EXPERIMENTAL CHARACTERIZATION OF DEFORMATION MECHANISMS IN MAGNESIUM AND THE EFFECT OF ALLOYING ON DUCTILITY

by

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Abstract

Magnesium (Mg) is a promising structural material with low density and high specific strength. The use of wrought Mg products has been stunted by poor formability, which is related to underlying anisotropic deformation mechanisms. The number of independent easy glide basal slip systems does not satisfy the Von Mises criterion, and activation of \(<c+a>\) slip and twining holds the key to creating formable Mg.

The current study provides experimental observations of the deformation mechanisms activated in commercial and developmental Mg alloys. \(<c+a>\) dislocations in pure Mg were observed to non-conservatively dissociate onto the basal plane, resulting in a sessile configuration. By contrast, the dislocations in AZ31 do not dissociate, and the dissociation in Mg-3Er is also much smaller than for pure Mg. HREM images revealed that the suppressed dissociation may be related to the spreading of partial dislocation cores on pyramidal planes. The more compact \(<c+a>\) dislocations maintain their mobility and lead to improved ductility.

Extension twinning is another significant deformation mechanism that affects the ductility of Mg. Observations made in this study indicate that the strain concentration at the tip of a
ABSTRACT

twin can be released by the formation of dislocations. The high density of dislocations observed in and around twin tips indicate that twin-dislocation and twin-GB interactions play an important role in twin propagation.

For Mg-0.1Ca, texture weakening was observed to be a critical mechanism that improves ductility. Ca was observed to segregate at high-angle grain boundaries, which retards GB mobility and activates the nucleation of static recrystallization in deformed grains. The GB energy of the decorated boundaries are less dependent on misorientation, which enables the growth of randomly orientated grains and weakens the texture.

In total, investigations of the deformation mechanisms in hot-rolled polycrystalline pure Mg, AZ31, Mg-3Er and Mg-0.1Ca presented in this thesis have elucidated the mechanisms that govern ductility. Control of $<c+a>$ dislocation cores, deformation twinning, and texture reduction highlight promising paths for the design of ductile Mg alloys.

Advisor: Professor Kevin J. Hemker

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1.1 Motivation

The first discovery and use of magnesium (Mg) can be dated back to ancient Greece, but the first production was reported in 1808 by Sir Humphrey Davy and commercial production in larger amounts started in Germany by 1886 [1]. As Mg is the “lightest structural metal”, 75% lighter than steel and 33% lighter than aluminum, and the 8th most abundant element in the earth’s crust by mass, Mg is a promising structural material for the automotive industry. The vehicle market is rising due to the booming global economy, and stringent emission and fuel economy regulations are driving the market of lightweight materials for the automotive industry from the current 89 billion dollars to an estimated 158 billion dollars by 2027 at a compound annual growth rate of 7.4% [2]. The increasing demand for lightweight materials is a historic opportunity for growth in the Mg industry. The annual gross production of Mg has been steadily increasing (Figure 1.1); however, the increased consumption of Mg for structural applications in industry ranges from about 20%
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to 50%, which is dramatically lower than the proportion of aluminum (Al, >90%) [3] and iron (Fe, >99%) [4]. The largest portion of Mg is used for Al alloying and as a manufacturing agent (e.g. desulfurization in steel and as a reducing agent for titanium, zirconium, hafnium, etc.). Of the limited proportion used in structural applications, cast Mg products are the great majority (~90%). Moreover, the use of Mg in the automotive industry has remained constant over the last twenty years with the content of cast Mg components per vehicle lower than 0.3% of the total weight (Figure 1.2). The most significant factor that limits the wider application of wrought Mg and Mg alloys for structural use is the its low formability at ambient temperature.

Figure 1.1: Annual gross production and the main consumptions of Mg; the numbers indicates the proportion of the consumption partition (data from USGS).

Pure polycrystalline Mg fails in a brittle manner after limited deformation at ambient temperature [5]. In contrast to the substantial formability of cold-rolled Al, 100 µm thick
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Al beverage can walls and Al foil are everyday items, cold-rolled polycrystalline pure Mg fractures after only ~30% reduction in thickness [6, 7]. The brittleness of pure Mg can be overcome by forming at an elevated temperature (>400°C) [8], but a strong basal texture forms during hot forming [9]. The mechanical properties of strongly textured materials are anisotropic and generally have low ductility and are not commonly employed as structural materials. Therefore, the wider use of structural Mg will require reduction in anisotropy and improvement of ductility and formability.

Figure 1.2: Material content per vehicle (data from [10])

To develop formable Mg, a variety of approaches have been attempted, including advanced processing techniques [11], directional precipitation [12, 13] and alloying design [14], amongst which, the development of Mg alloys has drawn the most attention (Figure 1.3).
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The addition of rare-earth (RE) elements have been shown to dramatically improve the room-temperature formability and simultaneously weaken the forming texture [15]. However, the mechanisms by which the properties of Mg are enhanced by the addition of RE and RE-like elements still need further experimental investigation. This dissertation describes the efforts to decipher the fundamental mechanisms of ductility improvement and texture weakening in Mg alloys. Particular attention in this dissertation has been focused on the influence of alloying on the microstructure, including dislocation behavior during deformation and recrystallization kinetics during annealing, both of which determine the macro-scale properties.

Figure 1.3: Approaches that have been employed to produce ductile Mg alloys. The dislocation behavior and texture weakening mechanisms will be focused in this thesis.
1.2 Background

The development of Mg alloys with improved ductility requires an understanding of the inter-dependent relationships between microstructure, processing and mechanical properties (Figure 1.4). The key to linking the three are the deformation mechanisms of materials. In metallic materials, the deformation is accommodated by the behavior of defects. The defects are categorized as either 0-D point defects (e.g. solute atoms or vacancies), 1-D line defects (e.g. dislocations) or 2-D planner defects (e.g. stacking faults (SF) and twins). The dominant deformation mechanisms of Mg are dislocations and twinning. The concept of alloy design is to investigate the influence of the alloying element on the deformation mechanisms and to optimize the composition to obtain the desired properties.

Figure 1.4: Key to understand the inter-dependent relationship between microstructure, processing and property of materials science, deformation mechanism.
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1.2.1 Deformation mechanisms of Mg

Crystalline Mg forms a hexagonal-closed-packed (HCP) structure, with lattice parameters of $a = 3.209\text{Å}$ and $c = 5.211\text{Å}$. The $c/a$ ratio of 1.624 is slightly less than the ideal $c/a$ ratio of 1.633 [16]. The available deformation modes include $<a>$ dislocation slip on the basal, prismatic or pyramidal planes, $<e + a>$ dislocation slip on pyramidal planes (pyramidal I \{10ar{1}1\} or pyramidal II \{1\bar{2}12\}), extension twinning \{10\bar{1}2\}<10\bar{1}\bar{1}>$ and compression twinning \{10\bar{1}1\}<\bar{1}012> (Figure 1.5).

![Deformation mechanisms and unit cell of HCP Mg](image)

**Figure 1.5:** The deformation mechanisms and unit cell of HCP Mg. The first row shows dislocation slip modes and the second row for twinning modes.
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1.2.1.1 Dislocation slip systems in Mg

In HCP materials, \(<a>\) slip dominates deformation at room temperature and the activation of basal or prismatic plane slip is governed by the relative magnitude of stacking fault energy (SFE), \(\gamma\), on the two planes. In Mg, the SFE on the basal plane is 34–54 mJ/m², which is dramatically lower than that of the prismatic plane (129–218 mJ/m²) [17]. Therefore, room-temperature deformation is dominated by basal \(<a>\) slip [16], with Burgers vector \(b = <a> = \frac{1}{3} \langle 11\overline{2}0 \rangle\). However, the basal \(<a>\) dislocation provides only three independent deformation modes that only allow for strain along the \(<a>\) axes [18], and this does not satisfy the von Mises criteria of five independent deformation modes for plastic deformation. The limited number of easy-glide slip systems in Mg underpins the low plasticity during conventional deformation. \(<c>\)-axis deformation cannot be accommodated by basal \(<a>\) dislocation due to the low Schmid factor, and can be primarily accomplished by pyramidal \(<c + a>\) dislocation slip or twinning.

The pyramidal dislocation has Burgers vectors \(b = <c + a> = \frac{1}{3} \langle 11\overline{2}3 \rangle\), which provides five independent slip systems when activated [19-21]. However, the CRSS of these \(<c + a>\) dislocations is approximately 20 times that of the basal slip systems [22] and the \(<c + a>\) dislocation can only be active under \(<c>\)-axis compression on single crystal Mg when the low Schmid factor on the basal plane suppresses the easy-glide basal slip. Reasons for the larger CRSS includes the large spacing of pyramidal planes and the large magnitude of the Burgers vector. Another reason for the low mobility of \(<c + a>\) dislocations is related to
CHAPTER 1. INTRODUCTION AND BACKGROUND

glissile-to-sessile core transformations [19]. The \(<c+a>\) dislocations were observed to
dissociate on the basal plane [22-25] and the SF loops can be in size of hundreds of nm.

The dissociation should be affected by SFE such that increasing SFE leads to less
dissociation. In Mg, it is generally accepted that three types of basal-plane SFs exist,
including two intrinsic SFs, I₁ and I₂, and one extrinsic SF E [26]. The intrinsic SF I₁, also
known as a growth fault, forms by the removal of a basal line followed by slip of \(\frac{1}{3}(10\bar{1}0)\),
leading to the sequence of (Figure 1.6 (b) and (c))

\[ I₁: \ldots ABABAB\mid CBCBCB\ldots \]

The intrinsic SF I₂, or deformation fault, results from shearing of \(\frac{1}{3}(10\bar{1}0)\) in the crystal,
yielding the sequence of (Figure 1.6 (d) and (e))

\[ I₂: \ldots ABABAB\mid CACACA\ldots \]

And the extrinsic SF E forms by inserting an extra C plane, yielding

\[ E: \ldots ABABAB\mid C\mid ABABAB\ldots \]

The SFEs of these three faults have been predicted to be 21, 44 and 69 mJ/m² for I₁, I₂, and
E respectively [27], and the SFE roughly follows \(\gamma_E \approx \frac{3}{2}\gamma_{I₂} \approx 3\gamma_{I₁}\) according to published
results [18, 27-29]. The I₁ intrinsic SF has the lowest SFE. The spacing between glide
dissociated partials is often approximated by \(d \approx \frac{Gb_p^2}{4\pi \gamma}\), giving a value of \(d\) in the range of
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1~3nm. This value is significantly smaller than the partial spacing of basal dissociated \(<c + a>\) dislocation observed in TEM images, which is on the order of hundreds of nm.

