MECHANICAL PROPERTIES AND INFLUENCES OF IRRADIATION IN DILUTE NANOGRAINED ALUMINUM ALLOYS

BY

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DISSERTATION

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ABSTRACT

The aim of this dissertation is providing information to help develop alloys that are dimensionally stable in extreme environments. For example, nuclear reactors are exposed to high temperatures and high irradiation damage levels that can cause mechanical and microstructural instabilities such as creep, embrittlement, void swelling, and so on. If more knowledge regarding how materials behave in such extreme environments becomes available, the development of stable materials can be expedited.

To achieve this goal, mechanical properties characterization of dilute nanocrystalline (nc-) aluminum alloys will be the primary focus of this work under various thermal treatments, along with additional characterization of these alloys under irradiation. These works include the thermal creep and irradiation induced creep responses of various Al alloy systems at elevated temperatures.

For the hardness measurements, standard nanoindentation methods were employed. For creep measurements, a novel thin film bulge test technique was used due to many advantages. Microfabrication process was employed to make free standing thin films for creep tests, and DC sputtering was used to deposit a metal layer.

The first part of this work concerns the strengthening mechanisms operating in nc-Al alloys which are promising materials for nuclear power plant application. Microstructure and mechanical characterizations under various annealing temperatures were performed. The results suggest that various mechanisms can strengthen nanocrystalline alloys, for example, solute doping of grain boundaries and solid solution strengthening.

The second part presents the thermal creep response of various nc-Al alloys at various temperatures, and the results suggest Coble creep is a dominant mechanism over the range studied.
For a creep test, a thin film bulge test method was employed. The work explores the effects different solute additions on creep rates and specifically, both in solid solution and in precipitates.

Lastly, the effects of irradiation on nc-Al alloys are investigated. This irradiation study includes change of mechanical and microstructural properties under irradiation. Here, the importance of irradiation induced mixing on alloy hardness is demonstrated. The results of these studies are complementary to my work on the strengthening of these alloys during thermal annealing. Irradiation was also employed to examine self-organization in nc-Al-Sc and nc-Al-Sb alloys. The work provides strong evidence that these alloys do self-organize under irradiation and it raises interesting questions regarding the role of grain boundary diffusion in this process. Lastly, irradiation induced creep (IIC) measurements were performed using heavy ions to explore the role of alloys additions on creep response.

These characterizations for Al alloys provide valuable information in the design of promising nanostructured materials for high temperature and nuclear applications.
To my family
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<td>APT</td>
<td>Atom Probe Tomography</td>
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<td>BF</td>
<td>Bright Field</td>
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<tr>
<td>DPA</td>
<td>Displacement(s) per Atom</td>
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<td>EDS</td>
<td>Energy-Dispersive Spectrometry</td>
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<td>FIB</td>
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<td>Irradiation Induced Creep</td>
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CHAPTER 1
INTRODUCTION

1.1 Irradiation Damage In Metals

The threats of global warming have created an urgent need to develop new sources of energy that do not contribute to increase of carbon in the atmosphere. Many possible technologies have been suggested ranging from solar energy to wind power to biomass, and while these technologies are all promising, it remains questionable how quickly they can provide the increasing world needs for energy over the next few decades. It is likely therefore that nuclear energy will continue to play an important role in the generation of electric power over the next several years. Two major problems now facing the nuclear energy industry are the economics and the safety of nuclear power. It is well recognized that critical to the field of nuclear energy is development of new materials that can withstand the more extreme environments to which current reactor components are being exposed, e.g., higher dose, and also to even harsher conditions expected in future advanced reactors, higher irradiation fluences and temperatures, and possibly more hostile chemical environments.

The unique feature of nuclear reactors is the prolonged bombardment of material in the reactor with energetic neutrons. As Wigner pointed out in 1946 [1], energetic neutrons displace atoms from their equilibrium lattice sites and this changes the properties of the material. Since these changes are most often detrimental, this process has been denoted as radiation damage. More specifically, irradiation of materials with energetic neutrons leads to the creation of point defects (vacancies and interstitials) in the crystal lattice via collision cascades. Energetic displacement of atoms also leads to clustering of these defects and to atomic mixing of atoms. Irradiation can thus lead to huge supersaturations of point defects, dislocation loops, and chemical disordering. The
processes will be described in more detail in chapter 4, but it is useful to qualitatively describe here how they lead to radiation damage to provide a perspective for the research in this thesis. An overview of the important irradiation effects relevant to this work is therefore in Fig. 1.1.

**Ion beam mixing**

![Ion beam mixing](image)

**Radiation-enhanced diffusion**

![Radiation-enhanced diffusion](image)

Irradiation of a metal with energetic incident ions generally leads to the relocation of atoms in a solid, by ion beam mixing (IM) at low temperatures and by radiation enhanced diffusion (RED) at high temperatures. Ion beam mixing refers to the recoil mixing of atoms, and it is directly related to phase stability and nonequilibrium processing of materials, as it induces precipitate dissolution and chemical disordering of the system, as illustrated at Fig. 1.1. High temperature irradiation
leads to RED, as point defects created by irradiation are mobile, thus *enhancing* diffusion processes, for example accelerated precipitation and growth, and grain growth in nanocrystalline materials. RED can also *induce* non-equilibrium behavior, such as solute segregation and void swelling. For example, the flow of point defects sinks can couple to solute atoms causing them to enrich (or deplete) at the sink sites, often inducing non-equilibrium precipitation [2, 3]. Long term evolution of irradiation induced defects (damages) by RED can also result in irradiation creep, which is strongly accelerated by the excess defect production. As illustrated in Fig. 1.1 above, the formation and growth of loops and voids plays important roles in the creep process. In SIPN (Stress induced preferential nucleation), interstitial loops (blue) and vacancy loops (red) nucleate with preferred direction with respect to applied stress and eventually creep [4]. In SIPA (Stress induced preferential absorption), which is dominant in metal, interstitial and vacancy are absorbed by dislocations oriented perpendicular (red) and parallel (blue) to the direction of the applied stress respectively [5], as illustrated in Fig. 1.1. This SIPA, contributes to irradiation creep by the formation of dislocation climbing.

Irradiation damage in nuclear materials under extreme conditions has become of recent interest for the design of generation IV nuclear reactor. Materials in these reactors will be exposed to temperatures that reach up to 1000 °C as well as irradiation doses exceeding 200 DPA (displacements per atom) [6, 7]. Consequently, explosive demand for developing alloys that are dimensionally stable in these extreme environments does exist, and many studies have been conducted so far. Previous research focused on the microstructure for avoiding defect fluxes by adding point defect traps or sinks [8]. Solute atoms were adopted in early studies for this purpose [9], but more recent works have focused much more on incoherent or semi-coherent boundaries in nanostructured materials [10-13]. Currently researchers are focusing on finely precipitated
nanostructured alloys due to their resistance to extreme conditions: irradiation, high temperature and etc. [7].

1.2 Why Study Nanocrystalline Alloys

Nanocrystalline materials, which have a mean grain size in the range 1-100 nm, are promising for a wide range of applications in various fields of technology. The advantages of these materials for irradiation environments are easy to recognize by considering Fig. 1.2. For example, most of the detrimental effects of irradiation derive from a large supersaturation of point defects. The high density of defect sinks associated with grain boundaries in nanocrystalline metals, however, suppresses these supersaturations. Grain boundary sinks, moreover, are considered to be both unsaturable, i.e., persist in steady state, and unbiased, thus avoiding void formation. A second important characteristic of nanocrystalline materials is that they inherently possess high strength, owing to the Hall-Petch behavior. The strength of nanocrystalline metals, in fact, has been an area of active interest ever since the pioneering work of Gleiter some forty years ago [14]. A quick search on “strength and nanocrystalline metal” shows that two papers with these search words were published in 1992, while last year, 2018, over 9,000 papers were published [15]. Much of the recent attention has focused on the roles of solute additions, precipitates, and heterogeneous interfaces on strengthening and stabilization of grain size, but these materials also have come under intense study for irradiation effects as well. Part of the motivation for this research, beyond the applied aspects, is a consequence of the rapidly increasing capabilities of atomistic level computer simulations to examine carefully the relationship between the unique structure of nanocrystalline alloys and their properties. Recent advances in experimental techniques, moreover, aberration corrected transmission electron microscopy, atom probe tomography, and nanohardness
indentation, have similarly greatly enhanced the ability to study these materials and to make direct contact with the simulations.

![Diagram](image)

Fig. 1.2 Schematic of nanocrystalline (a) movements of interstitials and defects towards grain boundaries (b) grain boundaries can serve high diffusivity path to the direction of applied stress

While nanocrystalline metals have definite advantages for applications involving energetic particle irradiation, they also have several potential weaknesses. For example, grain boundaries provide paths for fast diffusion at very modest temperatures. This can lead to grain growth unless they are stabilizers by solute additions [16], or by precipitates (Zener pinning) [17]. Small grain sizes and fast diffusion in grain boundaries can also lead to thermal creep, either by Nabarro-Herring creep [18, 19] or Coble creep [20]. There also is the question whether nanocrystalline materials are subject to irradiation-induced creep. Older work had suggested that defect annihilation at grain boundaries cannot lead to creep, as equal fluxes of vacancies and interstitials flow to all grain boundaries, cancelling any net absorption of atoms. For example, if it is assumed that grain boundaries can be described by a network of dislocation, vacancies can cause these dislocations to climb in one direction, but interstitials cause them to climb in the reverse direction. The high energies of grain boundaries in nanocrystalline materials make this picture less clear, and it has been reported that irradiation induced creep can indeed be activated in nanocrystalline metals,
even when equal fluxes of vacancies and interstitials are absorbed in the grain boundaries. The research in this thesis is directed at gaining a better understanding of these various processes by examining model alloy systems.

1.3 Choice Of Al Alloys For Investigation

Dilute aluminum alloys were selected for study in this thesis for a number of reasons. Most importantly, the research is fundamental, focused on providing the materials understanding necessary to design structural materials for applications in extreme environments, more specifically, for nuclear reactors. As mentioned already in this introductory material, nanocrystalline metals are inherently strong, at least at low temperatures, but they are susceptible to creep at high temperatures, both thermal creep and irradiation-induced creep, and rather little is known about either. In fact, remarkably little is known about irradiation damage in nanocrystalline materials more generally. The research in this thesis, therefore, is designed, in part, to fill this gap in knowledge by performing creep measurements on nanocrystalline metals. As I will discuss in Chapter 3, the bulge-test method is ideally suited for creep measurements on thin film specimens, however, for the reasons cited in Chapter 3, the apparatus selected for this work is practical for measurements up to a temperature of only ~ 300 °C. For this reason, I selected Al and Al alloys for this study, since creep scales with melting temperature, T_m, and for Al T_m ~ 660°C. Al, moreover, is relatively stable against oxidation, which is also an important practical consideration for controlled experiments on thin film specimens. A third reason for selecting aluminum concerns defect production mechanisms in metals. While this topic is discussed in more detail in Chapter 4, suffice it here to note that defects produced by ions in Al are predominantly isolated Frenkel pairs, whereas in heavier metals such as Cu, Ag and Au, the defects tend to be clustered, or even condensed into dislocation loops. The simpler damage structure in Al greatly facilitates
comparison with theoretical models. Finally, Al has a low atomic number, 13, and therefore ion penetration is greater in Al than in other structural materials. This allows a somewhat thicker specimens to be used, and this is helpful in reducing the (unwanted) effects of surfaces.

Lastly, I point out that while this thesis is not directly concerned with the practical aspects of structural materials in nuclear reactors, it is of some significance to note that Al (specifically Al 6061), owing to its low neutron absorption cross section, high thermal conductivity, and good resistance to aqueous corrosion, has been used as a cladding material in various experimental reactors, including the High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory and the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) [21]. It is also presently being used in the construction of the Jules Horowitz material testing reactor (JHR) in France [22]. Al 6061 had also been planned for use in the Advance Neutron Source at Oak Ridge National Laboratory, but this facility was cancelled in favor of the Spallation Neutron Source (SNS).

1.4 Thesis Overview

This dissertation focuses on the study of the hardening mechanism of nanocrystalline dilute Al alloys subjected to various solute (different intermetallic phase) and behavior under thermal creep of those alloys. Additionally, understanding fundamental irradiation effects on solute behaviors in Al alloys are also a primary goal of this thesis. The overall goal of this dissertation is to provide better background for helping developing alloys that are dimensionally stable in these extreme environments.

First, in Chapter 2, I focus on elucidating the strengthening mechanism of highly immiscible dilute Al alloys, i.e Al-Sc, Al-Sb, Al-Cr and Al-W, by using microstructural and
mechanical characterization. Unrevealed strengthening mechanisms can provide valuable
knowledge about how to obtain better and stable properties in engineering material for various
applications. In chapter 3, I continue my studies of mechanical properties by measuring thermal
creep response of candidate Al alloys, using an in-situ thin-film bulge technique. I analyze the data
to extract meaningful effect of pre-heat treatment on nanocrystalline alloys. In addition to this
study on thermal creep in Al and different highly immiscible Al alloys (Al-Sc, Al-Sb and Al-W) I
also investigate irradiation creep on Al and Al-Sc in Chapter 4. Chapter 4, moreover, also employs
irradiation to complement and better understand the hardness studies presented in Chapter 2.
Another important part of Chapter 4 is the characterization of the microstructure of dilute
nanocrystalline Al alloys under irradiation, from which several contributions to our understanding
of self-organization in irradiated alloys are derived. Chapter 5 summarizes the results of the
dissertation and discusses perspectives.

1.5 References


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CHAPTER 2

MECHANICAL PROPERTIES OF DILUTE NANOGRAINED ALUMINIUM ALLOYS

Mechanical properties are directly related to the microstructures of materials. In crystalline materials, deformation mostly takes place through the motion of dislocations [1], and these dislocation motions under stress govern the plastic response of materials. The dynamics of dislocation motion is determined by various microstructural features, including precipitates, grain boundaries, and alloy solute additions. While the influence of these microstructural features have long been investigated and are well understood in conventional bulk alloys, strengthening mechanism in nanocrystalline materials remains controversial, particularly in situations where these various mechanisms act in concert. It is possible, however, to study such synergies if the microstructural features of test samples can be systematically and controllably altered. The methodology employed in the present study therefore has been to investigate how the strengthening mechanisms are affected by systematic variation of the solute concentration, and by performing controlled annealing and ion irradiation treatments of these alloys. Irradiation treatments will be reported in Chapter 4. Before reporting the results of this study, I will briefly describe the relevant strengthening mechanisms in nanocrystalline materials.

2.1 Strengthening Mechanisms

2.1.1 Hall-Petch And Inverse Hall-Petch Relations

In polycrystalline materials, and nanocrystalline materials in particular, grain boundaries play a fundamental role in the strengthening mechanisms. For one, grain boundaries generally impede the movement of dislocations and this results in the high strength [2]. Decreasing grain
size also results in the decrease the number of dislocations available per grain that can be piled up. This increases the required applied stress for dislocations to cross grain boundaries [3]. In addition, decreased grain size means that increasing the density of the barriers to dislocation motion because the ratio of the grain boundary volume to the total volume increases. The stress increase can be explained by Hall-Petch equation [1], which explains the inverse relationship between grain size and yield strength, i.e.,

\[
\sigma_y = \sigma_0 + \frac{k}{\sqrt{d}}
\]  

(2.1)

where \(\sigma_y\) is the yield stress, \(\sigma_0\) is a frictional stress required to move dislocations, \(k\) is the strengthening coefficient specific to each material, and \(d\) is the grain size.

While the Hall-Petch relation is often employed to explain strength in nanocrystalline materials, it is likely that this mechanism is no longer operative when the grain size is extremely small. For example, dislocations are thought to be unstable in nanocrystalline materials in this regime [4-6]. Moreover, when \(d < \sim \) 15 nm, an inverse Hall–Petch behavior is often reported [7, 8], i.e, the strength decreases with further reducing \(d\). The inverse Hall–Petch effect has been attributed to various factors: (i) a decrease in dislocation line tension with decreasing grain size [9]; (ii) the difficulty of generating dislocation pile-ups within grains having sizes less than a critical value [7]; (iii) a contribution to plasticity from grain-boundary diffusional creep [10-12], grain-boundary sliding [13, 14] or grain-boundary shear [15]; (iv) an overall softening with decreasing grain size due to the increase in the density of triple junctions [16, 17] or grain boundaries [8, 18]; (v) atomic ordering near grain boundaries and triple junctions [19]; and (vi) the competition between dislocation emission (from within the grain boundaries) and grain-boundary sliding [20]. It is noteworthy that inverse Hall-Petch is observed when small-grained
nanocrystalline materials are annealed at high temperature, possibly suggesting that grain boundary relaxations in addition to grain growth are involved [21-26].

2.1.2 Solid Solution Strengthening

Solid solution strengthening is a widely used technique which can be achieved by adding solute atoms to the crystalline lattice of a solvent and forming a solid solution. Adding solute atoms usually strengthens crystals owing to more difficult dislocation movement. When solute atoms are introduced, local stress fields are formed and the dislocation propagation will be hindered at these sites, impeding plasticity and increasing yield strength proportionally with solute concentration. This enhanced strength is a result of both lattice distortion and a modulus effect. Remarkable solution strengthening, hence, can be achieved by: (i) increasing the local shear modulus via alloying with solutes of higher shear modulus; (ii) raising the local stress fields introduced by alloying with solutes with far different equilibrium lattice constants.

Solid solution strengthening theory in coarse-grained alloys, such as those from Fleischer [27] and Labusch [28], are based on the concept that dislocations move freely through the grain interior and that strengthening results from local interactions with solute atoms due to size and elastic modulus mismatches. According to Fleischer’s model, solute atoms are treated as obstacles for dislocation glide owing to the lattice distortion around each solute atom. Mukai et al. [29] observed lattice distortion in the interior of grain, when initially solute are added to the system using Fe solute in Al (Al–1.5at.%Fe alloy), and confirmed that solute atoms in host matrix can act as a barrier against dislocation motion.

Compared to the strong pinning model of Fleischer, the Labusch model is a weak pinning model. In the Labusch model, each individual solute alone would not be strong enough to pin the
dislocation at the same stress level and the collective interaction of many solutes around the dislocation is considered. Strengthening, thus, occurred with favorable statistical fluctuations in the solute configuration. For explaining this model, solutes in the glide plane of the dislocation is considered.

As for the type of solid solution, two different cases can be formed depending on the size of the alloying element, a substitutional solid solution or an interstitial solid solution. In case of substitutional solid solution, the solute atom is large enough that it can replace solvent atoms in their lattice positions. The effect of substitutional solute is mainly attributable to interaction of the solutes with the dilatational stress field around edge dislocations. For substitutional solutions in copper, as shown in Fig. 2.1, the yield strength increases proportionally to the solute concentration.

![Effect of solute concentration on shear yield strength in dilute Cu base alloys](image)

Fig. 2.1 Effect of solute concentration on shear yield strength in dilute Cu base alloys [30]

### 2.1.3 Precipitation Hardening

Precipitation hardening, $\Delta H_{ppt}$, refers a strengthening process involving the formation of hard precipitate particles in the host alloy and these restrict dislocation slip. For intermetallic particles, even when coherent, are typically not susceptible to shearing. In this case, precipitation
strengthening is related to Orowan looping [31] as shown in Fig 2.2. When the precipitate is strong enough to resist dislocation penetration, dislocation bows around precipitates and bypasses the particle, as seen in Fig. 2.2(a-c). Finally, as shown in Fig. 2.2(d), the dislocation releases in the higher stress value owing to the resistance of closely spaced hard particles to the passing of dislocations. Ashby [32] developed this theory and included system parameters (i.e. shear modulus, burgers vector). This led the expression of precipitation hardening, with the presence of obstacles spaced at a distance, \( l \) nm apart (L in Fig. 2.2), as follows [33],

\[
\Delta H_{ppt} = T_1 T_2 \frac{G_{solvent} b}{l} \frac{1}{2\pi} \left( \frac{l}{r_c} \right) \tag{2.2}
\]

where \( T_1 \) is Tabor factor (= 3) [34], \( T_2 \) is Taylor factor (= 3.06) [35], \( b \) is burgers vector and \( G_{solvent} \) is the shear modulus of the matrix. Spacing \( l = d_p \left[ \left( \frac{1}{2f} \right)^\frac{3}{2} - 1 \right] \) [36] with precipitate volume fraction \( f \) and precipitate size \( d_p \), and \( r_c \approx 2b \) [37].

Fig. 2.2 The situation that dislocation meets hard undeformable second phase particles (a) dislocation is approaching (b) dislocation meets particles (c) Tension is balanced with resistance force (d) dislocation is escaping [38]

\* T= the line tension of the dislocation
The critical size of the precipitated particles is decreased as the stiffness of particles increases, hence, if precipitates are harder, Orowan looping is observed for smaller particles size [33]. Precipitation hardening is a remarkably effective strengthening mechanism, for instance, the strength of Al alloy can be increased from about 150 to over 500 MPa (or more than 300 %) [39].

2.1.4 Strengthening Mechanisms In Dilute Nanocrystalline Alloys

The strengthening improvements observed in nanocrystalline thin film Al alloys have been attributed to a number of mechanisms, either acting singly, or in combination. The first mechanism, as just discussed, is the Hall–Petch (H-P) relation. It will be convenient in what follows to express the H-P relation, eq. (2.1), in the form,

\[ \Delta H_{HP} = T_1 T_2 k_{HP} / \sqrt{d} \]

(2.3)

where \( T_1, T_2 \) is already defined above and \( d \) is the average grain size and the value of \( k_{HP} \) for Al alloys is reported in a range between 0.06 and 0.28 MPa \( \sqrt{m} \) [40-45]. The value of \( \sigma_0 \) in eq. (2.1) is typically small and is neglected. As noted above, MD computer simulations [14, 46] and some experiments [8, 47] have shown that when grain sizes are smaller than ~ 15 nm, nanocrystalline metals sometimes begin to soften. Since the Al films investigated here all have grain sizes significantly larger than 15 nm, inverse H-P should not be important, and this effect will not be discussed further.

Another important finding of MD simulations is that when the grain size becomes small, there cease to be sources of dislocations within the grain interiors [48]. Even existing dislocations are unstable. This means that deformation by dislocation glide requires that the dislocations be nucleated at the grain boundaries. This led Rupert et al. [49] and others [50], to suggest that the
Grain boundaries serve as strong pinning points for these dislocations, so that the alloy strength can be associated with the stress required to drive the dislocation across the grain, [51], i.e.,

$$\tau = G b^2 / d$$  \hspace{1cm} (2.4)

This, notably, does not consider the nucleation of dislocations.

Rupert et al.[49], further addressed solid solution effects for these grain sizes by adding a grain boundary pinning term to traditional Fleisher model. This model can be applied many nanocrystalline cases [49, 52].

With the aid of eq. (2.4), it is quite straightforward to show how solute additions contribute to the strength, as G and b both depend on solute concentration. Following Rupert and Schuh [49],

$$\Delta H_{nc} \approx T_1 T_2 \frac{G_{solute} b_{solute}}{d} \cdot \epsilon_{nc} \cdot c$$  \hspace{1cm} (2.5)

where $T_1$, $T_2$ and $d$ are defined above, and $\epsilon_{nc}$ accounts for the strain due to change in the stiffness and the lattice parameter. To first order,

$$\epsilon_{nc} = \left( \frac{1}{G_{solute}} \frac{\partial G}{\partial c} + \frac{1}{b_{solute}} \frac{\partial b}{\partial c} \right).$$  \hspace{1cm} (2.6)

As before, $G_{solute}$ and, $b_{solute}$ are the shear modulus and burgers vector of the matrix.

In addition to these two mechanisms, solid solution hardening and precipitate hardening also contribute to the strengthening. These mechanisms were described in the previous section and will be treated simply as additive [49, 50].

An additional strengthening mechanism in nanocrystalline alloys concerns the strength of the grain boundaries, themselves. This topic falls within the broader topic of grain boundary
engineering [53, 54], however, the present discussion is limited to nanocrystalline materials, and mostly nanocrystalline alloys. It has long been questioned whether deformation in nanocrystalline materials is determined by grain boundary sliding, or by dislocation glide [55-57]. This question was examined by Vo et al. using MD simulation [58]. An important result from this study is reproduced in Fig. 2.3, where it is observed that while grain boundary sliding is the dominant mode of deformation at small grain sizes, dislocation glide becomes dominant at ~ 20 nm. Consequently, dislocation glide will be the dominant mechanism of deformation in the present study, although grain boundary sliding may be important to accommodate the emission and absorption of dislocations in the grain boundaries. A second important work by Vo and co-workers [59] for the present discussion concerns the doping of grain boundaries with solute. These results are shown in Fig. 2.4. It is observed here that additions of solute to the grain boundaries lowers the grain boundary energy, Fig. 2.4(a), and as a consequence, the yield stress increases (Fig. 2.4(b)). One of the predictions of this work is that the size misfit of the solute in the host matrix was a key factor in the effectiveness of this strengthening mechanism.

Fig. 2.3 Percentage of the total plastic strain due to dislocation solid symbols and GB sliding open symbols for different samples at a strain rate of $1 \times 10^{10} \text{s}^{-1}$ [58]
It is important to recognize that the MD simulations have considered only very small grain sizes, ~ 4 - 12 nm. The grains orientations, moreover, were created in a nearly random fashion, which means few, if any, low energy boundaries were sampled. In contrast, the Al grains sizes in the present work are greater than ~ 50 nm, and low-energy grain boundaries are observed.

While Vo et al. revealed the importance of solute doping of grain boundaries, they did not explicitly explore the atomistic mechanisms of strengthening, although they did imply that the strengthening derived from suppressing grain boundary sliding. This possibility had also been reported in simulations using Lennard-Jones potentials [60]. In larger grained Al samples, it is also possible that solute suppress nucleation of dislocation in the boundaries. In this regard, Borovikov et al.[61], used MD simulations to examine the effect of Cu (Ag) solute additions on dislocation emission from grain boundaries in Ag (Cu). These authors indeed showed, albeit for a very specific grain orientation and at small grain size ~ 20 nm, that solutes, in fact, do influence dislocation emission. This is shown in Fig. 2.5. Note that whether the solute is oversized or undersized makes little difference on this large effect.
Fig. 2.5 MD simulations of yielding in (a) dilute Cu-Ag, and (b) Ag-Cu alloys. In (c) the yield stress is plotted as a function of solute concentration. Taken from ref. [61].

2.2 Most Relevant Previous Studies Of Selected Al Alloy Systems

2.2.1 Al-Sc Alloys

2.2.1.1 Strengthening In Dilute Al-Sc

Precipitation strengthening of Al-Sc alloy are investigated by Seidman et al. [62]. According to them, the coherent Al$_3$Sc precipitates increase the room temperature flow stress of aluminum, from about 20 MPa for pure Al to 140 – 200 MPa for Al(-Sc) alloys with peak strengthening precipitate size ~ 1.5 nm. Regarding to the strengthening mechanism, Seidman et al. [62] also observed a transition of strengthening mechanism from precipitate shearing mechanism to Orowan dislocation bypass hardening based on precipitates sizes, like other Al alloy system coherent, shearable precipitate phases [63]. In their study, they confirmed that shearing mechanism is applicable for 1.4 nm whereas Orowan hardening can explain the result in 7.8 nm precipitate case. Indeed, the large precipitates serve as effective pinning points of dislocation as confirmed by dislocation loops around the precipitates. However, in small precipitates, dislocations can travel in pairs with coherent L1$_2$ precipitates.
2.2.1.2 Irradiation Effects In Dilute Al-Sc Alloys

Along with improved mechanical properties, superior radiation resistance is also attainable by Sc addition to Al alloys. Platov et al. [64] observed remarkable increment of irradiation resistance AlMg$_{2.8}$Sc$_{0.24}$(at.%) using neutron irradiation. After the irradiation, the mechanical property remained same.

