depending on context. Here, we examine three aspects of stability that are particularly relevant for nanocomposites under extreme conditions. In the first section to follow, Section 4.1, we examine phase stability in oxide ceramic composites. Oxide ceramics belongs to one of many classes of materials that exhibit phase transformations under irradiation. Of particular interest here, the interfaces within oxide nanocomposites can both accelerate and retard such transformations, rendering the overall phase stability of the nanocomposite very different from the component phases. In the next Section 4.2, we discuss how irradiation can alter the overall morphological stability of the composite. Particularly at low temperatures, irradiation can lead to the complete mixing of the two component phases, destroying the initial composite morphology and interfacial structure that give rise to the desired enhanced defect annihilation in the first place. Finally in Section 4.3, we discuss crystallographic stability of interfaces under severe plastic deformation (SPD). If specific interfaces are identified as being particularly beneficial for, e.g. radiation damage mitigation, then one would like those interfaces to be stable against bulk processing techniques, such as SPD. Or vice versa, it would be desirable for the mechanically stable interfaces created in SPD to also be thermally stable and radiation tolerant. It is therefore important to identify such interfaces. In all three cases, we discuss factors that influence the stability of interfaces and the corresponding composite structure.

4.1. Phase stability of oxide interfaces under irradiation

In the metallic composites considered thus far, the interfacial structure and the consequent thermodynamic interactions dominate the response, while in the oxide composites considered in this section, the kinetic effects dominate. For this reason, in studies of metallic composites reviewed in this article, the focus has been on the role of the interfacial structure on interface interactions with point and line defects. Such interactions are driven by thermodynamic considerations. Irradiation studies of interfaces in oxides, however, have focused on coherent interfaces. These types of interfaces have negligible thermodynamic interactions with defects. Even so, irradiations of these interfaces show dramatic effects on the overall radiation response of the material. This outcome is rationalized in terms of differences in the defect kinetics on each side of the interface. While the interface does not directly influence the energetics of defects, it acts as a transition region from one material to another.

In any composite, both thermodynamics and kinetics would play a role to varying degrees. Thus, it is useful to consider the following oxide systems as a limiting case for examining a different regime of behavior. At present, irradiation studies that focus on a more direct role of interfaces and grain boundaries on radiation damage response in oxides are rare. To serve as a useful contrast to analogous work on metals, a few of these studies are also discussed below.

Radiation damage studies on oxides have a long history. This is a consequence of the fact that oxides play an important role in nuclear applications, most obviously as the primary type of fuel in fission reactors [269], but also because of their potential role as nuclear waste forms [270] and in fusion energy systems [271]. Further, because of the large variations in crystal structure and chemistry exhibited by oxides, they serve as excellent materials for fundamental studies of radiation damage processes. As in metallic systems, researchers have shown that oxides irradiated at higher temperatures are prone to void swelling. This phenomenon has been demonstrated in a number of oxides, such as Al_2O_3 [272]. The propensity for void swelling varies dramatically among different oxides, even oxides that have similarities in basic structure. For example, Al_2O_3 is very susceptible to void swelling while MgAl_2O_4 spinel is not [273]. The reasons for this, summarized in a recent review by Sickafus [274], seem to be related to the difference in energetics of interstitial dislocation loops in the two materials.

A second failure mechanism that dominates at lower temperature is amorphization (the loss of long-range crystalline order), a phenomenon not present in single-component metallic systems. While covalent oxides, materials in which the interatomic interactions are dominated by covalent bonds, are more susceptible to amorphization than ionic oxides, materials in which long-range electrostatics dominate atomic bonding, [275], amorphization occurs in a wide variety of oxide compounds. One of the goals of designing oxide-bearing nanocomposites is to increase the phase stability of the component oxide phases. Thus, to understand the phase stability of nanostructured oxides, one must first examine phase stability in irradiated bulk oxides.

4.1.1. Background on ion irradiation-induced amorphization in oxides

4.1.1.1. Bulk oxides

Amorphization of oxides under irradiation has been studied for many years, both via subjecting the oxide to external irradiation or via natural radiation due to the decay of either U or Th within the structure, referred to as metamictization. Metamictization, in particular, has been studied for well over a century, from the initial recognition in 1864 that the properties of zircon (ZrSiO_4) vary depending on their physical origin [276] to the classification and definition of metamict materials in 1893 as materials that had originally been crystalline but became amorphous with time [277]. In 1914, it was suggested that the amorphization was due to alpha decay [278]. Later studies of zircon examined the precise relationship between radiation damage and changes in physical properties [279, 280] and is still an active area of research [281]. Correlating the degree of amorphization to the decay process in such materials has been of great interest precisely because it allows for a mechanism to date the materials [282].

External irradiation sources have been extensively used to examine crystal-to-amorphization transformations in oxides. Of particular interest is how this transformation depends on temperature, dose, and electronic versus nuclear stopping. While today many such studies use ion beams to damage the material, early studies either utilized neutron irradiations, via placement in a reactor (or “in-pile”) [283-285], or distributed a radioactive dispersant, such as UO_2 or Cm within the material [286, 287]. However, even in the 1930s Stackelberg and Rottenbach tried to bombard zircon with alpha particles [288, 289], in what Wang and Ewing [290] describe as one of the first “ion beam” experiments. More conventional ion beam irradiation experiments of oxides were in place at least by 1966, when Matzke and Whitton used Kr and Xe beams to irradiate several oxides and examine ion-beam induced phase changes in those materials [291].

Since that time, ion beams have been used extensively to complement neutron- and self-irradiation experiments of oxides to understand the fundamental mechanisms of damage production, damage accumulation, and phase stability, and how all of these affect various properties of the material as a function of dose.

Upon irradiation, the properties of oxides change dramatically. A multitude of properties ranging from electrical and thermal conductivity, strength and toughness, dielectric response and optical properties in oxides, and ceramics more generally, are modified by radiation damage. These changes are reviewed by Hobbs et al. [272] and Zinkle and Hodgson [292]. It is beyond the scope of the current review article to go into any detail of these changes. It suffices to say that some properties, such as electrical resistivity, are extremely sensitive to damage levels as small as 10^{-3} dpa.

The structural changes that accompany amorphization lead to even greater changes in the properties of the material. Along with the change in structure, many properties of the oxide phase can also change, including hardness, which can increase [293] or decrease [294]; the leach rate [295]; and the thermal conductivity [283]. Of particular importance is sample volume. Upon amorphization, oxides generally swell, or experience a significant increase in volume, due to the fact that the amorphous phase has a different volume than the crystalline phase, although compaction has also been observed [272].

While the exact mechanisms by which radiation damage induces a crystalline-to-amorphous transformation are not very clear, it is generally accepted that amorphization proceeds either directly in-cascade or via defect accumulation, or a combination of processes, such as cascade overlap [294, 296]. In the case of defect accumulation, in which each cascade leads to the generation of some number of point defects and defect clusters, amorphization is assumed to occur once a critical defect concentration is achieved. When this happens, the free energy stored in the defect structure is greater than the amorphous phase and a phase transformation occurs [294]. As might be expected, amorphization is more difficult to achieve as the temperature is raised, since the rate of defect recombination increases with temperature, leading to greater recovery of the crystalline state. This leads to the definition of a critical temperature for amorphization, T_C , above which the material simply cannot be amorphized. Many studies have focused on determining how T_C varies across different oxide structures and within a given family of oxides that have varying chemistry [297, 298]. However, complicating these studies is the fact that the response of the ceramic is sensitive to the irradiation spectrum, in particular the ratio of electronic to nuclear stopping [286, 299, 300] and the mass of the implanted ion [301]; thus, T_C is not uniquely defined for a given material, but depends on many factors.

Amorphization studies have been performed on a wide range of oxide compounds, from garnets [302] to the so-called δ -phase compounds, such as $\text{Sc}_4\text{Zr}_3\text{O}_{12}$ and Y_6UO_{12} [303]. The most systematic studies have focused on pyrochlores and other fluorite derivatives, such as bixbyite, as well as perovskites. Pyrochlores and perovskites have received greater attention because of their incorporation into waste forms such as Synroc [304]. For this reason, the amorphization of these materials under irradiation is reviewed in detail below. For reference, the structures of many of these oxides are shown in Fig. 4.1.

Amorphization in fluorite derivatives - pyrochlore

Pure fluorites, such as CeO_2 and UO_2 , do not amorphize under irradiation. Many fluorite derivatives, however, readily amorphize and the propensity to amorphize is very sensitive to the chemistry of the compound. One of the most studied families of oxides is the pyrochlore family. With a chemical formula of $\text{A}_2\text{B}_2\text{O}_7$, pyrochlores can be viewed as oxygen-deficient fluorites. Compared to pure fluorite, pyrochlores have a larger unit cell due to the ordering of A and B cations on the cation sublattice and the ordering of structural oxygen vacancies on the anion sublattice. Under irradiation, pyrochlores often first undergo an order-to-disorder transformation, in which the two cation species mix and the oxygen vacancy positions are essentially randomized on the anion sublattice. In this state, the structure of the compound, from a diffraction point of view, is indistinguishable from fluorite and is often referred to as disordered fluorite.

Upon further irradiation, many pyrochlores also exhibit an amorphization transformation. The propensity for amorphization of pyrochlores has been observed to be very sensitive to the nature of the B cation. For example, titanium pyrochlores ($\text{B} = \text{Ti}$) are very susceptible to amorphization [301], while zirconium and hafnium pyrochlores ($\text{B} = \text{Zr}$ or Hf) are not [305]. The role of B cation chemistry is dramatically demonstrated in a series of irradiations on $\text{Gd}_2(\text{Ti}_{2-x}\text{Zr}_x)\text{O}_7$, in which the resistance to amorphization of the pyrochlore was a direct function of the relative Zr content [306]. Further, as shown in Fig. 4.2, there is some dependence of the critical amorphization temperature on A cation chemistry. T_C has a non-linear relationship with A cation radius [298, 307]. All of the $\text{B} = \text{Ti}$ pyrochlores had a critical dose for amorphization of less than 1 at 293 K when irradiated with 1 MeV Kr^+ ions, but $\text{Gd}_2\text{Ti}_2\text{O}_7$ experienced the greatest susceptibility for amorphization amongst the lanthanide pyrochlores. Interestingly, this compound also has the highest energetic penalty for cation disorder [308-310], a point that will be discussed in more detail below. In contrast, Sn pyrochlores exhibit a wide range of behavior, with some amorphizing relatively readily ($\text{A} = \text{Gd}$, Nd , and La) and others very resistant to amorphization ($\text{A} = \text{Y}$ and Er) [311]. The different behavior of $\text{B} = \text{Sn}$ pyrochlores to the other families investigated has been proposed to be linked to the more covalent nature of the Sn-O bond [311]. Like the TiZr pyrochlore mentioned above, increasing Sn content has been correlated with radiation tolerance [312].

Molecular dynamics (MD) simulations of pyrochlore have focused on two aspects: the role of pyrochlore chemistry on damage production [313] and the effect of defect accumulation on pyrochlore stability [314]. For instance, MD simulations of ion tracks formed when a single high-energy ion traverses the solid, modeled via thermal spikes, show complex track morphologies [313] that are reminiscent of experiments [315, 316]. Complementing these dynamical simulations are numerous calculations using both pair potentials and density functional theory, which have examined various defect properties in pyrochlore, including defect formation energies [308, 317, 318] and kinetics [319].

Amorphization in other fluorite derivatives

Amorphization has been studied in other fluorite derivatives, although not to the extent as pyrochlore. The amorphization susceptibility of $\text{A}_6\text{B}_1\text{O}_{12}$ δ -phase compounds depends strongly on chemistry. Tungsten-bearing δ -phase compounds amorphize readily [303], but compounds containing uranium – $\text{RE}_6\text{UO}_{12}$ with $\text{RE} = \text{Y}$, Gd , Ho , Yb , and Lu [320] – do not. Atomistic calculations again correlated this with the formation energy of cation antisites [321].

Experiments on the $A_4B_3O_{12}$ δ -phase compounds $Sc_4Zr_3O_{12}$ and $Lu_4Zr_3O_{12}$ did not observe any propensity for amorphization [322].

Extensive irradiation studies performed on another fluorite derivative, bixbyite, showed no evidence of amorphization, though radiation damage was observed to induce phase transformations consistent with the thermal phase diagram [323].

Amorphization in perovskites

As with the pyrochlores, large numbers of chemistries of perovskites (ABO_3) have been subjected to irradiation to determine phase stability in this class of oxides. The amorphization susceptibility of perovskites is very sensitive to the chemistry of the compound. For example, $KTaO_3$ is readily amorphized even at temperatures as high as 700 K while $SrTiO_3$ cannot be amorphized above temperatures of 425 K [324]. Recrystallization of the amorphous perovskite has been induced either by temperature [297] or via electron beams [325]. Interestingly, when $B = Ti$, the recrystallization occurs epitaxially at the crystalline-amorphous boundary, but when $B = Nb$ or Ta , new crystals nucleated within the amorphous regions directly. In contrast to the pyrochlore family of oxides, where significant attention has been given to the factors that differentiate the response of different pyrochlore chemistries to irradiation, no such examination has been performed for perovskites, beyond the calculation of defect formation energies [326].

As our later discussion will emphasize radiation damage results on composite structures containing $SrTiO_3$, here we delve into more detail on the irradiation studies of this material. While the critical dose to amorphize $SrTiO_3$ depends on the irradiation conditions [325], bulk $SrTiO_3$ amorphizes by a dose of 3-4 dpa (for Ne irradiations assuming a displacement threshold energy, the minimum energy to permanently dislodge an atom, of 40 eV) [297, 327]. Analysis of the amorphous content versus fluence suggests that defect-stimulated amorphization (or defect accumulation) drives the amorphization transformation in $SrTiO_3$ [328]. MD and accelerated MD simulations with pair potentials examined a number of defect properties, including the displacement threshold energy and point defect migration energy, finding significant differences for each of the species [329, 330]. For example, while the displacement threshold energies for O and Sr were found to be similar – 50 and 70 eV, respectively – that of Ti was much higher, 140 eV. This suggests that O and Sr defects will be produced in much higher quantities than the stoichiometry of the material suggests, relative to Ti.

A final comment regarding $SrTiO_3$ is in order. As with many oxides, $SrTiO_3$ can exhibit non-stoichiometry and one manifestation of non-stoichiometry in $SrTiO_3$ is the formation of Ruddlesden-Popper (RP) phases and faults [331], which can be viewed as extra planes of SrO within the $SrTiO_3$ structure. Two recent studies have shown that the radiation tolerance of a material such as $SrTiO_3$ is very sensitive to the presence of RP faults. Individual RP faults were observed to amorphize more readily than the surrounding matrix, which was attributed to the attraction of radiation-induced point defects to the RP faults [332]. When a high density of RP faults is present, such as in the case of the RP phase, $Sr_3Ti_2O_7$, the material amorphizes significantly faster than stoichiometric $SrTiO_3$ [333].