**Figure 1.6:** (a) unit cell and lattice parameters of Mg; (b) sliding of layer A above layer B and (c) dissociation of a perfect dislocation to form \(I_1\) SF; (d) sliding of layer B and above layers and (e) dissociation of a perfect dislocation to form \(I_2\) SF.

Wu and Curtin [19] suggested that a \(<c + a>\) dislocation core is unstable on the original pyramidal II \(\{1 \bar 2 1 2\}\) slip plane. Their molecular dynamics (MD) simulation results suggest that the \(<c + a>\) edge dislocation transforms to lower-energy partials dissociation on the basal plane by \(1/3(1123) \rightarrow 1/6(2023) + SF + 1/3(0223)\) via a thermally activated process (\(\geq 500\) K). The two partials are immobile and obstruct the motion of other dislocations [23] because the Burgers vectors are out of the slip plane. As a result, the dissociation transforms the \(<c + a>\) edge dislocation to sessile configurations, which result in low mobility of these dislocations and leads to high hardening under \(<c>\)-axis compression. However, the core transformation was set up to start from two half \(<c + a>\) dislocation on pyramidal II slip
plane, which was observed by Kumar et al. [30] at a twin boundary. No direct experimental evidence of the pyramidal II SF has been reported in the pristine Mg [31], but the $I_1$ intrinsic SF has been observed experimentally [22, 23, 31, 32] and simulated computationally [19, 33]. Moreover, the size of the SF loops they predicted is only several nanometers in width, which is dramatically smaller than that was observed experimentally.

Geng et al. proposed another mechanism that the formation of SF loops is related to the movement of the super jogs [31]. The super jogs were recently observed in MD simulation by Srivastava et al. [34] and in-situ TEM characterization by Zhang et al. [35]. Super jogs form due to an inhomogeneous shuffling processes and the dragged out dipoles from by the motion of screw dislocations sometimes can create and leave behind debris and long faulted loops [34]. This super jog induced fault formation was suggested to be an athermal process that can occur at a large range of temperature (0-600K). The SF loops on the basal plane can exert a strong drag effect on dislocation glide and result in strong hardening. However, the super jog induced loops are predicted to be thin and long with no apparent growth with loading or temperature, which contradicts the large loops seen in TEM observations.

The observation that large dislocation loops formed by $<c + a>$ dissociation on the basal plane have a Burgers vector out of the resident plane implies that climb should be involved in the growth/collapse of the loops [31]. The ‘climb-like’ transition is atomistically complicated, involving significant atomic motion within the core region, but does not involve vacancy or interstitial diffusion from the surrounding bulk [19]. The
CHAPTER 1. INTRODUCTION AND BACKGROUND

nonconservative ‘climb-like’ dissociation should be thermally activated, and room temperature may be high enough to generate the distant partials.

1.2.1.2 Deformation Twinning

In addition to \(<\mathbf{c} + \mathbf{a}\>\) dislocations, deformation twinning is another mechanism that accommodates non-basal plastic deformation. It is also an important process for \(<\mathbf{c}>\)-axis straining when easy-glide basal slip is not available. The twinning systems that have been observed most frequently include \{10\overline{1}2\} extension twinning, which rotates the crystal by 86°; \{10\overline{1}1\} and \{10\overline{1}3\} contraction twinning, which rotates the crystal by 56° and 64° respectively; and \{10\overline{1}1\} – \{10\overline{1}2\} and \{10\overline{1}3\} – \{10\overline{1}2\} double twinning, which rotates the crystal by 38° and 22° respectively. All of the crystal rotations introduced by twinning are along a \langle 1\overline{2}10 \rangle\) direction.

Twinning plays an important role in HCP metals, especially under high strain-rate deformation and at low temperatures when dislocation glide is frozen. However, twinning can also be activated in Mg under quasi-static deformation. The \{10\overline{1}2\} extension twinning dominates under \(<\mathbf{c}>\)-axis tension [36-38], and contraction twins are generated under \(<\mathbf{c}>\)-axis compression [39-41]. Extension twins can nucleate and grow to take over the original orientation of the whole grain under sufficient deformation, which leads to negligible strain hardening (see Figure 1.8). In contrast to extension twins, contraction and double twins display a submicron size needle shape with no apparent thickening. Double twinning is also frequently observed with formation of extension twin inside the contraction twins. The twin volume fraction of contraction and double twins increases much less with strain than
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extension twins, presumably requiring further nucleation events and yielding strain hardening [39]. The contraction and double twins also act as favorable sites for void and crack nucleation [42] and make little contribution to ductility.

The nucleation of extension twins at grain boundaries (GBs) in single crystal Mg is believed to rely on the transformation of grain boundary defects (GBDs) under stress into the required number of twinning partials to create a twin nucleus. The GB nucleation depends on the tilt angle of the GB and the GBD state [43-47]. The nucleation and propagation of twins are predicted computationally to be related to twinning dislocations and disconnections (TDs) [48-54]. The simultaneous nucleation and glide of multiple layers (believed to be 2 layers) of TDs on the twinning plane generates a twin nucleus, and the motion of TDs under further loading propagate the twin nucleus into the matrix.

Another mechanism of twin nucleation and propagation, atomic shuffling, is also described by simulation [55-57]. The process of shuffling is similar to that of TDs but instead of the formation of definable dislocations at the twin boundaries, local atomic shuffling reconstructs the twin lattice from the parent matrix on the basal/prismatic plane interface [55, 57]. Even though the nucleation and propagation of twinning in HCP Mg is still attracting attention, all the hypotheses are based on simulations with very little direct experimental evidence provided. The high rate and small scale of the localized transfer of atoms from matrix to twin makes it very difficult for experimental characterization.

The nucleation of twinning in polycrystalline Mg is also influenced by the interactions between GBs and twins [58-60]. The intersection of twins and GBs produces a stress
concentration and acts as a source for defects. Under continued straining, the growth of the twin exacerbates the strain localization and can possibly stimulate the formation of another twin on the other side of the GB, appearing as if the twin has propagated across the boundary. This process is termed as adjoining twin pairs (ATP). The formation of ATP is determined by the misorientation of the GB and anisotropy of the material. The GB misorientation has a cutoff angle for twin transmission which is reported to be $50^\circ$ in Mg [61], and the increase in crystal plastic anisotropy enhances the probability of twin transmission [62].

1.2.1.3 Anisotropy of deformation mechanisms

The low symmetry of the hcp crystal structure results in anisotropic deformation in Mg. The critical resolved shear stresses (CRSS) of dislocation slip and the activation stresses of twinning in Mg are listed in Table 1.1. The contraction twin includes $\{10\bar{1}1\}$ and $\{10\bar{1}3\}$ systems and the activation stresses for both systems are estimated to be close in the range of 100-150MPa [63]. The CRSS of basal slip is dramatically lower than that of other deformation systems so it dominates most of the plastic deformation, but basal slip makes no contribution to $<$c>-axis strain. $<$c>-axis tensile strain can be accommodated by extension twins, which have about six times higher activation stress than that of basal slip; the $<$c>-axis compressive strain is accommodated by $<$c + a> slip and contraction twinning, with the former dominant due to its lower CRSS.
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Table 1.1: Critical resolved shear stress (CRSS) of slip and twinning systems in Mg at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>Basal slip</th>
<th>Prismatic slip</th>
<th>&lt;c + a&gt; slip</th>
<th>Extension twin</th>
<th>Contraction Twin</th>
</tr>
</thead>
<tbody>
<tr>
<td>CRSS (MPa)</td>
<td>0.5-2</td>
<td>17.5</td>
<td>40-80</td>
<td>12-18</td>
<td>125</td>
</tr>
<tr>
<td></td>
<td>[22, 64, 65]</td>
<td>[66, 67]</td>
<td>[22, 68]</td>
<td>[64, 69]</td>
<td>[63]</td>
</tr>
</tbody>
</table>

Figure 1.7: Inverse pole figures (IPFs) and pole figures (PFs) of (b) ND, (c) TD and (d) RD acquired from an as-rolled AZ31 Mg alloy with 50% reduction in thickness.

One significant consequence of the anisotropic deformation mechanism in Mg is the formation of strong texture after forming [70-72]. For example, strong basal texture is formed after hot rolling with the <c>-axis along and <a>-axis perpendicular to the normal direction (ND), as shown in Figure 1.7. More details of the basal texture will be discussed.
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in Section 1.2.2. The stress-strain curves for compression tests on hot-rolled AZ31 with strong basal texture are shown in Figure 1.8. The ND compression is a ‘close-to-<c>-axis’ test, which activates <c + a> dislocations; and the TD compression is dominantly <a>-axis compression, which activates extension twins. Due to the high CRSS of <c + a> dislocations and consistent with a glissile-to-sessile transformation of the dislocation core, the ND compression test shows a high yield strength, large initial strain hardening and a low strain to failure. On the contrary, the TD compression curve illustrates an obvious yield point and more modest hardening after yielding, consistent with the nucleation and growth of extension twins. The extension twins can only contribute up to 6% strain in theory. The extension twins rotate the orientation the matrix by 86° (close to 90°), and consequently, after all of the original material is twinned, the TD compression is now a close-to-<c>-axis compression, and subsequently the last stage of the TD compression curve shows an apparent strain hardening and strength to failure identical to that of ND compression. As a result, the ND and TD of hot-rolled Mg alloy exhibit anisotropic mechanical properties.