More detailed study was carried out by Ivanov et al. [65] with AlMg$_{2.24}$Sc$_{0.23}$Zr$_{0.04}$, AlMg$_{2.24}$Sc$_{0.12}$Zr$_{0.04}$(at.%) using neutron irradiation as a following research of Platov et al. [64]. Firstly, they showed recombination effect of Sc in the solid solution matrix, as can be seen in Fig 2.6. $K_v$ and $\eta'$ shown in Fig 2.6. represent absorption of vacancies and recombination parameter, respectively. Note ($\eta' \propto \frac{1}{K_v K_i}$).

![Fig. 2.6 The concentration dependences of the $K_v$ and $\eta'$ in electron irradiated Al-Sc, Al-Mg and Al-Zn alloys [64]](image-url)
As can be observed in Fig. 2.6, Sc is more effective to enhance the mutual recombination of point defects and this enhancement is mainly related with decrease of interstitial mobility \(K_v\) because Sc does not interact with vacancy in a given ranges. Owing to that The dilatation volume of Sc in Al is \(> 0\) \cite{66}, the diffusion transport of scandium atoms to sinks by the interstitial mechanism \cite{67} is not an effective. Consequently, Sc induced better irradiation resistance of Al.

For another reason for better irradiation resistance of Sc addition, Ivanov \textit{et al.} \cite{65} observed the stability of \(\text{Al}_3\text{Sc}\) with respect to radiation enhanced coarsening. Along with serving as a recombination center for point defects, \(\text{Al}_3\text{Sc}\) itself is stable under irradiation coarsening. When \(\text{AlSc}0.2\text{ at.\%}\) alloy is irradiated at 180 °C using 1 MeV electrons, \(\text{Al}_3\text{Sc}\) size (200 nm) remains constant up to \(1.1 \times 10^{26} \text{ m}^{-2}\). Also, additional \(\text{Al}_3\text{Sc}\) was not formed during the irradiation. This behavior also found in Al-Sc-Mg alloys with neutron irradiation \((4.7 \times 10^{24} \text{ m}^{-2})\) at 150 °C in Ivanov \textit{et al.} \cite{65}’s study.

### 2.2.2 Strengthening In Dilute Al-Sb Alloys - Focused On Irradiation

While most studies of GaAs concern its electronic properties, particularly in regard to strained quantum dots on GaAs, there are few, if any, studies regarding the mechanical properties of the AlSb system. On the other hand, radiation-induced precipitation (RIP) of AlSb in Al has been studied, and indeed, these studies motivated my interest in the Al-Sb system. These early RIP studies have focused on the precipitation behavior during implantation of pure aluminum with Sb \cite{68, 69}, suggesting that Sb solutes in aluminum can be an effective trap for vacancies, and consequently this system represents a potentially useful radiation-resistant alloy. Nelson \textit{et al.} \cite{69} studied the formation of AlSb precipitates (second phase) during the ion implantation, using 80 keV Sb\(^+\) ion to Al thin films. Total dose was \(5 \times 10^{16}\) ions/cm\(^2\) with dose rate was \(- 4 \times 10^{13}\) ions cm\(^{-2}\)/s, which equivalent to about 15 at. % Sb in the implanted region. They reported that at
low temperature, radiation-enhanced diffusion is an important factor whereas thermal diffusion is negligible, and thus radiation diffusion may be responsible for rapid precipitate growth at this temperature range ~ 40 °C. Not only find radiation enhanced diffusion is significant at lower temperature range, but also find that dislocations are common structures below 300 °C. Picraux et al. [68] followed up on this initial work, mainly focusing on the formation and evolution of AlSb precipitates in Sb-implanted Al by implanting 50 keV Sb ion at temperatures ranging from room temperature to 300 °C. Firstly, they observed that precipitation occurs during implantation at roughly the same temperature as during annealing of a sample implanted at room temperature, as well as that the size distribution of the precipitates is strongly dependent on temperature (of sample) during the implantation. The mean size of the precipitates increases with increasing implantation temperature and increasing fluence, but with decreasing flux. Secondly, larger and fewer precipitates were observed at high temperature under same flux. At higher temperature, flux dependence is weak. At the same temperature, higher flux induces smaller precipitate and the extent of the variation with fluence is less for the lower-temperature implantation. The precipitate size distribution also depends strongly on Sb fluence, high fluence results, as might be expected, in larger and fewer precipitation. In terms of the precipitate evolution, flux and temperature are more important during the nucleation and/or early growth (5 nm) of precipitates - under increasing Sb fluence. Lastly, Picraux et al. [68] also observed disordered structure by heavy ion irradiation. The very dense network of dislocations which may be produced during irradiation. The overall AlSb evolution phenomenon is related to diffusivity of Sb solute. Because $D_t$ increases more rapidly with time as the temperature is raised, nucleation should occur at an earlier stage in the implantation, and hence at a lower Sb concentration. Therefore, at a given flux, fewer precipitates should nucleate at higher temperatures, consistent with the observed behavior. In addition to
precipitation, at higher flux the precipitate dissolution processes are also accelerated, and this might inhibit precipitation until an even higher solute concentration is reached.

### 2.2.3 Previous Study In Dilute Al-Cr Alloys

When it comes to strengthening, Beckerdike et al. [70] showed that the solid solution strengthening and precipitation hardening led to high tensile strength and Young’s modulus in the Al-C-Fe ternary system. Partridge and McConnell [71, 72], did further study using vapor quenched super-saturated Al-Cr binary (2.8-5.6 at.%Cr) and the Al-Cr-Fe ternary (2.5-6.1 at.%Cr and 0.45-0.92 at.%Fe) alloys. According to their research, although higher Cr at.% results in the increment of Young’s modulus, the conversion of Cr in solid solution to Al$_7$Cr intermetallic precipitates has negligible effect on Young’s modulus value. Below ~ 280 °C, the solid solution microstructure could be retained, and higher temperatures spherical shape Al$_7$Cr equilibrium phase is started to form at the grain boundaries in supersaturated solid solution. They also claimed the yield stress increment enhanced by this solute addition, $\sigma_{0.2} = mC_{cr} + \sigma_0$, where $m = 44.7$ Mpa/at.%Cr, $\sigma_0 = 283$ MPa and $C_{cr} =$ at.% of Cr. This yield stress is also related with precipitation, it reduced at temperature above 270 °C where precipitation starts to be observed. They also found the lattice parameter(a) change, $a = 4.0494 - 0.0083C_{cr}$. As $C_{cr}$ increases, the grain size reduction was also observed at $3 < C_{cr} < 5$.

### 2.2.4 Previous Study In Dilute Al-W Alloys

Rajulapati et al. [73] studied nc AlW (up to 4 at. % W) alloy powders containing pure Al with second-phase pure W particles were synthesized by ball milling. After ball milling, they did o high-pressure torsion (HPT) at room temperature or n hot compacted (HC) at 300 °C. They claimed Orowan hardening results in max. 30 % hardening effects. Although no data on diffusion
of W in Al has been found, it can be assumed that low diffusivities exist in this system. It follows that the diffusivity of W in Al should be negligible during milling, to the extent that the presence of a high concentration of vacancies and dislocations does not facilitate the formation of intermediate phases or metastable solid solutions.

2.3 Experimental Methods

2.3.1 Sample Preparation And Alloy Selection

In the present study, the alloys were prepared by magnetron sputtering, which enabled a simple means to prepare highly supersaturated Al alloys. By annealing these samples, the solubility could be reduced as precipitates formed, thereby controllably changing the dominant strengthening mechanisms. Since the grain sizes of these samples are greater than ~ 50 nm, the solute concentration could be reduced during annealing by solute flowing to grain boundaries, or by precipitating within the grain interiors, but this will be discussed for the specific alloys investigated. Annealing at sufficiently high temperatures also led to increases in grain size, which of course needed to be taken into account.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic size (pm)</th>
<th>( \Delta V/V^* )</th>
<th>Young’s modulus (GPa)</th>
<th>Maximum solubility (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>143</td>
<td>-</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>128</td>
<td>-0.72</td>
<td>279</td>
<td>0.35</td>
</tr>
<tr>
<td>Sb</td>
<td>140</td>
<td>0.63</td>
<td>55</td>
<td>1.2</td>
</tr>
<tr>
<td>Sc</td>
<td>162</td>
<td>0.27</td>
<td>174.4</td>
<td>0.21</td>
</tr>
<tr>
<td>W</td>
<td>139</td>
<td>-</td>
<td>411</td>
<td>0.02</td>
</tr>
<tr>
<td>Mg</td>
<td>160</td>
<td></td>
<td>45</td>
<td>16</td>
</tr>
</tbody>
</table>

Other alloys

Table 2.1 Solute properties of Al alloys

* \( \Delta V/V = \left( V_{Al}^X - V_{Al}^{Al} \right) / V_{Al}^{Al} \) [74]
The choice of alloys for this work reflect considerations of strengthening mechanisms, creep, and radiation damage. The complete set of alloys studied in this thesis is provided in Table 2.1, along with key properties. A first consideration in selecting these solutes was to begin with scandium, since a large body of work already exists on the mechanical properties of this classic age-hardening alloy.

<table>
<thead>
<tr>
<th></th>
<th>(D_0(10^4\text{m}^2\cdot\text{s}^{-1}))</th>
<th>(Q\ (\text{kJ} \cdot \text{mol}^{-1}))</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>1.71</td>
<td>142.4</td>
<td>[75]</td>
</tr>
<tr>
<td>Cr</td>
<td>1.85\times10^3</td>
<td>253</td>
<td>[76]</td>
</tr>
<tr>
<td>Sb</td>
<td>0.09</td>
<td>121.7</td>
<td>[77]</td>
</tr>
<tr>
<td>Sc</td>
<td>2.65</td>
<td>165</td>
<td>[78]</td>
</tr>
<tr>
<td>W*</td>
<td>14</td>
<td>250</td>
<td>[79]</td>
</tr>
<tr>
<td>Mg</td>
<td>1.24</td>
<td>130.4</td>
<td>[80]</td>
</tr>
</tbody>
</table>

*Data for W assume is actually for Mo, but assumed similar.

Table 2.2 Diffusion data of Al alloys

The other alloys were selected to test the different strengthening models described above, i.e., the role of atomic volume, effect on Young’s modulus. Also of interest in this study was the annealing behavior, i.e., precipitation kinetics, and therefore the thermal diffusivity of the alloying elements was also considered. The thermal diffusion data are shown in Table 2.2.

2.3.2 Thin Film Deposition

The DC magnetron sputtering was performed to grow Al, Al-0.7 at.% Sc, Al-1.1at.% Sc, Al-1.7 at.% Sc, Al-1.2 at.% Sb, Al-1 at.% W, Al-4 at.% W, Al-11 at.% W, Al-4 at.% Cr, and Al-10 at.% Cr thin films. An AJA DC magnetron sputtering system, is employed to grow nanocrystalline films. For the mechanical tests and microstructural characterization, ~ 600 nm metal films were deposited on [100] Si substrates, which had been oxidized to form a 1 µm thick
oxide layer. The deposition chamber base pressure was below at $5 \times 10^{-8}$ Torr and the Argon gas pressure was maintained at $2 \times 10^{-3}$ Torr during the deposition. The deposition rate of each element was calibrated using Rutherford backscattering spectroscopy (RBS) method, see section 2.2.6.1, below.

2.3.3. Heat Treatment

For investigating effects of heat treatment, 1 hour annealing was performed at various temperatures after film growth. This annealing was performed at a base pressure of $\sim 5 \times 10^{-8}$ Torr and annealing pressure was maintained below $1.5 \times 10^{-7}$ Torr to minimize oxidation. In order to maintain a good vacuum level, a liquid nitrogen (LN) cooled shroud was used during the annealing. Temperature was increased at a rate of $\sim 8$ °C/min and after annealing samples for 1 hour, they were cooled at a rate of about $\sim 4$ °C/min.

2.3.4 Atom Probe Tomography Sample Preparation

The specimens used for Atom Probe Tomography (APT) were prepared from the thin films using a Helios 600i Nanolab Focused Ion Beam (FIB). Prior to the fabrication, (15 μm X 1.5 μm X 2 μm) a Pt layer was deposited on the top surface of sample to protect the thin film. Then, wedge shaped cuts were made using a Ga ion beam with 30 kV and 22° tilt angle at rotation angles of 0° and 180°. After finishing cutting out the wedge sample (which consists of a film and some parts of Si wafer), it was transferred to a microtip on the micro coupons using an omni-probe needle. At this step, creating a wedge cut can facilitate the weldability of sample piece to the micro coupon by increasing the probability that during tip shaping the Pt is redeposited at the surface where the sample was originally attached to the microtip coupon. The hemi-spherically shaped tips were fabricated by ion beam milling from outer to inner direction. Note that the ion beam current and
voltage were decreased as the tip became sharper, from 21 nA to 1.1 pA and 30 kV to 5 kV, respectively to minimize the damage and the implantation of Ga. Tip shaping by annular milling is shown in Fig 2.7. Tip shank angle at Fig. 2.7 is ~ 50° - 100° for laser induced heat dissipation.

Fig. 2.7 Shaping by Annular Milling on Al-Sc alloys; step1: at 30 kV all the way down to 10 μm below tip apex. Step 2: at 16 kV all the way down to 2-3 μm below tip apex. Step 3: at 5-8 kV all the way down to 2-3 μm below tip apex.

The final tip was needlelike, with diameter ~ 75 nm at top and ~ 250 nm at the bottom, and L is less than ~ 2 μm, as seen in Fig. 2.8.

Fig. 2.8 SEM of an APT sample after FIB fabrication
2.3.5 Nanoindentation

2.3.5.1 Overview Of Nanoindentation

Nanoindentation, is widely used for characterizing materials on a microscopic length scale [81]. During the nanoindentor measurements, a sharp diamond tip, usually a Berkovich diamond tip - a three-sided pyramid with a half angle of 65.35°, indents the sample surface and the indentation depth and load are constantly measured. With this displacement and load relation, the contact area can be approximated [82] and hardness value can be determined. Conventional nanoindentation provides a single hardness value and elastic modulus per one indentation. But continuous stiffness measurement technique enables continuous values from a single indentation.

The yield strength can be obtained by the following equation [83].

\[ \sigma_y = \frac{H}{3} (0.1)^n \]  

where \( \sigma_y \) is the yield strength and \( n \) is the strain hardening exponent [83]. Analyzing of hardness measurement, however, is difficult because stress state near the indenter tip is complex. Nevertheless, determining the difference between the strengths of different materials is generally reliable, and so with appropriate standards, absolute hardness values can be obtained.

There are various artifacts in nanoindentation testing on thin films on a substrate [84], related to the indentation depth. If indentation depth is below 50 nm, the values are not reliable because of the effect of tip irregularity and the sample roughness. Another rule of thumb regarding nanoindentation is not to indent a film beyond one-tenth of its thickness [82], since the plasticly deformed region during the indentation is larger than indentation depth [85]. Consequently, nanoindentation results with very thin films on substrates may give erroneous values and it may
depend significantly on samples properties. For correcting these artifacts issues, several theoretical models are used for studies [86-88]. Pileup behavior near the indenter tip and the stress in the thin film can also affect the results. Previous researchers discussed these artifacts and described key factors to obtaining reliable information from nanoindentation measurements [88-93].

2.3.5.2 Hardness Measurement Using A Nanoindentor

A Hysitron TI950 triboindenter with a Berkovich diamond tip was used for my hardness measurements of samples. During the indentation, the sample surface and the indentation depth and load are constantly measured, providing information on both the hardness and elastic modulus [82] as a function of depth [89].

Before the actual measurement of hardness, the load was selected to achieve sufficient plastic deformation and then hardness values were measured at 9 locations on each sample, using a calibrated force, \( \sim 400 \mu N \) for nanocrystalline Al alloys. From the measured reduced modulus \( (E_r) \), the modulus of the sample was obtained using the relation,

\[
\frac{1}{E_r} = \left( \frac{1-\nu^2}{E} \right)_{\text{sample}} + \left( \frac{1-\nu^2}{E} \right)_{\text{indenter}}
\]

(2.8)

where Poisson’s ratio \( \nu \) is about 0.07 and indenter modulus is 1140 GPa from the diamond probe’s characteristics [94]. Reproducibility of results on different specimens was \( \sim \pm 10\% \) and \( \pm 15\% \) for the hardness and modulus, respectively. Note that a standard basic QS trapezoid loading function was employed for getting a better approximation of hardness and modulus.
2.3.6 Characterization Techniques

Various characterization techniques were performed, such as RBS, XRD, SEM, TEM, STEM and EDS in STEM were used to characterize samples.

2.3.6.1 Rutherford Backscattering Spectrometry (RBS)

Rutherford Backscattering Spectrometry (RBS) is a useful method to check overall composition of samples and determine/calibrate deposition rates. RBS was able to determine film thickness information within a few percent and composition information within ± 0.5 at.%, although this depends on the various factor such as sample thickness, alloy constituents, surface roughness, and available stopping power data. A HVE van de Graaff accelerator and NEC Pelletron were employed to perform RBS using He$^+$ ions. Both systems employ the same backscattering geometry, incident beam angle is at 22.5° from the plane normal direction and the scattering angle is 150°.

In order to obtain clear element peak profile, I collected data until the count rate was ~1500 per channel in the region of interest. SIMNRA software was used to for fitting and analyzing RBS spectra. The plot in Fig 2.9 is an example of the calibration plot, Al-0.7 at.%Sc alloy, using SIMRA software. While simple “eyeball” fitting is usually sufficient, I integrated the counts under different regions of the spectrum to obtain more accurate results see e.g., refs. [95, 96] for details.
2.3.6.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) was employed to identify the solubilities and alloy phases in the film after different processing steps. In particular, grazing incidence angle X-ray diffraction (GIRXD) was employed due to small film thickness and low atomic number of Al. A Philips X’pert 2 with Cu $K_{\alpha 1}$ $K_{\alpha 2}$ was used for XRD measurements and the peak positions were corrected with reference values. Grain diameters, $d$, were estimated in selected Al-Sc alloys by using the Scherrer equation ($d = \frac{K\lambda}{\beta \cos \theta}$), $K$ is dimensional shape factor, typically 0.9, $\lambda$ is the X-ray wavelength (0.154 nm), $\beta$ the peak broadening, and $\theta$ the Bragg angle, although all values employed for analysis derived from TEM measurements. Fig. 2.10 is an example of GIXRD measurement.
Microstructural characterization was conducted primarily using TEM and STEM methods. Comprehensive information of samples, such as, grain size, precipitate size, composition, phase, were obtained by analyzing TEM images and electron diffraction patterns. In particular, JEOL TEM series were employed to obtain the micrographs. General bright field and dark field images were obtained using JEOL 2010 LaB6 as well as nanobeam diffraction. A Gatan ultrascan 2k x 2k CCD was used for imaging with 2010 LaB6. For High Resolution Transmission Electron Microscopy (HRTEM) imaging, especially, JEOL 2010F EF-FEG was employed for high angle annular dark field (HAADF)-STEM. This JEOL 2010F EF-FEG was also used for Energy dispersive spectrometry (EDS) chemical analysis to identify each element and correlate compositions with phases. Typically, solute concentrations as low as ~ 0.5 at.% could be detected, but depending on the specific solute atom.

Image J and Digital Micrograph software programs were used to analyze TEM images, mainly focused on measuring grain size and precipitate size. Size distribution and average size
were determined with the assumption of a spherical shape, for example, the area of each grain (or precipitate) was converted into effective diameter of spherical shape. For Al-Sb alloys, which had very small precipitates, a Digital micrograph software were mainly used for precipitate analysis.

TEM samples were prepared typically by a Gatan Precision Ion Polishing System (PIPS). For films that underwent creep testing, the film was attached to Cu or Mo TEM grids (1 x 1 mm²) using M-bond and then PIPS was used to thin the sample. Since the thickness of film for the bulge test is ~ 300 nm, fine polishing was conducted with 2 keV Ar⁺ for 10 mins to minimize surface damage. In the case of annealed samples, samples were first polished by Allied Multiprep to around 40 μm and then attached on TEM grids. Ion milling was carried out with ion 4-5 keV until a hole first appeared and then fine polishing was employed. For preparing cross-section view TEM samples, standard lift out techniques using FEI Helios 600i NanoLab Focused Ion Beam (FIB) was employed. First, Platinum was deposited as a protection layer about 2μm thick and milling processes were followed with different voltages and currents in order to minimize the implantation of Ga⁺ ions and irradiation damage. These cross-sectional samples were mostly used for examining the columnar structure of Al-Sc and Al-Sb alloy systems.

2.3.6.4 Scanning Electron Microscope (SEM)

Hitachi 4800 and JEOL 6060 SEM’s were used on occasion for confirming film thickness and/or film composition, although it was mainly used to confirm compositions of sputtering targets, which were too large for convenient RBS analysis, and too expensive to fragment.
2.4 Experimental Results

2.4.1 Nanocrystalline Al

Before presenting results on Al alloys, it will be useful to first provide a basic characterization of a pure Al thin films to serve as a reference. The grain size, $d$, of as-grown, pure Al films, which was $\sim 600$ nm in thickness, was determined by both TEM micrographs and X-ray diffraction and found to be $d \sim 100$ nm. Figs. 2.11(a-d) show STEM micrographs after annealing to successively higher temperatures. After 1 hour annealing at 150 °C the grain size has increased to $\sim 180$ nm, but little additional grain growth is observed at higher temperatures, reaching only $\sim 250$ nm at 300°C. The slow grain growth at high temperatures is likely a consequence of stabilization by the columnar structure [97].

Hardness measurements were also performed. The as-grown samples, with grain size $\sim 100$ nm, have a hardness $\sim 0.7$ GPa. As reported in Fig. 2.12, annealing at 250 °C results in a decrease in hardness to $\sim 0.55$ GPa, or about 20 %.
Fig. 2.11 TEM images of the Al after annealing at (a) 150 °C for 1 hour (b) 200 °C for 1 hour (c) 200 °C for 3 hours (d) 300 °C for 1 hour

Fig. 2.12 Grain size and hardness of Al as a function of annealing temperature
2.4.2 Al-Sc Binary Alloys

2.4.2.1 Thermodynamic And Kinetic Properties Of Al-Sc Alloys

Aluminum alloyed with scandium (dilute Al-Sc alloys) [98] shows excellent mechanical properties at room temperature, due to the presence of elastically hard and coherent nanometer size Al$_3$Sc precipitates that can be obtained at a high number density [99, 100]. These precipitates impede dislocation movement and stabilize a fine-grain structure [98] and furthermore, enable this Al-Sc alloys to be stable at elevated temperatures. Hence, precipitation strengthened Al-Sc alloy can be used at temperatures significantly higher than conventional aluminum alloys. Furthermore, Sc provides better temperature stability. Interestingly, adding small quantities (0.1 - 1.0 %) of scandium as a ternary addition to a number of Al alloys, can also significantly improved their mechanical properties [101]. Superior corrosion resistance, light weight and weldability make this system a promising candidate material for extreme environments.

The phase diagram binary Al-Sc system is shown in Fig. 2.13. In this binary system four compounds exist: Al$_3$Sc, Al$_2$Sc, AlSc and AlSc$_2$ and all these intermetallic compounds have high a melting point > 1000 °C. Of interest here for dilute Al-Sc alloys is the Al$_3$Sc (L1$_2$) phase, which has a peritectic temperature of 1283 °C [102]. The detailed phase diagram on the Al-rich end is shown in Fig. 2.13(b). Al-rich primary solid-solution of the Al-Sc binary phase diagram exhibits a very narrow solid-solubility in equilibrium Al$_3$Sc phase. The maximum solid-solubility of Sc is 0.21 at.%, occurring at the eutectic temperature, which is only 1 °C below the melting point of pure aluminum.
For the present study, I selected 3 different dilute Al-Sc compositions, nominally Al-0.7at.%Sc, Al-1.1at.%Sc, and Al-1.7at.%Sc, referred to hereafter as AlSc\textsubscript{0.7}, AlSc\textsubscript{1.1}, and AlSc\textsubscript{1.7}, respectively, to investigate mechanical and microstructural behaviors under harsh environments. Due to the high concentration (supersaturations) of Sc in these alloys, they cannot be simply homogenized in the solid state and quenched, the standard treatment for age-hardening alloys; however, under irradiation solubilities are enhanced, and thus very high supersaturations become necessary for parts of this study. Sc solubilities at the annealing temperatures employed here are shown in Table 2.3.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>RT</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (%)</td>
<td>1.2 x 10^{-5}</td>
<td>8.2 x 10^{-5}</td>
<td>3.8 x 10^{-5}</td>
<td>1.3 x 10^{-3}</td>
<td>3.8 x 10^{-3}</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3 Sc solubility in Al at the annealing temperatures [104]

The crystal structure of the Al\textsubscript{3}Sc intermetallic phase was first described by Rechkin et al. [105] and is shown in Fig. 2.14. As seen in this figure, the L\textsubscript{12} structure of Al\textsubscript{3}Sc phase is based
on face centered cubic unit cell, with one Sc atom at cube corners. The lattice spacing of this compound is 4.105 Å [106] which is only 1.6 % greater than that of Al, 4.04 Å. As a consequence, Al₃Sc precipitates are expected to be coherent up to a critical diameter, 20 ~ 30 nm. Marquis and Seidman [104] observed the perfect coherency between Al matrix and Al₃Sc precipitates in dilute Al-0.3wt% Sc alloys by TEM observations. According to their research, Al₃Sc precipitates, which grows to 40 nm in diameter after 120 hours aging at 400 °C, are still coherent in Al. If the precipitates maintain coherency with the surrounding matrix, coherency strains can be large [103], and this too can enhance strengthening.

![Fig. 2.14](image)

Fig. 2.14 (a) Atomic arrangement of the Al₃Sc [107] (b) schematic drawing of the strains around a coherent precipitates which has smaller lattice constant than the matrix [103]

Seidman *et al.* [62] studied hardness behavior in large-grained Al-0.3wt% Sc alloys. According to their study, which is shown in Fig. 2.15(a), as the aging temperature increases from 275 °C to 400 °C, the incubation time for precipitation decreases, the time to reach peak hardness decreases, and the rate of hardness drop after peak aging increases (as observed at 300 °C and 400 °C). The maximum hardness is ~ 800 MPa and this increment is stable with prolonged heat treatment at 275 °C and 300 °C. In fact, other studies [101, 108] also reported similar behavior
that heat treatment in 250 °C – 350 °C can lead to significant precipitation hardening of Sc supersaturated alloy. Seidman and his coworkers [62] also reported precipitate size effect on hardness, as seen in Fig. 2.15(b). The maximum hardness value increase, 500 MPa, is achievable when the precipitate size ~ 1 nm (after annealing at 300 °C). If temperature is above 350 °C, precipitates drastically coarsen (at 300 °C is ~ 1 nm but at 400 °C, ~ 10 nm) and “hardness increment value” decreases. In fact, Al₃Sc precipitates do not coarsen significantly at temperatures < 350 °C, unlike most common hardening phases in Al alloys where coarsening is observed from 150 °C – 200 °C [103], owing to the relatively low diffusivity of Sc in Al, e.g., compared to Cu, Ag, and Mg. All these studies claimed that maximum hardness is achievable with combination of smaller precipitates size and heat treatment at 150 °C – 350 °C.