Amorphization in other materials

While amorphization and radiation-induced order-to-disorder transformations have been studied in a large number of other materials, most have not received as much systematic study. Some of these studies have been discussed in other reviews [272, 274, 294, 334]. Here, we summarize studies of MgO, Al₂O₃ and MgAl₂O₄ spinel, as these are among the most studied oxides and MgO, in particular, forms a component of the some of the composites that are discussed below.

As summarized by Sickafus [274], the amorphization susceptibility of Al₂O₃ and MgAl₂O₄ are very different. MgAl₂O₄ is a very radiation-tolerant material; under prolonged exposure to neutrons, only small dislocation loops [273] and cation disordering is observed [335]. MgAl₂O₄ can only be amorphized at very low temperatures, below about 100 K [336]. In contrast, Al₂O₃ experiences catastrophic void swelling when irradiated to higher temperatures [273]. While it is still relatively amorphization resistant as compared to titanate pyrochlores, for instance, it can be amorphized more readily than MgAl₂O₄, with a critical temperature for amorphization of about 170 K [337]. To the best of our knowledge, there has never been a report of MgO amorphizing under irradiation.

Factors that determine susceptibility to amorphization

One of the goals of the large number of studies on the phase stability of oxides under irradiation is to identify factors that promote phase stability. Thus, a number of authors have proposed parameters that can be used to distinguish tolerant versus intolerant materials.

As mentioned above, one of the most important factors is covalency. As originally proposed by Naguib and Kelly [275], covalent oxides tend to amorphize much more readily than ionic oxides. This has been expanded upon in great detail by Trachenko [334] who notes that not only do covalency arguments explain broad differences, such as between SiO₂ and MgO, but also within a family of compounds, such as pyrochlore. The Ti-O bond is significantly more covalent, as determined from electronic structure calculations, than the Zr-O bond. Thus, one would expect Zr-bearing compounds to have a higher degree of phase stability than Ti compounds, as is observed in the experiments. The same basic idea lies behind topological rules for identifying structures that will easily amorphize, as developed by Hobbs [338]. Structures that are flexible and able to accommodate multiple arrangements are inherently more stable than those that are not. Covalent materials, with directional bonding, are less flexible. However, this approach does not easily distinguish the amorphization resistance in structurally similar compounds, such as the pyrochlores.

As discussed by Trachenko, the definition of covalency is not precise and, while it can be used to give some indication of relative tolerance, the fact that it is not easily quantifiable limits its predictive power. As a consequence, there has been more focus on identifying structural or defect properties that correlate with radiation stability. For example, in the case of pyrochlores, the deviation from ideal fluorite, as measured by the x positional parameter of the oxygen ions, has been correlated with amorphization resistance [339]. So too has differences in Pauling electronegativities between the anion and cations, with larger differences suggesting greater stability [340].

Finally, fundamental energetic properties of the oxide have been correlated to amorphization resistance. In particular, two quantities have received attention in the literature. First, the formation enthalpy of the oxide has been shown to correlate with the radiation tolerance of

various pyrochlores [311]. Oxides with lower enthalpies of formation are also more tolerant against amorphization. Second, the energetics of disordering (how the A and B cations mix while still retaining the crystalline structure) has been identified as a key parameter in the amorphization resistance of spinel, pyrochlore, and other fluorite derivatives [310, 341]. Cation and anion disorder are more costly for instance in Ti pyrochlores than Zr pyrochlores. This disorder occurs naturally under irradiation, so Ti pyrochlores build up more stored energy than their Zr counterparts, eventually leading to instabilities and amorphization. However, this is only part of the picture. For instance, Sn pyrochlores, while exhibiting extremely high energies for disordering [308], can be very amorphization resistant [311]. This suggests that disordering alone is not the only factor, but that it is the relative competition between the disordered and amorphous structures of the oxide that govern the response to irradiation. The idea that disordering is intimately linked to amorphization has also been examined in the context of intermetallic compounds [342].

For oxides in which amorphization occurs directly in-cascade, the amorphization process has been compared to the glass forming process. Oxide compositions that are more likely to form glasses from the melt are also more likely to undergo a crystalline-to-amorphous transformation under irradiation [343].

For very complex minerals with large structural units, such as neptunite $[\text{Na}_2\text{KLi}(\text{Fe},\text{Mn})_2\text{Ti}_2(\text{SiO}_3)_8]$, the structural complexity has a direct bearing on the amorphization susceptibility [290]. In particular, the larger the number of unique cation sites and the number of different atom types, the greater the complexity of the mineral and the greater its susceptibility to amorphization.

4.1.1.2. Grain boundaries

As has been discussed above, the goal of using nanomaterials for radiation damage environments is to exploit the sink properties of the interfaces and GBs to enhance the overall radiation tolerance of the material. In the case of oxide ceramics, this potential was dramatically demonstrated in irradiation experiments of MgGa_2O_4 spinel [344]. As shown in Fig. 4.3, two spinel specimens, one comprised of large grains (about 10 μm in diameter) and a nanocrystalline sample with grains ranging in size from 4-12 nm, were implanted with 300 keV Kr^{++} ions at a temperature of 100 K. The large-grain sample amorphized by an estimated dose of 12 dpa. The small-grain spinel, however, retained its crystallinity to doses of 96 dpa. This is a particularly surprising result in that defect mobility in spinel at 100 K should be so slow [345] that the boundaries are not effective sinks for, at the very least, vacancies. Indeed, in experiments on Au, the radiation tolerance of nanograined material was worse at low temperature than large grain material [41]. This suggests that complex defect-boundary interactions might be occurring in the spinel, consistent with the “interstitial emission” mechanism recently discovered through long-time scale MD simulations and discussed in section 2.1.2 [46, 91].

The vast majority of studies on the role of GBs on radiation damage evolution in oxides have focused on higher temperatures where the dominant failure mode is not amorphization but rather void swelling. In materials, such as Al_2O_3 and MgAl_2O_4 , experiments have observed interstitial loop and void denuded zones near GBs as well as enhanced void content at the boundaries

themselves [63, 272, 273, 346], very similar to the behavior seen in pure metals such as Cu [64, 65].

Very few studies have examined phase stability at GBs in irradiated oxides. To the best of our knowledge, only one study observed amorphization at grain boundaries. Ion implantation of $\text{YBa}_2\text{Cu}_3\text{O}_x$ thin films lead to preferential amorphization of the material at the GBs [347]. Higher doses lead to amorphization across the thin film, but doses as low as 100 times less lead to amorphization at the boundaries. Further, amorphization seemed to initiate at “kinks or sharp turns” at the boundary. The reduced phase stability at internal interfaces observed in this material is similar to that observed at the RP faults in SrTiO_3 [332].

4.1.1.3. Oxide composites and heterointerfaces

While one of the primary motives for understanding phase stability in oxides under irradiation relates to their potential use in composite waste forms, rather limited work has been performed on irradiated oxide composites. Synroc, a composite waste form developed in Australia, contains a variety of oxide phases, including zirconolite ($\text{CaZrTi}_2\text{O}_7$), perovskite (CaTiO_3), hollandite ($\text{BaAl}_2\text{Ti}_6\text{O}_{16}$), and rutile (TiO_2) [304]. Direct studies on Synroc have examined macroscopic swelling of the material under α -decay and neutron irradiation and found significant swelling with dose [348]. However, the evolution of the component phases within the material was not distinguished; rather, the response of irradiated Synroc has been correlated with the response of the individual constituent phases [294]. Similar studies have been performed on related oxide composites, such as Supercalcine [294]. Certainly, none of these studies attempted to correlate any radiation damage response with the nature of the interfaces in the composite.

The other potential application that drives much of the radiation damage research on oxides is for inert matrix and composite fuel forms. To this end, researchers studied the radiation damage behavior of a model fuel form comprised of layers of MgO and HfO_2 [349, 350]. Neither of these materials readily amorphize, so it was no surprise that amorphization was not observed in the composite structure. However, the interfaces did mitigate radiation damage accumulation as compared to single crystals of each material. Again, no attempt was made to correlate the damage accumulation with the specific properties of the interface.

A final set of experiments on oxide composites involved nanoparticles of ZrO_2 embedded in an amorphous SiO_2 matrix [351]. Normally, ZrO_2 is very radiation tolerant, withstanding doses of 680 dpa in bulk form [352] and at least 80 dpa in nanocrystalline form [353]. However, in the ZrO_2 - SiO_2 composite, the ZrO_2 nanoparticles amorphized at a dose of only 0.5 dpa. It was hypothesized that this enhanced amorphization susceptibility was a consequence of a high interfacial energy between SiO_2 and ZrO_2 . Shen argued that the irradiation stability of a nanocomposite was inversely related to the energy of the interfaces within the composite [354]. However, no direct measurement of the interfacial energy was available to support this hypothesis.

4.1.2. Phase stability at coherent interfaces in oxide composites

To optimize the performance of nanostructured composites for nuclear energy applications, the role of interfaces in influencing radiation-induced defect evolution must first be understood. While several of the studies described in the previous section demonstrated the promise of

nanocomposites for extreme environment applications, none of them examined the role of the interfaces in determining the behavior of the composite. To address this gap in knowledge, a systematic study of a series of bilayer composite structures was performed, both experimentally and theoretically, in order to determine the precise role of the interface. These are reviewed below.

4.1.2.1. Experimental studies

The bilayer composite structures all contained SrTiO_3 (STO) as one of the component phases. The other phases were anatase TiO_2 , BaTiO_3 (BTO), and LaAlO_3 (LAO). All were synthesized via pulsed laser deposition using SrTiO_3 as the substrate, except for the case of STO/LAO, as higher quality films are obtained using LAO as the substrate. Final film thicknesses were typically about 300 nm. These samples were all implanted with Ne ions ranging in energy from 250 to 300 keV, the energy chosen to maximize the damage at the interface, as guided by SRIM (Stopping and Range of Ions in Matter) calculations [237]. The samples were then characterized via TEM. Multiple fluences were implanted into the various samples; here, the results after about 3 dpa are summarized. The original experiments are discussed in Refs. [355-358].

The microstructures of the three bilayer structures after a dose of about 3-4 dpa are shown in Fig. 4.4. The radiation-induced structure at the interface is very different in each case. In the case of TiO_2 /STO (Fig. 4.4a), there is a denuded zone on the TiO_2 side of the interface while the STO side of the interface has amorphized. For BTO/STO (Fig. 4.4b), there is no discernable effect at the interface. Neither BTO nor STO has amorphized and there is no indication of any kind of denuded zone. Finally, for STO/LAO, as shown in Fig. 4.4c both materials have experienced significant amorphization. Thus, depending on the interface in question, the interface either enhanced or degraded the radiation tolerance of the component materials. In the case of TiO_2 /STO, the interface did both at the same time.

Importantly, although STO is common to all three bilayers, its phase structure after irradiation is very different. The BTO/STO interface did little to the phase stability of STO. The TiO_2 /STO interface degraded the phase stability of STO, but only slightly, with a relatively thin amorphous layer at the interface. In contrast, the phase stability of STO was dramatically affected by the STO/LAO interface. Near this interface, an amorphous layer with a thickness of about 70 nm formed in the STO after about 3 dpa. These results indicate that the phase stability of STO is very sensitive to the nature of the composite, either via the structure of the interface and/or the properties of the other material.

4.1.2.2. Atomistic modeling

In order to elucidate the role of interfaces in bilayer films, atomistic models of TiO_2 /STO and BTO/STO interfaces were constructed and used to calculate the properties of point defects near these interfaces. In the case of the STO/LAO interface, the atomistic models used could not adequately describe the charge transfer that stabilizes that interface. In this case, the insight gained from the other two systems was used and only bulk effects were explicitly considered.

Upon irradiation, the experiments on the TiO_2 /STO interfacial system revealed a thin amorphous layer on the STO side of the interface. This implies that whatever misfit dislocation structure may have existed in the pristine interface did not play a dominant role in the damage evolution at

the interface as those misfit dislocations would not be present once the amorphous layer formed. It is possible that the misfit dislocations played a role in the initial formation of the amorphous layer itself. However, due to the relatively large dislocation spacing at the interface and the fact that an amorphous layer forms at the interface at low dpa, the atomistic models focused on calculations of point defect energetics in the constituent phases assuming coherent interfaces.

Figures 4.5a-b show typical profiles for defect formation energies near the coherent TiO_2/STO interface for both vacancies and interstitials. Being absent of any defect trapping sites, such as misfit dislocation intersections or disconnections, a coherent interface is not expected to act as a strong point defect sink. There are strong variations in the energy as a function of the distance of the defect from the interface, but these are dominated by the behavior in each of the bulk phases. Further, there is no deep energy well at the interface itself. Similar behavior is observed for the coherent BTO/STO interface [357]. As argued above, even if there were misfit dislocations, because of the amorphization that often occurs at the interface, a well-defined misfit dislocation network would be destroyed and hence can have only a transient influence on defect evolution.

Thus, these atomistic calculations indicate that defect evolution in these oxide bilayers is not driven by the interface itself, but by the component phases. Specifically, differences in defect formation energy, at 0K and the dilute limit, or more generally the chemical potential for each species within each phase, drive the defect evolution. In the case of the two Ti defects in the TiO_2/STO system, Ti vacancies are driven from the TiO_2 phase into the STO phase, while the opposite is true for Ti interstitials.

While these chemical potential differences provide the thermodynamic driving force for defect evolution, whether the defect flow can actually occur is a function of the migration barriers of each defect. Using temperature accelerated dynamics [88], the migration barriers for all of the relevant defects in the component phases of the bilayer systems were calculated [357-359]. A few results are worth highlighting. First, the migration energies of the various point defects within one material vary significantly. For example, oxygen interstitials diffuse much faster than Ti interstitials in TiO_2 [359]. Thus, at a given temperature, some defects will be able to respond easily to the thermodynamic driving forces embodied by the chemical potentials and others will not. Second, and more importantly, the mobility of a given defect is very different in the two component materials. While Ti vacancies are relatively mobile in TiO_2 , their mobility is essentially zero in STO [357]. This means that a defect that might be fast in TiO_2 and that can respond to a chemical potential gradient driving it to STO, may not diffuse at all once it reaches the STO phase.