In summary, the anisotropy of deformation mechanisms in Mg results in the low formability at ambient temperature, strong texture after forming at elevated temperature and strongly anisotropic mechanical properties of the formed materials, all of which limits the wider application of Mg.
1.2.2 Texture

Generally, Mg and Mg alloys develop basal texture during plastic forming. The mechanism for the texture formation and evolution during processing has been subject to a number of studies [6, 73-78], but due to the complicated deformation geometry and the low crystal symmetry, the mechanism for the formation of basal texture remains an open question.

1.2.2.1 Origin of texture

In principle, crystallographic texture can be formed or changed during solidification, deformation, recrystallization, and phase transformations. Since Mg alloys do not undergo massive phase transformations or a change of crystal structure, and solidification textures are usually weak except for special processing conditions, the consideration can be confined to textures produced by either deformation or recrystallization [79].
CHAPTER 1. INTRODUCTION AND BACKGROUND

The deformation texture can be intuitively attributed to the strong anisotropy of the deformation mechanisms in Mg that the CRSS of basal slip is significantly lower than the other. The ultimate deformation texture can be effectively simulated by manipulating the relative CRSS or activation stress of dislocation slip and twinning systems in Mg [73, 74, 79]. When the relative CRSS of different deformation mechanisms changes, various textures can result. The strain compression textures for HCP materials, including basal slip, prismatic slip, \(<c + a>\) pyramidal slip and \(\{10\bar{1}2\}\) extension twinning with various ratios of CRSS were simulated and are shown in Figure 1.9 [79]. The starting texture of the simulations was random, and the total thickness reduction was 40%. If basal slip is dominant, a basal texture forms, which is similar to the texture that was observed in hot-rolled Mg. When the ratio of other deformation systems versus basal decreases and
multiple deformation systems are activated, the basal texture disappears and split of peaks forms. This splitting texture fiber is obtained by equal channel angle extrusion (ECAE) when \(<c + a>\) dislocations are activated [74]. However, thermomechanical processing of Mg alloys is usually performed at elevated temperatures to improve workability, and therefore dynamic recrystallization (DRX) must also be considered.

DRX can be categorized, based on the nucleation and growth characteristics, as continuous DRX (CDRX) and discontinuous DRX (DDRX) [80-82]. CDRX proceeds by a recovery process with dislocation rearrangement to form subgrains and the continuous absorption of dislocations into low angle grain boundaries (LAGBs). This leads to the formation of high angle grain boundaries (HAGBs) and thus new DRXed grains. In contrast, DDRX is a process with nucleation at serrated HAGBs by bulging and grain growth through GB migration. The DRX process is largely controlled by deformation conditions such as temperature and strain [83]. It has been stated that CDRX dominates during the hot forming process in Mg [9, 81, 84]. However, as I will show in Chapter 6 that DDRX also exists during hot rolling, but it is overwhelmed by CDRX and grain growth due to the high mobility of boundaries at elevated temperatures. Although the texture formation is related to recrystallization and to a lesser extent, deformation, the exact mechanism in polycrystalline alloys is complicated due to the influence of solute atoms, precipitates and deformation localization.
1.2.2.2 Influence of deformation localization

The main deformation localization mechanisms in Mg during hot forming are shear bands and deformation twins. In shear bands, the dislocation density is much higher. Similarly, twinned areas that reorient off the matrix are also favorable sites for dislocation nucleation. The constrained dislocations inside the twin and the stress concentration introduced by the dislocation pile-up from the matrix leads to relatively higher dislocation density around the twinned area than in the far-away matrix. As a result, the twin and shear band regions possess higher stored energy and are thermodynamically favorable for recrystallization. Accordingly, the nucleation from deformation twins and shear bands are termed as deformation twin induced nucleation (DTIN) [85-87] and shear band induced nucleation (SBIN) [88, 89], respectively.

Shear bands and deformation twins can facilitate texture weakening. Both cut the texture fiber and the nucleated recrystallization grains are more likely to have a random orientation as compared to the textured matrix [75, 80, 90]. However, the effect of DTIN and SBIN on texture weakening is generally limited. One reason is that the small size of the deformation twins and shear bands constrains the volume fraction of the recrystallized grains. The other possibility is that the nucleated grains with random orientation are not likely to grow at elevated temperature because GB energy in HCP Mg is dependent on misorientation angle, and the recrystallized grains surrounded by GBs with large misorientation are not energetically favorable to grow [76, 84, 91].
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1.2.2.3 Influence of solute atoms

The addition of solute atoms in Mg can change the relative CRSS values of the different deformation systems. For example, rare-earth (RE) alloying can possibly increase the activity of \(<c+a>\) dislocations (see Section 1.2.3.2) and consequently weakens the rolling texture or stretches the pole figure contour along the rolling direction.

In addition, some alloying elements like RE and Ca can segregate at GBs and influence the nucleation and growth of recrystallization. The decorated GBs experience solute drag and which suppresses DRX [92, 93] and slows down the formation of texture during forming. The GB segregation of solute atoms can also level out the dependence of GB energies on misorientation encountered in traditional Mg alloys, and thus promote equal growth opportunities for recrystallized grains [76, 84, 91]. Both processes introduced by GB segregation can weaken the texture.

1.2.3 Mg alloys

The research and development of Mg alloys for practical industrial applications have increased worldwide during the past decade [14, 94]. Mg alloys are categorized into cast and wrought Mg based on the processing approach. Even though considerable efforts have been devoted to the development of wrought Mg alloys, more than 90% of structural Mg alloy components are produced by casting, especially by various die-casting processes (Figure 1.1). The development of usable novel wrought Mg alloys remains a holy grail to Mg researchers.
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The alloying elements in wrought Mg alloys can be divided into three categories [95]. First, the elements that improve both strength and ductility of Mg: Al, Zn, Ca, Ag, Ce, Ni, and Cu. Second, the elements that improve ductility and have little effect on strength: Cd and Li. Lastly, the elements that enhance strength but decrease ductility: Sn, Pb, Bi, and Sb. Compared to these conventional alloying elements, RE elements are unique and have given promising results in terms of weaker texture and better formability, which may create a pathway to increased use of wrought Mg alloys.

1.2.3.1 Commercial alloys

The main commercial Mg alloys are the AZ series (Mg-Al-Zn), AM series (Mg-Al-Mn), AE series (Mg-Al-RE), EZ series (Mg-RE-Zn), ZK series (Mg-Zn-Zr), and WE series (Mg-RE-Zr). Commercial cast Mg alloys for automotive applications are the AZ and AM series (e.g. AZ91D, AM50A, and AM60B) due to their excellent combination of mechanical properties, corrosion resistance, and die castability [14]. The main concern of cast components used for engine parts is their creep resistance, which can be improved by adding alloying elements, including but not limited to RE, Sr, or Ca. The development of wrought Mg alloys has mainly focused on plastic deformation behavior, microstructure evolution and the effect of the alloying elements on the mechanical properties. The wrought Mg alloys AZ31, AZ61 and ZK60 have been extensively studied and AZ31 attracts the most attention.

The wrought Mg alloys can be formed by hot/cold rolling [96], extrusion [78], or ECAE [97, 98]. The influence of processing parameters on microstructure and properties has been
systematically studied [78, 99, 100]. In general, elevated temperature facilitates the formability of Mg alloys [97, 101]. Grain refinement can be achieved by increasing the rolling angle and number of extrusion passes [96], and the decreasing grain size results in higher strength and hardness as well as a greater elongation.

With the help of advanced characterization techniques, the influence of deformation mechanisms including dislocation slip and twinning on microstructure evolution and mechanical properties has been investigated. Agnew et al. found that the activity of \(<c+a}\) dislocations is increased in AZ31 alloys [73]. As will be shown in Chapter 3, we have found that the fundamental mechanism for the increased activity of \(<c+a}\) dislocation in AZ31 is related to the fact that the addition of alloying elements suppresses the formation of dissociated \(<c+a}\) dislocations on the basal plane [102].

1.2.3.2 Mg-RE alloys

The influence of various RE additions (e.g. Y, Ce, Gd, La, Er, Nd and Dy) on microstructure and mechanical properties has been investigated thoroughly [103-114]. In general, the addition of RE has been shown to increase the ductility and decrease the strength after secondary processing (e.g. extrusion, hot rolling, etc.), but each RE behaves uniquely and affects the properties to various extents when added as dominant alloying elements. For a RE element with high solubility (Y, Gd, Er and Nd), the strength and ductility increase with increasing content of the RE element. For a RE element with low solubility (Ce and La), hard eutectic phases are formed as a result of the RE addition and this increases the strength but decreases the ductility.
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The generally lower yield strength of the Mg-RE alloys after processing when compared to that of pure Mg is attributed to the weaker texture introduced by the RE (‘RE texture’) [25, 110]. The alloys with RE texture can be strengthened by grain refinement, higher solute content and precipitation [113-115].

In addition to the influence of RE texture on ductility, the activation of multiple slip systems also appears critical. Sandlobes et al. [116] proposed that RE alloying decreases SFE and that activated \textit{I}\textsubscript{1} SF serve as sources for non-basal dislocation nucleation. Wu et al. [117] predicted that RE additions (as well as Ca and Mn) decreases the energy barrier of non-basal dislocation cross-slip, and that the promoted cross slip prevents the \textit{<c + a>} dislocations from dissociating on the basal plane, increasing the mobility of \textit{<c + a>} dislocations and mitigating the anisotropy of Mg alloys and increases the ductility.

1.2.3.3 Mg-Ca alloy

The high cost of RE metals make it almost impossible for Mg-RE alloys to be widely adopted for industrial applications. Sandlobes et al. [5] examined over 60 solute atoms to identify the one that behaved most similarly to yttrium, by comparing atom volume, electronegativity, and bulk modulus, but also compared the cost and radioactivity and cost as a means to find a suitable replacement. The most suitable element on the list turned out to be calcium (Ca). Moreover, Wu et al. [117] predicted that Ca alloying can also assist cross-slip of \textit{<c + a>} dislocations in the competition between glissile-to-sessile dissociation of \textit{<c + a>} dislocations, which resembles the effect of RE alloying. Experimentally, there is a comparable effect between alloying Mg with Ca and alloying Mg with RE on the
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texture weakening [77, 118-120], GB segregation [76, 84, 91-93, 121], grain refinement [122, 123], precipitate hardening [124] as well as the increased overall properties. Therefore, Ca appears to be a promising cheaper substitute for RE in Mg alloying.