![Fig. 2.15 (a) Vickers micro-hardness versus aging time for an Al-0.3 wt.% Sc alloy as a function of aging temperatures. (b) increase in ambient temperature microhardness versus precipitate radius for an Al-0.3 wt.% Sc alloy aged at different temperatures [62]](image-url)
2.4.2.2 Evolution Of Microstructure Of AlSc_{0.7}, AlSc_{1.1}, And AlSc_{1.7} Alloys During Thermal Annealing

*As-grown AlSc_{1.1} Films*

TEM micrographs of the as-grown AlSc_{1.1} films are shown in Fig. 2.16. The mean grain size is ~75 nm, as can be seen in the plan-view TEM images in Fig. 2.16(a) (HAADF) and (b) (bright field). The size distribution is plotted in Fig. 2.16(f); over 100 grains were included in the distribution. Fig. 2.16(c), which is a HAADF cross sectional view of the as-grown film illustrates that these thin films have a columnar grain structure, as is typical of films grown at room temperature by magnetron sputtering. This TEM sample was prepared by focused ion beam lift out methods using a Ga beam. The bright contrast observed in this image, i.e., the precipitates, are in fact Ga precipitates. The integrated intensity of selected area diffraction (SAD) pattern taken on this sample prepared in plain view corresponds to FCC aluminum, as shown in Fig. 2.16(d). No evidence for precipitation of Sc is observed in either the HAADF image or the bright field image, Fig. 2.16(a) and (b), or in the selected area diffraction (SAD) pattern in Fig. 2.16(d). The bright contrast in Fig. 2.16(a) arises from diffraction contrast and not Z-contrast.
While the TEM images in Fig. 2.14 provide strong evidence that Al₃Sc has not precipitated during film growth, it does not determine whether Sc has undergone segregation, for example to
grain boundaries during the film growth. Energy dispersive spectroscopy (EDS) was thus used to verify that the Sc atoms were homogeneously distributed in the sample, and indeed no segregation was observed. Determining the solute concentration on grain boundaries in dilute alloys, however, is difficult, and since knowing precisely the initial state of the alloy is crucial for understanding the hardness behavior, I also used atom probe tomography (APT) to characterize the nominally AlSc$_{1.7}$ alloy in the as-prepared state. Measurements were performed using a pulsed laser mode in an ultra-high vacuum environment, $\sim 10^{-10}$ Torr, while the APT tip was cooled to -223 °C, see ref. [109] for details. The energy of the laser was 100 pJ. Under 250 kHz laser pulsing, atoms are evaporated from the surface, by an electric field effect, and projected onto a Position Sensitive Detector (PSD) with a very high detection efficiency, $\sim 80\%$. Generally, the number of atoms collected from each tip was more than 10 million atoms. The APT data were analyzed using IVAS software and the open source software 3Depict, which allowed for tip reconstruction using the atom position file and the range file which contains the mass spectrometry data.

The APT results are shown in Fig. 2.17 and Table 2.4. Fig. 2.17(a) provides a qualitative sense of the homogeneity of the Sc atoms by showing a cross sectional slice of the atom locations, while Fig. 2.15(b) provides the pair distribution function (pdf) of Sc atoms. The pdf for this alloy indeed looks very similar to that for a random distribution. Also provided by the APT characterization is a chemical analysis of the alloy. This is reported in Table 2.4. An important finding of this analysis is the very low concentration of oxygen in the sample, $< 0.01$ at.%. This value is typical of oxygen contamination in other sample grown in the magnetron sputtering system [110]. In other studies of the mechanical properties of Al thin films grown by vapor deposition, oxygen contamination was significant [111]. Similarly, ball milling processing of nanocrystalline alloys often leads to oxygen contamination of the order 1 at.%. The finding of Ga in the sample
derives from the FIB processing of the APT tip; most Ga is found near the surface of the APT specimen. The Pt in Table 2.4 is due to the thin film of Pt deposited on the specimen that is used to avoid direct implantation of Ga. Lastly, the hydrogen is a common element observed during APT; however, it mostly derives from hydrogen in the APT vacuum system that adsorbs on the tip; it is not a contaminant.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Al</th>
<th>Sc</th>
<th>Ga</th>
<th>O</th>
<th>C</th>
<th>Pt</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (at.%)</td>
<td>98.17</td>
<td>1.37</td>
<td>0.1</td>
<td>0.01</td>
<td>0.01</td>
<td>0.04</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Table 2.4 Composition of as-grown AlSc$_{1.7}$ alloy deduced from APT

![Atom probe reconstruction of the as-grown AlSc$_{1.7}$ alloy. The green dots represent Al atoms, while the black dots (enlarged) show Sc atoms; (b) nearest neighbor distribution (Sc): comparison of the pdf for the as-prepared sample and a random distribution](image)

Fig. 2.17 (a) Atom probe reconstruction of the as-grown AlSc$_{1.7}$ alloy. The green dots represent Al atoms, while the black dots (enlarged) show Sc atoms; (b) nearest neighbor distribution (Sc): comparison of the pdf for the as-prepared sample and a random distribution.
Before continuing on with the characterization of the annealed Al-Sc films, it is worth discussing briefly why the Ga forms precipitates during FIBing at room temperature, but the Sb and Sc do not precipitate during film growth at room temperature. First, the diffusion coefficient of Ga in Al is \( \sim 4.31 \times 10^{-4} \text{ m}^2\text{s}^{-1} \) [112], is 10 times larger than that of Sc, \( 0.49 \times 10^{-4} \text{ m}^2\text{s}^{-1} \) [112]; this is sufficient in itself to explain the result. On the other hand, Sb also has a high diffusivity in Al, presumably similar to Ga, and it does not precipitate during thin-film growth. Ga, however, is implanted into the Al during FIBing and this creates point defects, enhancing the diffusion coefficient. The local concentration of Ga during FIBing, moreover, is also very high, contributing to precipitation, although this has not yet been quantified.

**Annealed Al-Sc Films**

**AlSc\(_{1.1}\)**

The \( \text{AlSc}_{1.1} \) films were annealed for one hour at various temperatures between room temperature and 350 °C. The work of Marquis and Seidman [104] had previously reported that bulk, intra-granular precipitation begins at \( \sim 350 \) °C, and so higher temperatures were not investigated. Micrographs of the heat-treated AlSc\(_{1.1}\) films are shown in Fig. 2.18(a-d) below, while Fig. 2.18(f) shows the grain size distributions of these annealed films. After 150 °C treatment, Sc appears to remain in solutions as there is no evidence of the \( \text{Al}_3\text{Sc} \) phase. Again, the bright contrast in the HAADF image in Fig. 2.18(a) is diffraction contrast. The lack of precipitation is not surprising, at least within the grain interior. Using the diffusion data in section 2.3.1, above, the diffusion distance of a Sc atom during annealing at 150 °C for 1 hour is only \( \sim 2 \times 10^{-2} \) nm, i.e., less than one atomic jump – see Table 2.5. Figs. 2.18 (a) and (e) show that average grain size after annealing at 150 °C is also not much changed from that of the as-grown film.
Figs. 2.18(b, c, and f) show that the grain sizes in these Al-Sc films do not increase, in fact, until annealing reaches 250 °C. Precipitation, on the other hand, begins at ~ 200 °C, although the size and density of precipitates at this annealing temperature are very small. By 250 °C, precipitation has become far more pronounced, although similar to annealing at 200 °C the precipitates appear to be confined mostly to the grain boundary regions. This is illustrated in Figs. 2.18(b) and (c), where the precipitates are marked by dashed red circles. EDS measurements (in STEM mode) confirm that the bright contrast are regions of higher Sc concentration, as reported in Table 2.6. Electron diffraction, moreover, confirms that the precipitates after annealing at 250 °C are Al$_3$Sc, see Fig. 2.19. It is noteworthy that the diffusion data in Table 2.5 yields Sc diffusion distances of ~ 0.3 nm and 3 nm during the 1 hour anneals at 200 °C and 250 °C, respectively. This small amount of diffusion is insufficient for precipitation in the grain interiors, or even for much transport of solute from the grain interior to the grain boundaries. The precipitates mostly likely arise, therefore, from grain boundary diffusion of Sc initially located within ~ 2-3 nm of the grain boundaries. The activation of grain boundary diffusion at 200 °C - 150 °C may thus explain the onset of both precipitation and grain growth. It is worthwhile noting that the diffusion data in section 2.2.1 derives from ref. [104], which was determined at temperatures as low as 300 °C. My estimate of diffusion distances at 250 °C, therefore, does not require extended extrapolations and should thus be considered reliable.

<table>
<thead>
<tr>
<th>Temp.[°C]</th>
<th>150</th>
<th>200</th>
<th>250</th>
<th>300</th>
<th>350</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ [nm$^2$/s]</td>
<td>9.89 x 10$^{-7}$</td>
<td>1.41 x 10$^{-4}$</td>
<td>7.78 x 10$^{-3}$</td>
<td>2.13 x 10$^{-1}$</td>
<td>3.44</td>
</tr>
<tr>
<td>$\sqrt{D\tau}$ [nm]</td>
<td>5.97 x 10$^{-2}$</td>
<td>7.12 x 10$^{-1}$</td>
<td>5.29</td>
<td>27.71</td>
<td>111.26</td>
</tr>
</tbody>
</table>

Table 2.5 Tracer diffusion data for Sc in Al [104]
During annealing above ~ 300 °C the grain size begins to increase more rapidly, reaching a value of more than ~ 200 nm by 350 °C; these results are found in Figs. 2.18(d-f). Precipitation is observed in these same figures to become more copious. Again, Sc-rich precipitates are marked by dashed red circles. It is also observed at these higher temperatures that Sc-rich precipitates are no longer only located at grain boundaries, but also in the grain interiors. With the higher volume fraction of Sc-rich precipitates at 350 °C, it becomes possible to confirm their phase identity as Al$_3$Sc from grazing incidence x-ray diffraction. This is shown in Fig. 2.22. It is again interesting to consider whether the precipitates found in the grain interior had undergone (homogeneous) nucleation within the grains or if they had nucleated at the grain boundaries, and the boundaries migrated away from them during grain growth. The data for Al-Sc, however, are not as clear as for Al-Sb in Fig. 2.32(e), below, although Fig. 2.18(d) shows that the distance between precipitates is smaller than the grain size after annealing at 250 °C, suggesting that intragrain precipitation is likely. A summary of the grain size and precipitate size in AlSc$_{1.1}$ films as a function of annealing temperature is provided in Table 2.7.
Fig. 2.18 STEM image of AlSc$_{1.1}$ after 1 hour annealing at (a) 150 °C (b) 200 °C (c) 250 °C (d) 300 °C (e) 350 °C (f) grain size distributions.

Fig. 2.19 AlSc$_{1.1}$ after annealing at 250 °C (a) HAADF Z-contrast (b) reversed diffraction pattern of encircled spots are indexed corresponding to the Al$_3$Sc phase
Table 2.6 EDS analysis of precipitates. Point number refers to locations identified in Fig. 2.18.

<table>
<thead>
<tr>
<th>Annealed Temperature (°C)</th>
<th>point</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>99.4</td>
</tr>
<tr>
<td>250</td>
<td>3</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>99.2</td>
</tr>
<tr>
<td>300</td>
<td>5</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>99.7</td>
</tr>
<tr>
<td>350</td>
<td>7</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>99.6</td>
</tr>
</tbody>
</table>

Table 2.7 Summary of grain size and precipitate size as a function of annealing temperature in Al-Sc films.

At higher temperatures, 350 °C, the volume fraction of precipitates becomes sufficiently high that superlattice reflections can also be identified using x-ray diffraction. This is shown in Fig. 2.20.
2.21, where a grazing incidence geometry has been employed. Note, Al$_3$Sc phase cannot be confirmed by GIXRD method until the sample was heat-treated at temperature of 350 °C.

![GIXRD of AlSc$_{1.1}$ film after annealing at 350 °C for 1 hour](image)

**Fig. 2.21** GIXRD of AlSc$_{1.1}$ film after annealing at 350 °C for 1 hour

Columnar structure of AlSc$_{1.1}$ films and twin structure were confirmed by cross sectional view TEM images as shown in Fig. 2.22(a) for 350 °C heat-treated AlSc$_{1.1}$. Within the grain shown in Fig. 2.22(a), the twin structure is confirmed by the diffraction pattern in Fig. 2.22(b).

![AlSc$_{1.1}$ after annealing at 350 °C for 1 hour](image)

**Fig. 2.22** AlSc$_{1.1}$ after annealing at 350 °C for 1 hour (a) cross section bright field TEM (b) diffraction in a given grain at (a)
Especially, for a 350 °C annealing film, JEOL 2200FS (S)TEM is used to see Al₃Sc in detail, as shown in Fig. 2.23 below. Sc enrichment at grain boundaries is clearly confirmed using this cross section TEM imaging.

![Cross section STEM](image)

**Fig. 2.23 Cross section STEM of AlSc₁₁₁ annealing at 350 °C for 1 hour**

**AlSc₀.₇**

AlSc₀.₇ films were annealed at the same temperatures as the AlSc₁₁₁ samples. TEM images for AlSc₀.₇ films under various annealing conditions are shown in Fig. 2.24. It is observed that phase evolution during annealing was similar with AlSc₁₁₁, for example, precipitates are clearly found after 300 °C heat treatment. The composition of the red marked spots in images were indicated in Table 2.8. Data for the grain size and precipitate size as a function of annealing temperature are included in Table 2.7 and it shows that the average grain sizes are normally ~ 30 % larger and precipitate size is smaller than AlSc₁₁₁. In this AlSc₀.₇ case, the precipitate coarsening are observed at 350 °C heat treatment as well.
Fig. 2.24 STEM images of AlSc0.7 after 1 hour annealing at (a) 150 °C (b) 200 °C (c) 250 °C (d) 300 °C (e) 350 °C (f) grain size distribution

<table>
<thead>
<tr>
<th>Annealed Temperature (°C)</th>
<th>point</th>
<th>At. %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>93.74</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>99.48</td>
</tr>
<tr>
<td>250</td>
<td>3</td>
<td>95.70</td>
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<td></td>
<td>4</td>
<td>99.39</td>
</tr>
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<td>300</td>
<td>5</td>
<td>97.69</td>
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<td>6</td>
<td>99.71</td>
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<td>350</td>
<td>7</td>
<td>88.18</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>99.66</td>
</tr>
</tbody>
</table>

Table 2.8 Atomic concentration of annealed AlSc0.7. Points refer to locations in Figs.2.23(a)-(e)

\textit{AlSc}_{1.7}

Annealing on AlSc1.7 films were also performed at same conditions with other Al-Sc dilute alloys. TEM images under various annealing conditions are shown in Fig. 2.25. Average grain sizes noticeably increase over 300 °C heat treatment as can be seen in Fig. 2.25 and the detailed
sample information in Table 2.7. This condition thus shows the same behavior with the preceding studies on 0.7 at.% Sc and 1.1 at.% Sc.

Fig. 2.25 STEM images of AlSc_{1.7} (a) as-grown film after 1 hour annealing at (b) 150 °C (c) 200 °C (d) 250 °C (e) 300 °C and (f) grain size distribution

In addition to APT characterization of as-grown sample, APT characterization was also carried out on a specimen pre-annealed at 180 °C to do unambiguously determine whether solute comes out of solution in the grain interiors. The pre-annealing temperature was selected since the hardness had dropped significantly at this temperature and precipitation was not yet observed. The APT reconstruction of this sample, which contains ~ 1.0 x 10^7 atoms or a volume of ~ 2 x 10^5 nm^3, is shown in Fig. 2.26.
Fig. 2.26 APT reconstruction of AlSc$_{1.7}$ tip annealed at 180 °C for 1 hour. Mass spectrum is shown at right. Atom identity in reconstruction correspond to colors in mass spectrum.

Closer analysis of this tip is shown in Fig. 2.27. In Fig. 2.27(a), only Ga atoms; these atoms were introduced into the tip during FIB sample preparation. Ga is mobile in Al during implantation and this results in a nonhomogeneous distribution, as is observed. An expanded view of pinkish rectangle in this figure is shown in Fig. 2.27(b), but now showing only Al and Sc atoms that are in clusters. For the most part, the fraction of Sc in clusters in the entire tip is small, only ~ 1.3 %, but somewhat more than in the as-prepared sample, ~ 0.61 %. Fig. 2.27(c) quantifies this further, showing the pair distribution function (pdf) for this annealed sample as well as that expected for a random distribution. Note this nearest neighbor distribution of Sc atoms was calculated using an average Sc atom separation distance 0.52 nm, which was then ultimately used to identify clusters inside the sample.

It is observed that the pdf is less random than that of the as-prepared sample, but still quite similar to the random distribution. Most of the clusters are observed in a location of the tip that
also shows a high concentration of Ga. It is reasonable that Ga has migrated to some defect, presumably grain boundaries, and this suggests the Sc clustering results from mobility in the grain boundary.

The clustering analysis of an entire tip is shown in Fig. 2.28 and Table 2.9. Here, larger clusters were observed compared to as grown sample. While ~ 400 clusters were found using the IVAS software [113], the size, composition and location of the largest clusters are presented in Table 2.9. The largest cluster contains ~ 2800 atoms and has roughly the composition expected for Al₃Sc. Rotation of the tip reconstruction, moreover, reveals that this large cluster is 2-dimensional, certainly suggesting that this cluster/precipitate has formed on a grain boundary. Unfortunately, the volume sample analyzed by APT is small and one expects to locate only about one grain
boundary in a tip. The size of this cluster Table 2.9, moreover, is small ~ 15 nm³, and probably not observed by STEM HAADF imaging. It should also be realized that precipitates in this alloy are observed after annealing at 200 °C, and so the APT characterization is very much in line with what should be expected from the TEM results.

![Atom probe reconstruction of an AlSc₁.₇ annealed at 180 °C. Clusters are identified by color.](image)

**Table 2.9 Cluster information after APT reconstruction of annealed sample**

<table>
<thead>
<tr>
<th>Total ions in cluster for some of the largest clusters</th>
<th>Position (nm)</th>
<th>Cluster volume (nm³)</th>
<th>Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>2819</td>
<td>-4.0182</td>
<td>-8.0713</td>
<td>3.9837</td>
</tr>
<tr>
<td>198</td>
<td>-11.8658</td>
<td>0.0544</td>
<td>44.5836</td>
</tr>
<tr>
<td>174</td>
<td>-6.5921</td>
<td>-5.3056</td>
<td>4.486</td>
</tr>
<tr>
<td>115</td>
<td>-12.6598</td>
<td>0.1261</td>
<td>40.7386</td>
</tr>
<tr>
<td>92</td>
<td>4.0128</td>
<td>-11.4938</td>
<td>4.8969</td>
</tr>
<tr>
<td>70</td>
<td>-11.5127</td>
<td>0.306</td>
<td>42.6207</td>
</tr>
</tbody>
</table>

Table 2.9 Cluster information after APT reconstruction of annealed sample
2.4.2.3 Nanohardness: AlSc$_{1.1}$, AlSc$_{0.7}$ And AlSc$_{1.7}$ Alloys As A Function Of Annealing Temperature

An AlSc$_{1.7}$ as-grown sample has the highest value of hardness, as shown in Fig. 2.29 below. Fig. 2.29(a) shows mean grain size as a function of temperature in the case of AlSc$_{1.1}$. As the annealing temperature increases from room temperature to 200 °C, hardness values decrease from 2 GPa to 1.3 GPa. On annealing at 200 °C, 250 °C and 300 °C, in contrast, the hardness value remains almost constant. At 350 °C, hardness decreases slightly, but only about 10 %. A plot in Fig. 2.29(b) for AlSc$_{0.7}$ shows the same behavior as those for AlSc$_{1.1}$. Initial hardness of as-grown AlSc$_{0.7}$ is around 1.6 GPa and it dropped ~ 30 %, to 1.0 GPa after annealing at 200 °C. Over 200 °C the hardness again does not change significantly. For AlSc$_{1.7}$, hardness behavior follows the same trend as the other Al-Sc alloys. Further discussion will be presented below.

Fig. 2.29 Hall-Petch plot of Al-Sc alloys (a) AlSc$_{1.1}$ (b) AlSc$_{0.7}$, and (c) AlSc$_{1.7}$
The as-grown film hardness is plotted over the function of Sc concentration in Fig. 2.30. AlSc$_{1.7}$ has higher hardness as we can expect, and the hardness of as-grown sample shows a proportional relationship with Sc concentration.

![Fig. 2.30 Effect of Sc at.% on hardness of as grown film](image)

2.4.3 Al-Sb Binary Alloys

2.4.3.1 Thermodynamic And Kinetic Properties Of Al-Sb Alloys System

Al-Sb is an interesting binary alloy system as it has only one intermediate phase, AlSb, which is a line compound, and very limited solubility in the FCC Al phase (less than 0.02 at.%) below ~ 630 °C [114]. Above 1000 °C Al and Sb are miscible, as seen in Fig. 2.31, the phase diagram of Al-Sb system. I selected an alloy concentration of, Al-1.2 at.% Sb, or simply AlSb$_{1.2}$, in light of a previous ion implantation studies of Sb into Al [68]. These studies showed that implantation of Sb into Al to an average concentration of 1.2 at.% at room temperature remained a single phase solid solution. On annealing, this alloy showed a high density of small coherent AlSb precipitates. No hardness measurements on this alloy have been previously reported.
AlSb, which is a brittle intermetallic compound, consists of a face centered lattice of antimony of side intermeshed with an identical lattice of aluminum, as shown in Fig. 2.32 [115]. AlSb compound is FCC with lattice parameter of 6.126 Å. For this compound phase, Sb lattice contract slightly because Sb is on two intermeshed face centered rhombohedral lattices [2] with 6.20 Å. Since AlSb is coherent with Al matrix- one of Sb lattices is replaced by a lattice of aluminum- AlSb melts congruently at $T = 1060^\circ$C [116]. The distance of Al and Sb atoms in AlSb is $\sim 2.65$ Å, whereas the closest distance of approach of atoms are $2.87$ Å for Sb and $2.86$ Å for Al, respectively. The molecular volume of AlSb increases 20 % compared to the sum of the atomic volume of its constituent elements.
2.4.3.2 Effect Annealing Temperature On Microstructural Evolution

The microstructures of the nanocrystalline AlSb$_{1.2}$ alloys were characterized by TEM examination during annealing from the as-grown state at room temperature to 250 °C. Annealing times were 1 hour. Grain size and precipitate size were again obtained using STEM-HAADF imaging. Images for the various samples are shown in Fig. 2.32(a-e), while Fig. 2.32(f) shows the grain size distributions for the different samples. The average grain and precipitate sizes are reported in Table 2.10. The addition of Sb does suppress grain growth somewhat. At 250 °C the grain size is only 148 nm, compared to 210 nm for pure Al at 200 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>As grown</th>
<th>75</th>
<th>100</th>
<th>150</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm)</td>
<td>52 ± 1.85</td>
<td>58 ± 2.16</td>
<td>83 ± 3.46</td>
<td>96 ± 4.6</td>
<td>148 ± 5.45</td>
</tr>
<tr>
<td>Precipitate size (nm)</td>
<td>N/A</td>
<td>N/A</td>
<td>3.5 ± 0.25</td>
<td>5 ± 0.3</td>
<td>15 ± 1.2</td>
</tr>
<tr>
<td>Precipitate density (x 10$^5$/nm$^2$)</td>
<td>N/A</td>
<td>N/A</td>
<td>50</td>
<td>235</td>
<td>86</td>
</tr>
</tbody>
</table>

Table 2.10 Microstructural evolution in AlSb$_{1.2}$ during thermal annealing.
Fig. 2.33 HAADF STEM images of AlSb$_{1.2}$ films (a) as prepared and after annealing for 1 hour at (b) 75°C (c) 100 °C (d) 150 °C and (e) 250 °C (g) grain size distribution
Evidence for precipitation of AlSb is first observed after annealing for 1 hour at 100 °C. This is recognized by the bright, (Z-) contrast in Fig. 2.33(c), mostly observed along the grain boundaries. Note, however, that this contrast is not yet sharp. By 150 °C, Fig. 2.33(d), distinct precipitates are observed, and again, mostly on the grain boundaries; these precipitates could be identified by electron diffraction to be AlSb, as expected, see Fig. 2.35. The size distributions of the observed precipitates in AlSb$_{1.2}$ as a function of annealing temperature are reported in Fig. 2.34. To help understand this annealing behavior, the bulk diffusion distances at the different annealing temperature were calculated using the diffusion data in Table 2.11.

<table>
<thead>
<tr>
<th>Temp.[°C]</th>
<th>75</th>
<th>100</th>
<th>150</th>
<th>250</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ [nm$^2$/s]$^{[77]}$</td>
<td>4.86E-06</td>
<td>8.14E-05</td>
<td>8.42E-03</td>
<td>6.30E+00</td>
</tr>
<tr>
<td>$\sqrt{Dt}$ [nm]</td>
<td>0.13</td>
<td>0.54</td>
<td>5.5</td>
<td>150.5</td>
</tr>
</tbody>
</table>

Table 2.11 Tracer diffusion data for Sb in Al

The diffusion distances are quite consistent with the precipitation behavior. At 100 °C, the diffusion distance in the Al grains is too small to enable precipitation, and little precipitation is observed. The precipitation that is observed is restricted to grain boundaries, presumably made possible by grain boundary diffusion. At 250 °C, the bulk diffusion distance is sufficiently large for Sb in the grain interiors to segregate to the grain boundaries; this can explain the far more significant grain boundary precipitation, and limited precipitation in the grain interiors. By 250 °C, diffusion of Sb in the bulk has become significant, and indeed, extensive precipitation is observed in the grain interiors. Recall, AlSb is coherent in the Al matrix. It is possible, perhaps that intra-grain precipitates are created during grain growth by grain boundary migration; however, this seems unlikely since grain growth between 150 °C and 250 °C is relatively minor; see Fig. 2.33(f) and Table 2.10.
2.4.3.3 Hardness Evolution Of Al-Sb Alloys

The nanohardness data for AlSb1.2 are reported in Fig. 2.36 as a function of annealing temperature along with the grain size data from Table 2.10. The as-grown film has the highest value, 1.5 GPa, but as the annealing temperature increases from room temperature to 150 °C, the nanohardness gradually drops from ~1.5 GPa to ~1.0 GPa. At annealing temperatures greater than 150 °C, the hardness remained nearly constant at 1 GPa. This behavior is thus very different from that of typical Al-based age-hardening alloys, where the hardness rises on initial aging of the alloy as precipitates begin to form, reaches a maximum, and then decreases as precipitates grow large.
and their density decreases. These data thus demonstrate that nanocrystalline Al alloys behave far differently than their corresponding polycrystalline alloys. Two details in Fig. 2.36 are most noteworthy. First is that on annealing at 75 °C the hardness drops significantly from its as-grown value, i.e., $\Delta H / \Delta H_0 \sim 70 \%$, where $\Delta H = H(\text{asgrown}) - H(T)$ and $\Delta H_0 = H(\text{asgrown}) - H(T = 250 \degree \text{C})$. This is significant because precipitates are not yet observed, and grain growth is negligible. The second point is that the hardness at $T > 150 \degree \text{C}$ is $\sim 1.0 \text{ GPa}$, which (a) is substantially greater than that the pure Al sample $H_{\text{Al}} \sim 0.7 \text{ GPa}$, and it appears to be independent of grain size. I will defer further explanation of these results until all of the results on Al alloys have been reported so that more general conclusions can be drawn.