Thus, atomistic modeling revealed two parameters that dictate the evolution of radiation-induced defects in composites in which the interface does not act as a trap for defects: the relative formation energy, or chemical potential difference μ , of the defects in the component phases and the migration barriers E^m of the defects within the component phases. These factors can be conceptualized in a schematic energy landscape for defects in these composites, illustrated in Fig. 4.5c. In this schematic, which is for some arbitrary defect, the defect migrates quickly (i.e., it has a smaller migration barrier E^m) in one phase (labeled A) but is thermodynamically driven to the second phase (B), where the chemical potential μ is lower. However, in phase B, the migration energy is higher so defect migration will be slower. This combination of migration energies and chemical potentials will lead to a complex response in which the defect is driven to diffuse to the

phase in which its migration is slow, potentially leading to defect accumulation within the interface region. As discussed in the next section, this accumulation is driven not by traps at the interface but by changes in kinetics. This concept can be extended to include the effects of interfacial structure by accounting for defect-trap sites within the interfaces, as schematically illustrated in Fig. 4.5c, and thus generalized to more complicated two-phase composite systems.

Importantly, we note that while the context for these results is phase stability of the component oxides at the interface, this conceptual landscape applies to other scenarios. In particular, in metallic nanocomposites, in which amorphization is non-existent, the defect concentration gradients that arise from the energetic landscape in Fig. 4.5c would lead to, for example, spatially varying void distributions and may contribute to the formation of void denuded zones in metallic systems.

4.1.2.3. Continuum modeling

To understand how these two parameters, migration energy and chemical potential, influence damage evolution, a simplified continuum model of defect evolution in a multilayer composite was constructed in [360]. Such a continuum model, which coarse-grains the properties of individual atoms and instead focuses on homogenized concentrations of defects, has significant advantages over a fully atomistic description of the system in that it can simulate longer times and larger system sizes. The model developed in [360] is a reaction-diffusion model in which the concentration of a single interstitial and vacancy species is tracked as a function of their relative energetics – chemical potentials and migration barriers – in the component phases. It accounts for both defect production and defect annihilation, via encounters between interstitials and vacancies. Two arbitrary phases, labeled A and B in Fig. 4.6, are represented in the model. The input parameters are the migration energy of interstitials and vacancies in Phase A and Phase B as well as the difference in formation energy (or chemical potential) for each defect in Phase A versus Phase B. The simulation results show that the steady-state defect concentrations within the model system depend significantly on the relative defect energetics in the two component phases in the composite.

To understand the different ways that the phase composition of the composite can influence the overall radiation-induced defect evolution, the steady-state defect concentration profiles as a function of the materials parameters that define the model were determined. Figure 4.6 illustrates two extreme scenarios for defect content within the composite. In Fig. 4.6a, the difference in chemical potentials for both vacancies and interstitials in the two phases are of the same sign – both defects are driven from Phase A to Phase B – while in Fig. 4.6b, the difference has the opposite sign, so that interstitials and vacancies are driven to different phases.

In the first case, the defect concentrations near the interface are very different than in the center of each layer. When going from Phase A to Phase B, we first observe that there is a drop in the concentrations of both interstitials and vacancies and then, on the other side of the interface, there is a spike in the concentrations of both. On the A side of the interface, there is a defect-denuded zone, and on the B side of the interface, there is an enhancement in defect content which, depending on the material, would lead to enhanced amorphization at the interface (or, in a metallic composite, enhanced void nucleation). This scenario is reminiscent of the TiO₂/STO bilayer composite described above and in Fig. 4.4. This defect structure is a consequence of the

fact that, while both defects are driven to Phase B, the migration barriers are higher in Phase B, so that once defects reach Phase B, their flow is impeded and their concentrations grow.

In contrast, for the case in which the chemical potentials are of opposite sign as illustrated in Fig. 4.6b, in Phase A the interstitial concentrations are maximized while the vacancy concentrations are minimized. The opposite behavior is observed in Phase B. In this case, interstitials are driven to Phase A and vacancies are driven to Phase B and they are effectively segregated in the material. This minimizes the probability of annihilation and both defect concentrations reach a maximal concentration. This scenario, which is the worst-case scenario for such a composite, is similar to the observations for the STO/LAO bilayer composite, in which both constituents exhibited significant amorphization.

The case of BTO/STO is not represented by either model in Fig. 4.6. In this bilayer, the differences in defect formation energies (chemical potentials) between the two phases are rather minimal and there is no driving force for defects to flow across the interface. Thus, there is no accumulation or depletion of defects at the interface, just as observed in the experiments [357].

4.1.2.4. Implications for nanocomposites

Together, the experiments, atomistic modeling, and reaction-diffusion model indicate that the radiation damage evolution within a multiphase composite depends on the phase composition of the composite. Further, the defect evolution in one of the component phases depends on the defect properties of the other phase. By changing Phase B and thus the formation and migration energies of defects in Phase B, relative to Phase A, the defect content in Phase A also changes. This means that the overall stability of the composite to irradiation depends not simply on the individual responses of the component phases, but is a more complex aggregate response of the entire system. That is, the response of a composite of A and B to irradiation is more than the simple sum of the responses of A and B.

This result provides new avenues for designing radiation-tolerant composites. If the phase structure of the composite is not chosen appropriately, one may be in a situation represented by Fig. 4.6b, in which defect annihilation is minimized and defect concentrations reach maximum values. With the appropriate choice of Phase B, the radiation tolerance of Phase A can be improved, per the scenario in Fig. 4.6a. In this case, Phase B acts as a three-dimensional getterer of defects, attracting both interstitials and vacancies and enhancing their recombination, much in the same way that one-dimensional (dislocations) and two-dimensional (interfaces) microstructural features can act as sinks for defects.

One advantage of using the phase structure of the composite to control radiation damage evolution, as opposed to interfacial structure, for instance, is that the phase structure of the composite is easier to control during synthesis. At this time, engineering materials to have specific types of interfaces is still challenging and, while one cannot synthesize a composite with arbitrary combinations of two phases, the possibilities of creating such a composite are greater than engineering specific interfaces.

4.1.3. Structured interfaces in oxide composites

The results described above focus on a very special class of interfaces in which the interfacial structure itself does not play a dominant role in the behavior of defects at the interface. A few

more recent studies have examined the role of interface structure on the evolution of radiation damage and the behavior of defects at interfaces in oxide composites.

One structural interface feature known to have influence are steps. Experiments on the $\text{CeO}_2/\text{SrTiO}_3$ interface [361] revealed that this interface contained a high density of atomic steps. Upon irradiation, it was observed that SrTiO_3 began amorphizing precisely at these steps, a result that was linked with the local stoichiometry of the materials at the steps. Atomistic calculations on the same system [362] indicated that steps at the interface are strong traps for defects. However, the nature of this trapping is rather complex. Steps with slightly different local structure had significantly different interactions with defects, with one set of steps interacting strongly with both anion interstitials and vacancies, and the other set interacting more strongly with cation defects. This indicates a tendency for different defects to segregate to different steps, possibly leading to local changes in stoichiometry and thus instability of the material.

Another structural aspect is the crystallography of certain domains in the interface. This is manifested in the interesting behavior observed at the $\text{SrTiO}_3/\text{MgO}$ interface [363, 364]. STO thin films were grown by pulsed laser deposition on single crystal MgO substrates. The resulting morphology contained two domains of STO, oriented in the (100) and (110) directions relative to the substrate. Upon irradiation, the (110) domains amorphized at doses about an order of magnitude smaller than the (100) domains. Further, a crystalline layer of (100)-oriented STO developed across the entire interface. At this time, the origin of this behavior is not clear, but it seems to be intrinsic to the electrostatic properties of these materials. In particular, the polar (110) grains of STO become destabilized under irradiation, presumably because of the accumulation of charged defects at the interface. Atomistic calculations [364] reveal that these interfaces can have complex structures that depend not only on the orientation relationship between the two materials, but also the termination chemistry. Clearly, more work is necessary to develop a complete understanding of the behavior of these interfaces under irradiation.

Together, the foregoing results indicate the complex interaction of defects with all types of interfacial features and the need to account for them to develop a full understanding of the radiation response of these materials. Further, they highlight some of the peculiarities that occur in ionic systems as a consequence of electrostatic effects. However, these studies only hint at the complexities underlying these systems and significant work is needed to understand precisely how the interplay between interfacial structure, charge, and defect kinetics promote the radiation stability of oxide composites.

4.1.4. Outstanding questions

While the work described above provides new insights into the response of oxide nanocomposites to irradiation, there are a number of complications that real systems exhibit that are still unexplored. We describe some of these outstanding questions that still need to be addressed to fully understand how these composites behave under extreme conditions.

First, as the composite microstructure evolves and some regions of the composite become amorphous, the composite essentially becomes a three-phase composite, with the original A and B phases and a new amorphous C phase. Phase C will have its own defect energetics (formation and migration properties) that must be accounted for in order to predict the overall response of the composite to irradiation. However, to predict the formation of the Phase C itself, a better

understanding of the precise mechanisms of amorphization within the relevant materials must be obtained. While, as discussed above, a great deal of work has been devoted to understanding amorphization in oxides, there is still a lack of understanding of the critical defect concentration for the onset of amorphization in a given oxide. These types of parameters must be known to make quantitative predictions of the phase evolution in these composites.

Second, the model presented above was developed for dilute defect concentrations. That is, defects were assumed not to interact except via recombination. Neither long-range electrostatic interactions nor defect clustering reactions were taken into account. As the defect content evolves, and in particular in ionic oxides, as charged defects migrate from one part of the system to another, electrostatic effects will become important. Specifically, space charges [365] will almost certainly form at the interfaces, influencing the subsequent evolution of the defects. Further, ionization effects [299] will change the dominant charge state of each defect, changing both the relative defect energetics but also the response to any electrostatic fields within the material. Finally, defect-defect interactions can lead to defect clustering and those defect clusters will have their own energetic landscapes [366] that would need to be considered for quantitative predictions.

Third, while the defect evolution in the systems presented in Fig. 4.4 seems to be dictated by bulk defect energetics and not by the structure of the interface, the interfacial structure is still anticipated to play a role. Whether that structure is characterized by features such as misfit dislocations [363, 364] or atomic steps [361, 362], these features will act as sinks for defects and further modify the evolution of defects. Correlating the atomic structure of the interface with defect behavior at the interface in oxide heterostructures is the subject of ongoing work.

Finally, not only can the phase structure of the composite evolve with irradiation, but so can the chemical structure. If an interstitial species produced in one phase diffuses to another, it will change the chemical composition of that second phase, possibly leading to either complexions (new phases) at the interface [367] or even a complete transformation of the entire phase into a new phase. Again, predicting the evolution of the composite depends on knowing how the individual phases interact with one another as the composite evolves under irradiation.

4.2. Morphological stability under heavy ion bombardment

Layered composites of insoluble metals are thermodynamically metastable, so long as the layers remain continuous. Morphological stability breaks down if one of the layers “pinches off,” forming a bridge between neighboring layers, as illustrated in Fig. 4.7 [368]. Pinchoffs eventually lead to complete phase separation under high temperature annealing [261]. They may be created by plastic deformation [369, 370], misfit strain [371], and GB grooving [372, 373]. They may also be caused by mixing under heavy ion or neutron irradiation [374]. This section will review the state of knowledge on radiation-induced mixing (RIM) at interfaces in low solid solubility metals and how it relates to interface morphological stability under heavy ion or neutron irradiation.

Displacement damage in crystalline solids caused by high-energy heavy ions and neutrons is qualitatively different from that caused by high-energy light ions, such as hydrogen (H) or

helium (He) [375-378]. While the latter generates isolated vacancy-interstitial pairs, the former may give rise to collision cascades sufficiently dense to initiate thermal spikes (TSs): volumes on the order ~ 10 nm in diameter whose temperature reaches thousands of Kelvin for several picoseconds [379]. The core of a TS behaves as a nano-scale droplet of equilibrium liquid during this time [375]. TSs were first proposed by Brinkman [380] and later confirmed in molecular dynamics (MD) simulations by de la Rubia *et al.* [381]. TSs give rise to distinct forms of damage, such as vacancy and interstitial clusters [377]. They also lead to forced mixing at heterophase interfaces.

The steady-state morphology and composition profile across interfaces under heavy ion bombardment is governed by a competition between collision-induced mixing and thermodynamically driven, thermally activated de-mixing. Above a critical temperature, hypothesized to be proportional to the average cohesive energy [382], intermixing is driven by thermally assisted, radiation enhanced diffusion [382, 383]. Below this temperature, mixing is temperature independent and dominated by collision-induced mixing [384].

Two kinds of models were initially proposed to explain mixing in the low-temperature regime: ballistic mixing (BM) and liquid phase mixing within thermal spikes (TSM). BM is due to atomic displacements induced directly by two-body scattering and may be characterized by an effective diffusivity [385]. Sigmund *et al.* described relocation of impurities based on BM, finding that it is strongly dependent on the mass ratio of the mixed species [386]. However, Cheng *et al.* showed that metallic bilayers with similar mass ratios nevertheless exhibit rather different mixing rates, undermining the BM model [387].

In support of TSM, Seitz and Koehler calculated that liquid phase diffusion might occur within thermal spikes [379]. Vineyard then developed a theoretical model for the number of jumps inside a thermal spike by solving the heat equation [388]. To account for chemical driving forces, Cheng *et al.* proposed adding a Darken term into the effective diffusivity [387]. Later, the same authors reported that for bilayers with zero heats of mixing, RIM is inversely proportional to the square of average cohesive energy [389], in agreement with Vineyard's model. Based on this model, Johnson *et al.* [390] derived a phenomenological expression for mixing as a function of average cohesive energy and the heats of mixing. Nastasi and Mayer then calculated liquid interdiffusivity from a hard sphere model based on the kinetic theory of Enskog, and used it to explain the amount of mixing inside thermal spikes [391]. Averbach *et al.* further proposed that RIM may be reduced in materials composed of elements with a liquid phase miscibility gap [392].

RIM has also been extensively studied using MD, generally supporting the TSM picture [393], but also giving rise to new insights. Gades and Urbassek confirmed the inverse-square dependence of mixing on cohesive energy and found a stronger-than-linear relation with heats of mixing [394]. Nordlund and Averbach found an inverse Kirkendall effect at Cu/Co and Cu/Ni interfaces driven by different recrystallization rates due to differences in melting temperature [395]. On the other hand, Sule *et al.* reported that mixing does not depend on chemical driving forces in Ti/Pt and Al/Pt bilayers [396], but seems to be highly dependent on the mass ratio between the overlayer and substrate [397]. They argued that asymmetry of intermixing in the nearly equal mass Co/Ti system might be due to differences in atomic size [398]. These authors also reported abnormal enhanced nanoscale intermixing in Pt/Ti bilayers [399].