1.3 Thesis overview

This thesis work was an interdisciplinary research project undertaken by an international interdisciplinary research team from Johns Hopkins University (Baltimore, USA), Texas A&M University (College Station, USA), Lehigh University (Bethlehem, USA) and Max-Planck-Institut für Eisenforschung GmbH (Düsseldorf, Germany). This project is funded by the National Science Foundation. The primary objective of the project is to address the mechanisms of low formability in Mg and the improved properties in Mg alloys by experimentally measuring and observing the influence of solutes on non-basal dislocation mechanisms, e.g. \(<c + a>\) dislocations and twins, across a variety of length scales. Ultimately, the goal is to utilize the understanding developed from this study to guide alloy design of ductile Mg alloys for a wider industrial application. In order to achieve the defined objectives, a collaborative effort was organized, which utilized the expertise of the three groups: (1) alloy synthesis and processing by Professor Dierk Raabe’s group, (2) multi-scale mechanical testing and microstructural characterization using state-of-the-art TEM techniques, by Professor Kevin Hemker’s group, and (3) high-resolution TEM characterization of dislocation core and GB segregation by Dr. Christopher Marvel’s and Prof. Kelvin Xie’s groups. The synergistic efforts of the teams from diverse backgrounds
CHAPTER 1. INTRODUCTION AND BACKGROUND

working towards a common goal set the stage for an enriching experience in learning and understanding the fundamental mechanisms of Mg alloying and ductilization.

Chapter 1 provides background and outlines the anisotropic deformation systems, mechanisms of texture formation and modification, and history of Mg alloy development.

Chapter 2 introduces the material systems selected for this study and presents the experimental methods employed. Hot-rolled polycrystalline pure Mg, AZ31, Mg-3Er and Mg-0.1Ca Mg alloys were chosen to investigate the influence of alloying on deformation mechanisms. Multi-scale mechanical testing techniques including MTS macro-testing, milli-scale testing and in situ micro-compression testing are discussed in detail. This is followed by the details of sample preparation methods used, including the traditional mechanical polishing, electropolishing, and ion milling processes and the novel focused ion beam (FIB) technique. Microstructural characterization was primarily carried out through use of a scanning electron microscope (SEM) equipped with energy dispersive x-ray spectrum (EDX) and a scanning/transmission electron microscope (S/TEM) including nano beam electron diffraction (NBED), EDX and weak beam dark field (WBDF) imaging.

Chapter 3 presents the effect of Al and Zn alloying on the \(<c + a>\) dislocation behavior in the widely studied commercial AZ31 wrought Mg alloy. The dissociation of \(<c + a>\) dislocations, which is extensively observed in pure Mg, is suppressed in AZ31 alloy. The compact dislocation core increases the activity of \(<c + a>\) dislocations and contributes to the enhanced ductility.


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**Chapter 4** details the influence of a RE element, Er, on the behavior of $<c + a>$ dislocations in a Mg-3Er binary alloy. The addition of Er suppresses the dissociation of $<c + a>$ dislocations. Atomic resolution imaging of the dislocation cores also points to the fact that the Er solute spreads the core of $<c + a>$ partials and thus increases the stability on pyramidal planes. Both the suppression of glissile-to-sessile dissociation on the basal plane and the stabilization of partial dislocation cores on pyramidal planes in Mg-3Er can improve the mobility of $<c + a>$ dislocations and increase the ductility.

**Chapter 5** provides the microscopic characterization of extension twin tips in pure Mg. Elastic strain concentration is observed at the in-grain twin tip but is not as large as expected. The density of dislocations inside and surrounding the twinned area was found to be dramatically higher than that in the matrix far away from the twin. High density of dislocations formed at twin tips that terminates inside a grain and at twin tip-GB junctions with neighboring grains appear to release the elastic strain at the early stage of twin propagation. Twin-dislocation and twin-GB interactions also point to possible mechanisms for inter and intragranular twin propagation.

**Chapter 6** investigates the mechanisms of texture weakening in a Mg-Ca alloy. Ca addition is shown to enhance the activity of $<c + a>$ dislocations and change the texture from DRX. GB segregation of Ca atoms was found to dramatically decrease the mobility of GBs in the Mg-Ca alloy and level out the dependence of GB energy on misorientation. The low GB mobility leads to in-grain recrystallization nucleation in highly deformed areas and increased evenness of GB energy, all of which allow for relatively equal probability of
growth of recrystallized grains with texture weakening orientations. Both processes explain the SRX induced texture weakening in Mg-Ca alloy.

Chapter 7 provides a summary of the key findings and suggests possible future directions for this study.
1.4 References for Chapter 1

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Chapter 2.
Experimental Procedures and Materials

To experimentally investigate the influence of alloying elements on the behavior of dislocations and twins in Mg alloys, one must possess a clear understanding of Mg alloying and experimental characterization methods. This chapter introduces the materials selected for investigation, followed by a detailed description of the mechanical testing techniques employed to introduce defects. Detailed sample preparation processes for different characterization techniques are described. The chapter concludes with a detailed introduction of microstructural characterization approaches.

2.1 Materials selection

To evaluate the influence of alloying elements on deformation mechanisms in Mg alloys, the materials investigated included: 99.9% pure Mg, AZ31B, Mg-3Er and Mg-0.1Ca. The pure Mg serves as the reference material for comparison of deformation mechanisms and mechanical properties. AZ31B, one of the most widely used commercial wrought Mg alloys, was used to investigate the influence of Al and Zn on the dislocation behavior. The
nominal composition of AZ31B is shown in Table 2.1. To uncover the mechanisms of improved ductility and formability of Mg-RE alloys, Mg-3Er with 3 wt.% Er in Mg was studied due to the reason that Er has decent solubility in Mg to avoid precipitation and because improved properties have been reported for Mg-Er alloys. Lastly, Mg-0.1Ca with 0.1 wt.% Ca in Mg was included because Ca behaves similarly to RE elements when the atom volume, electronegativity and bulk modulus are compared [1]. The low solubility of Ca in Mg determines the low Ca content for one phase solute without precipitation.

<table>
<thead>
<tr>
<th>Table 2.1: Chemical composition of AZ31B Mg alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
</tr>
<tr>
<td>Content (wt.%)</td>
</tr>
</tbody>
</table>

All the materials characterized in this study were hot rolled with 50% reduction at 450°C. After rolling, both pure Mg and AZ31B alloy have a strong basal texture with the crystallographic <c>-axis aligned along the normal direction (ND) and the <a>-axes in the sheet plane with negligible difference between transverse direction (TD) and rolling direction (RD). The grains are generally equiaxed with an average grain size of about 30 μm for AZ31B and 15 μm for pure Mg, respectively. The characterization of microstructure will be detailed in Chapter 3. The Mg-3Er and Mg-0.1Ca alloys exhibit weaker texture after hot rolling, and the details will be discussed in Chapter 4 and Chapter 6.
2.2 Mechanical testing

Multi-scale mechanical testing techniques were utilized to introduce defects into the Mg and Mg alloys. All mechanical tests were performed at quasi-static strain rate. Compression along ND or tension along RD were carried out to activate \( <c+a> \) dislocations, and compression along the RD was used to stimulate extension twinning.

2.2.1 Macro-scale testing

All of the samples were cut by wire electrical discharge machining (EDM), and the surfaces in the gage were then mechanically polished with SiC abrasive grinding paper (1200 for standard ANSI grit or P4000 for European P-grade) to remove the recast layer from cutting and then chemically polished with 10% nitric acid in methanol for 2min to eliminate the damage layer from mechanical polishing.

Quasi-static compression tests were performed on a servo-hydraulic MTS machine (Figure 2.1). The force applied on the specimen with dimension of 3 mm x 3 mm x 6 mm was measured with a load cell and the displacement was captured by a linear variable differential transformer system. A nominal strain rate of \( 10^{-4} \text{ s}^{-1} \) was imposed by the velocity of the cross head. The interfaces between the top and bottom surfaces of specimen and compression platens were carefully lubricated with Vaseline to prevent friction and avoid barreling. Data collection was straightforward in the quasi-static testing. The engineering strain (e) was calculated from measured displacement divided by the total gage length, and engineering stress (s) was computed using the force measured with the load.
cell divided by the original cross-sectional area. By assuming incompressible plastic flow, the engineering stress and engineering strain were converted to the corresponding true stress ($\sigma$) and true strain ($\varepsilon$) using standard equations:

$$\sigma = s(1 - e) \tag{2.1}$$

$$\varepsilon = -\ln(1 - e) \tag{2.2}$$

Figure 2.1: MTS machine for macro-scale quasi-static mechanical testing.
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2.2.2 Micro-scale compression

Micrometer-sized pillars were fabricated using annular milling with a Thermo Scientific Helios G4 UC Dual-Beam SEM (Figure 2.2). Large trenches with an outer diameter of 30 μm and an inner diameter of 15 μm were milled using 9.3 nA current. Successive milling was then performed using 2.3 nA, 230 pA, 130 pA and 100 pA current to narrow down the pillar diameter to a mid-height diameter of 10, 8, 7.5 and 6 μm, as shown in Figure 2.2 (b). Finally, the pillars with average diameter of 5.4 ± 0.1 μm, average height of 11.8 ±0.2 μm and 1-2° taper angle were fabricated using a final milling current of 80 pA.