Fig. 2.36 Measured hardness and grain size of the AlSb$_{1.2}$ metal film as a function of annealing temperature
2.4.4 Al-Cr And Al-W Binary Alloys Systems

2.4.4.1 Thermodynamic And Kinetic Properties Of Al-Cr And Al-W

The hardness of dilute, nanocrystalline Al-Cr and Al-W alloys were also measured as a function of annealing temperature and related to the microstructure of the alloys. For the Al-Cr system, Al-4 at.% Cr and Al-10 at.% Cr were studied, while for A-W, Al-1 at.% W and Al-4 at.% W and Al-10 at.% W were all studied. The phase diagrams of these two systems are shown in Fig. 2.37, and selected compositions are indicated with red arrows in the figure. As it can be seen, the solubility of Cr in Al is extremely small, ~ 0.35 at.% at the peritectic temperature, \( T_P \), ~ 661 °C [117]. The alloy system forms several intermetallic phases in equilibrium, however, the monoclinic Al\(_7\)Cr phase should co-exist with the FCC Al rich phase in equilibrium for the alloy compositions employed here. Cr is significantly undersized in FCC Al; it has an atomic volume 8.3 nm\(^3\), in Al, roughly half that of host Al atoms [74]. Another key feature of Cr in Al for the present study is its very low diffusivity in Al, nearly seven orders of magnitude lower than self-diffusion in Al at low temperatures. This feature influences the better stability of nanoparticles.
In Al-W binary alloy, W solute atoms diffuse even slower than Cr atoms and have very low solubility (less than 0.02 at.%) [114]. This alloy system is interesting as it undergoes chemical ordering at temperatures below ~ 1300 °C but above ~ 1327 °C significant amounts of W can be dissolved in liquid Al, as illustrated in Fig. 2.37(b). Although Tonejc et al. [120] have extended the solubility up to ≈ 0.95 at.% W by rapid quenching of liquid alloys, it is still one of the Al alloys with very low solubility (less than 0.02 at.%). I selected 3 different W at.% supersaturated dilute composition, 1at.%W, 4at.%W and 11at.%W. These concentrations are marked with red arrow as seen in Fig. 2.37(b). Al12W intermetallic compound, body centered cube (BCC) with 7.58 Å [121] does exist up to ~ 8 at.%W and ~ 660 °C. Al5W phase, which has hexagonal shape (a = 4.9058 Å, c = 8.8558 Å) [121] is started to be observed if 8 < W at.%.
2.4.4.2 Microstructural Evolution Of Al-Cr And Al-W Binary Alloys Systems

Solid solutions of Al-Cr (4 at.% Cr and 10 at.% Cr) and Al-W (1 at.% W, 4 at.% W, and 11 at.% W) were also systemically annealed up to 400 °C owing to the limited diffusivity of Cr and W. Those systems are referred to hereafter as AlCr₄, AlCr₁₀, AlW₁, AlW₄ and AlW₁₁, respectively.

Grain sizes of the AlCr₄ films and AlCr₁₀ films were determined using STEM HAADF images-Z contrast similar to those shown in Figs. 2.38(a-e). The average grain size of the as-grown films was ~ 70 nm, and it did change much with annealing until ~ 300 °C. After 1 hour annealing at 400 °C, the grain growth size had increased to ~ 120 nm. Compared to Al-Sb and Al-Sc alloys, the onset of grain growth is delayed somewhat in temperature, ~ 50 °C, and overall, it is less rapid. The grain size distribution is plotted in Fig. 2.38(e).

Fig. 2.38 STEM micrograph of AlCr₄ (a) as prepared (b) 150 °C (c) 250 °C (d) 300 °C (e) 400 °C and (f) grain size distribution
Identification of the precipitates in the Al-Cr alloys is more difficult than in Al-Sb and Al-Sc, using STEM HAADF imaging, as seen in Figs. 2.39. Possibly this is due to a cancellation of the higher atomic number with the low density of Al$_{13}$Cr$_2$ and small fraction of Cr. Consequently, electron diffraction was employed. The results are shown in Figs. 2.39. Here, no indication of precipitation is found at 150 °C or 250 °C, but by 300 °C, reflections corresponding to the Al$_{13}$Cr$_2$ phase begin to appear in addition to those from the FCC matrix. This temperature is significantly higher than that required for precipitation of Al$_3$Sc (200 °C) and AlSb (100 °C), although owing to the far smaller diffusivity of Cr in Al, this is expected. Past results on vapor quenched dilute Al-4.1 at.%Cr-0.6 at.%Fe alloys showed, for example, precipitation of Al$_{13}$Cr$_2$ at ~ 275 °C. This is slightly lower temperature, but those samples were annealed for 1000 hours [122]. The precipitation of Al-Cr alloys with ~ 4 at.% Cr at ~ 300 °C is also consistent with results on rapidly quenched Al-Cr alloys [123]. Consequently, only the FCC Al phase can be observed up to 250 °C in the selected area diffraction patterns, but the formation of a new phase was observed at 300 °C, as seen in Fig. 2.39 below.

![Fig. 2.39 TEM diffraction of AlCr$_4$ at (a) 150 °C (b) 250 °C (c) 300 °C](image)

The AlCr$_{10}$ alloy was not examined in detail, although grain size was determined from STEM HAADF images, as shown in Fig. 2.40. The average grain of differently annealed samples
was nearly constant, ~65 nm, below 400 °C. The grain size distributions can be found at Fig. 2.40(e) and for this alloy, there were no shifts in the distribution.

Fig. 2.40 STEM micrograph of AlCr$_{10}$ (a) as prepared (b) 250 °C (c) 300 °C (d) 400 °C and (e) grain size distribution

Intermetallic phase, Al$_{13}$Cr$_2$, was clearly identified using GIXRD of AlCr$_{10}$ film after annealing at 400 °C. Abundant Al$_{13}$Cr$_2$ phase may increase intensity of XRD peaks and facilitates the measurements. Interestingly, peaks of Al$_{13}$Cr$_2$ are broadly scattered at several ranges as can be seen Fig. 2.41.
Microstructural evolutions of Al-W alloys under various were analyzed using HAADF-STEM images as shown in Fig. 2.42 for AlW$_1$ and Fig. 2.43 for AlW$_4$, respectively. Initial grain size of AlW$_1$ is ~ 80 nm and this size remained nearly constant up to 300 °C, as seen in Fig. 2.42(a-e). After annealing at 400 °C, the grain size slightly increased ~ 100 nm, see Fig. 2.42(f). Regarding behavior of W, no distinct precipitation of Al-W phases was observed over the range studied except a sample that underwent 1 hour heat treatment at 400 °C. No other phase was observed at diffraction ring in Fig. 2.42(g) after annealing at 300 °C. EDS-TEM measurement in 400 °C, only at the spot 1, 2 and 8 in Fig. 2.42(h), W solutes were detectable.
For the AlW\textsubscript{4} film, Fig. 2.43(a-e), the grain size was initially \(~60\) nm, \(~25\) % smaller than AlW\textsubscript{1}, and it did not change after samples underwent annealing under different temperatures. No W precipitation at the grain boundaries was observed up to \(300\) °C as observed in Fig 2.43(e). After heat treatment at \(400\) °C for 1 hour, however, two different discrete colored regimes, white-W rich area and black - W depleted regime, were observed. EDS analysis was able to confirm W
content in this Fig. 2.42. W concentration t spot 1 is ~ 0.3at %, whereas W concentration at spot 2 is ~ 8%.

HAADF-STEM images of AlW$_{11}$, are shown in Fig. 2.44, and again no distinct precipitation was observed. Especially, EDS mapping was employed to investigate W behavior for 250 °C sample in Fig. 2.44(a). Purple dots in Fig. 2.44(b) represents W solute distributions and it moves toward to the grain boundaries but still W distributed in all the matrix. An EDS line scan in Fig. 2.44(c), shows, perhaps, slight W enrichment near grain boundaries after 250 °C annealing. However, owing to low mobility of W in Al matrix, it can be assumed that no precipitation occurs, and thus diffraction pattern in Fig. 2.44(d) shows only the Al phase.
Fig. 2.44 AlW\textsubscript{11} after annealing at 250 °C for 1 hour (a) TEM micrograph (b) EDS line scan (c) EDS map (d) diffraction pattern

2.4.4.3 Strengthening Of Al-Cr And Al-W Alloys Under Various Annealing Temperatures

The mechanical behavior of the solid solution thin film Al-Cr alloys with 4 at.% Cr and 10 at.% Cr solutes were investigated by nanoindentation. The results of these experiments are plotted against annealing temperatures in Fig. 2.45(a). The evolution of grain size is also plotted in Fig. 2.45 to reveal possible relationships between hardness and grain size. The initial hardness of two different compositions, AlCr\textsubscript{4} and AlCr\textsubscript{10}, are ~ 2.7 GPa (red circle) and ~ 4.8 GPa (red triangle), respectively. In both cases, noticeable hardness drops occur after annealing at 300 °C – the hardness of AlCr\textsubscript{4} dropped to 1.2 GPa, while that of Al-10 at.% Cr decreased to ~ 3.5 GPa. At 300 °C, Cr diffuses ~ 0.1 nm after 1 hour [124], which suggests that the small amount of precipitation is associated with grain boundary diffusion and not bulk diffusion. The hardness reduction, therefore, is most likely loss of Cr solute in the grain boundaries. Unfortunately, APT was not
performed on this alloy and hence it is uncertain whether my estimate of Cr bulk diffusion, which requires extrapolation of literature data, is sufficiently accurate. This conclusion, however, does agree, with that for Al-Sc and Al-Sb. In other work on nc-Al-Cr alloys Partridge and McConnell [72] claimed that in vapor quenched Al-5 at.% Cr, which was subsequently rolled, the large reduction in strength after annealing at \( \sim 300 \) °C can attributed to the combined effects of reductions in the dislocation density and loss of solute solution hardening resulting from precipitation. Their specimens, however, were heavily rolled and contained a high concentration of dislocations, which provide an alternative fast diffusion path to grain boundaries.

The hardness in AlCr\textsubscript{10} behaved similar to that of AlCr\textsubscript{4}, the small drop in hardness observed in AlCr\textsubscript{4} at 250 °C, was not observed in AlCr\textsubscript{10}. This may difference may stem from the excess solute in the grain boundaries in AlCr\textsubscript{10}, i.e., a small loss of Cr due to grain boundary precipitation may not much effect hardness. More significant, perhaps, is the large difference in hardness between these two Al-Cr alloys after high temperature annealing, \( \sim 450 \) °C; the hardness of the 4 at.% alloy drops to nearly the same value observed for pure Al of similar grain size, while the 10 at.% retains a hardness of nearly 4 GPa. Presumably, this is due to the much higher density of precipitates in the 10 at.% alloy, however, this was not investigated here in detail and will not be discussed further.
Fig. 2.45 Hardness and grain size change of (a) Al-Cr alloys (b) Al-W alloys

Hardness tests were also carried out for all Al-W alloys and results are seen in Fig. 2.45(b); the behavior is similar to that of the Al-Cr alloys. All three different W concentrations, grain did not grow much after heat treatment. In fact, only after annealing at 400 °C did the least concentrated alloy show any grain grow, i.e., the AlW₁, grain size increased ~ 20 %, from 80 to 100 nm. While the grain size seems to be stabilized, hardness behavior in accordance with W concentration is interesting, as seen in in Fig. 2.44. Here it is observed that hardness begins to drop at increasingly high temperatures as the W concentration increases. The hardness reduction in AlW₁ can probably be explained by solute doping on grain boundaries since diffusion of W in Al is too small to cause loss of W from the grain interior. For the higher concentrations of W, bulk diffusion can begin to play a role, but like the Al-Cr alloys, this aspect of the hardening was not closely examined and will not be discussed in further detail.
2.5 Discussion

2.5.1 Nanohardness Measurements

As an overview of the hardness results for the nanocrystalline Al alloys, hardness is first plotted against the lateral grain size\(^{-0.5}\) for all alloys; this shown in Fig. 2.46. An immediate initial conclusion is that Hall-Petch behavior is not the dominant strengthening mechanism in these nanocrystalline alloys. Solid solution hardening is next considered. The annealing results on the Al-Sc alloys and the AlSb\(_{1.2}\) alloy similarly rule out the possibility that classical models of solid solution hardening [27], or even the modified model by Rupert and Schuh [49] to account for grain boundary effects, underlie hardening mechanism in these systems. Specifically, during the early stages of annealing, when the hardness decreases the most, our estimates of diffusion distances show that solute in the Al matrix is essentially immobile. The ATP measurements, moreover, provide direct evidence in the Al-Sc alloys that Sc remains in solution during film growth and after annealing for 1 hour at 180 °C. TEM results further indicate that during this low temperature annealing, no precipitates form and that grain growth is negligible. Recall, the Rupert and Schuh model is linear in both solute concentration and inverse grain size. Before discussing what I believe is controlling mechanism of hardness in these systems, it is nevertheless interesting to estimate the expected hardness change using the Rupert-Schuh model, i.e., eq. 2.5. This is found in Table 2.12 along with the enhancement of hardness compared to pure Al. For this calculation, \(G_{\text{Al}} \sim 28\) GPa, \(b_{\text{solvent}} = 2.86\) Å and \(D = \) grain size of each binary alloys are used. The calculated values appear far too small, further suggesting that the Rupert-Schuh model does not explain hardening in these very dilute Al alloys. Precipitate hardening need not be considered here, since the as-grown samples do not have precipitates. This leaves only the possibility that solute additions strengthen the grain boundaries, as I will now discuss.
I am unaware of any current theories for the strengthening of nanocrystalline alloys by solute doping of grain boundaries. There are, however, a number of MD simulations concerning this question as outlined in section 2.1.4. While these simulations are performed at extremely high strain rates, $\sim 10^9$ s$^{-1}$, and consider grain sizes generally no larger than $\sim 20$ nm, they appear to explain the current results. First we see both in the studies by Vo et al. [58] on Cu-Nb and by Borovikov et al. [61] on Cu-Ag and Ag-Cu that the addition of $\sim 1$ at.$\%$ solute increases the yield strength by $\sim 1$-2 GPa. These increases are the same order of magnitude as observed in the Al alloys, possibly somewhat larger, but this can possibly be accounted for by the larger shear modulus of Cu than Al, although the moduli of Ag and Al are similar. In addition to the MD
simulations, the importance of the nucleation of dislocations in the deformation of pure nanocrystalline Al has been experimentally verified [125]. These results are summarized by Mompiou et al. [125] in Fig. 2.46.

Fig. 2.47 Schematic of the sequential mechanisms involved in the plastic deformation of UFG Al films (a) interfacial dislocation activity emitted from sources S1 leads to GB sliding (b) intragranular dislocation activity is triggered by sources S2 located in the GBs, and in parallel, stress-coupled GB migration leads to grain growth (c) extensive plasticity and dislocation interaction starts to settle in grains that have undergone significant growth. Cavitation occurs at triple junctions when strain incompatibilities cannot be accommodated by dislocations [125]

This work reveals by in situ TEM observations of the straining of nc-Al that initial deformation is mediated by the nucleation of GB dislocations and their glide in the grain boundaries, Fig. 2.47(a). The authors note by measuring the stress on the dislocations, that nucleation is the limiting mechanism in this grain boundary sliding mechanism. As the strain increases to a few percent, the deformation mechanism switches to the nucleation of dislocations in GB’s and their glide across grains, Fig. 2.47(b). In larger grains, dislocations can intersect in the grain interior and create dislocations sources Fig. 2.47(c), but these grains are larger than those observed in the present study. Both experimental and MD simulations thus point to the nucleation of dislocations in the GB’s as the main mechanism controlling the strength of nc-Al and nc-Al alloys.
The preceding picture of strengthening in nc-Al alloys also appears consistent with the annealing behavior. As discussed above, the hardness in these alloys decreases before the onset of grain growth or precipitation. This could be explained simply by assuming solute diffusion in the grain boundaries, concomitant with solute clustering and precipitation. Until the precipitates are sufficiently large, $\sim 1$ nm, this would be difficult to observe by TEM observations, without extensive studies. Preliminary evidence of such clustering, however, was noted in APT results on AlSc$_{1.7}$ annealed at 180 °C reported above, although additional work will be necessary to confirm these results. Lastly, a brief comment on the role of grain size is appropriate. Most importantly, for the mechanism proposed, the grain size must be sufficiently small that no dislocations sources are present in the grain interiors. While an extensive search for dislocations was undertaken in the present research, some samples were examined for dislocations, but none found. The work of Mompiou et al. [125] also did not find dislocations source in the grain interiors for grain sizes less than $\sim 150$ nm. It is also likely that strengthening increases with decreasing grain size, presumably requiring a stress $\sigma = \mu Gb^2/d$ to operate the source in the boundary.

Annealing the samples at higher temperatures results in extensive precipitation, and an increase in grain size, but with little change in the hardness. These results are attributed, most naturally, to precipitate strengthening, as there remains little solute in solution either in the grain boundaries or in the grain interiors. In light of the extensive work performed on precipitate hardening in large grained Al-Sc alloys [see e.g., Seidman], this subject matter was not pursued. It is noteworthy, however, that hardness reaches its minimum value in this work, just as precipitates begin to appear.
2.6 Conclusion

In conclusion, we have presented extensive study of microstructural and mechanical character evolution under various annealing conditions with different solute atoms in nanocrystalline dilute Al alloys. Our experiments and analysis suggest strengthening mechanism of dilute nanocrystalline Al alloys are related with solute behaviors. Initial high strength is mainly due to the solute doing of grain boundary. Annealing allows the solutes to come out from the grain boundaries and the system soften. Although further annealing induces precipitation coarsening, the hardness value unchanged.

2.7 References


[94] TI 950 TriboIndenter User Manual
Revision 9.3.0314, 2014.


CHAPTER 3

THERMAL CREEP IN NANOCRYSTALLINE DILUTE ALUMINIUM ALLOYS

3.1 Introduction

In Chapter 2, the strengthening behavior of Al dilute binary alloys was investigated as a function of annealing temperature. These works provided a deeper understanding of the fundamental mechanisms that underlie solute strengthening in dilute, nanocrystalline (nc) Al alloys. With this foundation, it becomes possible to shift focus to creep behavior. Recall that the strengthening mechanism was shown to derive from solute in the grain boundaries, and not from solute in the grain interiors. MD simulations have suggested this occurs due to lowering the grain boundary energies, although precise mechanisms remain uncertain, e.g., the relative importance of suppressing the nucleation of dislocations in the grain boundaries compared with the suppression of grain boundary sliding was not explored. Nevertheless, this behavior does suggest that solute in the grain boundaries may also play an important role in thermal creep. For example, the Borisov model [1] suggests that grain boundary diffusion connected to grain boundary energy by the relation,

\[
D_{\text{gb}} = D_L \exp \left( \frac{2\gamma}{\lambda RT} \right)
\]

(3.1)

where \(D_L\) is the self-diffusion coefficient, \(\gamma\) is the grain boundary energy, and \(\lambda\) is the effective atomic density in the grain boundaries. Several systems appear to obey this relationship [see e.g., [2]]. Since Coble creep and grain boundary sliding are expected to operate in nanocrystalline metals, solute doping of the grain boundaries could be an effective means to suppress thermal creep.
3.1.1 Diffusional Creep Mechanisms

The mechanism of creep depends on temperature and stress. Under the conditions of different temperature and applied stress, dislocation glide, dislocation climb, or diffusional-flow mechanisms may dominate creep deformation. At high temperatures and low stresses, atomic diffusion in the lattice controls deformation, i.e., Nabarro-Herring (N-H) creep, as shown in Fig. 3.1. As stress is applied, vacancies move along the dashed lines and atoms will follow solid line in opposite direction. The creep rate by the N-H mechanism is given by the relation,

\[ \dot{\varepsilon} \sim 7D_{\text{vol}} b^3 \frac{\sigma}{kT} \frac{1}{d^2} \]  \hspace{1cm} (3.2)

Fig. 3.1 Schematic of (a) vacancy and atom flow between grains (b) aligned with directions of applied stress [1]
In this expression, $d$ is the grain size, $\sigma$ is the applied stress, $D_{vol}$ is the lattice diffusivity, $b$ is the Burger’s vector, and $k$ and $T$ are Boltzmann’s constant and the absolute temperature. At lower temperatures, but still low stress, grain boundary diffusion dominates mass transport and Coble creep controls the creep rate [3]; in this case the creep rate is given by,

$$\dot{\epsilon} = 47 \frac{D_{gb} \delta_{gb} \Omega \sigma}{kT d^3}$$

(3.3)

$\delta_{gb}$ is GB thickness, $D_{gb}$ is GB diffusivity, and $\Omega$ is the atomic volume. Note that while the stress dependence is the same as for N–H creep, the grain size dependence is $d^{-3}$ rather than $d^{-2}$. In this Coble creep, as shown in Fig. 3.2 atomic diffusion flows along the grain boundaries.

The ratio of lattice diffusion to grain boundary diffusion increases with temperature because the activation energy for grain boundary diffusion is always lower than that of lattice diffusion. Therefore, GB diffusion, Coble creep will predominate [3-6] over N–H creep at low temperature and very small grain size. Coble creep, consequently, is expected to be responsible for creep of nanocrystalline materials. In fact, Gleiter [7] suggested that Coble creep as a prevailing
mechanism on nanocrystalline materials even at low temperature, ~ room temperature. In earlier studies on creep of nanocrystalline metals claimed that Coble creep - diffusion along grain boundaries [8-11] – with a grain size effect [12, 13], is a main mechanism. Other studies [14, 15] showed that GB diffusion plays a dominant mechanism; Jiang showed GB diffusion in valid at room temperature. MD simulation result also reported a predominant role of Coble creep [16, 17]. For thin films, experiments [4], theoretical modeling [5], simulations [16, 17] show that GB diffusion has a key role in plastic deformation in Cu film. GB diffusion in aluminum is faster than in copper [18], thus Coble creep mechanism (GB diffusion) should have a significant influence on Al alloys.

To prevent the formation of internal voids or cracks during diffusional creep, additional mass transfer must occur at the grain boundaries to accommodate the mass relocation on boundaries. This results in grain boundary sliding. The diffusional creep rate, therefore, must be balanced exactly by the grain boundary sliding (GBS) rates if internal voids are not to form. Diffusional flow and GBS can be considered sequential processes in which mass is first transported by NH and/or Coble creep and a grain shape change and separation are affected. This will be followed by crack healing via GBS. Since the grain boundary sliding and diffusional flow processes occur sequentially, the net creep rate is the lesser of the separate creep rates. GBS creep rate is inherently less than the diffusional flow creep rate and it takes place rapidly relative to the diffusional flow creep. However, the grain boundary itself plays an important role in the deformation and fracture of polycrystalline materials at elevated temperatures, hence, grain-boundary sliding may contribute substantially to creep deformation in fine grained materials. The diffusional flow processes causing sliding are the same as those causing Coble or NH creep, except possibly when GBS is restricted by second phase particles.
If impurities are present in the boundaries, it is anticipated that these impurity elements would affect the creep behavior of materials because their segregation to grain or subgrain boundaries could weaken the boundaries [19] and thus deteriorate the creep properties. However, recent studies have focused on the beneficial role of impurities [20, 21]. Along with strengthening enhancement by impurity addition, thermal stability of nanocrystalline microstructure is also attainable though impurities. For example, pure nanocrystalline Al prepared by ball milling shows microstructural stability up to 0.78 $T_m$ [22], but this stability was attributed to the impurities introduced by the milling process. If solutes exist at GB, improved stability can thus likely be achieved by forming impurity drag associated with grain growth [22, 23] or by eliminating the driving force for grain coarsening via metastable status [24].

Previous researchers did some experimental work [25-31] on creep in nanocrystalline materials although data remain scarce, especially for the relationship between steady-creep rates and grain boundary doping. One study, however, employed MD simulations to investigate the role grain boundary doping in diffusional creep in dilute nanocrystalline Cu alloys [32]. This work showed that solute atoms lower the grain boundary free volume in nanocrystalline Cu. This leads to a lowering of the grain boundary energy and consequently to a reduced atomic mobility (eq. (3.1)) and higher creep resistance (eq. (3.3)). They also reported that an increase in creep resistance scales with atomic size of segregating solutes. Surprisingly, however, this work also reported that the atomic diffusion processes in the boundaries were similar to those in amorphous materials, including a quite low activation energy for creep, just 0.3 eV in Cu.
3.2 Experimental

3.2.1 Free Standing Film Preparation For Creep Bulge Test

Photolithography and micro-fabrication methods were employed to prepare free standing thin film specimens [33]. In this study, some of procedures were modified from the method originally proposed in ref. [33]. Fig. 3.3 illustrates the procedure. A (1 0 0) silicon wafer with Si$_3$N$_4$ layers on both sides is initially prepared. The Si$_3$N$_4$ layer thicknesses are $\sim$ 300 nm. Photolithography is then employed to make rectangular windows for the freestanding film. One of the Si$_3$N$_4$ coating layers within the marked area of the windows is removed by using a Reactive Ion Etching (RIE) process. The next step employs anisotropic wet etching, performed at 65°C using a potassium hydroxide (KOH) 20% solution, to remove the Si wafer substrate. For anisotropic etching, isopropyl alcohol (IPA) is added to the solution. Then a freestanding a Si$_3$N$_4$ film is left in a window membrane. The membrane size is 2.75 x 0.5 mm$^2$. DC magnetron sputtering was next performed to grow Cu-1.5at.% W, Cu-50at.%Ti, Al, Al-3.6at.%Ag, Al-0.7at.%Sc, Al-1.1at.%Sc, Al-1.7at.%Sc, Al-1at.%W, Al-4at.%W, Al-11at.%W, Al-4at.%Cr, and , Al-10at.%Cr, thin films on this Si$_3$N$_4$ membrane. The thickness of thin films was $\sim$ 300 nm; the thickness was selected to allow homogeneous damage in the irradiation portion of this work, see Chapter 4. The Argon gas pressure was maintained at $2 \times 10^{-3}$ Torr during film growth. In order to obtain a completely freestanding alloy film, RIE was applied as a final step to remove the remaining Si$_3$N$_4$ layer. For heat-treated samples, annealing was conducted on freestanding films at the desired temperatures using a halogen lamp. During annealing, the pressure was maintained below $1.5 \times 10^{-7}$ Torr to avoid oxidation from the free surface of the sample. The key requirement in this procedure is obtaining a flat, wrinkle-free, thin film, and achieving it is somewhat of an art, requiring patience and experience.
A plan view image of the actual prepared sample is presented in Fig. 3.4, which was acquired using an optical microscope. Again, the membrane size is 2.75 x 0.5 mm$^2$.