4.2.1. Fundamental mechanism of radiation-induced mixing between low solubility metals

Since RIM is thought to occur mainly within TSs, it may be expected that liquid phase properties affect RIM rates [392, 400]. The atomic scale mechanisms of RIM at interfaces between low-solubility metals have recently been investigated, focusing especially on the effect of liquid phase properties [401]. MD was used to model the effect of many thousands of 10 keV collision cascades impinging on a single interface, corresponding to high dose, heavy-ion or neutron bombardment. These simulations represent the low temperature limit of RIM, where no thermally activated diffusion occurs. In immiscible metals, these conditions give an upper bound on RIM rates, since the effect of thermally assisted diffusion would have been to cause thermodynamically driven de-mixing.

To isolate the effect of liquid phase properties on RIM from the influence of other factors, such as atomic mass ratios or solid phase properties, these simulations were conducted on just one model interface, namely Cu-Nb. Three well-characterized EAM [241] potentials are available for this binary system [242, 402]. All three provide comparably accurate descriptions of the elemental properties of Cu and Nb as well as the solid-phase portion of the equilibrium phase diagram of Cu-Nb [403]. Short-range interactions in all three potentials follow the Ziegler-Biersack-Littmark (ZBL) form [237], yielding identical high-energy scattering cross-sections.

However, all three potentials exhibit markedly different liquid phase properties [402]. Only one of these potentials provides the best description of the Cu-Nb binary system, namely the one developed in Ref. [402]. It has a fully miscible liquid phase and a eutectic point on the Cu-rich side (20% at. Nb) at 830°C. In contrast, one of the remaining two potentials predicts a large miscibility gap in the liquid phase with a critical temperature near 3500°C [242, 402]. The third potential predicts a completely miscible liquid phase, but with a eutectic point so deep that it cannot be determined using conventional atomistic methods because the liquid vitrifies into an amorphous solid before the solidus is reached [402]. Taken together, these three potentials provide an extremely convenient computational model system that enables the effect of liquid phase properties on RIM to be determined unambiguously, independent of other factors.

Qualitative mixing histories were similar for all potentials and interfaces studied. Figure 4.8 illustrates a typical mixing history at four successive dose levels: 0, 1, 3.5, 5 dpa (computed following the steps proposed by Stoller *et al.* [404]). Figure 4.8a-d show the distribution of Cu and Nb atoms at each dose, Fig. 4.8e-h visualize the location of fcc, bcc, and amorphous atomic environments, determined using adaptive common neighbor analysis [405], and Fig. 4.8i-l show composition profiles as a function of distance normal to the original location of the interface. The simulation begins with a perfectly sharp interface, as shown in Fig. 4.8a, 4.8e, and 4.8i. As the dose increases, the neighboring Cu and Nb gradually mix and the composition profile broadens. Numerous isolated impurity atoms may be seen in the crystalline Cu and Nb layers. Furthermore, an amorphous layer grows by consuming the neighboring fcc and bcc layers.

To characterize mixing rates quantitatively, the mixing parameter (MP), defined by Averbach and Peak in Ref. [392], was computed:

$$MP = \frac{D^{eff} t}{\phi F_D}.$$

Here D^{eff} , is the effective mixing interdiffusivity, t is irradiation time, ϕ is ion fluence, and F_D is the deposited nuclear energy per ion per unit depth. The MP therefore has units of $\text{\AA}^5/\text{eV}$. It relates the effective interdiffusion length, $\sqrt{D^{eff} t}$, to the mixing volume per unit energy deposition ϕF_D . It is a convenient means for quantifying RIM rates because it does not depend on the details of the irradiation conditions, specifically the type and energy of the irradiating ion (provided that it is a heavy ion, capable of generating TSs in the target material).

Two different methods for computing MPs from MD simulations, such as those illustrated in Fig. 4.8, were developed [401]. MPs for Cu-Nb interfaces of three different crystallographies using the three different EAM potentials mentioned above were then computed. To within the uncertainty of the calculations, interfaces with differing crystallographies have identical MPs. Thus, in the absence of thermally activated de-mixing processes, interface crystallography does not affect RIM.

On the other hand, the MPs for the three different EAM potentials differed markedly, indicating that RIM does depend on liquid phase properties. In particular, RIM rates are found to be well correlated with liquid phase interdiffusivities. Figure 4.9 plots the effective mixing interdiffusivity, D^{eff} —computed on a “per TS” basis (units of $\text{\AA}^2/\text{TS}$)—against the liquid phase interdiffusivity, $\bar{D}$, found at 4000 K (the temperature when the TSs are largest) for each potential. These two quantities are approximately linearly related with slope of $\kappa \approx 1.3 \text{ ps/TS}$, corresponding to the approximate duration of an individual TS.

A closer analysis of the time dependence of mixing within individual TSs showed that mixing is indeed due to interdiffusion, although over timespans closer to 3 ps, rather than 1.3 ps. However, for all three potentials, the initial mixing stage was followed by partial de-mixing over times of ~ 10 ps. This de-mixing was attributed to the segregation of impurities to the liquid core of TSs as they cool and solidify. The net effect of mixing by interdiffusion followed by partial de-mixing by impurity segregation on MPs may be captured by the phenomenological relation

$$MP \approx \frac{\kappa V_{TS} \bar{D}}{E_D}.$$

Here, V_{TS} is the average TS volume, and E_D is the deposited energy per TS. In all the simulations, the contribution of ballistic displacements to mixing was found to be negligible.

These results demonstrate that to design nanocomposites with greatest morphological stability under neutron or heavy ion irradiation, it is desirable to choose low solubility metals with minimal liquid phase interdiffusivity as the constituents. This choice is expected to minimize RIM and therefore to reduce the likelihood of initiating a layer pinchoff under irradiation.

4.2.2. Critical layer thickness for onset of morphological instabilities

To assess the limits of morphological stability of Cu-Nb layered composites under heavy ion or neutron irradiation, 100 keV collision cascades in models such as the one shown in Fig. 4.10a were simulated [374]. The TSs generated in these simulations are large enough to span multiple

interfaces in the model, as shown in Fig. 4.10b. Multilayers of four different thicknesses were simulated, namely: 10 Å, 18 Å, 32 Å and 37 Å. These simulations used the EAM potential developed in Ref. [402] because, of all the available potentials, it best represents the liquid phase properties of the Cu-Nb binary system.

An example of the kind of damage created by TSs in these simulations is shown in Fig. 4.11a. To determine if this damage will lead to the pinchoff of a layer, its evolution in time through thermally activated processes must be modeled. The time scale for this damage evolution is too long to capture using conventional MD. Furthermore, the complex damage state in Fig. 4.11a is not well suited for modeling with lattice kinetic Monte Carlo (kMC) or accelerated MD methods. Therefore, phase field simulations [406], implemented in 3-D in the COMSOL finite element method (FEM) code were used to estimate how the morphology of the multilayer is affected by radiation-induced damage.

These phase field simulations use the Cahn-Hilliard equation [407] with a single order parameter, ϕ , representing the local Cu/Nb composition. The local free energy density has a double-well form,

$$f(\phi) = 4\Delta f \phi^2 (1 - \phi)^2,$$

where Δf is the average of the free energies of mixing of Cu and Nb in fcc and bcc crystal structures at 600 K [403]. The interface thickness is set to ~ 2 Å: comparable to the spacing between Cu {111} and Nb {110} planes and small enough to allow for convergence with respect to mesh element size. The elastic energy from the lattice mismatch between Cu and Nb as well as local distortions due to defects and defect clusters created during collision cascades were ignored. Since only the final state of the multilayers (pinched off or not) is of interest, all simulations were performed in reduced time units.

The initial order parameter distribution is obtained from atomic structures created by MD simulations, as illustrated in Fig. 4.11b. Pinchoff channels connecting some cascade-affected layers (mostly Nb) are formed during the phase field simulation while other layers return to their initial, flat morphology, as shown in Fig. 4.11c. The width of the pinchoff channels continues to increase with time, consistent with onset of the breakdown of the layered morphology and eventual spherodization [261, 408]. No cases of precipitate formation inside layers were found.

By analyzing all layers in all the simulations, the layer pinchoff frequency and multilayer survival probability were obtained as functions of layer thickness. A multilayer is considered to have survived if no layers in it have pinched off. Only $\sim 30\%$ of the 10 Å-thick multilayers survived after one collision cascade, while all other thicker layers above 18 Å are morphologically stable. Thus, multilayer composites may be expected to remain morphologically stable under heavy ion or neutron irradiation, provided that their layer thicknesses are above ~ 2 nm.

The layer-thickness dependence of morphological stability under irradiation may be explained based on liquid phase interdiffusion in TS cores. As described in the previous section, interdiffusion in TS cores is responsible for RIM at isolated interfaces. In multilayers with small thicknesses, regions of interdiffusion formed at neighboring interfaces during a thermal spike may overlap. The characteristic interdiffusion distance over the lifetime of a thermal spike is ~ 10 Å. Thus, regions of interdiffusion at neighboring interfaces are expected to overlap in multilayer

models with layer thicknesses of 10 Å and, occasionally, 18 Å. Such synergistic mixing across adjacent interfaces gives rise to frequent pinchoffs.

4.2.3. Outstanding questions

It is now understood that low-temperature RIM of low solid solubility metals is governed by liquid phase interdiffusion. Multilayers made of such metals are expected to remain morphologically stable under heavy ion and neutron irradiation down to layer thicknesses of ~2 nm. Nevertheless, several outstanding questions about RIM—and therefore about morphological stability of interfaces under irradiation—remain to be answered.

The simulations described above focused on the low-temperature limit, where thermally assisted de-mixing processes are negligible. The mechanisms governing RIM at elevated temperatures are relatively less well studied, largely because the longer times over which they occur make them inaccessible to MD modeling. Their effect on patterning and nanoscale morphology evolution has been modeled extensively using lattice kMC methods [409-414]. However, off-lattice kMC methods capable of modeling de-mixing within the complex local structures found at heterophase interfaces have yet to be developed.

Most modeling and experimental studies of RIM have been carried out on bilayers. An exception is the body of work led by Averbach and Bellon that used morphological instabilities arising from ion-induced mixing to create compositionally patterned microstructures [409-414]: a prediction they later confirmed experimentally [415, 416]. They also developed “phase diagrams” for alloys driven by irradiation, identifying ranges of temperatures and displacement rates where collision-induced mixing and thermally-assisted de-mixing compete, giving rise to steady state patterned microstructures [417]. Such investigations may be extended to assess the stability of defective multilayer morphologies, e.g., ones with slip offsets, or to account for microstructural features, such as grain boundaries, voids, or impurity precipitates.

Morphology evolution has been studied in multilayers in the long-time limit where complete recovery of collision-induced mixing is expected [374]. At high dose rates, however, interfaces might not fully relax after each recoil event and defects created by multiple collision cascades may accumulate. Impurity precipitation and growth may also initiate morphological instabilities [217, 409]. The effects of incomplete de-mixing on morphological stability of interfaces have yet to be fully understood.

Liquid phase interdiffusivity is responsible for RIM in low solubility metals. The factors that affect liquid phase interdiffusivity are well understood. These are the liquid-phase heats and entropies of mixing as well as single-element diffusivities [418]. However, there are presently no models for the non-equilibrium solute segregation that occurs during the partial de-mixing stage of TSs. Solute segregation at solidification fronts with velocities up to 10-20 m/s may be described using the continuous growth model (CGM) [419]. In contrast, the solidification front at the edge of a TS moves at $\sim 10^2$ m/s. Other factors besides solidification front velocity may also influence de-mixing, e.g., capillary effects arising from the high curvature of TS boundaries [420] or volumetric changes occurring during solidification [421]. These effects remain to be investigated in detail. An improved understanding of them will lead to more accurate predictions of morphological stability of multiphase nanocomposites under heavy-ion and neutron irradiation.

Several studies have investigated the stability of layered composites of low-solubility solids as a function of temperature and stress. For example, the stability of multilayers under internal and external stresses depends on layer thicknesses and elastic mismatch between the layers [371, 422]. The evolution of the internal morphology of unstable layers further depends on material properties and growth conditions, leading to pinch-off in some cases, but not others [423]. In some materials, stability at elevated temperature further depends on interface crystallography. For example, the temperature to solutionize Ni/Ni₃Al multilayers is 100 K lower for multilayers with Ni-Ni₃Al interfaces formed along {100} planes than along {111} planes [424]. The effect of stresses and interface crystallography on the morphological stability of irradiated materials has yet to be investigated in detail. Such considerations are important for the development and assessment of structural composites intended for service under irradiation, e.g., in nuclear energy applications.

4.3. Crystallographic stability in extreme strains

4.3.1. Processing effects on texture and interface evolution

An important aspect in developing next-generation metallic materials with superior properties is the ability to control the microstructure [163, 425-428]. Changes in microstructure can be achieved by changing chemistry (alloying), processing method, processing conditions (temperature and rate), or sequences of processing steps. Two important and related geometric aspects of microstructure are the distributions of crystallographic orientations (texture) and of grain boundary or interface character. Both aspects are critical to understanding and predicting the deformation behavior of nanomaterials.

Thermodynamic, near-equilibrium processes, such as solid-state phase transformation, epitaxial growth or solidification processing, can produce highly textured microstructures with structurally ordered boundaries or interfaces at the atomic scale [144, 194, 195] that result in properties such as good thermal stability [429, 430], radiation damage tolerance [50, 431], and high flow strengths [190, 432-434].

For structural metals, the common manufacturing methods involve mechanical work, which drive the microstructure far-from-equilibrium [435-437]. Unlike the aforementioned thermodynamic processes, mechanical deformation involves plastically straining the material and tends to create microstructures consisting of a distribution of orientations (called texture) and large fractions of dislocation-rich, high-energy (i.e., non-CSL) boundaries [438-442]. Within the grains, the dislocations generated in deformation tend to self-organize into dislocation patterns or networks of “cells”, “cell blocks”, or lamellae [443-446]. The boundaries of these substructures are disordered [447-449], generally comprised of ledges and tangles of interlocked dislocations. They are presumed to be in a lower energy state [450] compared to a uniformly random arrangement of dislocations.

Imposing severe levels of plastic strain via mechanical processing can lead to grain refinement, in which the new ultra-fine or nanosized grains contain little substructure. Yet still, the newly formed grain boundaries are high-energy, possessing a disordered structure and have often been referred to as ‘non-equilibrium’ boundaries [441, 451]. While deformation-induced intra-

granular substructure and nanostructuring can result in increases in material strength [440, 452], they are observed to be unstable with respect to heating and hence the material loses strength [453, 454].