Figure 2.2: (a) Thermo Scientific Helios G4 UC FIB used for micropillar fabrication; (b) top view of micropillars shows the diameters of successive milling; and (c) the dimension of the micropillar with average diameter of 5.4 ± 0.1 μm and average height of 11.8 ±0.2 μm.
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In situ micropillar compression was performed using an indenter head module that is designed based on the InForce 50 actuator (Figure 2.3). The actuator has a maximum load of 50 mN with a resolution of 3 nN, and a displacement range of 50 μm with a low electronic noise less than 0.1 nm. The in-situ load frame was placed inside a Tescan Mira 3 GM SEM. A 10 μm x 10 μm diamond flat punch was used to compress the pillars to a user prescribed depth and then unloaded. Loading was performed at a nominal strain rate of $10^{-4}$ s$^{-1}$ with a data acquisition rate of 500 Hz. Three of the pillars were compressed to failure for the stress-strain curves and the other seven were compressed to prescribed 3% strain for FIB lift-out and dislocation characterization.

![Figure 2.3: The InSEM cradle setup and mounting scheme. (a) Actuator installed on the cradle and (b) the SEM stage after the rotational substage. [2]](image-url)
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2.3 Characterization techniques

2.3.1 Electron backscatter diffraction (EBSD)

EBSD samples of pure Mg and Mg alloys were cut from rolled sheets using wire EDM. The samples were then mechanically thinned using SiC abrasive grinding paper (1200 for standard ANSI grit or P4000 for European P-grade) under zero nominal load (read from the force meter in an Allied automated polisher) and then polished using a 0.2 μm water-free silica colloidal until obtaining a mirror-like surface.

EBSD was performed using a Thermo Scientific Helios G4 UC SEM equipped with an EDAX EBSD detector. EBSD scans of all the as-rolled and annealed samples were performed at 20kV. The EBSD results were analyzed using TSL OIM 8 software, which provides information including: grain orientations (inverse pole figure maps, IPF), texture strength (pole figure, PF), grain size distribution, grain boundary (GB) misorientation and recrystallization fraction. The grain orientation spread (GOS) in each grain is determined by calculating the average misorientation (angle) for all points sampled within the grain. This operation is performed by computing the average (macroscopic) grain orientation and then by calculating the average deviation between the macroscopic grain orientation and the (microscopic) crystal orientations of each point within the grain. The threshold GOS of dynamically recrystallized grains typically is typically 1° – 2° [3].
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2.3.2 Transmission electron microscopy (TEM)

The Mg and Mg alloys samples were cut to 1mm thickness from rolled sheets using a diamond wire saw with a wire thickness of 0.12 mm. The slices were then mechanically polished using SiC abrasive grinding paper (1200 for standard ANSI grit or P4000 for European P-grade) on both sides of the sample under zero load to a thickness of 150 μm. The samples were subsequently punched into 3 mm discs using a TEM disc punch. Twin jet electropolishing is applied, using an electrolyte of 5.3 g lithium chloride, 11.16 g magnesium perchlorate, 100 mL 2-butoxyethanol and 500 mL methanol, at -35°C and 100 V. A small hole was created in the center of the disc by the twin jet electro polisher, which is controlled by the luminous flux (light stop value = 100). Finally, a Gatan precision ion polishing system (PIPS II) was utilized to clean the thin area around the hole and to further reduce the specimen thickness to electron transparency using 0.5 and 0.2 keV at liquid nitrogen temperature to produce artifact-free TEM foils [4].

Conventional TEM micrographs of dislocations were acquired using a FEI Tecnai 12 TEM operating at 100 keV to minimize electron beam damage. Bright field (BF) two-beam conditions and weak beam dark field (WBDF) \( g-3g \) diffraction conditions were used to characterize the dislocations [5]. Two-beam conditions can be obtained by tilting the TEM foil from the zone axis and highlighting only the incident and \( g \) spots. The diffraction patterns of a \( \{11\overline{2}0\} \) zone axis and two beam condition of \( g = [1\overline{1}00] \) for Mg are shown in Figure 2.4 (a) and (b). After the sample was tilted to two beam condition, the \( g-3g \) WBDF
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condition can be acquired by switching the microscope to dark-field mode, diffraction shifting the 1g spot to the center and highlighting the 0g and 3g diffracted spots.

![Diagram showing diffraction patterns](image)

**Figure 2.4:** (a) diffraction pattern of a (11̅20) zone axis for Mg, (b) diffraction pattern of two beam condition for g = 11̅00 and (c) diffraction pattern of the WBDF g-3g condition for g = 11̅00. The incident point that is aligned with the center of column is highlighted by red cross.

2.3.3 High-resolution scanning transmission electron microscopy (HRSTEM)

Thin lamella were extracted and thinned from polished cross-sections via the in-situ lift out technique using a FEI Scios focused ion-beam (FIB) instrument in Lehigh University [6-10]. They were then ion polished using a Fischione 1040 NanoMill instrument and a 500 eV Ar-ion beam to remove implanted Ga induced by FIB milling [7, 11].

Scanning transmission electron microscopy (STEM) was conducted using a JEOL JEM-ARM200CF instrument fitted with a CEOS ASCOR aberration-corrector and a cold-field emission electron gun. The ARM200CF was operated at 200 kV. Probe current decay was measured using a Keithley model 6485 picoammeter recorded at a rate of 0.1 Hz. The probe current utilized in this work was measured to be 112 pA, decayed at a rate of 2% per hour, and was assumed to be 1 Å in diameter at full width half maximum (FWHM). A current
decay correction was implemented into all analyses. Prior to loading into the ARM200CF chamber, all thin specimens were plasma cleaned with a SPI Plasma Prep III™ unit for approximately two minutes to minimize hydrocarbon contamination. High-angle annular dark field (HAADF) and bright-field (BF) STEM imaging were used to image the microstructures. The angular range of HAADF imaging was 68–280 mrad. X-ray energy dispersive spectrometry (EDS) was conducted using a single JEOL large-angle silicon drift detector that has a solid-angle of approximately 0.64 sr, a take-off angle of 19.2°, and an atmospheric thin window.

Single spectra (hereafter referred to as rastered spectra) were acquired by rastering the probe in 100 nm × 100 nm regions for 60 s with a decay-corrected probe current of 112 pA. Spectrum images of 256 × 256 pixels were acquired totaling 2000 frames with a 50 μs frame time and a decay-corrected probe current of 112 pA. Subpixel scanning was not applied. Spectrum images were subsequently binned from 256 × 256 pixels to create 128 × 128, 64 × 64, 32 × 32, 16 × 16, and 8 × 8 pixels to enhance statistics in quantification. The total acquisition times per spectrum in the binned spectrum images were 25.6 s. All spectra were recorded without tilting the specimen to avoid detector shadowing.

2.3.4 Automated crystal orientation mapping (ACOM)

Automated crystal orientation mapping (ACOM) in the TEM relies on narrowing down the electron beam to a small spot on the specimen and recording a selected area electron diffraction (SAED) pattern on the phosphor screen collected with an external high-resolution camera. The SAED pattern contains the symmetry needed to determine the
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orientation and phase of the crystal. Once the beam raster is scanned on the TEM foil, the SAED information of each pixel is recorded and compared to a library comprised of simulated SAED patterns for known phases. Each experimental diffraction pattern is compared to the simulated patterns to maximize the correlation index ($Q$):

$$Q_i = \frac{\sum_{j=1}^{m} P(x_j, y_j) T_i(x_j, y_j)}{\sqrt{\sum_{j=1}^{m} P^2(x_j, y_j)} \sqrt{\sum_{j=1}^{m} T_i^2(x_j, y_j)}}$$ (2.3)

where $P(x, y)$ represents the intensity of the experimental diffraction pattern at spatial coordinates $(x, y)$ and $T_i(x, y)$ represents the intensity of simulated (template) diffraction pattern $i$ at coordinates $(x, y)$. The correlation index, $Q$, is calculated for each of the $i$ template patterns, and the orientation with the highest value is chosen as the solution. When indexing a series of diffraction patterns, an orientation is assigned to each regardless of the aptness of the fit. To quantify how well the chosen template pattern fits the experimental data compared to other possible template patterns, ‘reliability’ ($R$) is used [12]:

$$R = 100\left(1 - \frac{Q_2}{Q_1}\right)$$ (2.4)

where $Q_1$ is the correlation index of the assigned orientation (best guess), and $Q_2$ is the correlation index of the second-best guess. A reliability of 0 signifies that there are multiple orientations that fit the experimental pattern equally well, indicating poor confidence. A reliability of 100 indicates a completely unique solution. In practice, a reliability of 15 is sufficient to ascertain the validity of the matching. An example of a SAED pattern (left)
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and the pattern overlaid with the simulated pattern (right) is shown in Figure 2.5. When the orientations of all pixels are identified from the acquired and simulated pattern comparison, a full orientation mapping can be reconstructed. This technique was developed and automated by researchers at NanoMEGAS and is sold as the ASTAR system [12-15].

![Figure 2.5: Example of (a) an experimental SAED pattern collected using ACOM (left) from a Mg grain with [11\overline{2}0] orientation and (b) the same pattern (with inverted colors) with the simulated SAED pattern (indicated by red circles). The reliability is 36 for this matching.](image)

The spatial resolution of ACOM depends on the minimum probe size obtainable by a given TEM. A probe size of 1 nm could be obtained using the available TEM (Thermo Scientific TF30) and a field emission gun (FEG) source of 300kV. To accomplish the high spatial resolution with enough intensity of the diffraction pattern, a 10 \( \mu m \) condenser aperture and spot size 9 were used. To reliably resolve the orientation of small size features, at least 2 x 2 pixels in theory (practically 3 x 3) are required, which means the 1 nm beam size scan has an actual spatial resolution of 2-3 nm.
Beam precession can be used to increase the reliability of ACOM [17]. The procession is actuated by an input AC signal that rotates the electron beam about a cone of a given angle. After interacting with the specimen, the beam is ‘descanned’, forming a diffraction pattern in the back focal plane [13, 18, 19]. The conically precessed beam substantially reduces dynamic contrast and increases the intensity of spots in reciprocal space with signal integration, allowing for spots in the first-order Laue zone (FOLZ) to be differentiated from those in the zero-order Laue zone (ZOLZ). Figure 2.6 illustrates the improved pattern quality with precession collected from a Mayenite crystal: one taken with no precession, one using 0.6° precession. However, precession increases the acquisition time and decreases spatial resolution [20, 21], so it is preferable to only use it when required [22, 23]. The angular resolution of ACOM is routinely ~1°, which is lower than the Kikuchi diffraction-based techniques, but sub-angular spatial resolution has been achieved through careful data analysis [24]. Due to the limited view of reciprocal space, ACOM is much less...
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sensitive to minor changes in orientation, which can be resolved by the newly developed technique, ambiguity resolver, in the new version of data analysis software.