Fig. 3.3 Fabrication procedure of thin film sample (a) Si wafer with Si$_3$N$_4$ coating on both sides is prepared. (b) The PR coated wafer is exposed to UV light (PR patterning). (c) Si$_3$N$_4$ layer is developed, and exposed PR is removed. RIE is used to remove Si$_3$N$_4$. (d) 200 µm Si wafer is etched using KOH solution. (e) Thin film is grown by DC magnetron sputtering. (f) Another Si$_3$N$_4$ layer is removed using RIE.

Fig. 3.4 Optical image (top view) of actual creep-test specimen
3.2.2 Characterization And Analysis

All deposition rates and alloy concentrations were calibrated using RBS. Transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and high angle annular dark field (HAADF) analysis were again employed for microstructural characterizations. Most of the TEM samples were prepared in plain view by using Multi-Prep polishing machine and PIPS machine. Nanoindentation measurements of these films were performed using a Hysitron triboindenter with a diamond Berkovich tip.

3.2.3 In-situ Thermal And Irradiation Induced Creep Measurement Using The Thin-Film Bulge Test Apparatus

3.2.3.1 Thin Film Bulge Test

Nowadays, thin films are applied to many industrial fields, for example, microelectrochemical system, electrical device, biomedical devices application and so on [34, 35]. Thus, a better understanding of mechanical characteristics and behaviors are required. In thin film forms, most material behave in different ways than they do in bulk [36], so careful characterization of thin-films is important to obtain accurate values. Furthermore, the fabrication process and microstructure also affect mechanical properties. Thus, traditional mechanical testing methods of bulk material are not usually applied to thin films. The freestanding thin-film bulge test is very powerful technique to study plasticity since stress-strain behavior is isothermal. Also, only innate properties of films can be measured as well as constitutive behavior can be measured with relatively large applied strains [33]. Hence, in this study, thin film bulge test method was used to investigate mechanical properties but focusing on creep.
3.2.3.2 Michelson Interferometry

Michelson interferometry is an optical device using laser light source, which is used in many different scientific applications, owing to its potential high accuracy. It has even been used for the measurement of gravitational waves. The Michelson Interferometer is illustrated in Fig. 3.5(a). A laser beam is split into two arms, one reflected from a reference mirror and the other from the sample. These laser beams are brought back together and interfere with each other, depending on their relative phases. As the position of the sample changes, the relative phases providing a displacement resolution of roughly the wavelength of the (JDS Uniphase, Model 1122P) He-Ne laser light 635 nm.

3.2.3.3 Experimental Setup For The Creep Test

Thin film bulge test experimental setup and schematic of measurement setup are shown in Fig. 3.5(a,b). The experimental setup is placed at the end of HVE Van de Graaff accelerator.
Fig. 3.6(a) is a schematic of this interferometric measurement setup [37] for thermal creep and irradiation induced creep measurements. While irradiation induced creep is discussed in Chapter 4, I describe it here, as thermal creep is measured exactly the same way, but with the ion beam turned off. A freestanding film is placed at the middle of a sample holder. After gas is added to the ‘pressure’ side of the film and stabilized, an ion beam penetrates from the opposite side - ‘ion beam’ side. The free-standing film bulges as the ion beam impinges on the thin film (or the temperature is raised sufficiently high). \( h \) in Fig. 3.6(a) is the bulge distance. A 1.8 MeV Kr\(^+\) ion beam was obtained using an HVE Van de Graaff accelerator. To affix the sample holder part to the experimental table, an aluminum support was designed as shown in Fig. 3.6(b). The support uses a micrometer slide the support in the longitudinal direction (transverse to the laser beam) and provides accurate positioning of the sample.

![Fig. 3.6(a) Schematic of thin film bulge test (b) Aluminum Support](image)

The freestanding film sample was attached to a sample holder using vacuum sealant. The sealed sample divides the volume of sample holder into two separated volumes. One side of the sample is in vacuum for irradiation and the other side is for applying gas pressure. Ar - 7\% H\(_2\) gas was used for applying and sustaining pressure. The H\(_2\) gas prevents samples from oxidizing during
the heating. Joule heating was used to control the specimen temperature. For this, an insulated W wire was wrapped tightly around a collar of the stage. The temperature was limited to $T < 300^\circ$C, owing to differential expansion of the Si wafer and sealant, but this temperature is sufficient for both thermal and IIC measurements in Al based alloys.

### 3.2.3.4 Measurement Of Thermal Creep And Irradiation Induced Creep

Michelson interferometry is employed to measure bulge distance. Bulge distance at the center of film, $h$, is obtained using Michelson interferometry. Interference pattern is directed to a photodetector (OT-301 Position Sensing Amplifier). The photodetector detects how many fringes pass a given location on the detector, where the distance change $\Delta h$ of the film is related to the number of fringes by,

$$ h = 635 \ [nm] \times \frac{n}{2} \ , $$

where 635 nm is the He-Ne laser wavelength. $n$ is the number of lines passing at a certain spot. If $n$ is even number, constructive interference occurs and the intensity is a maximum. On the contrary, if $n$ is odd number, destructive interference is observed, and intensity is a minimum. This phenomenon results in interference pattern and can be used to extract desired information. A typical interference pattern is shown in Fig. 3.7. LabView was employed for data acquisition.
Mechanical analysis of the thin film bulge test has been published in the literature [4]. If a freestanding thin film is used, intrinsic film properties can be measured without any substrate effects, as mentioned above. If membranes have a rectangular shape with aspect ratios greater than 4, deformation results in plane strain. In plane strain condition, stress and strain are distributed uniformly across the width of the membrane and this make this method useful to study in plastic behavior of thin films [37]. For a film with rectangular shape and aspect ratio greater than \(~ 4\), the stress can be approximated quite well using the expression:

\[
\sigma_x = \frac{p \left( a^2 + b^2 \right)}{2ht}
\]  

(3.5)

where \( h \) is bulge height at the center of film, \( t \) is the sample thickness, \( p \) is applied gas pressure, and \( a \) is the half width of membrane. Notice that the stress is infinite when \( h = 0 \), i.e., at the initiation of the experiment, for any nonzero applied pressure. The strain is obtained from expression,

\[
\varepsilon_x = \varepsilon_0 + \frac{2h^2}{3a^2} \arcsin \frac{2ah}{(a^2 + h^2)} - 1
\]  

(3.6)

where \( \varepsilon_0 \) is residual strain. These stress and strain equations are valid in both the elastic and plastic deformation.

3.2.3.5 Analysis Of Creep Measurement

Fig. 3.8(a) shows one of the better interference results that was acquired during \textit{in-situ} irradiation measurement. More often, however, the signal contains significant noise, as shown in Fig. 3.8(b). In order to overcome this problem, signal processing with MATLAB is used to reduce noise and this is achieved by Fast Fourier Transforming (FFT) the signal. The frequency acquired
after FFT is shown in Fig. 3.8(c). Since the graph is shifted to the center for convenience of distinction of the frequency trend, the graph looks symmetric. For typical creep rates, the appropriate frequency range is 0.01 ~ 0.05 Hz and this selected frequency range is then used to Inverse Fast Fourier Transform (IFFT) for extracting deformation signal. Fig. 3.8(d) shows the result after signal processing from Fig. 3.8(a) and desired bulge height, $h$, can be acquired with this processed data.

![Graphs](image)

Fig. 3.8 (a) One of the better data set (b) Raw signal before signal processing (c) Frequency after FFT (d) After signal processing.

### 3.3 Experimental Results

While Chapter 2 studied the strengthening mechanism using different solutes in Al, thermal creep behaviors were also investigated at different temperatures using the same Al binary
alloys as well as pure nc-Al. As it will be discussed later in this chapter, most samples were pre-annealed to stabilize the microstructure. Creep tests were then performed at various temperatures, lower than the pre-annealing temperature.

For these thermal creep studies, I focused on AlSc$_{1.1}$, in particular, how the creep behaviors change if pre-existing phases are present. In this AlSc$_{1.1}$ system, precipitates were clearly observed, and the hardness remained constant for annealing temperatures $> 250$ °C, as reported in Chapter 2. Annealing was thus carried out at 250 °C for 1 hour for attaining the microstructural stabilization. Along with pre-annealed AlSc$_{1.1}$ films which have Al$_3$Sc intermetallic phase, the as-grown AlSc$_{1.1}$ alloy was also tested for comparison.

In addition to Al-Sc alloys, pure Al, Al-Sb and Al-W alloys were studied. Pre-annealing temperatures were selected based on the microstructural evolution studies in Chapter 2; the pre-annealing conditions for all samples are presented in Table 3.1.

<table>
<thead>
<tr>
<th></th>
<th>Pre-annealing Temp. (°C)</th>
<th>Annealing hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>200</td>
<td>1</td>
</tr>
<tr>
<td>Al</td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>AlSc$_{1.1}$</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>AlSb$_{1.2}$</td>
<td>150</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>AlW$_1$</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>AlW$_4$</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>AlW$_{11}$</td>
<td>250</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.1 Pre-annealing conditions for given Al systems
3.3.1 Microstructure Evolution

Before presenting the thermal creep experimental results in detail, the microstructures of the various alloys employed for the creep measurements will be discussed.

3.3.1.1 Nanocrystalline(nc)-Al

Pre-annealed pure nanocrystalline Al was studied to provide a basis for understanding the effects of solute additions on the creep response. For this, Al films underwent heat treatment at 200 °C for 1 hour and 3 hours, and creep tests were then performed at different temperatures below 200 °C. The microstructure of an Al specimen pre-annealed for 1 hour is shown in Fig. 3.9(a,b), before and after the creep test, respectively. An average grain size of ~ 200 nm was found after the creep test. After 3 hours pre-annealing, the grain size was ~ 220 nm. Therefore, we can assume that 3 hours annealing will not induce significant grain growth after thermal creep because all the test temperatures are below 200 °C. The results in Fig. 3.8 confirm that creep deformation to a few percent does not much enhance grain growth.

Fig. 3.9 TEM image of nc-Al film pre-annealed at 200 °C for 1 hour (a) before thermal creep (b) after thermal creep at 170 °C
3.3.1.2 \textit{AlSc}_{1.1}

For the as-grown \textit{AsC}_{1.1} film, one creep test was performed directly on the as-deposited film. However, most films were stabilized at a grain size of \sim 100 \text{ nm} by first annealing them at 250 °C. Grain sizes after thermal creep measurements were obtained using HAADF STEM image analysis, as shown in Fig. 3.10(a-c). Grain sizes did not change much after thermal creep tests at room temperature and 150 °C (Fig. 3.10(a)), but for creep tests at 170 °C and 200 °C, Fig. 3.10(b) and (c) respectively, some grain growth did occur, \sim 20 %. Grain size distributions are plotted in Fig. 3.10(d) and average grain sizes are reported in Table 3.2.

When grain growth occurs in a system, a driving force is always required, and the temperature must be sufficiently high to activate thermal diffusion processes in the grain boundary. If another phase is present at grain boundaries, as in pre-annealed \textit{AlSc}_{1.1}, it may effectively increase the activation energy barrier and retard additional grain growth by Zener pinning [38, 39]. Previous work on Al-Zr [40], for example, showed that Al$_3$Zr precipitates are effective in suppressing grain growth in nc-Al. Comparison of the grain sizes in pure and \textit{AlSc}_{1.1} shows that Al$_3$Sc precipitates at the grain boundaries apparently also suppress grain growth in Al.
Table 3.2 Average grain size after thermal creep of AlSc$_{1.1}$ pre-annealed at 250 °C for 1 hour

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>After pre-annealing</th>
<th>125</th>
<th>150</th>
<th>170</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm)</td>
<td>106 ± 3</td>
<td>109 ± 4</td>
<td>112 ± 3</td>
<td>125 ± 6</td>
<td>130 ± 10</td>
</tr>
</tbody>
</table>

For AlSb$_{1.2}$, two different pre-annealing temperatures, 150 °C and 250 °C, were employed. Firstly, thermal creep tests were carried out at various test temperatures from 75 °C to 150 °C, using samples pre-annealed sample at 150 °C for 1 hour. As seen in the previous chapter, Fig. 2.30(d), the mean grain size after pre-annealing is ~ 65 nm. The average grain size after creep at
75°C and 100 °C is virtually the same, Fig. 3.11 and Table 3.3. During the creep test at 150 °C, however, the grain size increased to ~ 75 nm, Fig. 3.11(c). Fig. 3.11(d) plots the grain size distributions after creep test; clearly, no significant shifts are observed.

![STEM images of AlSb\textsubscript{1.2} pre-heated at 150 °C after thermal creep at (a) 75 °C (b) 100 °C (c) 150 °C and (d) grain size distribution](image)

Table 3.3 Grain size after thermal creep of AlSb\textsubscript{1.2} pre-heated at 150 °C for 1 hour

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>After pre-annealing</th>
<th>75</th>
<th>100</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size (nm)</td>
<td>63 ± 2</td>
<td>65 ± 3</td>
<td>61 ± 3</td>
<td>72 ± 3</td>
</tr>
</tbody>
</table>
Recalling from Chapter 2, precipitation in the AlSb$_{1.2}$ alloy starts on pre-annealing at 150 °C for 1 hour. Precipitate phases, thus, are clearly observed in STEM micrograph in Fig. 2.30 after pre-annealing at 150 °C and after thermal creep tests, Fig. 3.11. The white spots, are seen in Fig. 3.11(a-c), implies that the precipitates are present within the grains and at the grain boundaries. A plot of precipitation size as a function of creep temperature is shown in Fig. 3.12(a). In case of creep test at 75 °C, precipitates did not coarsen much, and their size remained at 4 nm and 6 nm, within the grain and at the grain boundaries, respectively. However, if the creep test was performed above 100 °C, precipitates at grain boundaries coarsened, notably much more than in the grain interior. This coarsening is not too surprising since the creep test required ~ 6 hours, whereas the pre-annealing was performed for only one hour, and the activation energy for Sb diffusion in the grain boundary is expected to be on the order of 0.3 eV (see below). While the average precipitate size at the grain boundaries, 16 nm, did not change much during creep at 100 °C to 150 °C, the standard deviation at 150 °C is larger than at 100 °C possibly owing to the coarsening. Coarsening, in general, was rather limited at these low temperatures within the grain boundaries and at the grain boundaries. Precipitate size distributions at the GB’s and within the grains are presented in Fig 3.12(c) and (d). All grain sizes and precipitate sizes were determined from TEM images.
Fig. 3.12 (a) Precipitates behaviors after thermal creep of AlSb\textsubscript{1.2} pre-annealed at 150 °C for 1 hour, (b) precipitates size change, (b) precipitate distribution (c) at grain boundary and (d) within the grain.

Along with creep tests on Al-Sb films, which were pre-annealed at 150 °C, additional creep tests were carried out with a pre-annealing temperature of 250 °C. Except for the initial pre-annealing temperature, all other test conditions were same, such as test temperatures ranges, pre-annealing time (1 hour) and so on. STEM images in Fig 3.13, shows the comparison of grain size after creep testing. Fig. 3.13(a) is before the measurement and Fig. 3.13(b) is after the creep test. No significant growth was observed; the mean grain size remained ~ 75 nm as shown in Fig. 3.13(c, d).
Fig. 3.13 STEM of (a) preheated AlSb\(_{1.2}\) film at 250 °C for 1 hour (b) after creep test at 50 °C (c) grain size change (d) grain size distribution

### 3.3.1.4 Al-W Alloys

Grain sizes of Al-W alloys pre-annealed at 250 °C are unchanged after creep: for AlW\(_1\), \(d \sim 80\) nm, for AlW\(_4\), \(d \sim 65\) nm and for AlW\(_{11}\), \(d \sim 55\) nm. STEM images are shown in Fig. 3.14(a-e). Unlike Al-Sc and Al-Sb, Al-W does not form precipitates during the pre-annealing treatment, and therefore the grain size stabilization cannot be attributed to Zener pinning. Possibly, W lowers the grain boundary energy and thereby suppresses grain boundary diffusion (see eq. 3.1), or
possibly W solute adds a drag force to the grain boundary. The former explanation would be consistent with the high strengthening of Al-W alloys reported in Chapter 2.

Fig. 3.14 STEM images of samples pre-annealed at 250 °C: (a,c,e) before creep test and (b,d,f) after creep test: AlW₁ (a and b); AlW₄ (c and d); AlW₁₁ (e and f).
3.3.2 Thermal Creep Measurements

3.3.2.1 As Grown - AlSc

As-grown AlSc thin films were selected for the initial thermal creep tests, which were performed at 75 °C, 100 °C, 125 °C, 150 °C and 170 °C. For the sample deformed at 125 °C, the effect of stress was also investigated. In the creep test, strain was measured as a function of time. The initial strain value ($\varepsilon_0$) (mostly, due to the thermal expansion at the test temperatures) and the initial displacement value ($h_0$) were calculated using known Yong’s modulus (E) of Al (~ 75 GPa) and a $\sigma$-$\varepsilon$ relationship. During the measurement, two brief unloading cycles were applied. The slopes of these unloading curves is plain strain modulus ($M$) and can be assumed from following equation [41]

$$M = \frac{E}{1 - \nu^2} \quad (3.7)$$

where Poisson’s ratio, $\nu$, was taken to be 0.33 for Al [42]. If replace $h$ to $h_0 + \Delta h$ in eq.(3.5) and (3.6), and use $\sigma$-$\varepsilon$ relationship, then finally initial values can be calculated. Note, the ($\Delta h$) was measured by an interferometer. The following Fig. 3.15 is a typical stress-strain curve of thin film bulge test [33] which shows how unloading is performed.

![Fig. 3.15 A typical stress-strain curve [33]](image)
Strain according to the time is plotted in Fig 3.16 and 3.17(a). Also, strain rates under the same applied pressure, 1 kPa, are shown in Table 3.4. At 100 °C, the strain rate for an AlSc$_{1.1}$ film is $0.9 \times 10^{-7}$ s$^{-1}$, while at 170 °C, strain rate increases to $3.5 \times 10^{-7}$ s$^{-1}$. Note in Fig. 3.16 that the results at 100 °C are quite reproducible. The temperature dependence of the steady state creep rates are reasonably consistent with Coble creep. In Coble creep, the strain rate is proportional to $d^{-3}$ (d is unchanged here), it is linear in stress (observed in [43]) and diffusion is along grain boundaries. Assuming an activation enthalpy for grain boundary diffusion, $\Delta H_{GB} \sim 0.4 - 0.5$ eV in pure Al [44], we expect an increase of the creep rate of $\sim 5$ on increasing the temperature from 100 °C to 170 °C which is in good agreement with the measured steady state strain rates in Table 3.4. It should be noted, however, that $\Delta H_{GB}$ in dilute Al-Sc alloys has not been measured. The grain size in Table 3.4 was assumed to be constant, $\sim 75$ nm, the value for the as-deposited grain size, as all tests were performed below $\sim 200$ °C, where the grain sizes were found constant (refer to Chapter 2).

![Fig 3.16 Strain vs time plot after creep test at 100 °C and 170 °C](image)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Grains size (nm)</th>
<th>Strain rate ($10^{-7}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>$\sim 75$</td>
<td>0.6</td>
</tr>
<tr>
<td>100</td>
<td></td>
<td>0.9</td>
</tr>
<tr>
<td>125</td>
<td></td>
<td>1.63</td>
</tr>
<tr>
<td>150</td>
<td></td>
<td>2.25</td>
</tr>
<tr>
<td>170</td>
<td></td>
<td>3.5</td>
</tr>
</tbody>
</table>

Table 3.4 Strain rate vs temperature of ‘as-deposited AlSc$_{1.1}$ thermal creep’
Figs. 3.17(a-c) are 125 °C creep results and they show typical thermal creep results for AlSc
1.1 films. When the pressure was increased, strain rate and stress both simultaneously increased as plotted in Fig. 3.17(a and b). In all cases, the strain rate reaches steady state and these steady state strain rates and stress show a linear relationship (see Fig. 3.17(c)), also consistent with Coble creep. When a stress of 2.2 MPa was applied, the strain rate is ~ 1.13 x 10^{-7} s^{-1}. For 4 MPa and 7 MPa, strain rate were ~ 1.63 X 10^{-7} s^{-1} and 3.02 X 10^{-7} s^{-1}, respectively.-These results will be discussed in more detail in the following section.

3.3.2.2 Pre-annealed Alloys

At high temperatures, the precipitate structure and grain size of nanocrystalline metals become unstable, which can complicate studies of thermal creep. I therefore pre-annealed the as-deposited nc-Al binary alloys at selected temperatures for 1 hour to stabilize the microstructure. Pre-annealing temperatures were selected based on the microstructural evolution studies in Chapter 2 and the conditions are presented in Table 3.5.
Table 3.5 Pre-annealing conditions for given systems

<table>
<thead>
<tr>
<th></th>
<th>Pre-annealing Temp.(°C)</th>
<th>Annealing hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>200</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>3</td>
</tr>
<tr>
<td>AlSc\textsubscript{1.1}</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>AlSb\textsubscript{1.2}</td>
<td>150</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>AlW\textsubscript{1}</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>AlW\textsubscript{4}</td>
<td>250</td>
<td>1</td>
</tr>
<tr>
<td>AlW\textsubscript{11}</td>
<td>250</td>
<td>1</td>
</tr>
</tbody>
</table>

Pre-annealed Al alloys underwent thermal creep tests; the results are shown in Figs. 3.18(a-e). In Figs. 3.18(a-e) strain rates are plotted as a function of applied stress for samples tested at different temperatures between 50 – 200 °C. The thermal creep strain rates increase approximately linearly with stress. Strain rates were negligibly small at room temperature (not shown but strain rates were less than $10^{-7} \cdot s^{-1}$ order at the highest stresses). The maximum applied stress was limited to ~ 90 MPa, as the specimen fractured at higher stress levels.

For the pure Al sample, increasing the pre-annealing time from 1 hour to 3 hours, resulted in smaller strain rates (better creep resistance), as seen in Fig. 3.18(a) and 3.18(b). Similarly, pre-annealing AlSc\textsubscript{1.1} at 250 °C (See Fig. 3.18(c)) also suppresses creep rates compared to the as-grown samples. As we previously discussed in Chapter 2, intermetallic precipitates were observed in the matrix after pre-annealing at 250 °C, so that precipitates prohibit further grain growth for annealed AlSc\textsubscript{1.1} and possibly also affect the creep response. Specifically, the strain rate of as grown AlSc\textsubscript{1.1} is $\dot{\varepsilon} \sim 1.63 \times 10^{-7} \cdot s^{-1}$ at 125 °C for a stress of 5 MPa, as presented in Table 3.4 and Fig. 3.17, whereas, for pre-annealed AlSc\textsubscript{1.1} under the same conditions, $\dot{\varepsilon} \sim 0.05 \times 10^{-7} \cdot s^{-1}$. Comparison of strain rates at the same stress level (~ 10 MPa) is shown in Table 3.6. Note ‘a’ are from the experimental results and ‘b’ are calculated using eq.(3.3) with $D_b$ values taken from ref. [45].
Fig. 3.18 Strain rate vs stress during thermal creep. Al (a) pre-annealed 1 hour and (b) pre-annealed 3 hours; (c) AlSc; AlSb pre-annealed (d) at 150 °C (e) at 250 °C, (f) AlW (g) AlW (h) AlW.
Testing Temp (C) | 50 | 75 | 100 | 125 | 150 | 170 | 200 |
---|---|---|---|---|---|---|---|
Strain rate ($s^{-1}$) | *a: $\dot{\varepsilon}$ _exp_, b: $\dot{\varepsilon}$ _eq. (3.3)* |
Condition | a | b | a | b | a | b | a | b | a | b | a | b |
---|---|---|---|---|---|---|---|---|---|---|---|---|
Al 1hr | 5.00E-09 | 1.78E-07 | 1.10E-08 | 8.89E-07 | 5.70E-08 | 3.09E-06 | 6.00E-08 | 7.56E-06 | 8.00E-08 | 1.44E-05 |
AlSc | 4.00E-08 | 2.45E-05 | 3.33E-07 | 6.01E-05 | 4.44E-07 | 1.14E-04 | 7.00E-07 | 2.69E-04 |
AlSb$_{1.2}$ 150˚C | 2.00E-08 | 7.97E-07 | 8.00E-07 | 5.18E-06 | 7.00E-07 | 2.59E-05 | 7.00E-07 | 2.19E-04 |
AlSb$_{1.2}$ 250˚C | 1.00E-08 | 4.25E-07 | 4.00E-08 | 2.76E-06 | 7.00E-08 | 1.38E-05 | 5.00E-07 | 1.17E-04 |
AIW$_{1}$ | 2.00E-08 | 1.28E-05 | 4.00E-08 | 5.55E-05 | 9.00E-08 | 1.17E-04 | 2.00E-07 | 2.12E-04 |
AIW$_{4}$ | 3.20E-08 | 3.14E-06 | 5.70E-08 | 3.95E-05 | 1.00E-07 | 4.85E-05 | 1.55E-07 | 3.95E-04 |
AIW$_{11}$ | 1.00E-07 | 1.60E-04 | 1.40E-07 | 5.49E-04 | 2.50E-07 | 1.33E-03 |

Table 3.6 Comparison of strain rates. Stress is fixed at 10 MPa (a) experimental; (b) eq.(3.3).

For a comparison of the effects pre-annealing temperature on thermal creep, two different pre-annealing temperatures, 150 °C and 250 °C, were selected for AlSb$_{1.2}$; this is shown in Fig. 3.18(d,e). Specifically, thermal creep tests at 100 °C on AlSb$_{1.2}$ films, pre-annealed at 150 °C, were performed twice to check the reliability of the creep measurements and the results were quite similar. Remember from the Al-Sb study in Chapter 2 that pre-annealing temperatures, 150 °C and 250 °C, are both sufficiently high to produce precipitates. Chen et al. [46] studied the effect of Sb impurity on the creep properties of a 2.25Cr-1Mo steel. They claimed the segregation of Sb may reduce the boundary cohesion and promote the boundary sliding and cavitation, thereby deteriorating the creep behavior of the steel. Here, I observed the opposite, an improved creep resistance in AlSb$_{1.2}$. Back to the point, if strain rates under the same test conditions were compared in Fig. 3.18(d) and (e), the higher annealing temperature led to better creep resistance. This matches with a previous study reported by Yang et al. [47]. Yang and coworkers also observed the effectiveness of higher annealing temperature on creep properties. Inevitably, this enhanced creep resistance is related with microstructural evolution of system. Since the grain size for these
two pre-annealing conditions are very similar, ~ 10 %, this cannot be the main effect and some other factors must play a role. This will be discussed below.

Al-W alloys, AlW\textsubscript{1}, AlW\textsubscript{4} and AlW\textsubscript{11}, were selected to study the effects of solute concentration. Strain rate vs stress curves of these systems are shown in Fig. 3.18(f-h). Like the other two Al alloy systems, pre-annealing was carried out before the creep test, however, unlike Al-Sc and Al-Sb, precipitates did not form, see section 3.3.1. The different strain rates in the different alloys appear to be related to the grain size rather than to the solute (W) concentration, at least at first glance. Specifically, under the same test conditions, AlW\textsubscript{11} has the highest strain rate among the 3 different Al-W alloys, but a more complete discussion will be provided later in this chapter.