Both conventional deformation and severe plastic deformation (SPD) studies discussed in the foregoing focused on grain boundaries in single-phase pure and alloyed metals. In recent years, SPD techniques, such as wire drawing, high pressure torsion (HPT), equal channel angular extrusion (ECAE), and accumulative roll bonding (ARB), have been applied to many kinds of two-phase composite systems, including Cu/Ag and Cu/Nb [148, 181, 194, 455-457], Al/Zn [458], Cu-Al [459], Cu-Ni [460], Ag-Fe [461] and Zr-Nb [462, 463]. As for single-phase alloys, nanostructuring and the expected concomitant substantial increases in strength were achieved in these two-phase metal systems. In some cases, deformation textures were measured and these were found to exhibit a dispersion of orientations, not significantly different from those that developed within the constituents when deformed alone under the same conditions. The crystallographic character and properties of the bimetal interfaces after deformation have received even less attention compared to studies of material textures, grain structure, and flow stress, apart from a few exceptions. In the case of Cu-Nb wires formed using SPD involving repeated wire-drawing extrusions, the Cu-Nb interfaces in the Cu-Nb nanowires were studied via atom probe tomography and TEM. Several types of interface structures were reported, some characterized as disordered and some ordered [68, 464]. Similarly in HPT Cu-Nb, which imposes extreme simple shearing, atom probe tomography revealed that the interfaces of the refined 5-10 nm grains were not sharp, exhibiting some chemical variation [148]. No special interface structures were reported. In HPT processing of a Cu-Al alloy, Al was found to phase separate from Cu when the grains were refined below 10-15 nm [459]. Only a fraction of the Cu-Al phase boundaries were semi-coherent boundaries. Thus, from these studies, it appears that heterogeneity in interface character and structure results from extreme strains via extrusion or simple shearing.

4.3.2. Development of a crystallographically stable interface in extreme rolling

Recently it was reported that a two-phase nanostructured composite fabricated via ARB, an SPD technique that involves repeating rolling passes, exhibited a ubiquitous bimetal interface characterized by a specific crystallographic character and a highly ordered atomic structure with little-to-no detectable defects [146, 194, 465]. The ordering was first detected by a change in texture evolution from a typical rolling texture for mm and micron-scale layer thicknesses to an unusually sharp, atypical texture for submicron and nanoscale layer thicknesses [455]. Using various diffraction techniques, the highly oriented texture was later shown to correspond to the development of a preferred interface character [194, 466]. Surprisingly, these interfaces were not defective with extrinsic dislocations, contrary to what would be expected after severe plastic deformation [196]. In this respect, they were reminiscent of interfaces formed in thin composite films fabricated via deposition. Later experimental studies found these ARB-induced interfaces to be structurally stable under heating, subsequent mechanical deformation, and light-ion irradiation [22, 434, 467, 468], again much like the Cu-Nb composite thin films fabricated using deposition techniques. From a technological viewpoint, this result was exciting, because unlike thin films, ARB sheets can be made in bulk, suitable for structural applications.

It is also intriguing from a scientific point of view; texture and interface evolution appeared to be coupled and evolving in a non-conventional manner for a conventional plastic deformation

process, such as rolling. Interface effects and influences of grain neighbor interactions across the interface on plasticity have evidently become strong after extreme straining. As it represented a contradiction to conventional thought, this observation launched an investigation into texture and interface evolution during ARB. This study is described next.

4.3.3. Accumulative roll bonding for bulk nanolayered composites

Bulk sheets of layered Cu-Nb composites were fabricated by ARB [193, 455]. The ARB process begins with a clad, alternating stack of coarse-grained polycrystalline sheets of Cu and Nb in equal fractions [186] (Fig. 4.12a). A specially designed copper-cladding method was used so that no new interfacial area formed by deformation was exposed to air, thereby preventing the accumulation of oxides in the interface [432]. Through repeated rolling, cutting, and restacking, the ARB process imposes radically extreme strains, achieving 3-6 orders of magnitude refinement in the individual layer thickness, h , (from 10 mm to 10 nm) without changing the overall dimensions of the material (Fig. 4.12b). During the entire refinement process, the lamellar architecture is preserved and the bimetal interfaces remain planar and, due to immiscibility of these two metals, chemically sharp [146, 185] (Fig. 4.12c).

To test for co-deformation between the Cu and Nb phases, the thicknesses h of a large sampling of Cu and Nb layers within the same sample were measured via SEM and TEM [432]. This evaluation was repeated on heavily deformed samples with nominal layer thicknesses ranging from $h = 10 \mu\text{m}$ to 10 nm. It was found that both the Cu and Nb phase reduced in thickness at similar rates and to values expected from the applied percent rolling reduction. Thus, it can be concluded that from $h = 10 \mu\text{m}$ to 10 nm, the two phases co-deformed without debonding or sliding interfacially.

Another interesting feature of these composites was their extremely high aspect ratio grains. A high-resolution EBSD technique [466] revealed that the aspect ratio of the elongated grains for Cu and Nb exceeded 30 and 80, respectively. Thus, the nanolayered ARB composites consisted of an unusually high ratio of density of bimetal interfaces to density of grain boundaries.

4.3.4. Texture evolution in ARB

In the rolling deformation of a metal, there is a strong driving force for the individual crystals to assume stable crystallographic orientations. They reorient via crystallographic slip to more stable or so-called ideal orientations, where they in principle maintain this orientation with further straining. This phenomenon is generally called texturing. Deformation textures of heavily rolled materials typically consist of many of these ideal components or orientations and tend to remain stable with continued deformation. Rolling textures can differ in their relative fractions of these components, depending on applied strain level, stacking fault energy, and deformation mechanisms (whether the material is deforming by full dislocations, partial dislocations, or twins).

In the ARB process, the same deformation state as conventional rolling is imposed. For common metals like Cu and Nb, the stable orientations for rolling have been well studied [435, 436, 469]. The rolling texture of single-phase Nb consists of a range of orientations with a common axis $\langle uvw \rangle$ or plane $\{hkl\}$, referred to as the α $\langle 110 \rangle$ fiber and the γ $\{111\}$ fiber. Within these fibers, the $\{001\}\langle 110 \rangle$ and $\{111\}\langle 110 \rangle$ orientations are particularly strong [436, 469, 470].

Monolithically rolled Cu develops texture with strong intensities at the $\{112\}\langle 111 \rangle$ (called C), $\{4\ 4\ 11\}\langle 11\ 11\ 8 \rangle$ (known as D), $\{110\}\langle 112 \rangle$ (B), and $\{213\}\langle 364 \rangle$ (S) components [435, 436, 470, 471]. (These ideal components, C, D, B, and S, are defined using standard rolling $\{ND\}\langle RD \rangle$ nomenclature, where ND is the direction of the normal to the rolling plane and RD is the rolling direction.) For reference for the upcoming discussion, Table 4.1 lists the particular set of stable texture components that develop in *rolling* mediated by *slip* only (*RS*), which we denote here by $g_{fcc}(\theta, RS)$ for fcc Cu and $g_{bcc}(\theta, RS)$ for bcc Nb. For materials that accommodate rolling strains by slip and twinning, the peak texture components are different. Likewise we designate the special set of stable orientations generated in Cu in *rolling* mediated by *slip* and *twinning* (*RST*) by $g_{fcc}(\theta, RST)$ [472]. These are also found in Table 4.1.

Neutron diffraction was used to measure the texture of each phase in the Cu-Nb ARB samples. For samples in which h ranges from 100 μm to 1 μm , deformation textures of each phase closely resembled the rolling texture it would have developed when rolled alone [455, 473]. For these length scales, the layers were polycrystalline through-thickness; that is, many crystals span the thickness of the individual layers and the orientation distributions of the Cu and Nb phases in the composite corresponded to stable groups $g_{fcc}(\theta, RS)$ and $g_{bcc}(\theta, RS)$, respectively. For samples in which h had been refined below 1 μm , the deformation textures became unusually sharp, significantly deviating from $g_{fcc}(\theta, RS)$ for Cu and $g_{bcc}(\theta, RS)$ for Nb. At these fine length scales, the layers are no longer polycrystalline through thickness; that is, one crystal spans the distance between two adjacent bimetal interfaces [146, 466]. Component analyses of these textures revealed that the predominant orientations in the Cu phase range within an 8° span from the C $\{112\}\langle 111 \rangle$ component to the D $\{4\ 4\ 11\}\langle 11\ 11\ 8 \rangle$ component (in the $\{ND\}\langle RD \rangle$ nomenclature). In the Nb phase, the crystals lie within an even narrower 5° span, ranging from the $\{112\}\langle 110 \rangle$ component (which is called the I component) to the $\{225\}\langle 110 \rangle$ component.

The few orientations associated with the highly oriented textures corresponded to recognized ideal orientations in rolling. Attaining these ideal orientations involved crystallographic slip within the grains. Taken together, observations of texture evolution and development of familiar rolling components indicate that crystallographic dislocation slip was the dominant deformation mechanism even down to $h = 10\text{ nm}$ layer sizes.

4.3.5. Emergence of a crystallographically stable interface

Single crystalline layers and sharp textures suggested that the Cu and Nb preferred to be joined in a special way across the interface. Assuming that the layers are planar, lying parallel to the sheet, we can associate the crystallographic axes parallel to the ND with the interface plane normal. On this basis, a set of interfaces can be envisioned, by combining a Cu crystal, oriented from the $\{112\}\langle 111 \rangle$ component to the $\{4\ 4\ 11\}\langle 11\ 11\ 8 \rangle$ component (in the $\{ND\}\langle RD \rangle$ nomenclature), with an Nb crystal, lying within $\{112\}\langle 110 \rangle$ to $\{225\}\langle 110 \rangle$. An example of a particular interface character is illustrated in Fig. 4.13.

To determine the pervasiveness of this interface character, an automated heterophase interface character distribution (HICD) technique was employed [194]. HICD uses orientation and phase maps, such as those supplied by EBSD, to characterize the local interface character over large volumes of the material. The statistical analysis from HICD reveals that the distribution of interface characters is surprisingly narrow, in agreement with the characters presumed from the

texture analysis. It was concluded that the predominant interface was the C $\{112\}<111>$ component of Cu joined to the I $\{112\}<110>$ component of Nb, as illustrated in Fig. 4.13, within a $\pm 10^\circ$ span. Thus, in this highly oriented nanostructure, a majority of the crystals fall within 0.1%-0.2% of the entire orientation space.

Figure 4.14 shows HRTEM micrographs of typical interfaces formed in ARB nanocomposites: the $\{112\}<111>\text{fcc}||\{112\}<110>\text{bcc}$ and $\{338\}<443>\text{fcc}||\{112\}<110>\text{bcc}$ interface. These two interfaces are misoriented by $\sim 7^\circ$ about the $<110>\text{fcc}||<111>\text{bcc}$ axis [465]. As shown, they both possess a highly ordered atomic structure with a zigzag morphology. This type of pervasive atomically ordered structure has been demonstrated in thin films fabricated by epitaxial growth; however, it is not expected of material fabricated by a bulk metal working technique such as ARB.

In a few works, the interfaces that are generated in ARB were modeled by MD simulation [68, 131, 150]. This approach provided an explanation for the zigzag morphology seen in Fig. 4.14. Within the perfect crystal, the crystallographic planes that correspond to the interface planes (e.g., $\{112\}\text{fcc}$, $\{338\}\text{fcc}$, or $\{112\}\text{bcc}$) are also faceted, possessing a regular zigzag pattern of alternating flat faces [131]. Consequently when these planes are joined and relaxed in simulation, the final interface structure contains a periodic array of facets [158, 465]. The remarkable likeness with the relaxed equilibrium structure calculated via MD indicates that the facets in the actual deformed structure in Fig. 4.14 are an intrinsic part of the atomic structure and, more importantly, that overall the interfaces in the deformed structure contain minimal defects.

4.3.6. Two key variables for crystallographic stability

In [196], two criteria were proposed for the crystallographic stability of an interface: plastic stability in co-deformation and low formation energy. Plastic stability in co-deformation means that neither crystal reorients during co-deformation. Thus, the crystals on either side of the interface must be orientationally stable (Fig. 4.15). As the two crystals on either side of the interface co-deform, they create new interfacial area (Fig. 4.15). The energetic penalty for creating new interfacial area depends on its crystallographic character. When the interface is crystallographically stable in deformation, the new interfacial area they create after deformation will possess the same interface character as the original before deformation. Accordingly, both criteria are needed for crystallographic stability in high strain deformation. These two criteria are usually not considered in conventional modeling techniques. At present, a materials model does not exist that accounts for changes in interface formation energy that could accompany changes in the orientation of the two adjoining crystals during plastic deformation.

In what follows, each condition is discussed and numerically quantified in turn. To combine their effects, a map is then constructed to identify which interfaces satisfy both criteria. The results reveal that meeting both criteria represents a severe constraint, which explains why a prevailing interface character in Fig. 4.14 is naturally selected after extreme strains.

4.3.6.1. Plastic stability of an interface in a bicrystal

To test for the plastic stability of a particular interface character, a 3D full-field, crystal plasticity finite element model of a Cu-Nb multi-layer was constructed [204]. This method was selected

because stress and strain and orientation gradients in the layers and near the interface, should they occur, can be calculated.

In the model, the layers were single crystals of Cu and Nb with pre-assigned starting orientations. They are joined such that they create a particular interface crystallographic character. During straining, they are enforced to co-deform, maintaining compatibility at their common interface. However, the crystals on either side may distort and reorient, changing the interface character. The model permits the crystals to deform by a combination of anisotropic elasticity and thermally activated dislocation slip [474] on established crystallographic slip systems (the $\{111\}<110>$ slip systems in fcc and the $\{110\}<111>$ and $\{112\}<111>$ slip systems in bcc [153]. The resistance to slip evolves with strain following a hardening model that includes self-hardening and latent hardening. The material parameters associated with the hardening model were characterized by a comprehensive suite of tests on Cu and Nb for a wide range of strain rates and temperatures.

Bicrystals with different starting interface characters are subjected to plane strain compression, a two-dimensional idealization of the deformation state in rolling that best applies to the central volume of the sheet. The stability of the interface character requires that both crystals on either side of the interface reorient at most only a few degrees. As a means of quickly comparing the plastic stability of different interfaces under the same straining conditions, we adopt the following measure [196, 204],

$$\omega = \exp\left(\frac{\Delta\Omega_{Cu}}{\Delta\varepsilon}\right) \exp\left(\frac{\Delta\Omega_{Nb}}{\Delta\varepsilon}\right) \quad (4.3.1)$$

which ranges from 0 to 1, where 1 is indicative of a perfectly stable bicrystal. The angle $\Delta\Omega$ is the minimum re-orientation angle of a crystal from its starting orientation during a strain interval of $\Delta\varepsilon$. The more the quantity $\Delta\Omega/\Delta\varepsilon$ of each crystal deviates from zero, the more the interface character has been altered. It is recognized that in the strictest sense, an interface character with $\omega < 1$ after deformation is not stable with respect to this deformation. However, if after very large strains, an interface reorients a small amount, such that ω is slightly less than 1, then this suggests that it was close to its stable point. For this reason, we can assign an arbitrary and reasonable tolerance of 10° reorientation on both sides (after 75% strain), which would correspond to $\omega = 0.8$.