2.3.5 Automated nano beam electron diffraction (NBED) strain mapping

Nano beam electron diffraction (NBED) operates by producing a small probe of nearly parallel electrons and collecting SAED patterns from a specimen of the same orientation. The strain at various locations is calculated by comparing the location and symmetry of diffraction spots in the diffraction patterns and calculating a 2D elastic strain tensor, which can be plotted into strain maps with a strain resolution of ~0.1%. Strain resolution of 0.06% has been obtained for single crystal silicon, but actually decreases to 0.2% due to dynamical diffraction and bending [25]. Imaging processing methods that can be used to improve NBED resolution to 0.03% [26]. Initially NBED was performed by manually recording diffraction patterns and calculating relative strain from various locations generally in semiconductor materials [27-30]. Recently, NanoMEGAS has developed TOPSPIN, a platform that automates the collection and analysis of diffraction patterns for strain analysis [21].

This technique measures the relative two-dimensional strain between a reference region and the region of interest. This requires that the reference region and the region of interest have the same orientation. The microscope conditions suitable for automated NBED are nearly identical to those used to perform ACOM, as detailed in Section 2.3.3. In addition, the specimen must be tilted to a low-index zone axis and beam precession (usually with precession angle 0.8°) is required to obtain the largest number of diffraction spots. With
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proper alignment, 3 nm spatial resolution can be obtained using precession assisted NBED strain mapping.

The general operating procedure for utilizing TOPSPIN may be described as follows. The reference pattern is recorded in an area with the same orientation as the region of interest and away from any strain fields that are to be measured. Multiple reference patterns can be recorded and averaged to create a single reference pattern. Secondly, the region of interest is outlined, and the step size between each point is specified. The diffraction patterns from each point are automatically recorded and saved into an .app5 file using the TOPSPIN data collection program. Lastly, measured diffraction patterns of each pixel in the region of interest are compared to the reference pattern, and a proprietary non-linear optimization algorithm determines the 2D elastic strain tensor at each point. 2-D strain maps can be reconstructed and analyzed using the TOPSPIN Data Viewer software.

2.4 Dislocation analysis

Dislocation slip is the most prominent deformation mechanism in Mg. The Burgers vector and dislocation line vector are the two primary parameters used to characterize dislocations.

2.4.1 Burgers vector analysis

To distinguish the dislocation Burgers vectors and to get strong diffraction contrast, the specimen is tilted to two-beam conditions, in which only the transmitted beam and one diffracted beam are strong. In this case, the diffracted beam satisfies the Bragg condition.
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However, the best contrast cannot be obtained when we tilt the specimen to the exact Bragg condition (deviation parameter, \(s = 0\)). Optimal contrast requires a small and positive \(s\). A diffraction vector \(\mathbf{g}\) is associated with each Bragg reflection and crystal plane. For each Bragg reflection, a series of diffraction spots are periodically spaced along a line in reciprocal space with diffraction vectors \(\mathbf{g}, \mathbf{0}, 2\mathbf{g}, 3\mathbf{g}\), etc. And the two-beam condition highlights the \(\mathbf{0}\) and \(\mathbf{g}\) diffraction vectors for a selected Bragg reflection.

There are three prominent Burger’s vectors for dislocations in HCP Mg crystals: \(\langle \mathbf{a} \rangle = \frac{1}{3}(11\overline{2}0)\), \(\langle \mathbf{c} \rangle = [0001]\) and \(\langle \mathbf{c} + \mathbf{a} \rangle = \frac{1}{3}(11\overline{2}3)\). To distinguish the dislocations with different Burgers vectors, one \(\langle 11\overline{2}0 \rangle\) zone axis can be selected and \(\mathbf{g} \cdot \mathbf{b} = 0\) invisibility criteria for two-beam condition around that zone axis is utilized to deduce the Burgers vectors \([31]\). The diffraction vector \(\mathbf{g}_c = [0001]\) is used to image \(\langle \mathbf{c} \rangle\) dislocations and the \(c\)-component in \(\langle \mathbf{c} + \mathbf{a} \rangle\) dislocations, but not \(\langle \mathbf{a} \rangle\) dislocations, which are invisible. By contrast, for a \(\mathbf{g}_a = \langle 1\overline{1}00 \rangle\) diffraction vector, \(\langle \mathbf{a} \rangle\) dislocations and the \(a\)-component in \(\langle \mathbf{c} + \mathbf{a} \rangle\) dislocations are visible but \(\langle \mathbf{c} \rangle\) dislocations are invisible. The dislocation that is visible for both \(\mathbf{g}_a\) and \(\mathbf{g}_c\) are deduced to be \(\langle \mathbf{c} + \mathbf{a} \rangle\) dislocation.

WBDF is an important technique in TEM to characterize dislocations in crystalline materials. WBDF gives strong contrast between the dislocation and the background, with the contrast close to the dislocation core. In WBDF condition, the specimen is tilted with large \(s\), and the lattice planes of the specimen do not satisfy the Bragg condition. However, the planes near the core of the dislocation are locally bent into the Bragg condition and show contrast. This bending is only large close to the dislocation core, which results in a
strong contrast with a narrow line. When $s$ increases, the planes must bend more to satisfy the Bragg condition and the observed dislocation line appears narrower. In theory, this means that the larger $s$ is, the narrower the dislocation line that can be achieved. However, the practical operation of WBDF conditions is more complicated.

In the two-beam condition, the intensity of the diffracted beam $g$ in a perfect crystal can be written as function of the extinction distance ($\xi_g$), foil thickness ($t$) and effective extinction error ($s_{\text{eff}}$) [32]:

$$
|\phi_g|^2 = \left(\frac{\pi t}{\xi_g}\right)^2 \cdot \frac{\sin^2(\pi s_{\text{eff}})}{(\pi s_{\text{eff}})^2}
$$

(2.5)

where the effective excitation error

$$
s_{\text{eff}} = \sqrt{s^2 + \frac{1}{\xi_g^2}}
$$

(2.6)

and the extinction distance can be further expressed as a function of unit cell volume ($V_c$), structure factor ($F_g$), Bragg angle ($\theta_B$) and electron beam wavelength ($\lambda$):

$$
\xi_g = \frac{\pi V_c \cos \theta_B}{\lambda F_g}
$$

(2.7)

where
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\[ F_g = f \left| \cos \left( \frac{(h+2k) + \frac{1}{2}}{3} \pi \right) \right| \]  

(2.8)

The values of the coefficients are listed in Table 2.2 (wavelength is calculated for 100kV)

<table>
<thead>
<tr>
<th>g vector</th>
<th>( f (\text{Å}) )</th>
<th>( F_g (\text{Å}) )</th>
<th>( V_c (\text{Å}^3) )</th>
<th>( \theta_n (°) )</th>
<th>( \lambda (\text{Å}) )</th>
<th>( \xi_g (\text{nm}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1100</td>
<td>2.199</td>
<td>2.199</td>
<td>46.5</td>
<td>0.203</td>
<td>0.037</td>
<td>180</td>
</tr>
<tr>
<td>0002</td>
<td>2.049</td>
<td>4.098</td>
<td>46.5</td>
<td>0.217</td>
<td>0.037</td>
<td>96</td>
</tr>
</tbody>
</table>

Table 2.2: Coefficient to calculate excitation distance for the two \( g \) vectors

![Figure 2.7: Intensity of the diffraction beam applied in this thesis as a function of excitation error](image_url)

For a sample with a thickness of 150nm, the plot of intensity \( |\phi_{g}|^2 \) vs. excitation error \( s \) can be found in Figure 2.7. In theory, increasing \( s \) would enhance the contrast. However, the
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intensity decreases dramatically in the meantime when $s$ increases from 0.01 nm$^{-1}$ (example for BF) to 0.1 nm$^{-1}$ (typical value for WBDF). The result is that the exposure time needed to record the image on the CCD also rapidly increases and may introduce the issue of drift. For reasonable contrast with acceptable drift, the $g$-3$g$ WBDF condition was utilized with

$$s = \frac{1}{2}(n - 1)|g|^{2} \lambda$$  \hspace{1cm} (2.9)

where $n = 3.2$ for the WBDF condition [5] and

$$|g|^{2} = \frac{1}{d^{2}} = \frac{4}{3} \left( \frac{h^{2} + hk + k^{2}}{a^{2}} \right) + \frac{l^{2}}{c^{2}}$$  \hspace{1cm} (2.10)

The values of $s$ are 0.060 nm$^{-1}$ and 0.053 nm$^{-1}$ for $g_{c}$ and $g_{a}$, respectively. The exposure time was approximately 10-20s for the images that were acquired in this thesis.

The $g$-3$g$ WBDF condition can be obtained by the following procedure: (1) tilt the specimen in BF so that only the incident and $g$ diffraction spots are excited, and $s_{g}$ is slightly greater than zero. (2) Switch to dark-field (DF) mode and use the DF beam-deflecting coils (multifunction X and Y) to bring the $g$ spot on to the optic axis (center of the screen). Ideally, at this time, the 0$g$ and 3$g$ spots will be highlighted with no other spots visible. (3) Insert the objective aperture and use the binoculars to center the aperture over the weak $g$ spot. (4) Switch to imaging mode and acquire DF image with appropriate exposure time.
2.4.2 Line vector analysis for straight dislocations

Tomography is the ideal approach to determine the line vector of dislocations in complicated shapes. A 3-D reconstruction of a dislocation is created by stitching together a series of images of the same dislocation acquired with different tilting angles. With the known orientation of the area of interest, the line vector of the dislocation can be visualized directly. In addition, the reconstructed 3-D dislocation can be rotated onto a particular plane in which the dislocation appears as a single line. Then, the plane that is parallel to the dislocation line is the habitat plane of the dislocation.