3.3.2.3 Stress Dependence

As already mentioned in the introductory section, creep rates can be assumed to obey a power-law relation with stress $\dot{\varepsilon} \propto \sigma^n$. The stress exponent ‘$n$’ is an important parameter to understand the deformation mechanism in creep. Also, it can be directly compared with experimental data, providing a test of creep mechanisms.

The stress exponent $n$ for AlSc\textsubscript{1.1}, is determined as $n \sim 1$, as plotted in Fig. 3.19(a,b). The calculated $n$ of preheated AlSc\textsubscript{1.1} samples are in Fig. 3.19(a) and that of a single as-deposited AlSc\textsubscript{1.1} sample is in Fig. 3.19(b). In both cases stress exponents $n$ is $n \sim 1$, consistent with Coble [3] or Nabarro-Herring [48, 49] creep, but not most models involving dislocations.
Fig. 3.19 Stress exponent of AlSc$_{1.1}$ (a) pre-annealed, and (b) as-deposited and then tested at 125 °C

3.3.3 Hardness

While the effect of annealing on nanohardness was presented in Chapter 2, I measured hardness values after thermal creep on the as-grown and pre-annealed AlSc$_{1.1}$ samples to check for possible effects of creep damage and more generally for reproducibility of the results. The measurements are shown in Fig. 3.18(a), and (b), respectively. For the as-grown film, the initial hardness was ~ 2 GPa, and it decreases after undergoing thermal creep, specifically, higher temperature resulted in lower hardness values. This decrement of hardness is in accordance with the expected temperature dependence and can be explained by the same mechanism discussed in Chapter 2, i.e., no new features arise from the creep deformation. The hardness change of the pre-annealed film in Fig. 3.20(b) shows only a 10 % reduction, from ~ 1.4 GPa to ~ 1.25 GPa. It is apparent that very efficient hardness stabilization take place when the Al$_3$Sc intermetallic phase pre-exist in a given system.
Fig. 3.20 Hardness after thermal creep test of AlSc$_{1.1}$ according to the testing temperature (a) as grown (b) pre-annealed at 250 °C

AlSb$_{1.2}$ pre-annealed at 150 °C showed similar behavior of hardness after creep as before, as can be seen in Fig. 3.21. The initial hardness value is ~ 1.2 GPa and remained constant after thermal creep. Here, the grain size varied only 10%, from ~ 60 nm to ~ 70 nm. As previously pointed out for pre-annealed Al-Sc above, this behavior is due to the pre-existing AlSb intermetallic phase in the microstructure.

Fig. 3.21 Hardness and grain size of after creep tests on AlSb$_{1.2}$ film preheated at 150 °C according to testing temperature
3.4 Discussion

The primary goal of the thermal creep study is to find stable microstructure conditions that cannot deteriorate mechanical properties (i.e. creep resistance) under high temperature applications and to elucidate the thermal creep mechanisms operating in dilute supersaturated/two-phase Al alloys. I, thus, employed various solutes and parameters (such as annealing temperature, annealing duration, and so on).

**Diffusional Creep In Dilute Nanocrystalline Binary Al Alloys**

The thermal creep behavior in dilute nc-Al alloys is summarized in Fig. 3.22 in a comprehensive plot of creep rates in all of the Al samples. In Fig. 3.22(a) the strain rates are normalized by the applied stress, whereas in Fig. 3.22(b) the strain rates are normalized by both the applied stress the grain size to the inverse third power ($1/d^3$), in accordance with Coble creep. The grain size information of each condition is inscribed in the plot. Fig. 3.22(a) shows that there is some tendency for the strain rate to increase with inverse grain size for each specific alloy, although the grain sizes could not be varied significantly and so the effect of grain size is not overly dramatic. On the other hand, when grain size is included in the normalization, Fig. 3.22(b), it is observed that the four alloys systems fall into narrow bands on the normalized Arrhenius plot, representative of the different solute addition. Notably, the normalized creep rates are highest for pure Al, and they decrease progressively in the order Al-Sc, Al-Sb and Al-W; the change from pure Al to Al-W is more than one order of magnitude.
I briefly note one qualification to the above analysis. I have assumed the usual $1/d^3$ dependence for the strain rates according to Coble creep; however, since the thin films have a columnar structure (see Fig. 3.23(a)) and bulge test measures plane strain, this dependence may be incorrect. For plane strain, atom fluxes must originate on the surfaces and flow to the grain boundaries. Thus, the atom current between the grain boundaries and the surface yields

$$J_v \delta_{gb} \Omega = d^2 \frac{dL}{dt}$$

where $d$ is the grain size and $L$ is the specimen thickness. Then using

$$J_v = D_v \Delta C_v / L$$

and

$$\Delta C_v = \alpha \Omega / kT$$

the strain rate,

$$\dot{\varepsilon}_L = dL / L dt = AD_{gb} \alpha \Omega / kT L^2 d$$

yielding a weaker dependence of grain size. $A$ is constant combining geometric shape factors. The creep data are rescaled in Fig. 3.23(b) to reflect this weaker grain size dependence. Al-W alloys still show the lowest creep values, but pure Al, Al-Sc, and Al-Sb roughly the same. This would suggest solute in the grain boundaries can suppress creep for the reasons cited above, but that grain boundary precipitates are not effective in suppressing creep. The MD simulations in ref. [32] found similar
results, although as mentioned previously, the grain sizes in these simulations are very small and the strain rates extremely high.

![Image](a)

**Fig. 3.23** (a) Columnar grain of AlSc$_{1.1}$ pre-annealed at 250 °C for 1 hour (b) Normalized steady-creep rate according to $L^2d$

**Activation Energy**

Activation energy values systems were calculated and presented in accordance with grain size, as presented in Table 3.7. Different alloys are indicated by the color of the symbol. Although the microstructure of as-grown AlSc$_{1.1}$ was not stabilized prior to testing, the plot assumes a grain size of 75 nm. (Recall, Al-Sc grain size did not grow much below $T \leq \sim 200$ °C, thus it is reasonable assumption over the given test temperatures). Despite some data variations, all the calculated activation energies (Q) are between 0.38 – 0.52 eV and consistent with values reported in the literature [44]. This indicates that the rate controlling process in the current nc-Al alloys is associated with grain boundary diffusion not lattice self-diffusion ($\sim 1.45$ eV [50]) or vacancy diffusion.
Here, Al alloys exhibit activation energies of creep in the range 0.38 - 0.48 eV (with the exception of the most dilute alloy, AlW which is 0.52 eV). These values are somewhat lower than that found for pure Al (0.52 eV and 0.54 eV), as seen in Fig. 3.24. While the difference in activation energies between pure Al and the dilute alloys is small, two pure Al samples were tested as were several Al alloys, and consequently it appears the difference real; it will be assumed so here. The first conclusion that can be drawn from this result is that suppression of thermal creep in dilute alloys cannot be attributed to the Borisov model of grain boundary diffusion, since the activation energy for creep is lower in the alloys, whereas in the Borisov model, grain boundary diffusion in the alloys has a higher activation energy than in pure Al. I will next consider the Al-Sc and Al-Sb results separately from the Al-W as the former show precipitation on the boundaries and Al-W does not. For Al-W, I will assume the W is in solution in the grain boundaries. The solubility of W in Al, however, is negligible at the creep temperatures, and W has a negative heat mixing with Al, and forms compounds. Without significant diffusion, compound formation is difficult, and so it is reasonable to think that the grain boundaries tend to be amorphous, or at-least amorphous-like. A very small grain size, moreover, should contribute to such a grain boundary structure [32]. Recalling now the simulations of creep in nc-Cu-Nb cited above [32], the authors noted that creep in this alloy showed a very low activation energy compared grain boundary diffusion in Cu and that the transport of atoms in the boundary appeared amorphous-like. I therefore presently attribute the creep behavior in nc-Al-W alloys to a similar mechanism.

The creep mechanism in the Al-Sc and Al-Sb presumably related to the pre-existing clusters or precipitates in the system, although it may also be possible that the equilibrium grain boundary solubility is sufficient to suppress creep by the same mechanism as proposed for Al-W. A significant solubility in the grain boundaries, however, is probably not consistent with the
reduced hardness, and I will assume creep suppression is due to grain boundary precipitates. If a second phase does exist, it serves as grain boundary pinning point, and total free energy of intersecting portion of GB is reduced owing to the cross-section area. The grain size (radius R) for obtaining stability and precipitate size (radius r) has a relation by \( R/r \approx 3/4 \cdot f \), with volume fraction \( f \) [38], which means that if very fine inclusions are in system, microstructure stabilization can be achieved with just small volume fractions of it. Based on this idea, pre-annealed alloys can be considered in the metastable states because the location of each boundary corresponds to a local energy minimum if microstructure is stable. Consequently, systems are in metastable status, and this is could lower activation energies, as observed. It is also possible that the grain boundary precipitates simply prevent grain boundary sliding and as discussed above, this would suppress creep. The rate limiting step in this case is no longer grain boundary diffusion, but rather the complex motion of sliding past precipitates, which involves precipitate-matrix interfaces as well as grain boundary interfaces. Such a many bodied motion is likely to have a reduced activation energy.

<table>
<thead>
<tr>
<th></th>
<th>Condition</th>
<th>Grain size (nm)</th>
<th>Activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>200 °C 1 hour</td>
<td>~200</td>
<td>~0.54</td>
</tr>
<tr>
<td></td>
<td>200 °C 3 hours</td>
<td>~220</td>
<td>~0.51</td>
</tr>
<tr>
<td>AlSc1,1</td>
<td>250 °C 1 hour</td>
<td>~105</td>
<td>~0.4</td>
</tr>
<tr>
<td></td>
<td>As-deposited</td>
<td>~75</td>
<td>~0.48</td>
</tr>
<tr>
<td>AlSb1,2</td>
<td>150 °C 1 hour</td>
<td>~65</td>
<td>~0.44</td>
</tr>
<tr>
<td></td>
<td>250 °C 1 hour</td>
<td>~80</td>
<td>~0.45</td>
</tr>
<tr>
<td>AlW1</td>
<td>250 °C 1 hour</td>
<td>~80</td>
<td>~0.52</td>
</tr>
<tr>
<td>AlW4</td>
<td>250 °C 1 hour</td>
<td>~65</td>
<td>~0.38</td>
</tr>
<tr>
<td>AlW11</td>
<td>250 °C 1 hour</td>
<td>~53</td>
<td>~0.42</td>
</tr>
</tbody>
</table>

Table 3.7 Activation energy
3.5 Conclusion

In deformations of nanocrystalline materials, grain boundaries are considered having energetic roles in main mechanism of deformation process [9, 25, 30, 31, 51-56] and these studies are supported by the comparison of activation energy with grain boundary diffusion [25, 51, 52, 54-56].

This relation is complicated by the fact that not all impurities pin the grain boundaries with equal strength and that some impurities may precipitate. This attained solute pinning, increases the stress needed to initiate grain-boundary-mediated plastic deformation, such as creep, in nanocrystalline alloys. The activation energy obtained via this study shows grain boundary diffusion is a controlling mechanism and it is implying that grain boundaries are involved in the deformation process. This is similar to the results reported on various other nanocrystalline materials.
3.6 Supplementary Information: Finite Element Method (FEM)

To evaluate validity of eqns. (3.5) and (3.6), the finite element method (FEM) was performed using ABAQUS as shown in Fig. 3.25. For better visualization (exaggeration of displacement), the arbitrary stress was selected. As expected from the assumption, uniform distribution of stress across the width of the membrane is confirmed (see Fig. 3.A1(a)) and both eqns. (3.5) and (3.6) are valid. So, obviously maximum displacement is seen at the center of the film.

![Fig. 3.25(a) Stress distribution (b) Displacement](image)

3.7 References


[38] C.S. Smith, Introduction to Grains, Phases, and Interfaces—an Interpretation of Microstructure


[45] J. Hwang, R. Balluffi, Possible temperature dependence of the activation energy for grain boundary diffusion in metals, IBM Watson Research Center, Yorktown Heights, NY (USA); Cornell Univ …, 1978.


4.1 Introduction

4.1.1 Radiation Damage

Radiation damage events involve the transfer of energy from an incident energetic particle to the solid and the resulting redistribution of target atoms, leaving behind point defects (vacancy-interstitial pairs) and point defect clusters; this is schematically illustrated in Fig. 4.1. At elevated temperatures, diffusion of these non-equilibrium point defects can lead to various detrimental effects in an alloy microstructure, e.g., void swelling, embrittlement, and creep, and for this reason the process is generally referred to as radiation damage [1].

Fig. 4.1 Displacement cascade created by a Primary Knock-on Atom (PKA) [2-4]

The defect production process in metals has long been studied and the details of this process are well understood, at least in simple metals such as dilute Al alloys. The collision between an incoming particle, for example, a fast neutron, and a lattice atom results in the recoil of this atom
away from its original lattice site as now described. Initially, the energy is transferred from the incident particle to a lattice atom, referred to as the Primary Knock-on Atom (PKA). If the energy transferred during this first collision is greater than the *threshold displacement energy*, the PKA is displaced from original lattice site, and it collides with another lattice atom, thus initiating a collision cascade. This process continues until all the energies of all recoil atoms fall below the displacement energy. The energies of recoil atoms are lost not only by colliding with other lattice atoms but also by creating electronic excitations, but these excitations usually have little effect on the defect production process. The number of Frenkel pairs (FP’s), i.e., vacancy and interstitial pairs, created by this process is typically obtained by computer simulation, e.g., SRIM [5]; however, a rough estimate is provided by the Kinchin-Pease formula, which was proposed in ref. [6, 7],

\[ N_{FP} = \frac{0.8E_D}{2E_d} \]  \hspace{1cm} (4.1)

where \( E_D \) is the *damage energy* (i.e., initial primary recoil energy less the energy dissipated in electronic excitations) and \( E_d \) is the *displacement energy*, which is the average energy required to create a stable interstitial-vacancy pair, typically \( \sim 25 \text{ eV} \). Note that the average recoil energy from a fission neutron in steel is \( \sim 50 \text{ keV} \), which according to eq. (4.1), produces \( \sim 800 \) FP’s (neglecting energy loss from electronic excitation). Thus, a substantial number of atoms are displaced from their original locations in an energetic displacement cascade. Moreover, these defects are all created in a volume roughly 5 nm in spatial extent and on a time scale of a few ps. The amount of damage produced by a given irradiation can be quantified by the dose of the irradiation particles. Rather than specify the actual dose, e.g., neutrons/cm\(^2\) or ions/cm\(^2\), it is generally more convenient to specify the dose in displacements per atom (dpa). This quantity is simply the number of FP’s
produced during the irradiation divided by the number of atoms in the irradiated volume. Currently, the goal set for structural materials in nuclear reactors is to provide materials that can withstand a dose of \( \sim 200 \text{ dpa} \) during their service lifetime i.e., each atom will become an interstitial atom 200 times. Doses in this dissertation are specified in terms of dpa.

### 4.1.2 Atomic Mixing

The collision between an incoming particle and a lattice atom results in subsequent displacement of many atoms from their original lattice sites, far more than just the number of FP’s. Many atoms simply exchange places with other atoms, resulting in atomic mixing but no FP’s. Part of this atomic mixing results from diffusion in a localized thermal spike, which develops as the energy in the collision cascade thermalizes. Local temperatures generally exceed the melting temperature. This rather complex process of ion beam mixing affects phase stability and other nonequilibrium processes. For example, previous research has shown that metastable phases can be attained via low temperature irradiation on multilayered thin films [8-12]. Ion beam mixing in alloys systems with strong chemical interactions, i.e., large heats of mixing and liquid immiscibility, can lead to solute clustering and even precipitation in the thermal spike; several overlaps of cascades are required, however, to create large solute clusters since each atom undergoes only one or two jumps during the thermal spike. In case of alloy systems with weak to moderate chemical interactions, the cascade mixing can be assumed as random mixing, or *ballistic* mixing. In this process, the interaction energy is far less than that involved in the thermal spike, as a consequence, the alloy system is homogenized by this ballistic mixing [13]. Since ion beam mixing is related to phase stability in reactor components and nonequilibrium processing of new materials, the understanding of ion beam mixing is required to develop new engineering materials.
4.1.3 Radiation Enhanced Diffusion (RED)

When crystalline alloys are irradiated at elevated temperatures, the point defects are mobile and contribute to diffusion processes, i.e.,

\[ D_{RED} = f_i c_i D_i + f_v c_v D_v \]  \hspace{1cm} (4.2)

where \( c_{i(v)} \) is the concentration of interstitials (vacancies), \( D_{i(v)} \) is the defect diffusivity, and \( f_{i(v)} \) is the appropriate correlation factor; for convenience, \( f_{i(v)} \) will be assumed unity in what follows. The point defect concentrations include the equilibrium point defect concentrations plus the supersaturations of points defects created by irradiation. Most of the point defect pairs produced by irradiation are eliminated through self-recombination within the cascade, however, some, with fraction (\( \xi_{FM} \)), freely migrate in the lattice [14, 15]. These defects eventually also annihilate, either by recombination or by migrating to sinks such as precipitate/matrix interfaces, grain boundaries, surfaces and dislocations [16-18]. Those defects that recombine contribute to diffusion, but otherwise have little additional effect. The defects that flow to sinks have more detrimental effects, leading to void swelling, non-equilibrium segregation and creep.

Rate equations can be used to calculate radiation enhanced diffusion using eq.(4.2). With the assumption that equilibrium point defect concentrations are negligible, the appropriate rate equations are [19]:

\[
\frac{\partial c_{i(v)}}{\partial t} = K_0 - \frac{4\pi r_{i(v)}}{\Omega} (D_i + D_v) c_{i(v)} c_{v(i)} - \frac{4\pi r_{v(i)s}}{\Omega} D_{v(i)} c_{v(i)} c_s. \]  \hspace{1cm} (4.3)

The first term on the right, \( K_0 \), is the defect generation rate of freely migrating defects in dpa-s\(^{-1}\). The second term is the recombination rate; here, \( \Omega \) is the atomic volume, and \( r_{i(v)} \) is the vacancy-interstitial interaction radius, typically equal to \( \sim \) twice the lattice parameter. The last term
represents the loss of defects to sinks, assumed here to be spherical with concentration, $c_s$. If annihilation at heterogeneous sinks (i.e. grain boundaries, precipitates) is also considered, another term, $\nabla D_{i(v)} \nabla C_{i(v)}$ is required in the above equation. The steady state solutions to eq.(4.3) are given by the expressions,

$$c_v = -\frac{K_{i6}c_s}{2K_{i6}} + \left[ \frac{K_{v6}K_{i6}}{K_{i6}K_{v6}} \left( \frac{K_{i6}c_s}{2K_{i6}} \right)^2 \right]^{1/2}$$ (4.4)

$$c_t = -\frac{K_{v6}c_s}{2K_{i6}} + \left[ \frac{K_{v6}K_{i6}}{K_{i6}K_{v6}} \left( \frac{K_{v6}c_s}{2K_{i6}} \right)^2 \right]^{1/2}$$ (4.5)

where $K_{i6} = \frac{4\pi r_{i6}}{\Omega} (D_t + D_v)$ and $K_{v(i)_s} = \frac{4\pi r_{v(i)_s}}{\Omega} D_{v(i)}$.

Since interstitial atoms are typically far more mobile than vacancies, solution to eqs. (4.5-4.6) leads to a $D_{RED}$ that has very well-defined temperature regimes, as shown in Fig. 4.2 for Cu.

Fig. 4.2 Variation of diffusion coefficient as a function of temperature in irradiated Cu [1]. The different curves refer to different defect production rates and dislocation densities, $\rho_d$, as indicated. The dashed line refers to the thermal diffusivity.
At very high temperatures, the equilibrium defects are dominant and $D_{RED} \rightarrow D_{th}$. As the temperature is lowered, irradiation induced defects become predominant. In the high temperature regime, both vacancies and interstitials are highly mobile and quickly migrate to sinks and annihilate. Defect concentrations are too small in this regime to promote recombination; this regime is thus called the *sink-limited* regime. At lower temperatures, defects migrate more slowly to sinks and thus they build up high concentrations, thus giving rise to recombination. The low temperature regime is thus denoted *recombination-limited* regime. The boundaries for the different regimes are determined by the defect production rate, defect migration enthalpies, and the sink density. The different regimes are easily identified by the temperature dependence of $D_{RED}$. At high temperatures, thermal diffusion dominates and the activation enthalpy of diffusion $\Delta H_{RED} \rightarrow \Delta H_{eq}$, i.e., the activation energy for self-diffusion in equilibrium. In the *sink-limited* regime, $\Delta H_{RED} \rightarrow 0$ since all defects migrate a fixed distance to sinks, and $D_{RED}$ is given by,

$$D_{RED} = 2 \cdot \left( \frac{\Omega}{4\pi r_{eq}} \right) K_0$$  \hspace{1cm} (4.6)

At low temperatures, eqs.(4.4-4.5) lead to $\Delta H_{RED} \rightarrow \Delta H_{i,v}^m/2$ where $\Delta H_{i,v}^m$ is the enthalpy of migration of the slower moving defect, vacancy or interstitial. Since for most cases the vacancy is slower, $D_{RED}$ is expressed by

$$D_{RED} = 2 \cdot \left( \frac{\Omega}{4\pi r_{iw}} \right)^{\frac{1}{2}} \frac{1}{2} K_0^\frac{1}{2} D_v^\frac{1}{2}$$ \hspace{1cm} (4.7)
4.1.4 Irradiation Induced Creep (IIC)

While irradiation-induced creep has been extensively studied, most experimental work in this area was conducted between 1960 and 1990. These early studies employed neutron irradiations since measurements of creep and other mechanical properties required large specimens. Neutron irradiations, however, inevitably involve high costs and extensive irradiation times, and they are not conducive to well-controlled \textit{in-situ} measurements. A newer trend in irradiation damage research is to employ ion irradiations in combination with newly developed micromechanical testing on miniaturized specimens [20-24]. Ion irradiation offers many advantages: control of temperature, stress, dose rate, and recoil spectrum, and it is compatible with \textit{in-situ} testing, which is very useful for measurements of creep.

As noted above, the advantage of neutron irradiation for measurements of mechanical properties is that neutrons create homogeneous damage in large specimens. For ion implantation, producing homogeneous damage is far more difficult, even in highly miniaturized specimens. This limitation comes from the short penetration depth of ions, coupled with strong dependence of defect production rate with ion energy. Various methods have been tried to overcome this inherent problem of using ion irradiation for studies of mechanical properties. It is sufficient here to note that typically this is achieved using high energy light ions, protons or He ions. For example, the penetration of 2 MeV protons in Ni is \(\sim 17\, \mu\text{m}\). This damage depth is sufficient for measurements of nanohardness [25], but not creep on bulk samples. For creep measurements, Jung employed 6.2 MeV protons, which have a penetration depth of \(\sim 100\, \mu\text{m}\) on specimens that were rolled to \(\sim 50\, \mu\text{m}\) [26]. While this procedure was successful, the maximum defect production rate with high energy protons is \(\sim 1 \times 10^{-6}\, \text{dpa-s}^{-1}\), which limits the experiments to very low doses, typically \(\sim 0.1\, \text{dpa per day}\). An additional problem with light ion irradiation is that the primary recoil spectrum
is strongly weighted toward low energies, \(~ 1\) keV, owing to the Coulombic interactions, which is very unlike irradiations with fission neutrons, which are weighted toward high energy recoils, for example, \(~ 60\) keV in Ni. In the present work, creep measurements were performed using bulge tests on very thin Al films, \(~ 400\) nm, and employing 1.7 MeV Kr\(^+\) ions. As will be discussed below, the damage is nearly homogeneous in these thin Al films and ion doses of over 40 dpa could be obtained in a few hours.

4.1.5 Self-Organization In Dilute Al-Alloys

Nelson et al. [27] demonstrated nearly 50 years ago that two-phase alloys (Ni-Ni\(_3\)Al (i.e., \(\gamma-\gamma'\))) under irradiation can undergo self-organization reactions, whereby precipitate structures adopt a characteristic length scale in steady state that is independent of the initial conditions. This self-organization reaction is sometimes referred to as compositional patterning (CP) [28]. This idea for self-organization is significant since it implies that an alloy undergoing CP will acquire a fixed microstructure in steady state, one that will not deteriorate during irradiation regardless of how prolonged in time. Nelson et al. suggested that CP in irradiated alloys derives from a dynamical competition between high energy displacements processes in cascades, i.e. ballistic mixing, and thermally activated diffusion processes, i.e., radiation-enhanced diffusion. The high energy ballistic events in cascades tends to homogenize alloys since ballistic energies exceed chemical binding energies, whereas the thermally activated diffusion processes generally bring these systems back to equilibrium. Nelson’s model assumed that precipitate atoms recoil far from the precipitate and join a random distribution of solute atoms, this so-called “sputtering” rate of a precipitate being proportional to its volume (i.e., \(~ r^3\)). Solute atoms join the precipitate by radiation-enhanced diffusion, so the rate is proportional to \(r\). A simple derivation [29] shows that this competition leads directly to a steady state radius. While the model provides some qualitative
understanding, it has a number of shortcomings; for example, recoil distances are typically one or two lattice constants and so there is a high correlation for the recoiling precipitate atom to return to its nascent precipitate, either by RED or by ballistic mixing. For this reason, the Nelson model predicts that CP will always occur on some length scale. More rigorous models have since been developed, mostly notably those by Enrique and Bellon [28], Frost and Russell [30], and Heinig et al. [31]. For a review of these models, see refs. [32, 33].

In the theory of Enrique and Bellon, the competition between ballistic and diffusional atom jumps is described in terms of two control variables: the ratio of ballistic jumps to thermal jumps, $\gamma_b$, and the ballistic jump distance, R. Then using a Cahn-Hilliard like model they construct a dynamical phase diagram as shown in Fig. 4.3. For most ion irradiations, the recoil distance is greater than some threshold value, $R \sim 1$, required for CP. $R$ in Fig. 4.3 is shown in reduced units, but the threshold value in standard units corresponds to $\sim 1.5$ nearest neighbor distances. In this case it is seen that three different steady states can be stabilized depending on the value of $\gamma_b$: solid solution (SS), compositional patterning (CP) and macroscopic phase separation (MPS). If $\gamma_b \gg 1$, i.e., ballistic mixing is much larger than thermal diffusion, random mixing prevails, and a homogeneous solid solution is obtained. If thermal diffusion is dominant, $\gamma_b \ll 1$, the system approaches equilibrium, and the system undergoes macroscopic phase separation. The interesting regime occurs when $\gamma_b \sim 1$. In this case, thermal diffusion dominates ballistic diffusion at small length scales and phase separation occurs, but on longer length scales, ballistic mixing dominates and limits the size of the ordered domains, i.e., the system shows compositional patterning.
Fig. 4.3 Analytical dynamical phase diagram for an A\textsubscript{50}B\textsubscript{50} alloy as a function of the average forced relocation distance R and forcing intensity γ\textsubscript{b}, in units of the A and C physical constants of a Ginzburg-Landau free energy. Insets are (111) sections of 3D kinetic Monte Carlo simulations. From ref. [34].