To demonstrate, we consider the ARB interface in Fig. 4.14b: $\{112\}<111>fcc\parallel\{112\}<110>bcc$. The bicrystal model finds that after large strains, a new stable end state is achieved, which is close in orientation space to the original interface character. Specifically after 75% strain, the Cu crystal lattice rotates about the $<110>$ $\sim 6^\circ$ and the Nb crystal lattice about the $<111>$ $\sim 2^\circ$, which corresponds to $\omega = 0.86$. Starting from various 10° perturbations from $\{112\}<111>fcc\parallel\{112\}<110>bcc$ KS leads to nearly the same end state. In agreement, the predicted preferred end state lies within the narrow distribution of predominant interfaces observed in the ARB sample.

To probe the distribution of experimentally observed predominant interfaces, the calculation was carried out for several interface characters ranging from $\{112\}<111>fcc\parallel\{112\}<110>bcc$ to $\{4\ 4\ 11\}<11\ 11\ 8>fcc\parallel\{112\}<110>bcc$ in orientation space. The calculations find that they are all

stable, i.e., yielding $\omega \geq 0.8$. This result confirms that the predominant interfaces are plastically stable.

Another familiar interface is the KS interface that develops during deposition of Cu-Nb thin films. While this interface has very low formation energy, it is not naturally selected during severe plastic deformation via rolling. Repeating the bicrystal simulations for the KS (and Nishiyama-Wasserman, NW (see Sect. 2.2)) interfaces finds it to be highly unstable in plane strain compression. The Cu crystal reorients by 27° and the Nb crystal by 30° after 60% rolling reduction. This yields a value of ω of 0.434, indicating plastic instability. This result provides some explanation as to why this interface, despite its low formation energy, does not emerge in large-strain rolling deformation. In fact, these rotations are evolving the interface character towards the $\{112\}<111>\parallel\{112\}<110>$ orientation [204].

The bicrystal plasticity calculations were performed for several more interface characters. Among the vast lot, the interfaces investigated can be grouped into two mutually exclusive classes: group 1 consists of interfaces where both adjoining crystal orientations are stable components in the theoretical rolling texture of the corresponding monolithic material (Table 4.1) and 2) group 2 consists of interfaces where one or both crystals do not correspond to a stable rolling texture component. The orientations of the first group were present in the phases when the layers were polycrystalline through thickness [443]. Group 1 interfaces were tested in order to understand why so many of the stable orientations were not naturally selected when the layers were refined via severe plastic deformation to the nanoscale. The second group is included in the analysis to determine whether enforcing co-deformation with or between two theoretically unstable orientations in a bicrystal could stabilize these orientations.

For further insight, the question of whether the stability of a bicrystal correlates with the stability of its individual crystals is addressed. To this end, an analogous parameter ω^{SX} can be calculated wherein the reorientation angles $\Delta\Omega$ are obtained from interface-free, isolated single crystal simulations of the respective orientations, i.e.,

$$\omega^{SX} = \exp\left(\frac{\Delta\Omega_{Cu}^{SX}}{\Delta\varepsilon}\right) \exp\left(\frac{\Delta\Omega_{Nb}^{SX}}{\Delta\varepsilon}\right) \quad (4.3.2)$$

Obtaining one value for ω^{SX} requires two separate calculations, one for each constituent crystal.

For many candidate interface characters, Fig. 4.16 compares ω for a co-deforming bicrystal containing a single interface vs. ω^{SX} for its corresponding two crystals deforming independently. Interfaces in group 1 are denoted by squares and those in group 2 by circles. Interfaces lying on the diagonal line in Fig. 4.16 indicate that co-deformation did not constrain the two adjoining crystals from deforming as they would individually. For example, if $\omega = \omega^{SX} = 0.4$, then the two constituent crystals whether deforming separately or co-deforming together as a bicrystal are equally unstable. Likewise, when $\omega = \omega^{SX} = 0.95$, then the two crystals as individuals or bonded as a bicrystal are equally stable. In both examples, because when $\omega = \omega^{SX}$, enforcing the two crystals to co-deform had no effect on their orientational stability; they reoriented the same amount whether bonded or not. Calculations in Fig. 4.16 show that only the most stable of interfaces falls on the line ($\omega = \omega^{SX} \geq 0.95$), a result that may be a consequence of the fact that neither parameter can exceed unity. The vast majority of the remaining interfaces are less stable

and fall below the line. This result means that most often the less stable of the two crystals makes the bicrystal less stable, not the other way around. Thus, it is found that co-deformation can limit interface stability. The measure ω for the bicrystal is bounded by the minimum of ω^{SX} for the two crystals making up the bicrystal. This finding is also interesting because it shows that while ω^{SX} may be viewed as easier than ω to determine since no interface is involved in its calculation, ω^{SX} apparently is not indicative of the behavior of the bicrystal, i.e., most often ω does not equal ω^{SX} .

To compare with experiment, the interfaces observed in the material are marked with a black symbol. Notably, these observed interfaces have $\omega > 0.8$, indicating that they are plastically stable. However, there are many other equally plastically stable interfaces that are not observed. It turns out that these unseen yet plastically stable interfaces were comprised of crystal orientations that belong to the theoretical rolling textures. Thus, it is likely these orientations were pre-existing in the material when the layers were polycrystalline, before the preferred set of interfaces emerged when the layer became single crystalline. This implies that these unobserved plastically stable bicrystals in Fig. 4.16 are not interfaces that have yet to be discovered, but are simply those that were not chosen. This indicates that plastic stability, while necessary, is insufficient. Another factor must be intervening to dictate which interfaces stabilize. As mentioned earlier in Sect. 4.3.6, this second important factor is considered to be γ^{int} , the energy involved in forming new interfacial area (Fig. 4.15). This variable is discussed next.

4.3.6.2. Energetic landscape for bimetal interfaces

MD simulation of a Cu-Nb bicrystal is employed to calculate the relaxed atomic interface structures of a series of Cu-Nb interfaces and their associated interface formation energies. The model and methods are fully described in [131, 158, 465], Fig. 4.17 shows the variation in interface formation energy, γ^{int} , with the tilt angle of the Cu crystal about the $\langle 110 \rangle_{\text{fcc}} \parallel \langle 111 \rangle_{\text{bcc}}$ axis. As shown, γ^{int} has a non-linear dependence on the tilt angle, being strongly dependent on interface character. Most intriguing is the finding that the $\{112\} \langle 111 \rangle_{\text{fcc}} \parallel \{112\} \langle 110 \rangle_{\text{bcc}}$ and $\{338\} \langle 443 \rangle_{\text{fcc}} \parallel \{112\} \langle 110 \rangle_{\text{bcc}}$ interfaces, also seen in Fig. 4.14, correspond to local energy minima.

The association of the preferred interfaces with minimum energy cusps strongly supports the premise that interface formation energy is a key variable in the evolution towards stable interfaces. However, it is important to mention that there are Cu-Nb interfaces with lower γ^{int} than those corresponding to the cusps in Fig. 4.17. MD modeling has shown that the Kurdjumov-Sachs Cu-Nb interface has a formation energy of $\gamma^{\text{KS}} = 586 \text{ mJ/m}^2$ [48] and thus lies below the scale of Fig. 4.17. Interface formation energy, therefore, while critical, is not the only important variable responsible for determining the formation of ordered, characteristic interfaces under severe plastic deformation.

4.3.7. A map for crystallographically stable interfaces

To examine how interfaces compare with respect to both criteria, normalized interface energy $\gamma^{\text{int}}/\gamma^{\text{KS}}$ and plastic stability ω are plotted on each axis of the map in Fig. 4.18. Crystallographically stable interfaces are anticipated to lie in the upper left-hand corner, where interfaces have both low formation energy and high plastic stability. Notably the experimentally observed interfaces (black symbols) exclusively collect in this stable region. These interfaces

include the $\{112\}<111>\text{fcc}||\{112\}<110>\text{bcc}$ and $\{338\}<443>\text{fcc}||\{112\}<110>\text{bcc}$ interfaces (Fig. 4.14) and those lying in between in orientation space. A few interfaces that are observed in small fractions, such as the $\{552\}<115>\text{fcc}||\{225\}<110>\text{bcc}$ and $\{338\}<443>\text{fcc}||\{001\}<110>\text{bcc}$ interfaces, lie within a border region. It is expected that these interfaces could eventually reorient with deformation to another interface character that would fall within the stable region. Many interfaces that are not observed experimentally after large strain rolling are seen to lie outside of the stability region, such as the KS and NW interfaces.

The map indicates that the region of stability is small relative to the vast space of interface character. Mechanically stable interfaces must maintain crystallographic stability while co-deforming, and form relatively low-energy interfaces, preferably associated with cusps in an energy landscape. Only a few interfaces and bimetal systems can satisfy these criteria simultaneously – a limitation that explains why the Cu-Nb nanomaterial evolves to a highly ordered, oriented state in large strain rolling.

An interesting implication of the map is the connection between crystal orientation and the formation energy of the interfaces that bound it (see schematic in Fig. 4.15). For pristine and sharp interfaces in the Cu-Nb system, the effect of interface character on interface energy is found to be strong (e.g., Fig. 4.17 and [465]). The landscape is found to contain a few energy minima. While the value of the energy may be important, the depth of the energy wells is just as, if not, more important. Interfaces whose characters correspond to energy minima in formation energy will incur large increases in energy with small deviations in character, whereas those distant in orientation space from these cusps will not. When mechanical forces can form an interface character that also corresponds to a low-energy state, then this interface would clearly be resistant to leaving this state with continued straining. On the other hand, for a bimetal system in which the effect of interface character on interface energy is negligible, interface energy is not expected to play a dominant role. Texture stability alone may dominate instead. Because stable textures for each phase have several preferred orientations, many bimetal interface characters will emerge.

4.3.8 Crystallographically stable interfaces and deformation twinning

In the above analysis, the crystals on both sides of the interface were presumably deforming by slip. When metal crystals are refined to nanoscale dimensions, the chances of deformation twinning for strain accommodation increases [174]. This is particularly true for the ARB nanolayered composites with predominant $\{112\}<111>\text{fcc}||\{112\}<110>\text{bcc}$ interfaces.

Previously in Sect. 2.3 the strong propensity for these interfaces to twin was discussed. During the ARB refinement process, twins are first observed at $h = 200$ nm, and their frequency and thickness both increase as the layer thickness is refined to $h = 10$ nm [185, 455]. At $h = 10$ nm, texture analyses suggest that the twin volume fraction is around 30% [156, 475]. TEM and EBSD analyses indicated that twins expand to encompass wide segments of the layers [146, 475].

The observed size dependence on deformation twinning in Cu is consistent with observations on other Cu-based nanomaterials. In Cu-Ag layered composites, Cu-Nb wires, Cu nanowires, and nanocrystalline Cu, the Cu crystals have been observed to twin for sizes as large as ~ 150 nm [163, 181, 476, 477]. Stacking fault formation in such large size crystals (> 135 nm) due to the

nucleation of partials from grain boundaries has even been predicted with an atomistically-informed phase field dislocation dynamics technique [128, 142].

The interesting outcome is that another stable, predominant interface emerges after twinning, distinct from the one that develops when the crystals deform purely by slip. This post-twinning interface remarkably also exhibits a regular atomic structure. Figure 4.19 shows a TEM micrograph of two typical interfaces in the $h = 10$ nm composite: (a) $\{551\}\langle 1\ 1\ 10\rangle\text{Cull}\{112\}\langle 110\rangle\text{Nb}$ interface and (b) $\{110\}\langle 001\rangle\text{Cull}\{112\}\langle 110\rangle\text{Nb}$ interface. Remarkably, like the predominant interfaces that develop before twinning (Fig. 4.14), these interfaces are ordered in structure and comprised of a periodic array of facets.

A comparison of the relaxed, equilibrium interface structures obtained via MD reveals that these interfaces appear to be relatively free of extrinsic defects [185]. This coincidence suggests that this interface is able to recover from interactions with dislocations generated in deformation.

As a sign of its stability, nanomaterials with $h \leq 20$ nm exhibit outstanding stability in microstructure and hardness up to temperatures of 0.5 the melting temperature of Cu [10, 185]. Fig. 4.19c shows the $\{551\}\langle 1\ 1\ 10\rangle\text{Cull}\{112\}\langle 110\rangle\text{Nb}$ interface after the composite was annealed at 500 °C for one hour; the interface has clearly maintained its structure.

As before, the crystallographic stability of these interfaces were analyzed in order to locate them on the map in Fig. 4.18. As seen in the energy landscape in Fig. 4.17, the $\{551\}\langle 1\ 1\ 10\rangle\text{Cull}\{112\}\langle 110\rangle\text{Nb}$ interface corresponds to a low energy minimum (~ 739 mJ/m²). The $\{110\}\langle 001\rangle\text{Cull}\{112\}\langle 110\rangle\text{Nb}$ interface also is low in energy, being ~ 949 mJ/m² [196]. These values are comparable to the formation energies for the interfaces in Fig. 4.14 and again, higher than that of the KS and NW interfaces. This comparison has three implications: the formation of another interface character after twinning does not incur an additional energetic penalty and it is also not entirely driven by interface energy, and the second variable we have considered, plastic stability, must play a role. As before, for the latter, the crystal plasticity finite element (CPFE) model was used to examine the stability of bicrystals containing either the $\{551\}\langle 1\ 1\ 10\rangle\text{Cull}\{112\}\langle 110\rangle\text{Nb}$ or $\{110\}\langle 001\rangle\text{Cull}\{112\}\langle 110\rangle\text{Nb}$ interface [204, 475]. Both were found to be stable, where the stability value ω was calculated to be 0.853 and 1.0, respectively. With high plastic stability and low formation energy, both interfaces lay in the stable regime of the map in Fig. 4.18.

Thus, it is found that with or without twinning, crystallographically stable interfaces depend on the same two basic criteria: 1) both crystals on either side of the interface can deform without reorienting and 2) the interface energy corresponds to a local minimum. Taken together, the results from both this section and the previous one, Sect. 4.3.8, suggest that it is possible to tune interfaces via severe plastic deformation processing in a much broader class of material systems than considered before, including materials that not only deform easily via slip but also via slip and twinning.

4.3.9 Outstanding questions

This work shows that it is possible to deformation process a nanocomposite such that a characteristic interface evolves exhibiting a regular atomic structure that prevails ubiquitously

over the entire material. This finding leads to additional interesting questions that are worthy of pursuit.