Alternatively, a traditional projection approach can be used to analyze the line vector of straight dislocations. This method requires imaging of two or more different viewing beam axes that are as far apart as possible. Straight dislocations can be plotted and determined using a stereographic projection. But here we will discuss the solution algebraically. Using the diffraction pattern for imaging (either two-beam condition or exactly at zone axis, two-beam condition will be discussed as an example), we know at least the intersection of the image plane with one crystallographic plane \((h_{g1}k_{g1}l_{g1})\) is perpendicular to the \(g = h_{g1}k_{g1}l_{g1}\) vector in reciprocal space. The angle \(\theta_1\) between the plane that is parallel to the dislocation line \((h_1k_1l_1)\) and \((h_{g1}k_{g1}l_{g1})\) can be calculated as:

\[
\cos \theta_1 = \frac{h_1h_{g1} + k_1k_{g1} + \frac{1}{2}(h_1k_{g1} + k_1h_{g1}) + \frac{3}{4}l_1l_{g1}\left(\frac{a}{c}\right)^2}{\left[h_1^2 + k_1^2 + h_1k_1 + \frac{3}{4}l_1^2\left(\frac{a}{c}\right)^2\right]^{1/2} \cdot \left[h_{g1}^2 + k_{g1}^2 + h_{g1}k_{g1} + \frac{3}{4}l_{g1}^2\left(\frac{a}{c}\right)^2\right]^{1/2}}
\]  

(2.11)
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The incident beam direction \((u_1, v_1, w_1, t_1)\) is parallel to the plane that is parallel to the dislocation line are perpendicular, which means:

\[
0 = h_1 u_1 + k_1 v_1 + i_1 w_1 + l_1 t_1 \tag{2.12}
\]

The plane \((h_1k_1i_1l_1)\) that is parallel to the dislocation line \([UVWT]\) using the first incident direction can be calculated by solving equations (2.11) and (2.12). Similarly, another plane \((h_2k_2i_2l_2)\) can be solved for the second imaging condition. Now the dislocation line \([UVWT]\) is parallel to both \((h_1k_1i_1l_1)\) and \((h_2k_2i_2l_2)\) planes, which means the dislocation line is along the intersection of the two planes. The dislocation line \([UVWT]\) can be solved as:

\[
\begin{align*}
U &= (h_2 + 2k_2)l_1 - (h_1 + 2k_1)l_2 \\
V &= (2h_1 + k_1)l_2 - (2h_2 + k_2)l_1 \\
W &= (h_2 - k_2)l_1 - (h_1 - k_1)l_2 \\
T &= 3(h_1k_2 - h_2k_1)
\end{align*} \tag{2.13}
\]

2.4.3 Geometrical phase analysis (GPA)

Hutch et al. proposed a means of quantifying local displacement and strain field from high resolution TEM or STEM images [34, 35]. This section will briefly introduce the theory of GPA. The image intensity at position \(\mathbf{r}\) can be expressed as
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\[ I(r) = \sum_g H_g(r) \exp(2\pi i g \cdot r) \]  \hspace{2cm} (2.14)

where \( g \) is the Bragg position, and \( H_g(r) \) is the Fourier coefficient that can be described as

\[ H_g(r) = A_g(r) \exp(iP_g(r)) \]  \hspace{2cm} (2.15)

where \( A_g(r) \) and \( P_g(r) \) are amplitude and phase that represent the contrast level and lateral position of the fringes in the high-resolution image. The inverse Fourier transform of equation (2.15) results in the complex image \( H'_g(r) \):

\[ H'_g(r) = A_g(r) \{2\pi i g \cdot r + iP_g(r)\} \]  \hspace{2cm} (2.16)

Subsequently, the Bragg-filtered image intensity \( B_g(r) \), amplitude \( A_g(r) \), phase \( P_g(r) \), and raw-phase images \( P'_g(r) \) from the original image can be calculated by

\[ B_g(r) = 2\text{Real}[H'_g(r)] \]  \hspace{2cm} (2.17)

\[ A_g(r) = \text{Mod}[H'_g(r)] \]  \hspace{2cm} (2.18)

\[ P_g(r) = \text{Phase}[H'_g(r)] - 2\pi i g \cdot r \]  \hspace{2cm} (2.19)

\[ P'_g(r) = \text{Phase}[H'_g(r)] \]  \hspace{2cm} (2.20)
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where Real, Mod and Phase denote the real part, modulus and phase of $H'_g(r)$, respectively.

The two-dimensional displacement, $u(r)$ can then be calculated from equation (2.19) as follows:

$$u(r) = -\frac{1}{2\pi} \left[ P_{g_1}(r)a_1 + P_{g_2}(r)a_2 \right]$$ (2.21)

where the $a_1$ and $a_2$ are the lattice vectors in real space as defined by the reciprocal lattice vectors $g_1$ and $g_2$. The strain and rotation tensors can then be determined by the derivatives of the displacement.

$$e = \begin{bmatrix} e_{xx} & e_{xy} \\ e_{yx} & e_{yy} \end{bmatrix} = \begin{bmatrix} \frac{\partial u_x}{\partial x} & \frac{\partial u_x}{\partial y} \\ \frac{\partial u_y}{\partial x} & \frac{\partial u_y}{\partial y} \end{bmatrix} = -\frac{1}{2\pi} \begin{bmatrix} a_{1x} & a_{1y} \\ a_{2x} & a_{2y} \end{bmatrix} \begin{bmatrix} \frac{\partial P_{g_1}}{\partial x} & \frac{\partial P_{g_1}}{\partial y} \\ \frac{\partial P_{g_2}}{\partial x} & \frac{\partial P_{g_2}}{\partial y} \end{bmatrix}$$ (2.22)

\[
\varepsilon = \frac{1}{2} (e + e^T) \quad (2.23)
\]

\[
\omega = \frac{1}{2} (e - e^T) \quad (2.24)
\]
2.5 References for Chapter 2

[29] D. Cooper, A. Béché, J. Hartmann, V. Carron, J. Rouviere, Strain measurement for the semiconductor industry with nm-scale resolution by dark field electron holography and


Chapter 3.

Undissociated $<c + a>$ Dislocations in AZ31
Revealed by TEM

In this chapter, careful tilting experiments and weak-beam dark-field (WBDF) electron microscopy observations elucidated that $<c + a>$ dislocation in the commercial alloy AZ31 remains compact without apparent dissociation. The stabilization of the $<c + a>$ dislocation core structure with Al and Zn alloying may explain the improved strain to failure in the AZ31 alloy as compared to pure Mg samples.

3.1 Introduction

$c$-axis compression experiments have been performed on pure Mg single crystals to activate non-basal pyramidal slip [1-6]. The motion of $<c + a>$ dislocations on pyramidal planes (I and/or II) with Burger vectors along $<1\bar{1}2\bar{3}>$ directions accommodate $c$-axis compression and contraction twins [7] are occasionally observed at large deformation before failure [8]. TEM studies by Geng et al. [9] provided evidence to suggest that $<c + a>$ dislocations in Mg are mostly “basal bound” and non-conservatively dissociate on the
basal plane. The dissociation of $<c + a>$ dislocations onto the basal plane has also been observed by Xie et al. [10] in their TEM study of Mg single crystals. These observations are consistent with the simulations suggested by Wu and Curtin [11] that the core of a $<c + a>$ dislocation is metastable and undergoes either a thermally-activated transition to a sessile, basal-dissociated $<c + a>$ dislocation. The dislocation core transformation exhausts glissile $<c + a>$ dislocations and result in low ductility. However, the dissociation of $<c + a>$ dislocation was predicted to form at high temperature (300°C) and the spacing of partials was simulated to be several nanometers, dramatically smaller than the spacing observed by TEM. Another mechanism of stacking fault loop formation based on the movement of super jogs was originally proposed by Geng et al. [9] and recently observed in MD simulation by Srivastava et al. [12]. Super jogs form due to an inhomogeneous shuffling process introduced by local fluctuations in the dislocation core and the dragging out of super jog dipoles by the motion of screw dislocations can create and leave behind debris and long faulted loops [12]. These super jogs were suggested to athermally dissociate on the basal plane and to exert a strong drag effect on dislocation glide, resulting in strong hardening at a large range of temperature (0-600K). The super jog induced loops are predicted to be thin and long, which contradicts the large loops seen in TEM observations. In both the thermally activated dissociation and athermal super-jog models, the dissociation on the basal plane dramatically decreases the mobility of $<c + a>$ dislocations, which is harmful to the ductility of Mg. Therefore, stabilization of $<c + a>$ dislocation cores to improve mobility has emerged as a promising strategy for improving the general ductility and formability of Mg alloys, and it has been predicted that solid
solution alloying may be an effective approach to stabilizing the \(<c+a>\) dislocation cores [11].

AZ31 is a popular commercial wrought Mg alloy [13, 14] that contains 3% Al and 1% Zn, as shown in Table 2.1. Wu et al. [15] studied the correlation between cross-slip energy barriers of \(<c+a>\) dislocations and ductility for a large number of potential solutes and predicted improved cross-slip with the addition of rare earth elements, Mn, Ca and Zr, but their work did not provide definitive explanation for elements like Al or Zn, which are the main alloying elements in AZ31. In this chapter, to experimentally determine the influence of solutes (primarily Al and Zn) on the \(<c+a>\) dislocation activity, we studied the \(<c+a>\) dislocation behavior after close-to-\(<c>\)-axis compression of AZ31 and compared the findings with dislocations in pure Mg that were introduced and characterized under identical conditions to AZ31.