While the theory for CP is now established, it nevertheless includes many assumptions; for example, it neglects the role of grain boundaries, radiation induced segregation, and other complexities of real alloy microstructures. More importantly, very few experiments have been performed to explore CP in real alloys, and nearly all experimental work has been performed on immiscible alloys, most notably dilute Cu- based alloys [35]. Two-phase aluminum alloys, on the other hand, mostly involve intermetallics, and other than the work of Nelson et al. [27] on Ni-Al alloys, I am unaware of any experimental work establishing CP in a two-phase alloy involving an intermetallic phase. Some work even disputes that the work of Nelson et al. [27] indeed demonstrates CP [36]. It is quite surprising, therefore, that although the work by Nelson et al. [27] has been cited ~ 250 (Web of Science), and the work of Enrique and Bellon some 120 times, there have been extremely few experiments on CP, and I believe none involving intermetallic second phase particles aside from the work by Nelson et al. [27] mentioned above. In this chapter, I explore CP in a very different γ-γ’ alloy, nanocrystalline Al-Sc. Although the work must be
considered preliminary, as I will show, it does strongly suggest that CP indeed occurs in this system, but the small grain size plays an important role.

4.2 Experimental

4.2.1 Ion Irradiations

A High Voltage Engineering Van de Graaff accelerator was used for ion irradiation. The vacuum pressure in the beamline and target chamber was maintained below $1 \times 10^{-7}$ Torr and consisted mainly of Ar. The ion beam was scanned to provide homogeneity and measured using a faraday cup placed intermittently in front of the sample. For irradiation creep, a 6 mm circular aperture was selected to define the beam, while a 3 mm aperture was used for simple irradiations of the AlSc$_{1.1}$ films. 1.8 MeV Kr$^+$ ions were used for irradiation since they create a nearly homogeneous damage distribution in the sample, provide high damage levels, and are available from an RF ion source, which was used in the MRL accelerator. These ions also mostly pass through the sample, so they do not create gas bubbles or other effects of contamination, see Fig. 4.4.

To evaluate irradiation damage, the measured ion doses, which have units of ions-cm$^{-2}$, were converted to displacement per atom (dpa) using the simulation software, SRIM [5] along with the expression,

$$\text{displacement per atom (dpa)} = \frac{\text{displacement}}{\text{cm}^3} \times \frac{\text{atoms}}{\text{cm}^3} \times \frac{\text{cm}^2}{\text{ions}} \times \frac{\text{Å}}{\text{cm}^2}.$$

As seen in Fig. 4.4, SRIM yields displacements/ion-Å, and the experimentally measured ion doses yields ions/cm$^2$. 

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Some irradiations were performed at the 6 MeV Tandem accelerator at the CINT facility at Sandia National Laboratory (SNL). These irradiations were performed using 5 MeV Au ions. Similar to the Kr irradiations, the Au ions were transmitted through the thin film specimens. While there are differences in the primary recoil spectra for these two irradiations, these differences can be considered negligible for the present work.

4.2.2 Irradiation Creep Apparatus

The irradiation creep apparatus employed at the MRL Van de Graaff irradiation facility at Illinois was identical to that described in Chapter 3 for thermal creep; indeed, the same apparatus was employed. The bulge test is particularly advantageous for irradiation creep experiments since the vacuum side of the specimen, see Chapter 3, can be attached directly to an accelerator beamline.
4.3 Experimental Results And Discussion

4.3.1 Irradiation Effect On Alloy Microstructure And Hardness

**Irradiation Of AlSc\(_{1.1}\) With 1.8 MeV Kr Ions**

As grown samples of AlSc\(_{1.1}\) and samples pre-annealed at 250 °C were irradiated with 1.8 MeV Kr\(^+\) ions to a dose of ~ 40 dpa at various temperatures: room temperature (RT) ~ 25 °C, 75 °C, 150 °C and 200 °C. STEM images of the as-grown samples, after irradiation, are shown in Fig. 4.5(a-b). Irradiations at RT (not shown), 75 °C and 150 °C of the as-grown samples show a small change in grain size, ~ 40 nm, but no change in the precipitate structure, i.e., an absence of irradiation-enhanced precipitation at these temperatures. The increases in grain size are consistent with reported values of irradiation-induced grain growth in Cu [37], which should be similar to those in Al [38].

The microstructures of pre-annealed samples, in contrast, are clearly changed after irradiation, as shown in Fig. 4.6(b-d). EDS measurements show that the bright spots in these images are Sc rich, see Table 4.1. A small increase in grain size during irradiation is again observed, Fig. 4.7(a) and Table 4.2, but more importantly, the precipitate density has dropped a factor of ~ 5 for irradiations at 75 °C and 150 °C, but at 200 °C it is unchanged, see Table 4.2. Unfortunately, TEM images on the RT irradiated, pre-annealed, samples are not available; however, we show below for comparable irradiations (at SNL) that the precipitates density goes to zero for this condition. The average precipitate size, in contrast, appears to have remained approximately the same, ~ 22 nm, with a possible small shift downwards in the size distribution at lower irradiation temperature (75 °C) as indicated in Fig. 4.7(b,c). The decrease in density, even without change in precipitate size, indicates an increase of Sc in solution for low temperature irradiations. Indeed,
radiation induced dissolution of precipitates is not uncommon and can be found in other systems in previous research [39, 40]. Lastly, irradiation of the pre-annealed sample at 200 °C retains intragranular precipitates, see Fig. 4.8. Such precipitates were observed in the pre-annealed sample, and so this is not too surprising, especially since the precipitate density has not changed. It appears, therefore, that thermally activated diffusion is becoming far more dominant than ion beam mixing at ~ 200 °C.

Fig. 4.5 STEM images of as grown AlSc$_{1.1}$ films after irradiation to 40 dpa at (a) 75 °C; (b) 150 °C

Fig. 4.6 STEM of AlSc$_{1.1}$: (a) after pre-annealing for 1 hour at 250 °C; after pre-annealing at 250 °C plus irradiation to 40 dpa at: (b) 75 °C; (c) 150 °C; and (d) 200 °C
<table>
<thead>
<tr>
<th>Irradiation Temperature (ºC)</th>
<th>Al (at.%)</th>
<th>Sc (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>99.4</td>
</tr>
<tr>
<td>150</td>
<td>3</td>
<td>91</td>
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<tr>
<td></td>
<td>4</td>
<td>99</td>
</tr>
<tr>
<td>200</td>
<td>5</td>
<td>92</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>99.5</td>
</tr>
</tbody>
</table>

Table 4.1 EDS analysis irradiated, AlSc$_{1.1}$ films pre-annealed at 250ºC

![Graph 1](image1.png)

Fig. 4.7 Characterization of AlSc$_{1.1}$ (a) grain size after irradiation at selected temperatures of as-grown and pre-annealed specimens. Precipitates sizes of AlSc$_{1.1}$ (b) after pre-annealing (c) after irradiation of samples which were pre-annealed at 250 ºC

<table>
<thead>
<tr>
<th>Sample Condition</th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>Irradiation Temp. (ºC)</td>
<td>75</td>
</tr>
<tr>
<td>Precipitate density (x 10$^{-5}$/nm$^2$)</td>
<td>~ 6.3</td>
</tr>
</tbody>
</table>

Table 4.2 Precipitate density change after irradiation on annealed AlSc$_{1.1}$
The effect of irradiation on the hardness of AlSc$_{1.1}$ alloys is summarized in Fig. 4.9. It is first noticed that irradiation of the as-grown sample at RT has very little effect on hardness. The small increase observed is close to the uncertainty of the measurement, although some increase is expected by the introduction of point defect clusters. Defect clusters are known to cause hardening in many alloys [1]. Irradiation of the as-grown AlSc$_{1.1}$ films at 75 °C has a similarly small effect on the hardness. Increasing the irradiation temperature to 150 °C, however, begins to show a reduction in hardness, from 2.1 GPa to 1.75 GPa. Notably, thermal annealing (for 1 hour) of as-grown samples causes a similar reduction in hardness in AlSc$_{1.1}$, to about 1.62 GPa.

The sample pre-annealed at 250 °C was similarly irradiated. Recall from Chapter 2 that annealing AlSc$_{1.1}$ to 250 °C leads to a reduction of hardness to ~ 1.3 GPa; this value is included in Fig. 4.9. A first notable finding in these irradiations experiments is that RT irradiation of this annealed sample leads to a large increase in hardness, to ~ 1.95 GPa, which is very close to that of the as-grown sample. Increasing the irradiation temperature, moreover, parallels the behavior observed on the as-grown sample. Irradiation at 75 °C leads to the same increase in hardness of this annealed sample as that for irradiation at RT, while irradiation at 150 °C shows a smaller
increase at hardness. Interestingly, the hardness of the as-grown sample, annealed at 150 °C, or irradiated at 150 °C, has a very similar hardness as the pre-annealed sample irradiated at 150 °C. It should be appreciated, however, that the as-grown sample annealed (or irradiated) at 150 °C is softening, whereas the pre-annealed sample undergoing irradiation at 150 °C is hardening. The point is that at 150 °C ballistic mixing during irradiation is competing with thermally activated diffusion. Irradiation of the pre-annealed sample at 200 °C has little effect on the hardness, in fact, a slight reduction, if anything, revealing that at this temperature thermally activated diffusion is more significant than ballistic mixing.

Fig. 4.9 Hardness of AlSc1.1 after irradiated using 1.8 MeV Kr⁺

**Irradiation of AlSc1.7 with 5 MeV Au Ions (at Sandia CINT Facility)**

Irradiations on AlSc1.7 were performed at the CINT facility at SNL using a 5 MeV beam of Au ions. Microstructure characterizations of these samples were performed using a JEOL2010 HR-STEM. To facilitate observation of precipitation behaviors, cross sectional TEM samples were prepared. The initial grain size of the as-grown AlSc1.7 films was ~ 65 nm, as reported in Chapter
2. After room temperature irradiation of this sample with different doses, 0.5 x 10^{16}/cm^2 and 1.5 x 10^{16}/cm^2, the grain sizes have increased modestly, to ~ 70 nm and ~ 82 nm, respectively. (see Fig. 4.10(a,b) and Table 4.3. Note, the two white, round-shaped bright spots in Fig. 4.10(b) are due to residual contamination from EDS examination, and should be ignored. Grain size distributions for the three samples are presented in Fig. 4.10(c). After irradiation, the grain size distribution shifted upwards; the effect of dose, however is small, ~ 20 % for a factor of three difference in dose. This small increase is consistent with ref. [37], where grain size was reported to increase as the cube root of dose, i.e., \( \sqrt[3]{3} \approx 1.4 \).

Fig. 4.10 Irradiation of as grown AlSc_{1.7} sample with different doses (a) 0.5 x 10^{16}/cm^2 (b) 1.5 x 10^{16}/cm^2 and (c) grain size distributions

Since precipitate coarsening occurs during annealing at temperatures above ~ 250 °C, I selected a 300 °C heat-treatment to provide convenient-sized precipitates to study their dissolution/coarsening behavior under irradiation. Microstructure characterization of heat treated and irradiated AlSc_{1.7}, was performed using TEM imaging, STEM-HAADF, reported in Fig.
4.11(a-d) and Fig. 4.12(a,b). As can be observed in the Z-contrast images shown in Fig. 4.11(b-d) and Fig. 4.12(a,b), the precipitates that are present after irradiation are located mostly on the grain boundaries. No precipitates were observed after room temperature irradiation, as mentioned above. Overall, the sizes and densities of precipitates both decreased after irradiation at (b) 140 °C, (c) 175 °C and (d) 200 °C. While the overall changes are not large at these temperatures, the volume fraction of precipitates after irradiation is nevertheless reduced by ~ 85% from that of the pre-annealed, but unirradiated sample. It is also significant that the precipitates appear to be completely dissolved during RT irradiation. Two other observations of note are (i) the grain sizes increase somewhat during irradiation and this growth increases with irradiation temperature, and (ii) the final precipitate sizes are very similar to those in the AlSc$_{1.1}$ samples pre-annealed at 250 °C and irradiated with 1.8 MeV Kr. This latter point will be discussed in more detail below.

Fig. 4.11 HAADF STEM images of AlSc$_{1.7}$ pre-annealed at 300 °C and then irradiated at (a) RT, (b) 140 °C (c) 175 °C, and (d) 200 °C, respectively. (all 1.6 x 10$^{16}$/cm$^2$)

Fig. 4.12 Cross section STEM images of AlSc$_{1.7}$ pre-annealed at 300 °C and then irradiated at (a) 140 °C, at (b) 200 °C, respectively (both 1.6 x 10$^{16}$/cm$^2$)
### As grown

<table>
<thead>
<tr>
<th>Irradiation Temp.</th>
<th>Before</th>
<th>After</th>
<th>Annealed at 300 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT (25 °C)</td>
<td>64±3.13</td>
<td>70±4</td>
<td>128±5.18</td>
</tr>
<tr>
<td>RT (25 °C)</td>
<td>82±3.65</td>
<td>126±6.3</td>
<td>177±6.1</td>
</tr>
<tr>
<td>RT (25 °C)</td>
<td>140 °C</td>
<td>175 °C</td>
<td>200 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Grain size (nm)</th>
<th>a</th>
<th>b</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>12</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
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<th>N/A</th>
<th>25±1.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>N/A</td>
<td>N/A</td>
<td>20.34±0.77</td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td>17.35 ± 1.54</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Precipitate density (x 10^5/nm²)</th>
<th>N/A</th>
<th>N/A</th>
<th>12</th>
<th>4.99</th>
<th>5.2</th>
<th>7.12</th>
</tr>
</thead>
</table>

Table 4.3 Characterizations of irradiated AlSc₁.⁷

In addition to the TEM characterization of the pre-annealed specimens that were irradiated at SNL, one pre-annealed sample, the one irradiated at 140 °C, was also characterized in by APT. This sample was selected for APT since the results reported above on microstructure and hardness suggest that ballistic and thermally activated diffusion are competing at ~ 140 °C. The APT reconstruction of this sample, which contains ~ 17 x 10⁶ atoms or a volume of ~ 2 x 10⁵ nm³, is shown in Fig. 4.13. Unlike the reconstructions shown in Chapter 2, this sample reveals a highly nonhomogeneous microstructure. Recall, one of the specimens examined by APT in Chapter 2 was annealed to 180 °C, 40 °C higher than this irradiated sample. The different colors reveal Sc atoms belonging to different clusters. While ~ 4500 clusters were found using the IVAS software [41],

![Atom probe reconstruction](image)

Fig. 4.13 Atom probe reconstruction of a pre-annealed (at 300 °C) AlSc₁.⁷ irradiated at 140 °C. Various clusters are identified by color.
the size, composition and location of the largest clusters are reported in Table 4.4. The largest cluster contains \( \sim 46,000 \) atoms and has roughly the composition expected for Al\(_3\)Sc. If the cluster is assumed spherical, its effective radius would be \( \sim 5.8 \) nm, which is somewhat smaller than the average size found by TEM, \( r \sim 8.5 \) nm, but comparable. The size of less compact precipitates, moreover, are likely to be overestimated by TEM. It should also be realized that the number density of precipitates found by TEM in this sample was \( \sim 5 \times 10^{-5} \text{ nm}^3 \), which taken with the volume sampled by APT, \( 5 \times 10^4 \text{ nm}^3 \), indicates that only a few precipitates will be found by APT. A first new finding provided by the APT, therefore, is that in the CP regime, here is not a narrow distribution of precipitates sizes; rather the distribution is wide, with many small clusters distributed throughout the matrix.

<table>
<thead>
<tr>
<th>Total ions in cluster for some of the largest clusters</th>
<th>Position (nm)</th>
<th>Cluster volume (nm(^3))</th>
<th>Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>46158</td>
<td>0.2855</td>
<td>-5.4398</td>
<td>20.6857</td>
</tr>
<tr>
<td>24286</td>
<td>3.1135</td>
<td>-0.625</td>
<td>11.7043</td>
</tr>
<tr>
<td>25871</td>
<td>20.421</td>
<td>13.1387</td>
<td>147.7518</td>
</tr>
<tr>
<td>19470</td>
<td>12.1234</td>
<td>9.1655</td>
<td>100.0801</td>
</tr>
<tr>
<td>6236</td>
<td>6.9355</td>
<td>21.8354</td>
<td>134.9421</td>
</tr>
<tr>
<td>4981</td>
<td>5.8911</td>
<td>1.1952</td>
<td>6.1722</td>
</tr>
</tbody>
</table>

Table 4.4 Cluster information after APT reconstruction

The APT is also useful for determining the solubility of Sc in Al during irradiation in the CP regime. This is shown in Fig. 4.14, where the concentration of Sc is plotted as a function of distance along the axis of a cylinder, 10 nm in diameter Fig. 4.14(a). The location of the cylinder is indicated in Fig. 4.14(b). Here it is observed that the scandium concentration is \( \sim 1.4 \text{ at.\%} \) away from the precipitate, but that it drops to \( \sim 0.40 \text{ at.\%} \) just outside the precipitate, before rising rapidly at an apparent precipitate interface.
Along with microstructural analysis, nanoindentation was performed on the Au-irradiated AlSc$_{1.7}$ samples; these data are shown in Fig. 4.15. These data confirm the findings above on Kr-irradiation of AlSc$_{1.1}$. First, room temperature irradiation of as-grown samples has very little effect on the hardness, but on the pre-annealed sample, irradiation increases the hardness from ~ 1.7 GPa to ~ 2.2 GPa; this value is close to the hardness of the sample in the as-prepared state. The small difference may be due to the larger grain size in the pre-annealed plus irradiated sample. Irradiation of the pre-annealed sample at increasingly higher temperatures leads progressively to smaller increases in hardness. Above 200 °C, irradiation has little effect on the hardness.

Fig. 4.14 (a) Sc atom distribution as a function of distance along the axis of a cylinder marked in (b); (b) reconstruction of the AlSc$_{1.7}$ tip (red atoms = Sc atoms) showing the location of the test cylinder
Irradiation Of AlSb\textsubscript{1.2} With 5 MeV Au Ions (at Sandia CINT Facility)

For comparison, AlSb\textsubscript{1.2} samples were also irradiated using 5 MeV Au ions. As-deposited and pre-annealed samples (at 150 °C) were irradiated. As reported in Chapter 2, annealing AlSb\textsubscript{1.2} samples at 150 °C leads to precipitation of AlSb with size ~ 5 nm. The results are shown in Fig. 4.16 and summarized in Table 4.5. Table 4.5 shows that the grain size is not much affected by RT irradiation; the as-grown film maintains a grain size of ~ 50 nm and the annealed film has a grain size of ~ 80 nm. The outstanding feature in this experiment is that the precipitates are completely dissolved, see Fig. 4.16(b).
Fig. 4.16 STEM image of AlSb$_{1.2}$ (a) as grown and irradiated at room temperature (1 x 10$^{16}$/cm$^2$) (b) pre-annealed at 150 °C and then, irradiated at 125 °C (1.6 x 10$^{16}$/cm$^2$) (c) grain size distribution

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>As grown</th>
<th>Pre-annealed at 150 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td>Irradiation Temp.</td>
<td>Room Temp. (25°C)</td>
<td>125 °C</td>
</tr>
<tr>
<td>Grain size (nm)</td>
<td>50 ± 2</td>
<td>52 ± 5</td>
</tr>
<tr>
<td>Precipitate size (nm)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table 4.5 Characterization of AlSb$_{1.2}$

Nanohardness measurements were performed to check whether AlSb$_{1.2}$ samples behaved similar to Al-Sc. Fig 4.17 illustrates that the irradiation hardening behavior is indeed quite similar. RT irradiation of the as-grown samples results in a small increase in hardness, ~ 0.25 GPa, which is similar to the change in AlSc$_{1.1}$, and again probably due to irradiation hardening. More importantly, RT irradiation of the pre-annealed sample greatly increases the hardness, from the pre-annealed value of ~ 1.0 GPa to ~ 1.7 GPa, the same value as the RT-irradiated, as-grown film. Also similar to irradiation of Al-Sc, irradiation of pre-annealed AlSb$_{1.2}$ at elevated temperatures leads to a smaller increase in hardness. Specifically, irradiation at 125 °C increases the hardness from 1.0 GPa to only 1.55 GPa.
Discussion Of Irradiation Hardening In Dilute Al-Sc And Al-Sb Alloys

The irradiation hardening studies on dilute, nanocrystalline Al-Sc and Al-Sb alloys appear to support our understanding of solute strengthening in these systems reported in Chapter 2. The major findings of these studies are (i) RT irradiation of the as-grown alloys has little effect of hardness or the alloy microstructure; (ii) irradiation at temperatures below ~100 °C of pre-annealed samples result in the apparent dissolution of precipitates and the restoration of hardness to the same level as in the as-grown alloy; (iii) for irradiation above ~ 150 °C (125 °C for AlSb$_{1.2}$) the hardness increases are smaller, diminishing with irradiation temperature until ~ 225 °C, when irradiation begins to have little to no additional effect on hardness. The first finding is significant since it reveals irradiation-induced hardening from defect clustering is, in itself, not an overly important factor in these nanocrystalline alloys. Whether this is because point defect clusters are not stable in these nanocrystalline alloys, or because the increases from these clusters are small in comparison to the effect of solute, was not determined. The second observation provides the primary support for the proposed model of grain boundary strengthening in dilute nc-Al alloys, as described in
detail in Chapter 2. RT irradiation results in ion beam mixing that redistributes solute in the grain boundaries. Fig. 4.16 shows the dissolution of Al\textsubscript{3}Sc precipitates after 75 °C irradiation on pre-annealed AlSc\textsubscript{1.1}. This figure also reveals that some dislocations are formed near the grain boundaries during this dissolution process. A simple calculation illustrates that homogenization of the alloys is possible in Al at the ion doses employed ~ 40 dpa, as now illustrated.

The ion beam mixing efficiency, during heavy ion irradiation of Al at 10 K can be found in the literature; its value is $D_{IM}t/\phi F_D \sim 25 \text{ A}^5/\text{eV}$ \cite{42} or in units of dpa, $D_{IM}t/\phi F_D \sim 125 \text{ A}^2/\text{dpa}$; $D_{IM}$ refers to the ion beam mixing diffusion coefficient. Noting that ion beam mixing is ~ 3 times higher at RT than at 10 K \cite{43} and that the irradiations doses were ~ 40 dpa, $r = 2\sqrt{D_{IM}t} \sim 25 \text{ nm}$. Since the grain size after annealing is ~ 80 nm, this degree of mixing can nearly, fully homogenous the alloy. Moreover, since the precipitates are mostly contiguous with the grain boundaries, full mixing may not be required to restore the hardness to its value in the as-grown state.

Fig. 4.18 TEM analysis of AlSc\textsubscript{1.1} pre-annealed at 250 °C and then irradiated at 75 °C

Heat Treated (250 °C for 1 hour)

Dissolution of Al\textsubscript{3}Sc

Dislocation loops close to grain boundaries

Radiated at 75 °C ~ 40 dpa

50 nm

50 nm

40 dpa

250 °C for 1 hour
The third significant finding, that ballistic mixing at \( \sim 150 \, ^\circ\text{C} \) competes with thermally activated diffusion, is somewhat more complex. In large-grained samples, \( D_{\text{RED}} \) can be estimated using eqs. (4.4) and (4.5) and compared to \( D_{\text{IM}} \). In the recombination limited regime,

\[
D_{\text{RED}} = c \nu D_v = \left[ \frac{K_0 D_v}{4 \pi r_{iv}} \right]^{1/2} = \left[ \frac{\xi \hat{\nu} D_0 \exp(E_m^v/kT)}{4 \pi r_{iv}/\Omega_0} \right]^{1/2}
\] (4.9)

where, \( \xi \) (production efficiency) = 0.1; \( \hat{\nu} \) (dpa rate) = 10\(^{-2}\)/s; \( r_{iv} \) (recombination radius) \( \sim 0.4 \) nm; \( E_m^v = 0.62 \) eV; \( D_{0,\nu} = 1/6 \nu_0 \lambda^2 \); \( \nu_0 = 1 \times 10^{14}/\text{s} \); \( \Omega_0 \) (atomic volume) = 1.5 \( \times 10^{-2} \) nm\(^3\). If \( D_{\text{IM}} = 2.25 \times 10^{-2} \) nm\(^2\)/s is taken from above, and equating \( D_{\text{IM}} = D_{\text{RED}} \), yields \( T = 313 \) K \( \sim 50 \, ^\circ\text{C} \). The above calculation, however, assumes self-diffusion in Al, not Sc impurity diffusion. Since thermal diffusion of Sc in Al is 100 times smaller than self-diffusion at these low temperatures, a correction is required. Including this factor in eq.(4.9) yields for Sc in Al, \( D_{\text{IM}} = D_{\text{RED}} \) at \( T = 120 \, ^\circ\text{C} \) (393 K), which is in good agreement with my experimental findings. While it should be recognized that my calculation is very approximate, it does indicate that this calculated \( D_{\text{RED}} \) is consistent with the result. The complication alluded to above arises because the precipitates are located on the grain boundaries, and it is possible that GB-diffusion of Sc along with ion beam mixing may also explain these results. Unfortunately, \( D_{\text{GB}}^{\text{al}}(\text{Sc}) \) is not known. Data for \( D_{\text{GB}}^{\text{al}}(\text{Cu}) \), however, is available [44], and using this data shows \( D_{\text{GB}}^{\text{al}}(\text{Cu}) \cdot t \sim 3 \times 10^3 \) nm after 1 hour. Since Cu lattice diffusion in Al is presumably much larger than Sc diffusion, this large value may overestimate \( D_{\text{GB}}^{\text{al}}(\text{Sc}) \) significantly; nevertheless, this estimate illustrates that grain boundary diffusion, in combination with ion beam mixing may also explain my results.
4.3.2 Self-Organization In Dilute, Nanocrystalline Al-Sc Alloys

While the primary goals of this thesis concern the strengthening mechanisms in dilute nanocrystalline Al alloys, and how they are affected by irradiation, these data also provide insights about self-organization in these materials. First, I will present the evidence for self-organization and then highlight what new is learned from this effort. The evidence for self-organization derives from examination of the precipitation behavior in three temperature regimes. In the low temperature regime typified here by RT irradiation, i.e., $\gamma_b \gg 1$, the work provides clear evidence that pre-existing Al$_3$Sc precipitates in both AlSc$_{1.1}$ and AlSc$_{1.7}$ dissolve under irradiation. The nanohardness increases and TEM images fail to locate Sc-rich regions. It should be emphasized that the TEM evidence comes primarily from HAADF STEM imaging. This means that the irradiation did not simply disorder the Al$_3$Sc phase, but it homogenized the alloy. This is consistent with the increase in nanohardness. Unfortunately, the dose dependence of this dissolution process was not measured, and hence no information on the interplay between disordering and dissolution can be ascertained. Similar behavior was obtained for AlSb$_{1.2}$ irradiated at RT with 5 MeV Au.

At intermediate temperatures, $75 \, ^{\circ}C < T < 200 \, ^{\circ}C$, i.e., $\gamma_b \sim 1$, the experiments show that the precipitates in both the AlSc$_{1.1}$ and AlSc$_{1.7}$ alloys adopt a fixed size, $\sim 20$ nm. It should be mentioned that for the AlSc$_{1.1}$ alloy, the precipitate size in the pre-annealed sample, prior to irradiation, was also $\sim 20$ nm. It may be argued, possibly, that the growth rate under irradiation is simply slow and therefore the system is not in the compositional patterning regime. This does not seem consistent with the second finding that the precipitate density was reduced, i.e., why should some precipitates completely dissolve while others maintain a constant size, unless the system has reorganized into this steady state. Indeed pre-annealing the AlSc$_{1.7}$ to a higher temperature 300
°C, led to larger precipitates, ~25 nm (Table 4.3), and irradiation of these samples results in a reduction in precipitate size, to ~17 nm, and a small reduction in precipitate density.