1) Only one deformation pathway was considered. Can re-designing the deformation-processing route create other stable interfaces? Are there other more stable yet undiscovered interfaces?

2) Plastic deformation of other metals than those considered here can induce profuse deformation twinning or phase transformations. How would these other deformation-induced phenomena affect the development of stable interfaces?

3) Post-mortem characterization shows that the interface structures contain little extrinsic dislocations and hence no evidence of dislocation interactions. What role do the interfaces play in recovery? How do interfaces recover dislocations?

4) Plastic stability ω is affected by the boundary conditions placed on the interface and its adjoining crystals. Even under plane strain compression, the local boundary conditions may change as the interface spacing reduces to the very fine nanoscales $\ll 100$ nm. The interface could begin to slide or lattice dislocations may cross the interface. It may also be the case that the dislocations can no longer be aptly represented by a statistical distribution (as presumed in the present modeling case) and a discrete description may be more appropriate. How would these aspects affect the plastic stability of the interface and hence the likelihood that the interface emerges after extreme straining?

5. Summary Points:

- The ability of interfaces to absorb point defects is sensitive to both the interfacial crystallographic character and the type of defect being absorbed. The competition between defect trapping and annihilation at interfaces and their reemission affects interface sink efficiency, which is in general not the same for two different interface structures. Furthermore, all of these factors depend on the damage structure of the interface, which depends on radiation dose, radiation flux, temperature, and the nature of the damage process itself.
- In particular, the mobility of defects at interfaces depends on the nature and size of the defect cluster as well as the interfacial character. These in turn affect the recombination rate of defects within the interface, which directly controls the sink efficiency of the interface.
- The intrinsic defect structure of a bimetal interface can have a profound influence on the density of nucleation sites and which slip systems are activated in the adjoining crystals. For an interface with a well-defined misfit dislocation network, dislocations prefer to nucleate onto slip systems that have both a high resolved shear stress (high Schmid factor) and lines of intersection with the interface plane that are parallel with a misfit dislocation line. A map has been developed to indicate where a dislocation of a given slip system will nucleate within the interface.

- Experimental observations indicate that the structure of a bimetal interface plays an important role in deformation twinning. A combination of theory and simulation suggests two interface-mediated mechanisms for stress-induced twinning from a bimetal interface: dislocation transmission across the interface and dissociation of intrinsic interface dislocations. Maps were developed to indicate which interface structures have high transmissibility and twinnability.
- Misfit dislocation intersections (MDIs) at semi-coherent interfaces serve as preferred trapping sites for helium (He). Helium is detected in the form of bubbles at interfaces only above a critical concentration. Thus, the concentration of helium that can be stably stored at interfaces can be tuned via the lattice misfit since it controls the density of MDIs.
- The key to stable He storage at interfaces is the phenomenon of wetting: He wets high-energy regions of interfaces just like water on glass, but is repelled from low-energy interface regions, much like dew on a leaf. The point of transition from wetting to non-wetting behavior stabilizes interfacial He in the form of platelets that store He nearly three times more efficiently than He bubbles in single crystalline metals. Above a critical concentration, helium platelets transition into bubbles.
- Hardening due to He platelets is significantly suppressed in nanolayered composites (layer thickness below approximately 5 nm).
- Even in the case of fully coherent interfaces, point defect accumulation can still occur at the interface. This is a consequence not of trapping of defects at the interface, but rather restricted flow of defects when they cross the interface. The bulk defect mobilities and formation energies dictate the direction and speed of flow. An analogy would be a change in the speed limit along a highway. If the speed limit is suddenly reduced, defects will begin to accumulate precisely at the point of change, even if the defects prefer to exist in the second material. A model incorporating these defect properties qualitatively reproduces experimental observations of defect evolution near oxide/oxide interfaces.
- By changing the relative chemical potentials and migration energies of defects in component phases in a nanocomposite, defect evolution can be controlled. If the chemical potentials of interstitials and vacancies are of opposite sign, the two defects will be segregated to different regions of the material and defect annihilation will be minimized. This represents a worst-case scenario for radiation tolerance. However, if the chemical potentials for vacancies and interstitials are of the same sign and the flow of both defects is in the same direction, defect annihilation will be maximized. In this case, the attractive phase will act as a 3D sink for the defects. This provides another set of parameters to tune the radiation damage response within nanocomposites.
- Radiation-induced mixing at interfaces between low solubility metals increases as the liquid phase interdiffusivity of the neighboring metals increases and as the distance between neighboring interfaces decreases. These relationships are due to the nature of

liquid-phase mixing by interdiffusion in the molten cores of radiation-induced thermal spikes. Cu-Nb multilayered nanocomposites with individual layer thicknesses above 2–4 nm are predicted to remain morphologically stable when subjected to 100 keV collision cascades, characteristic of neutron or heavy-ion irradiation.

- A predominant interface character with nearly pristine atomic structure can emerge from large-strain rolling deformation. The interfaces naturally selected in deformation are shown to be stable with respect to elevated heating and continued mechanical deformation.
- Using crystal plasticity and atomic-scale modeling, two interface properties are found to drive the development of stable interfaces in large strain deformation. The first one is a plastically stable crystallographic interface character. This is achieved when the crystals on both sides of the interface co-deform and do not reorient during plastic deformation. The second one is relatively low interface formation energy. On this basis, a map has been constructed to reveal a regime where mechanically stable interfaces, which possess these two properties, may lie.

Figure Captions

Figure 1.1. The atomic structure of an interphase boundary largely determines its interactions with dislocations (D), vacancies (V) and interstitials (I). In composites such as laminates, dispersoids, and interconnected 3D networks, when the interface spacing is on the nanoscale, the bulk behavior becomes interface-dominated and can be controlled by the interface structure.

Figure 2.1. Variation in defect supersaturation, $c_v(x) - c_v^{eq}$, with distance from an interface, x , for sink efficiency values ranging from 0 to 1. The defect supersaturation is shown scaled by the far-field defect concentration K_0/K_{sv} while distance is shown scaled by the mean free path between distributed sinks, $\sqrt{D_v/K_{sv}}$.

Figure 2.2. A 22nm-wide void denuded zone (VDZ) near a GB in Cu [64].

Figure 2.3. Variation of VDZ widths with GB misorientation in Cu [64].

Figure 2.4. Schematic of the interstitial emission mechanism. (a) During a collision cascade, interstitials and vacancies are created. If the cascade overlaps with a grain boundary, the boundary will preferentially absorb interstitials, leading to a damage boundary structure (b).

Immediately after the cascade, interstitials remaining in the grain interior can either recombine with vacancies, diffuse to the boundary and become trapped, or even escape from the immediate region. (c) On times longer than the interstitial diffusion time scale but much shorter than vacancy diffusion time scales, the interstitials trapped at the grain boundary can react with the residual vacancies in the grain interior via the interstitial emission mechanism, leading to extra annihilation of those vacancies, leading to a defect structure (d) that is much reduced compared to a situation in which the grain boundary had not been present.

Figure 2.5. Consequences of differences in defect mobility in different grain boundaries on radiation damage response. (a) During electron irradiation, where isolated point defects are produced at relatively low rates, interstitials will either diffuse to or be directly created in grain boundaries. The relative mobility of interstitial defects and clusters are indicated by the thickness of the arrows. In tilt grain boundaries, where there are fast diffusion mechanisms, those interstitials can then escape the system by ultimately reaching a triple point or a free surface (as indicated by the thicker green arrow). In more general boundaries, the mobilities are slower (schematically indicated by the thinner green arrow) and such escape is less probable. This has direct impact on the sink efficiency as shown in (b). As the interstitial mobility increases, the sink efficiency decreases because there are fewer interstitials to annihilate with vacancies (they escape from the vicinity). If in addition the vacancies are only loosely bound to the boundary (less negative binding energies ΔE_b^V), they can emit back into the grain, leading to a smaller net flux of vacancies to the boundary. However, in heavy-ion irradiation (c), there will be higher concentrations of interstitials. At tilt grain boundaries, they will tend to cluster, leading to reduced mobilities to the point that the interstitials may be trapped where they are (schematically illustrated via the red arrow and the slashed circle). In contrast, at more general boundaries, the clustering tendencies are lower and the interstitials still retain some mobility. (d) If the interstitials are completely immobile, then the sink efficiency of the grain boundary is a function of the mobility of vacancies in the grain boundary and if that mobility is too low, the rate of emission back into the grain will be higher than the in-boundary annihilation rate with interstitials and the sink efficiency will again be less than ideal.

Figure 2.6. Dislocations nucleate from the $\{111\} \parallel \{110\}$ KS interface in order to relieve interface strain concentrations that develop around the interface dislocations when the interface is strained [139, 186]. (a) A Shockley partial dislocation loop is emitted into the Cu from the interface. Comparing (a) and (b) shows that the loop has nucleated where the slip plane of the loop intersects the interface along its misfit dislocation line. (c) Disregistry plot showing the interface under strain prior to nucleation of the loop. Shear displacements develop about the misfit lines. Taken with permissions from [186].

Figure 2.7. Three-dimensional MD simulations of Cu-Nb nanolayered composites (5 nm layer thickness) in shock-compression: (a) the $\{111\} \parallel \{110\}$ KS interface and (b) the $\{112\}fcc \parallel \{112\}bcc$ KS interface. Simulations were performed at 300 K. Taken with permissions from [138].

Figure 2.8. The relaxed atomic structures of the (a) KS interface and (b) NW interface. In both figures, the x -direction is the $\left[11\bar{2}\right]_{fcc}$ direction and the y -direction is $\left[\bar{1}10\right]_{fcc}$. The solid lines

mark interface dislocations where segments of the same color have the same Burgers vector. The three edges of the triangle in the center indicate the traces where the three $\{111\}$ planes of Cu intersect the interface. The methods used to determine the interfacial dislocation line orientation and Burgers vectors can be found in [151]. Taken with permissions from [160].

Figure 2.9. MD simulations of dislocation nucleation from misfit dislocation lines: (a) the KS interface under in-plane tension along the $\left[11\bar{2}\right]_{fcc}$ direction and (b) the NW interface under an applied in-plane tension along the $\left[11\bar{2}\right]_{fcc}$ direction. Each loop is emitted into Cu and forms an intrinsic stacking fault. Taken with permissions from [160].

Figure 2.10: MD simulations of dislocation nucleation from a junction line at a misfit dislocation intersection in the $\{112\}<111>\text{Cu}||\{112\}<110>\text{Nb}$ interface. The interface is strained by in-plane tension along the $\left[11\bar{2}\right]_{fcc}$ direction. Taken with permissions from [160].

Figure 2.11. Map of the potential dislocation nucleation site within an interface for a given slip system. The nucleation site is based on two structural relationships: 1) the alignment between the line orientation of interface dislocation (i) and glide plane trace of the lattice dislocations LD (j) represented by $S^{(ij)}$ and 2) the alignment between the Burgers vectors of interface dislocations and lattice dislocations represented by $A^{(ij)}$. For each region in this map, implications on the mechanism of nucleation and the relative degree of difficulty are also given. The screw/edge character weighting variable p lies within the range $0 < p < 0.5$. Taken with permissions from [160].

Figure 2.12. Calculated (111) pole figures of textures for a model fcc metal with (a) slip and at least 30% of the phase reoriented via twinning and (b) slip only and no twinning. X-ray diffraction measured (111) pole figures of the textures of Ag and Cu within the Ag-Cu composite after rolling to 75% reduction at room temperature (c) Ag and (d) Cu. The transverse direction (TD) is the 1-direction, the rolling direction (RD) is the 2-direction, and contour levels are 1.0/1.4/2.0/2.8 mrd. Taken with permissions from Reference [144].

Figure 2.13. TEM analysis of Ag-Cu layered eutectic composites after rolling to 75% reduction: (a) and (c) TEM Bright Field (BF) image of Ag and Cu lamellae. (b) Diffraction pattern from the same region showing a $<101>$ Zone Axis Pattern. The interface plane trace has a normal along (020) and is parallel to [202]. Taken with permissions from Reference [144].

Figure 2.14. Atomistic simulations of twin transmission across the Ag-Cu interface at a resolved shear stress of 100 MPa at room temperature: (a) Twinning partials in Ag approaching a (111) Cu-Ag interface with a cube-on-cube orientation relationship. (b) A four-layer twin in Cu and (c) the resultant interface plane $(001)_T$. The subscript “T” corresponds to the coordinates in the twinned crystal. The vector n is the normal direction of the resultant interface plane. Atoms are colored according to common-neighbor-analysis. Blue atoms represent fcc structure, red atoms represent hcp structure, and green atoms represent a defective structure. The symbol “ $\perp$ ” represents a dislocation. Taken with permissions from Reference [143].

Figure 2.15. (a) Schematic of the reaction mechanisms between the residual dislocations remaining after the transmission events and the misfit dislocations pre-existing at the interface

for the new (100) interface plane. (b) Fine twins emanating from the (100) interface are observed in the adjoining Cu and Ag layers. Taken with permissions from References [144] and [143].

Figure 2.16. (a)-(d) TEM images showing that deformation twins become evident when the layer thickness reduces to about 50 nm. The twin volume fraction continues to increase as deformation proceeds further until the Cu layers are significantly reoriented at a layer thickness of 10 nm. Scale bars: (a)-(b) 200 nm, (c)-(d) 100 nm. Taken with permissions from Reference [185].

Figure 2.17. (a) A magnification of a twin in the sample with 30 nm layer thickness, showing the initial interface $\{112\}\langle 111\rangle\text{Cu}\parallel\{112\}\langle 110\rangle\text{Nb}$ and the interface $\{552\}\langle 115\rangle\text{Cu}\parallel\{112\}\langle 110\rangle\text{Nb}$ after twinning. (b) An incoherent twin boundary contains twinning partials on neighboring $\{111\}$ planes with different Burgers vectors and a total zero net Burgers vector. This means that the total net Burgers vector of the corresponding trailing partials at the Cu-Nb interface is zero. Taken with permissions from Reference [185].

Figure 2.18. HRTEM images showing interface structure after twinning. (a) A $\{112\}\parallel\{112\}$ Cu-Nb interface with a twin in Cu. The image focuses on the tip of the twin. (b) –(d) Higher resolution areas of the twinned Cu||Nb boundary in (a). Taken with permissions from Reference [184].

Figure 2.19. Schematic of the alternate emission deformation twinning mechanism in the Cu layer. (a) a two-layer twin nucleus forms due to the emission of partial dislocations from the top interface; (b) in the same way, another two-layer twin nucleus labeled by “2”, (c) in between them, many more stacking faults or two-layer twins form by emission of partial dislocations from both the top and bottom interfaces between the first and the second twin nuclei, and (d) a thick twin is constructed. The b_1 , b_2 , b_3 are the three partial Burgers vectors sharing the same $\{111\}$ twinning plane. Taken with permissions from Reference [146].