The APT characterization of the sample irradiated at 140 °C provides a more detailed picture of the CP microstructure. As described in section 4.3, the microstructure in the CP regime is, locally, very messy. While TEM provide an average precipitate size, they fail to show the many clusters of smaller size and how these clusters are arranged in the sample. The complexity of this microstructure, however, is perhaps not overly surprising when one considers that in the CP regime, \( \gamma_b \sim 1 \), i.e., for every thermally activated atomic jump there is a random ballistic atomic jump. This can only occur, in practice, when defect concentrations are highly supersaturated, and this leads to defect clustering, and clustering generally includes solute atoms. These different clusters, moreover, may act as recombination centers, or even sinks for point defects. In other words, \( \gamma_b \) is likely to be very inhomogeneous and on a mesoscopic scale, spatially varying in time. These complexities are not included in present models of compositional patterning. The high density of grain boundaries, moreover, add yet additional inhomogeneities into this system, as well as the complications of fast diffusion paths on grain boundaries. It is worth noting that ATP revealed a similar complex microstructure in dilute Cu-Fe alloys during irradiation in the CP regime, suggesting that this complexity may indeed be a characteristic of the CP-regime, and it should certainly be investigated further.

The high temperature regime, where \( \gamma_b \ll 1 \), was explored only indirectly. Notice in Fig. 4.7 the precipitate size continues to increase with increasing temperature. This essentially establishes the condition that the system undergoes macroscopic phase separation when \( \gamma_b \ll 1 \), i.e., the precipitate size is not being constrained under thermal annealing. Irradiations were not
performed at these higher temperatures owing to the limitation on irradiation time and the very low probability that such data would provide additional insights.

Lastly, I comment on the finding that in the patterning regime the precipitate size remains nearly independent of irradiation temperature. This is most simply explained by assuming the system is in the sink-limited regime. In this case both ballistic mixing and $D_{RED}$ are nearly independent of temperature and therefore $\gamma_b$ is constant. Any changes in the steady microstructure in the patterning regime, therefore would need to derive from changes in the equilibrium solubility or dislocation (sink) structure with temperature. Over the small temperature range of the patterning regime ~150 °C, these effects are not expected to be large. On the other hand, most of the precipitates are observed near grain boundaries, suggesting a different mechanism, i.e., compositional patterning may result from a competition between ballistic mixing of solute in precipitates on the grain boundaries with thermally activated grain boundary diffusion. Again, we can assume ballistic mixing is independent of temperature. And since the activation energy for grain boundary diffusion is small, ~ 0.4 eV [45], the temperature dependence will be weak. For example, increasing the temperature from 150 °C to 180 °C results in only a factor of 2 change in the diffusion coefficient. With the limited data presently available, however, further speculation is unwarranted.

4.3.3 Irradiation Induced Creep (IIC) In Al Alloys- Using A Thin Film Bulge Method

**Irradiation Induced Creep**

A primary objective at the outset of this work was providing information to help develop alloys that are dimensionally stable in extreme environments. Understanding irradiation induced creep (IIC) was meant to be a major part of this goal; however, owing to major issues with the
MRL Van de Graaff accelerator, this portion of the work has remained in its preliminary stages. Nevertheless, the understanding gained could be useful for future studies. Irradiation induced creep compliance is defined here by eq.(4.10) [46].

$$\dot{\epsilon} = B_0 \bar{\sigma} \dot{\phi}$$

(4.10)

where $\dot{\epsilon}$ is strain rate. $B_0$ is creep compliance value, $\bar{\sigma}$ is effective stress and $\dot{\phi}$ is displacement rate per seconds. This equation is applicable if swelling is negligible. The definition, moreover, anticipates that the strain rate is nearly linear in stress, which is normally observed for applied stress levels well below the yield stress [1].

**Initial Testing Of The IIC Measurement System**

IIC was first measured on CuW$_{1.5}$ to test the performance of the irradiation-induced creep (IIC) apparatus, as previous data on this alloy had been reported earlier using an earlier version of the same apparatus [47, 48]. Thus, irradiation creep responses of CuW$_{1.5}$ was measured at 100 °C and 200 °C during irradiation with 1.8 MeV Kr$^+$ at a “bulge pressure” of 1 kPa. A typical result is shown in Fig. 4.19.

![Fig. 4.19](image)

Fig. 4.19 IIC of CuW$_{1.5}$ free standing film at 200 °C, 1.8 MeV Kr$^+$ ($\phi$: 1.76 x 10$^{-3}$ dpa/seconds) (a) strain vs time (b) stress vs time (c) creep compliance, $B_0$ vs dpa
Fig. 4.19 shows IIC results for CuW_{1.5} at 200 °C. The initial strain rate is very high but this is primarily due to the initially high stresses in bulge testing, see eq. (3.5). Plotting the normalized compliance, $B_0$, versus dose, Fig. 4.19(c), shows that at low doses, $B_0$ drops rapidly before becoming constant. This is most likely due to irradiation-induced relaxation of the as-grown film structure, i.e., primary creep, but it may be due to a systematic error in the initial measurement of stress. This error arises from the determination of initial stress, as discussed in Chapter 3. At high doses, the stain rate $\approx 3.7 \times 10^{-6}$ and stress varies more slowly and $B_0$ approaches $\approx 3.5 \times 10^{-5}$ MPa^{-1}dpa^{-1}. This result is in good agreement with previous studies [47, 48], for which $B_0$ for Cu_{99}W_{1} at 200 °C was reported as $\sim 4.8 \pm 0.2 \times 10^{-5}$ MPa^{-1}dpa^{-1} and $3.2 \pm 0.6 \times 10^{-5}$ MPa^{-1}dpa^{-1} for Cu_{93.5}W_{6.5} at 200 °C, as plotted in Fig. 4.20. As shown in Fig. 4.20, CuW_{1.5} alloy, what I used to testing this bulge system, shows a value of $3.0 \times 10^{-5}$ MPa^{-1}dpa^{-1} and $3.5 \times 10^{-5}$ MPa^{-1}dpa^{-1}, at 100 °C and 200 °C, respectively. These preliminary results illustrate that the creep apparatus is working and provides reproducible results.

Fig. 4.20 Comparison to previous studies (* from refs. [47, 48] )
**Irradiation Induced Creep Of AlSc<sub>1.1</sub>**

STEM_HAADF micrographs showing the final microstructure of AlSc<sub>1.1</sub> after irradiation induced creep (IIC) are presented in Fig. 4.21: (a) as prepared and IIC at RT to a dose of ~ 20 dpa; (b) as prepared and IIC at 75 °C to a dose of ~ 25 dpa; (c) Pre-annealed and IIC at RT to a dose of ~ 25 dpa. The corresponding grain size distributions and average grain sizes are plotted in Fig. 4.21(d) and Fig. 4.21(e), respectively. The grain size distribution shifts slightly upwards after 75 °C IIC of as-deposited sample. No precipitates were observed after IIC in the as-deposited samples, as expected. The grain size of pre-annealed AlSc<sub>1.1</sub> did not change after RT irradiation and precipitation is not observed.

Fig. 4.21 HAADF-STEM images of AlSc<sub>1.1</sub> after IIC (a) at room temperature: as grown, (b) at 75 °C: as grown (c) at room temperature (25 °C): pre-annealed at 250 °C, (d) grain size distribution, after IIC (e) average grain size
The as-grown AlSc\textsubscript{1.1} IIC tested samples were also examined by BF TEM and dislocations inside of grains were confirmed. Black spots in Fig. 4.22 represent dislocations (loops). Since dislocations have different atomic arrangement orientations so that it appears in dark in BF TEM images. Irradiation induced dislocations were observed in many studies [49, 50], and this is owing to the fact that irradiation increased vacancy concentration.

![Bright field TEM image](image)

**Fig. 4.22** Bright field TEM image of as grown AlSc\textsubscript{1.1} after IIC at 75 °C

Fig. 4.23 shows the irradiation induced creep results for AlSc\textsubscript{1.1}. Irradiation creep was again induced by 1.8 MeV Kr\textsuperscript{+} irradiation with dose rate $\dot{\phi} \sim 3.2 \times 10^{-3}$ dpa/s. A plot of strain versus dose (dpa) is reported at Fig. 4.23(a). Again, the initial high stress is mainly responsible for the very high initial strain rates. Along with strain, the creep compliance, $B_0$ is also plotted in Fig. 4.23(b). It is again observed that the initial values change rapidly, again for the reasons cited above, but at long times the values remain nearly constant. The measured creep compliances are reported in Table 4.6. Here, AlSc\textsubscript{1.1} as-grown IIC results showed temperature dependence. At room temperature $B_0 \sim 1.1 \times 10^{-4}$ MPa\textsuperscript{-1}\cdot dpa\textsuperscript{-1} and at 75 °C, $B_0 \sim 2.2 \times 10^{-4}$ MPa\textsuperscript{-1}\cdot dpa\textsuperscript{-1}. The third set of creep data refers to a pre-annealed sample (at 250 °C) irradiated at RT. This sample has a larger grain size, due to annealing, and it contains precipitates. The data for this sample, if correct, are indeed
intriguing, as the strain rates and values of $B_0$ slowly increase with dose and approach the value for $B_0$ for the as-grown sample irradiated at RT. I emphasize “if correct,” since the results are unusual and the experiment was not repeated, owing to accelerator issues. On the other hand, the value of $B_0$ approaches a very reasonable steady state value. With this caveat, the data possibly show that precipitates suppress creep – possibly by providing an effective sink for point defects, or precipitates on the grain boundaries preventing grain boundary sliding. As the irradiation dose increases, these precipitates dissolve, see above, and the creep susceptibility approaches that of the as-grown sample, which also does not contain precipitates. Without additional data, however, this explanation remains speculative, but perhaps it motivates additional work.

With only two data points, it is not possible to test models of IIC, but it is useful to see how these data fit into our understanding of IIC. For example, if I assume the system is in the recombination-limited regime, and creep is due to point defects annihilating at dislocations (SIPA) or at grain boundaries (Ashkenazy mechanism [51]), then the temperature dependence of IIC should follow eq. (4.7). Using the migration enthalpy of vacancies in Al, 0.62 eV, the value of $B_0$ should increase a factor of $\sim 5$ on raising the temperature from RT to 75 °C. On the other hand, if I assume that the system is in the sink-limited regime, IIC is controlled by eq. (4.6), and it should be independent of temperature. The data thus fall within these bounds, but with just two data points, little more can be said.
For comprehensive understanding of intermetallic precipitates behaviour under irradiation, far more work than what was accomplished in this thesis will be necessary. First, many more irradiation temperatures and doses will be required. For example, in the CP regime, very few irradiations temperatures and alloy concentrations were examined, leaving unclear how the solubility and precipitate size depends on these two control variables. This lack of data also prevented a thorough evaluation of the role of grain boundary diffusion in the CP regime. Moreover, along with Sc and Sb solutes, other solutes with different diffusivities and chemical properties in the Al matrix should be explored.
Another thing is that, here, we only studied steady-state, however, engineering materials in real will be exposed from 0 to 100 dpa and changes in reactor temperature will occur. It would therefore certainly be of significance to follow the microstructural evolution as the alloy passes from one state to another. Lastly, this thesis had the initial goal of measuring irradiation-induced creep in Al alloys. Only minimal progress was achieved toward this goal, but its importance has not diminished. I therefore believe this effort should continue. My work on the irradiation effects and thermal creep in Al alloys should help in these future studies.

4.4 Conclusion

In previous chapters, strengthening mechanism and solute diffusivity effects were studied. In present chapter, research on the irradiation effects in Al binary dilute alloys on hardness was performed. The main findings provide strong support for the model of solute strengthening of nanocrystalline Al alloys proposed in Chapter 2 \( \text{viz.} \), dissolution of precipitates by ion irradiation restores the hardness of Al-alloys to that of their as-grown states. This clearly shows that precipitation hardening is far less effective in alloy strengthening in nanocrystalline materials than is grain boundary strengthening.

The study on compositional patterning provides new information for understanding CP in nanocrystalline alloys. First, it provides direct evidence that CP does occur in two-phase alloys containing compound precipitates; this had previously been in doubt. The APT characterization, moreover, shows that the microstructure in the patterning regime is very complex, with a broad distribution of solute cluster sizes and precipitates sizes. This work also showed that the irradiation induced solubility is greatly enhanced in the CP regime over the equilibrium solubility, which seemingly explains why hardness is very high during irradiation in the CP regime, even though
Al₃Sc precipitation is observed. This does not occur during thermal annealing.

Also, we demonstrated reliable IIC measurement methods, based on the bulge test during heavy ion irradiation. Due to the breakdown of the MRL HVE accelerator, I could not finish the study of IIC, but I did find that pre-existing precipitates phase in Al appear to reduce the irradiation creep compliance. I also “may” have shown that dissolution of these precipitate by irradiation increases the creep rates, which is opposite of what occurs for the hardness, but this question remains for future efforts.

4.5 References


4.6 Supplementary Study: In-Situ TEM Study Of Irradiation Induced Creep

Due to the breakdown of the MRL Van de Graaff accelerator, I attempted *in-situ* IIC tests on AlSc$_{1.1}$ at Sandia National Laboratories [1], but using a different experimental method. While this effort is very preliminary, the findings could be useful for future research.

**Sample Preparation**

The irradiation creep tests using a cantilever beam geometry were performed inside of TEM. The method was recently published by ref. [2], and therefore only briefly described here. The method basically employs a three-point bend test, whereby a nanoindentor is used to press at the center of a nanobeam. The difficulty of this arrangement is measuring the temperature during the test. For creep tests the temperatures are too low to use the lattice parameter for this purpose, and hence, electrical resistivity is employed. Supplementary Fig. 4.1 illustrates the scheme to connect 4 point electrical leads to the test beam. After getting 4 pads, nanocrystalline Al alloys films were deposited near to the 4 lines using same method for film growth. Thinning down the sample is followed process. To reduce the time for next step-Focused Ion Beam (FIB), the film deposited side was polished below 30nm. Next, 4 pads and the film are connected using gold (Au) wire bonding at a Vespel® mechanical test specimen stage. These wires make connection between films the 4 pads and the specimen holder, thus enabling the resistivity measurements.
Supplementary Fig. 4.1 (a) The schematic of fabrication process of beam for IIC. In this study, Al alloy films are grown instead of HEA in the given figure [3] (b) fabricated 4 Au pads (lines) and the Pt lines connect Au pads and samples.

For the irradiation creep measurement performed in the transmission electron microscopy, cantilever beam shape film structures are fabricated using Helios 600i Nanolab FIB instrument. After finishing the process, the samples were mounted on the custom Vespel® mechanical test stage using heat durable silver paint. This stage was attached to the holder vertically and the “Si side” was polished with a distance ~ 10 - 15 μm with a 30 kV Ga ion beam. The ion beam current is gradually reduced from 2 nA to 21 pA to obtain desired thickness. At the last polishing step, the surface is cleaned with ~ 21 pA ion beam. To make the bridge structure, the sample stage is now
attached horizontally and polished to a trench shape with a current of ~ 30 pA. The final shape of the beam can be observed in Fig. A2 with length ~ 10 μm, width ~ 2 μm, and thickness ~ 550 nm.

Supplementary Fig.4.2 SEM of a microbeam for in-situ TEM irradiation test

**Measurement**

For the irradiation induced creep measurement with the beam bending method, a 6 MeV tandem accelerator, connected to a customized JEOL 2100LaB6 TEM, was used for *in-situ* ion irradiation. In this in-situ, ion irradiation TEM (I^3TEM), the sample is positioned with 20° tilt angle about the sample rod axis towards the ion beam line. This setup makes ion beam and TEM electron beam reach the specimen at the same location. The beams were irradiated with 1 MeV Al ions.

To measure the temperature effects on the irradiation induced creep, a 50 μm diameter size infrared laser, with wavelength 1064 nm was employed as a heating source. To investigate the deformation behavior as well as the strength, a Bruker PI–95 ECM picoindenter with diamond flat punch in Supplementary Fig. 4.3, was used. Previous work [4-7] had already verified that this is a reliable technique to measure mechanical behavior. In this study, a diamond punch approached the sample stage, and after contact the load was held constant for a certain interval. After ~ 300 s, the stress was increased. Like other indentation methods, an air indent is performed beforehand. The mechanical response (i.e-creep strain) was measured with ~ 5 nm displacement and ~ 1 μN load
sensitivities. Initially, the 4 leads were supposed to measure resistivity (temperature), however, due to the improper sample mounting, the electrical connection failed. Nevertheless, the relative temperature could be “roughly” approximately from the laser power using a calibration previously obtained. The data from the bulge test, both thermal and irradiation creep, provides an estimate of the absolute temperature. The sample’s deformation behaviors were also recorded as video image files. In order to exclude various artifacts, the creep deformations were determined directly from the acquired TEM images.

Supplementary Fig. 4.3 Bruker PI95 Pico indenter holder [3]

Results

Irradiations were performed using 1 MeV and 5.5 nA Al ion beam. Supplementary Fig. 4.4 shows diffraction data during in-situ measurement. As laser power increases, the innermost ring diameter increases and at SI 120 the diameter of innermost ring is the largest, i.e., smallest lattice spacing. Since SI 120 represents the highest temperature, this presumably is due to Sc coming out of solution, indicating the specimen temperature is greater than ~ 350 °C.
Supplementary Fig. 4.4 Diffraction rings at different laser power

The results for IIC are shown in Supplementary Fig. 4.5(a-c). TEM images in Supplementary Fig. 4.5(a) provide a typical example showing how the microbeam indentation creep tests are performed. The image on the right, #4, was obtained after the test and the deformation (beam bending) is clearly seen. The illustrated Supplementary Fig. 4.5(b) is the corresponding strain behaviors according to the time for samples tested at different stresses and laser power (temperatures) between SI 0 – SI 120. The higher laser power (temperature) results in higher strain rates as expected. During the measurement, stress was increased several times and corresponding points can be found as sudden ‘strain rate jumps’ in Supplementary Fig. 4.5(b). At SI 120, a dramatic increase in the strain is observed at ~ 400 s. Although, there was no rupture after the measurement, a crack was observed at the center of the beam, as seen in Supplementary Fig. 4.6. Based on this, the steep strain may be related with a crack and the combination of this temperature and pressure induce deformation quickly. A plot of strain rate versus stress is shown in Supplementary Fig. 4.5(c). The beam tested at room temperature shows very low strain rates. Again, high laser power results in a high strain rate.
Supplementary Fig. 4.5 (a) Beam deformation sequence of beam #10L_SI 80 (b) strain vs time (c) strain rate vs stress. SI X refers to power level.

Supplementary Fig. 4.6 TEM images sequence of beam #12L with power level SI 120

HRSTEM imaging of irradiated AlSc$_{1.1}$ was conducted to observe more detailed features of the grain structure and the grain interior after irradiation. STEM images and the SAD patterns, which were taken in JEOL 2100 BF TEM after the creep test, are shown in Supplementary Fig.
4.7(a). The grain size is $\sim 446 \pm 40$ nm, which is far larger than other AlSc$_{1.1}$ binary alloy discussed in this work (for the sample annealed at 350 °C for 1 hour, the size is $\sim 200$ nm), and thus it implies that the temperature was significantly above $\sim 400$ °C, which is already close to 2/3 the melting temperature of Al. Thus, I can conclude that this sample was in the macroscopic phase separation regime, i.e., dominated by thermal diffusion. In Supplementary Fig. 4.7(b), the magnified HAADF STEM image, more detailed microstructure inside of grain was observed. Unlike the other AlSc$_{1.1}$ samples, most of precipitates are now observed in the grain interior, which is due to the much larger grain size and higher temperatures. Also due to the large grain size, and irradiation, a high density of dislocation loops are now formed as indicated by the white thin lines in Supplementary Fig. 4.7(b).

Supplementary Fig. 4.7 AlSc$_{1.1}$ after microbeam IIC (a) STEM image and SAD (b) magnified STEM

Calculated creep compliances ($B_0$) using eq.(4.10) are provided in Supplementary Table 4.1. At room temperature, denoted as SI 0, $B_0$ is quite low, as expected. Since no other exact temperature information is available, I can only comment that (i) the creep tends to increase with
increasing temperature (power) and that the order of creep compliance, \( \sim 10^{-4} \text{dpa}^{-1} \cdot \text{MPa}^{-1} \), is in a very reasonable range. Recall the values from the bulge test were very similar. At SI 120, the compliance increased a factor of 10 compared to that obtained by the bulge test at 75 °C, indicating that it is dominated by thermal creep, although no thermal creep tests, in absence of irradiation were performed to determine whether the irradiation had any effect on the creep rate.

<table>
<thead>
<tr>
<th>Laser Power (SI)</th>
<th>( Bo \ (\text{DPA}^{-1} \cdot \text{MPa}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4R 100</td>
<td>( \sim 5.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>5R 80</td>
<td>( \sim 2.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>9L 0</td>
<td>( \sim 7.3 \times 10^{-5} )</td>
</tr>
<tr>
<td>10L 80</td>
<td>( \sim 3.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>12L 120</td>
<td>( \sim 1.8 \times 10^{-3} )</td>
</tr>
</tbody>
</table>

Supplementary Table 4.1 Creep compliance

In spite of lack of accurate temperature information, this study is useful for steering future work and highlighting some technical issues. The primary findings of this study on the irradiation induced creep behaviors of dilute Al-Sc alloy can be summarized as follows:

1) The bulge test and cantilever beam methods for measuring irradiation-induced creep are complementary. The bulge test is more accurate and simpler to perform and presently more accurate than the cantilever beam method, but it is restricted to thin films, low stresses and a maximum temperature of \( \sim 300 \) °C. The cantilever beam method can employ either thin films or bulk specimens, operate high stresses and temperatures up to the melting temperature.

2) The irradiation induced creep compliance determined at stresses in excess of 100 MPa are in rough agreement with those found by bulge testing at \( \sim 10 \) MPa, showing the low-stress
creep mechanisms are operative to very high stress levels.

4.6.1 References


CHAPTER 5

CONCLUSIONS AND PERSPECTIVES

This thesis work has focused on understanding behaviors of nanocrystalline materials for developing alloys that are dimensionally stable in extreme environments, specifically focusing on dilute supersaturated nanocrystalline binary Al alloys systems which have intermetallic precipitates phases. While nowadays researchers are focusing on precipitated nanostructured alloys due to improved properties [1-3] and high resistance to extreme conditions: irradiation, high temperature [4] and these past works have not been sufficient to understand why these materials show novel properties or how they will behave under irradiation. This research, therefore, aimed to expand data base about nc materials and to provide insight into fundamental mechanisms.

Firstly, this dissertation investigated the strengthening mechanism of nanostructured Al binary alloys through microstructural and micromechanical characterization techniques. To elucidate strengthening mechanisms, four different binary alloys, Al-Sc, Al-Sb, Al-Cr, and Al-W, were selected for the study and thermal annealing was performed systemically on these samples to evolve the microstructure. Extensive TEM characterizations were conducted on these many samples. To correlate microstructural evolution to strengthening, nanohardness measurements on these alloys were carried out using a triboindentor. Results indicated that usual solid solution strengthening is not governing strengthening in these Al alloys, rather it is solute in the grain boundaries that causes the strengthening. On low temperature annealing, before solute in the grain interior comes out of solution, the alloys soften due to grain boundary precipitation. It was also observed that during the softening process at low temperatures, the grain size remained constant, but during high temperature annealing, the hardness remained constant while the grain size
increased. The strengthening in nc-Al alloys, indeed, behaves very different from larger grained Al alloys.

This dissertation also investigated thermal creep response of nc binary alloys as part of the strengthening studies. Since creep only occurs at elevated temperatures, even for nanocrystalline Al alloys, the thin film samples were pre-annealed to assure a stable microstructure during the series of creep measurements. A modified thin-film bulge test technique was employed as the creep measurement apparatus. The creep response is consistent with that of diffusional creep, specifically, Coble creep. The observed creep rate varied linearly with the applied stress and consistent with a $d^{-3}$ dependence ($d$ = grain size). Also, the effectiveness of heat treatment for improving creep resistance confirmed by comparing as grown Al-Sc and annealed Al-Sc. The observed activation energy ~ 0.4 - 0.5 eV, provided strong evidence that grain boundary diffusion is responsible for creep deformation in these candidate alloy systems. The work also showed that solute additions, even very dilute, a few percent or less, has a strong influence on reducing creep rates. Notably, W additions, which remained in solution during the creep test, was most effective, reducing the creep rate more than an order of magnitude compared to pure Al. Sc and Sb additions did not remain in solution during the creep tests and were less effective in suppressing creep. While the experimental data indicates that the thermal creep mechanism is Coble creep, the magnitude of the observed creep rate is not the same order of magnitude as theoretical predictions, although uncertainty in the grain boundary diffusion coefficients prevents an accurate comparison. Clearly, much work remains to be done to gain a full understanding. Furthermore, if creep measurement on as-prepared samples are performed, it would offer a good comparison to work conducted on annealed alloys because thermal annealing obviously affects creep response.
Lastly, this thesis investigated how irradiation effects the structure and properties of nc alloys. To answer this question, ion irradiation was carried out, specifically focusing on Al-Sc. An important finding is that irradiation contributes to the dissolution of pre-existing Al$_3$Sc precipitates into the matrix and as a consequence, it induces strengthening in the alloy. This clearly showed that precipitate hardening is far less important in nanocrystalline alloys than is grain boundary strengthening from alloy additions. Pre-annealed Al-Sb exhibited very similar behavior. These observations both confirmed and strengthen and the conclusions concerning strengthening mechanisms developed in Chapter 2. This study also shed new light on the phenomenon of irradiation-induced self-organization. First it demonstrated that self-organization, or compositional patterning, can occur in a nanocrystalline alloys containing compound precipitates. My finding that in the patterning regime, precipitates formed mostly at the grain boundaries, and at temperatures when grain boundary diffusion becomes significant, even in absence of irradiation, suggests that patterning in these materials may be a consequence of a competition between ballistic mixing and grain boundary diffusion (possibly enhanced by irradiation). Such behavior had not previously been considered in the literature. Lastly, initial studies of irradiation-induced creep were begun and preliminary measurements were performed. While it could be demonstrated that the creep apparatus could be a valuable tool in measuring creep ion samples under irradiation, and some interesting observations on the effect of precipitates on irradiation induced creep rates in nanocrystalline alloys were found, the failure of the MRL HVE accelerator prevented the study from reaching definitive conclusions.

In conclusion, this thesis explained the strengthening behavior of nc and irradiation effect on these alloys for designing reliable materials. However, not all parameters were investigated and there are still more works that could be done especially under irradiation. This work represents an
important step in finding alternative materials for the reliable operation in extreme environmental applications, such as generation IV nuclear power plants.

5.1 References


APPENDIX

SUPPLEMENTAL VIDEO FILE

The supplementary file, “AlSc1.7_cluster positions annealed at 180C.avi”, shows reconstructed an APT tip image of pre-annealed AlSc\textsubscript{1.7} after annealing at 180 °C.

**AlSc1.7_cluster positions annealed at 180C.avi**: This file corresponds to APT results of AlSc\textsubscript{1.7} in Figs. 2.26-28.