Figure 2.20. Illustration of twin nucleation directly from an interface due to its intrinsic structure. The interface initially has two sets of intrinsic dislocations with different total Burgers vector $B^{(1)}$ and $B^{(2)}$. Both sets have a Burgers vector component that is non-planar to the interface. (a) Dissociation of the interface dislocations, each into a residual and a partial dislocation that extends into the upper crystal. The partial forms a stacking fault as it glides. The two neighboring stacking faults, SF1 on the left and SF2 on the right, are spaced a distance s apart that equals the spacing of the two dissociation sites. (b) The number of twin planes encompassed by s is equal to k . Nucleation of $k = 2$ partials in between SF1 and SF2. As the k partials glide away from the interface, they form a twin domain between SF1 and SF2. Taken with permissions from Reference [178].

Figure 2.21. Transmissibility map for bimetal interfaces. Interfaces lying in the region near the origin are not as likely to permit slip-twin transmission and those lying away are more likely. Other areas marked ‘difficult’ correspond to regimes where slip-twin transmission would be difficult, but not impossible, requiring high stresses or high temperatures. Some experimental points are shown as ellipses. In these cases, interfaces from which twins form are colored in black and those from which they did not are colored in blue. Other experimental points are

shown as rectangles due to the anisotropy of their interfacial shear strength. In such cases, like the KS or NW interface, it is appropriate to report a range of τ_{ISS} values, while for mildly anisotropic ones, reporting a single value suffices. Taken with permissions from Reference [178].

Figure 2.22. Twinability map for bimetal interfaces. Interfaces lying in the region near the origin are not likely to twin and those lying away are more likely to twin by the dissociation-induced (*D*) or transmission-induced (*T*) or both mechanisms. Regions where twinning occurs predominantly by the *D* or the *T* mechanism are also indicated. The figure-of-merit for the *T*-mechanism (x-axis) accounts for the number of effective transmission pathways, $T = \tau_{ISS} G_T$. (See Figure 2.21). Experimental points are shown as ellipses. Interfaces from which twins are observed to form easily and often are colored in black and those from which they did not are colored in blue. All cases are for compression or plane strain compression applied normal to the interface plane. The diamond symbols indicate predictions. NW and KS interfaces are predicted not to form twins when a tensile load is applied normal to the interface. Taken with permissions from Reference [178].

Figure 3.1. Bright field TEM image of (a) as-synthesized and (b) helium-implanted 1° (001) twist boundary in Au [222]. The under-focused image in (b) shows He bubbles at the misfit screw dislocation intersections.

Figure 3.2. Under-focused bright field TEM image of He implanted Cu-Nb multilayer with nominally 5nm-thick layers [236]. Helium bubbles appear as white dots, preferentially at Cu-Nb interfaces, over a depth range where helium concentration exceeds the critical to nucleate bubbles. No bubbles are seen below ~ 200 nm from the surface, even though the He concentration at this depth is around 1-2 atoms/nm³.

Figure 3.3. Critical He concentrations required to observe He bubbles at interfaces in the TEM [236] and critical He doses required to observe a drop of density at interfaces in NR [247] plotted as functions of bcc/fcc lattice parameter ratios. The inset on the left shows the in-plane structure of the Cu-V interface while that on the right shows the in-plane structure of the Cu-Nb interface. Atoms colored red are constitutional vacancies found at misfit dislocation intersections in these interfaces [236].

Figure 3.4. Atomistic modeling of the evolution of He–vacancy clusters at a misfit dislocation intersection at a Cu-Nb interface [251]. These clusters initially grow as flat platelets by wetting regions of high interface energy. The helium platelet transitions into a more equiaxed precipitate above approximately 20 He atoms (between (c) and (d) above).

Figure 3.5. Schematic illustration of the bubble hardening mechanisms in multilayers (the circles indicate bubbles) [44]. (a) When the layer thickness is a few tens to a few hundreds of nanometers, $h \gg l$ and deformation occurs via confined layer slip (CLS). Dislocations gliding in a layer confined by interfaces are pinned by nanometer-scale bubbles resulting in an additive term to the CLS stress. (b) When the layer thickness is only a few nanometers and $h \leq l$, the yield strength is determined by the crossing of single dislocations across interfaces containing a distribution of nanometer-scale He bubbles in the interface plane.

Figure 4.1. Structures of some of the oxides discussed in the text, for reference. In these figures, red spheres indicate oxygen, black spheres are A cations, and blue spheres are B cations. In the case of spinel, only one quadrant of the structure is shown, highlighted by grey and white octants. The other octants have the same atomic structure. In the case of bixbyite and pyrochlore, which have structures related to fluorite, only the positions of the oxygen vacancies, relative to fluorite, are indicated (by transparent red spheres). The real oxygen are not shown for clarity. These figures are adapted from figures appearing in Refs. [341, 478, 479].

Figure 4.2. Critical dose as measured in displacements per atom as a function of temperature for $A_2Ti_2O_7$ pyrochlores, where the A cation is indicated. There is significant dependence of the critical amorphization temperature (the temperature at which the dose to amorphize becomes infinite) with the chemistry of the A cation. Adapted with permission from Ref. [298]. Copyrighted by the American Physical Society.

Figure 4.3. Irradiation response of (top) large grain and (bottom) small grain $MgGa_2O_4$ samples when exposed to Kr ions. The large grain sample amorphized by a dose of 12 dpa while the small grain sample retained crystallinity to doses of 96 dpa. Reproduced with permission from Ref. [344]. Copyright 2007, AIP Publishing LLC.

Figure 4.4. Summary of experimental observations of phase stability at three bilayer films irradiated to a dose of about 3-4 dpa. (a) At the TiO_2 /STO interface, the TiO_2 side of the interface exhibits a defect denuded zone while the STO side shows enhanced amorphization. (b) The interface in the BTO/STO bilayer shows no enhanced accumulation or depletion of defects. (c) At the STO/LAO interface, both materials exhibit much higher levels of amorphization than in the other bilayers. Figures adapted from Refs. [355, 357, 358].

Figure 4.5. (a-b) Atomistic modeling of the relative formation energies of (a) vacancies and (b) interstitials at the TiO_2 /STO interface. The lines are guides for the eye for the behavior of Ti vacancies and Ti interstitials, illustrating that the significant differences in the energetics in the two component phases may drive the defect evolution at interfaces during irradiation. (c) Schematic illustration of the defect potential energy landscape as informed by the atomistic calculations. For a given defect, the behavior near coherent interfaces is dictated by the migration energy in each of the two phases comprising the composite ($E^{m,A}$ and $E^{m,B}$) and the difference in chemical potential μ for the defect in each of the two phases. In principle, the concept can be extended to include trap states at the interface to account for the properties of general interfaces that also contain structure.

Figure 4.6. Concentrations of interstitials (solid lines) and vacancies (points) in a model multilayer composite as determined by a reaction-diffusion model. In (a) the chemical potentials of both defects are such that defect formation energies are lower in Phase B than in Phase A. This leads to the formation of a “denuded zone” in Phase A and an “amorphous zone” in Phase B where the defect concentrations are accentuated. In (b), the chemical potentials of the two defects are of opposite sign, leading to maximum separation of interstitials and vacancies and thus minimal annihilation. In this case, the defect concentrations are maximized.

Figure 4.7. Pinched off layer in a Cu-Nb layered composite [368].

Figure 4.8. Radiation-induced mixing sequence in a Cu-Nb bilayer [401]. Snapshots at 0, 1, 3.5, 5 dpa show atoms colored by (a)-(d) type (yellow: Cu; blue: Nb) and (e)-(f) local structure (green: fcc; red: bcc; gray: amorphous). (i)-(i) show Cu concentration profiles.

Figure 4.9. Correlations between effective radiation-induced mixing interdiffusivities D^{eff} and liquid phase interdiffusivity $\bar{D}$ [401].

Figure 4.10. (a) An atomic model of a Cu-Nb multilayer nanocomposite with 18Å-thick layers. (b) A collision cascade initiated by a 100 keV PKA spans multiple layers [374].

Figure 4.11. (a) Cu and Nb atoms intermixed in a 10Å multilayer at the end of a 100 keV collision cascade. (b) Initial concentration distribution used in the phase field model, extracted from the atomic structure in (a). (c) During a phase field simulation, one Nb layer is pinched off by two neighboring Cu layers, while other layers remain stable [374].

Figure 4.12. (a) The severe plastic deformation process, accumulative roll bonding (ARB), used to synthesize, (b) Cu-Nb nanolayered composites of controllable layer thickness. (c) Transmission electron microscopy (TEM) micrograph displaying the planar Cu-Nb interfaces in an $h = 20$ nm composite. Taken with permissions from [186].

Figure 4.13. Schematic of a predominant interface character that emerges in Cu-Nb nanolayered composites after extremely large rolling strains.

Figure 4.14. Ordered interfaces after extreme strains. High-resolution transmission electron microscopy micrographs of preferred Cu-Nb interfaces: (a) $\{338\}<443>\text{Cu}||\{112\}<110>\text{Nb}$ and (b) $\{112\}<111>\text{Cu}||\{112\}<110>\text{Nb}$. The crystallography of the facet planes is indicated. Taken with permissions from [196].

Figure 4.15. Coupling of the plastic stability of an interface and the energy associated with forming the new interface area. The interface character is plastically stable when the crystals on both sides of the interface do not reorient with deformation.

Figure 4.16. Map of the dependence of plastic stability on bimetal interface character. The solid line corresponds to $\omega = \omega^{SX}$. Interfaces lying along this line correspond to the situation when the stability of the co-deforming bicrystal equals that of its constituents when deformed alone. Square and circle symbols correspond to simulated fcc/bcc interfaces under rolling strains. Interfaces with black triangles represent the observed predominant slip-fcc/bcc interfaces and with black stars the twin-fcc/bcc interfaces. The observation that many interfaces lie below the $\omega = \omega^{SX}$ line means that stability is limited by the less stable of the two crystals. Taken with permissions from [196].

Figure 4.17. Variation in interface formation energy with tilt angle about the $\langle 110 \rangle_{\text{fcc}} || \langle 111 \rangle_{\text{bcc}}$ as calculated using MD simulation. Preferred interfaces (yellow region) correspond to deep wells in interface formation energy. Molecular dynamics calculation of the variation in interface formation energy with tilt angle about the $\langle 110 \rangle_{\text{Cu}} || \langle 111 \rangle_{\text{Nb}}$, the direction normal to the micrographs in Fig. 4.14. The green region corresponds to stable interfaces observed after the onset of twinning in the Cu phase. Taken with permissions from [196].

Figure 4.18. Map of bimetal interface character stability. Squares represent interfaces created by pairing orientations from the stable orientation distribution (i.e., well developed rolling texture for the monolithic, single-phase metal) of the deformed crystals (Table 4.1). Circles represent interfaces formed when one or both orientations do not belong to the theoretical single-phase rolling texture. Interfaces with black triangles represent interface characters observed before the onset of twinning and those with black stars represent interface characters observed after the onset of twinning. Taken with permissions from [196].

Figure 4.19. High-resolution TEM micrographs of a typical nano-interfaces ($h = 10$ nm) (a) $\{551\}\langle 1\ 1\ 10\rangle\text{Cu}||\{112\}\langle 110\rangle\text{Nb}$ and (b) $\{110\}\langle 001\rangle\text{Cu}||\{112\}\langle 110\rangle\text{Nb}$. The crystallography of the facet faces is also shown. (c) $\{551\}\langle 1\ 1\ 10\rangle\text{Cu}||\{112\}\langle 110\rangle\text{Nb}$ after exposure to 500 C for 1 h. The scale bar in panel (c) is 2 nm. Taken with permissions from [185].

Table Captions

Table 2.1, The structural details needed for calculating $S_{\max}$. The relaxed equilibrium atomic structure was calculated for a variety of structurally ordered Cu-Nb interfaces using atomic-scale MD simulation [158, 178, 465]. For those interfaces that are faceted, additional energy minimizing procedures were invoked to create an even lower energy state in which the facet faces were extended [465]. Subsequent disregistry analysis was carried out to determine the characteristics of the interfacial dislocation network. The interfacial shear strengths τ_{ISS} were calculated via MD simulation by applying an in-plane shear [197]. For this work, a trend was established by estimating the interfacial shear strengths at zero K.

Table 4.1. Stable crystal orientations for fcc and bcc crystals. The components are written in the $\{\text{ND}\}\langle\text{RD}\rangle$ nomenclature, wherein $\{\text{ND}\}$ is the crystallographic plane corresponding to the rolling plane and $\langle\text{RD}\rangle$ is the crystallographic direction aligned with the rolling direction. The orientations belonging to each group are obtained from [435, 436, 471, 472].

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Figures for Defect-Interface Interactions

I. J. Beyerlein^{1*}, M. J. Demkowicz², A. Misra¹⁺, and B. P. Uberuaga¹

¹Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

²Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

Interface	Type	B_N and s associated with $S_{\max}$ (Å)	θ (degrees)	τ_{ss} (MPa)
{111}<110>Cull{110}<111>Nb	Flat	0	N/A	300-1000
{111}<110>Cull{110}<001>Nb	Flat	0	N/A	300-600
{112}<111>Cull{112}<110>Nb	Faceted	2.1, 6.3	19.47	1550
{338}<443>Cull{112}<110>Nb	Faceted	1.0, 23	26.28	1550
{110}<001>Cull{112}<110>Nb	Faceted	1.35, 15.5	35.45	1550
{551}<1110>Cull{112}<110>Nb	Faceted	1.0, 9.3	27.21	1550
{112}<111>Cull{001}<110>Nb	Faceted	1.48, 6.26	19.47	1550
{110}<111>Cull{001}<110>Nb	Flat	0	N/A	2000

Table 2.1.

$g_{fcc}(\theta, RS)$	Stable orientation group for fcc crystals expected under rolling when mediated by slip	S {123}<634>, Brass {110}<112>, C {112}<111>, D {4 4 11}<11 11 8>, orientations between C and D such as K {338}<443>
$g_{fcc}(\theta, RST)$	Stable orientation group for fcc crystals expected under rolling when mediated by slip and twinning	Brass {110}<112>, Goss {110}<001>, Z {551}<110> and orientations between Goss and Z
$g_{bcc}(\theta, RS)$	Stable orientation group for bcc crystals expected under rolling mediated by slip	{112}<110>, {225}<110>, {223}<110>, {111}<112>, and E {111}<110>

Table 4. 1.

Figure 1.1

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Figure 3.1

Figure 3.2

Figure 3.3

Figure 3.4

Figure 3.5

Fig. 4.1

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