3.2 Experiments

Hot-rolled pure Mg and AZ31 both have strong texture with the \(<c>\)-axis aligned along ND. For both Mg and AZ31, rectangular compression samples with their longitudinal direction aligned along ND were electrical discharge machined (EDM) with dimensions of 3 mm x 3 mm x 6 mm. Pure Mg was annealed at 300 °C for 3h and AZ31 for 40min due to the different initial grain sizes of as-rolled materials. The post annealed AZ31 and Mg have similar grain sizes and equally low dislocation densities. Quasi-static compression tests
were conducted in an MTS machine at a strain rate of $10^{-4}$ s$^{-1}$ and the full stress-strain curves were obtained for samples that were compressed to failure.

Electron backscatter diffraction (EBSD) was performed on the surface of as-annealed samples, and solute distribution was investigated using scanning transmission electron microscopy with high-angle annular dark field (HAADF) detector and an energy dispersive X-ray detector (STEM-EDX). Dislocation contrast was observed with the WBDF technique on a Tecnai 12 transmission electron microscope at 100 keV. TEM foils were cut from samples deformed to 2.5% strain and oriented with ND in the plane of the foil. To avoid damage, both EBSD and TEM samples were mechanically polished under very low loads (nominally zero readings on the Allied automated polisher), and then electro-chemically polished with 10% nitric acid in methanol at -50 °C.

3.3 Results and discussion

3.3.1 Microstructure and mechanical properties

The textures of the heat-treated pure Mg and AZ31 are described in Figure 3.1. The maximum intensities of the pole figures of pure Mg and AZ31 are 13.48 and 12.05 respectively. This means that both samples exhibited similarly strong basal texture after hot rolling and annealing. Moreover, the average grain size of pure Mg ($65.1 \pm 27.3 \mu m$) was comparable to that of AZ31 ($68.5 \pm 50.0 \mu m$), as shown in Figure 3.2. Thus, when considering the mechanical properties, the effects of texture and grain size can be largely excluded.
CHAPTER 3. UNDISSOCIATED <C+A> DISLOCATION IN AZ31

Figure 3.1: IPF maps of hot-rolled polycrystalline (a) pure Mg and (b) AZ31 after heat treatment with the normal of sample surface along ND. Inset PFs indicate similarly strong basal texture after rolling and annealing.

Figure 3.2: The cumulative grain size distributions for pure Mg (blue) and AZ31 (red) illustrate similar grain size for pure Mg (average grain size = 65.1μm) and AZ31 (average grain size = 68.5μm).
CHAPTER 3. UNDISSOCIATED <C+A> DISLOCATION IN AZ31

Figure 3.3: Bright-field TEM images of (a) pure Mg and (b) AZ31 after heat treatment obtained using one [1 1 2 0] zone axis.

In addition to grain size and texture analysis, the microstructure was characterized in TEM. The dislocation density of both samples was observed in BF images using a \{11\overline{2}0\} zone axis, as shown in Figure 3.3. The zone axis diffraction condition activates multiple beams and contrasts all the \(<c>, <a>\) and \(<c+a>\) dislocations. The dislocation density in pure Mg after heat treatment is very low throughout the sample with almost no dislocations observed either in the middle of grains or the areas close to boundaries. The speckles observed in Figure 3.3 (a) are artifacts from electropolishing. The dislocation density in the middle of grains in annealed AZ31 samples is as low as that of pure Mg. But higher density of residual dislocation was observed in the areas close to the boundaries. The dislocation density \(\rho\) at the areas close to the boundary in the example as shown in Figure 3.3 (b) can be estimated by [16]:
CHAPTER 3. UNDISSOCIATED \(<\text{C+A}\)> DISLOCATION IN AZ31

\[
\rho = \frac{\sum n}{t\sum L} \tag{3.1}
\]

where \(n\) is the number of intersections of dislocation lines with the grid lines, \(\sum L\) is the total length of the grid lines and \(t\) is the sample thickness. The dislocation density in AZ31 is estimated to be \(1.11 \times 10^{15} \text{ m}^{-2}\) by assuming that the thickness of the thin area is 150nm.

To analyze the pre-existing precipitates in AZ31 alloy, HADDF map is shown in Figure 3.3 (c). The HADDF contrast shows the atomic weight with the higher atomic number presenting brighter intensity. The precipitates in AZ31 include Al-rich precipitates (Mg\(_{17}\)Al\(_{12}\)) and precipitates that contain Mn (Al\(_4\)Mn, Al\(_{11}\)Mn\(_5\), Al\(_8\)Mn\(_5\)) [17]. All the precipitates contain heavy elements and were highlighted in the HAADF map. These precipitates are nanometer in size with the average diameter of 28.3 nm, which did not significantly increase compared to that before heat treatment (26.9 nm) [18].

The distribution of solute atoms in the matrix and precipitates in AZ31 were mapped using STEM-EDX with corresponding maps of Mg, Al, Mn and Zn shown in Figure 3.4. All precipitates are rich in Al and Mn. The amount of Al and Zn in the matrix was measured to be 1.1 and 1.9 wt.%, respectively. The lower Al and higher Zn content in the matrix than the nominal composition of AZ31 (3 wt% Al and 1 wt.% Zn) can be ascribed to the formation of Al-rich precipitates resolution limit of EDX composition measurement (~1%).

In summary, Mg and AZ31 share similar texture and grain size after heat treatment, but the AZ31 alloy contains Al and Zn solute atoms in the matrix, precipitates and residual dislocations.
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![HADF STEM image of AZ31 and corresponding maps of Mg, Al, Mn, and Zn](image)

**Figure 3.4:** HADF STEM image of a random area from AZ31 and the corresponding maps of Mg, Al, Mn, and Zn with respect to the area of interest marked as red box.

The \(<c>\)-axis compression stress-strain responses of heat-treated pure Mg and AZ31 are shown in Figure 3.5. The ultimate compressive strength of AZ31 (300 ± 5 MPa) was consistently higher than that of pure Mg (243 ± 7 MPa). The average strain to failure of AZ31 (9.9% ± 0.5%) was also consistently higher than that of pure Mg (6.4% ± 0.3%) with a 50% increase. The higher ultimate compressive strength of AZ31 can be attributed to the interaction of dislocations with precipitates, pre-existing dislocations, and to a lesser extent, solute atoms. The improved strain to failure in the AZ31 samples could be related to the fact that increased strain hardening inhibits plastic instabilities [19], but the affect that the solute atoms have on \(<c+a>\) dislocation cores geometry and the attendant mobility of \(<c+a>\) dislocations must also be considered.
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![Engineering Stress vs. Strain Curve](image)

**Figure 3.5:** Engineering stress-strain curves of polycrystalline AZ31 Mg alloy (red) and pure Mg (blue) under compression along ND indicate consistently higher ultimate compressive strength and strain to failure of AZ31 than that of pure Mg.

3.3.2 Non-dissociated \(<c+a>\) dislocations in AZ31

To unravel the effect of solutes on \(<c+a>\) dislocation behavior in commercial wrought Mg alloy, the dislocations in pure Mg and AZ31 samples that were deformed to 3% under identical deformation conditions were imaged with WBDF at a series of tilt angles. Orientation near one \((11\bar{2}0)\) zone axis was selected and the \(g \cdot b = 0\) invisibility criteria was utilized to deduce the Burgers vectors [2]. The diffraction vector \(g_c = [0002]\) was used to
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image ⟨c⟩ dislocations (bₜₐₜ = [0001]) and the c-component of ⟨c + a⟩ dislocations (bₕₜₚₚ = 1/3[1123]) with ⟨a⟩ dislocations (bₜₛₜₜ = 1/3[1120]) invisible. By contrast, for the gₐ = [1T00] diffraction vector, ⟨a⟩ dislocations and the a-component in ⟨c + a⟩ dislocations are visible but ⟨c⟩ dislocations are invisible. Dislocations that are visible for both gₐ and gₜ are ⟨c + a⟩ dislocations. Representative WBDF micrographs for pure Mg and AZ31 are given in Figure 3.6 with diffraction vectors illustrated by yellow arrows. Examples of ⟨c⟩ + a⟩ and pure ⟨a⟩ dislocations are marked with red dash lines and solid blue lines respectively in all images.

Figure 3.6 (a) is of pure Mg and was imaged using gₜ = [0002]; long straight intermittent thin white lines that appear to be ⟨c⟩ + a⟩ dislocations can be observed lying parallel to the basal plane, which for this imaging condition is parallel to the incident beam. By contrast, when the thin foil was tilted about gₐ = [1T00] and away from the [1120] zone axis with the two-beam condition maintained (e.g. the (1T00) plane remains parallel to the incident electron beam but the basal plane is inclined at 10°, 20°, 30° from the electron beam), the ⟨c⟩ + a⟩ dislocations that appeared to be long and straight in Figure 3.6 (a) can now be seen to be dissociated on the basal plane with stacking fault (SF) fringes visible, similar to what was reported by Geng et al. [8] and Xie et al. [20].

The nonconservative dissociation of ⟨c⟩ + a⟩ dislocation creates a SF loop that is cut off by the free surfaces at the top and bottom of the TEM thin foil. A few curved dislocation segments can be seen in Figure 3.6 (c, d), but most SFs only have partial dislocations visible at the ends. The long straight intermittent thin white lines in Figure 3.6 (a) receive their
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contrast from the SF. When tilted, the thickness of the SFs increases which indicates that the SF lies on basal plane. These basal dissociated <c + a> dislocations indicate a core transformation from pyramidal to basal planes. After the transformation, <c + a> dislocations transit from glissile to sessile and can no longer accommodate <c>-axis compression and can also retard the movement of glissile <c + a> dislocations on the pyramidal plane. As a result, the mobility of <c + a> dislocations and the attendant ductility of pure Mg is low.

In parallel to the dislocation core transformation, a number of dislocation loops formed in pure Mg under <c>-axis compression (speckles in Figure 3.6 a-d). The formation of these nano-scale loops is analogous to the formation of interstitial loops during pencil glide of bcc metals [21], the formation of nano-scale loops occurs during the glide of ordinary dislocations in TiAl [22] and during pyramidal glide in Ti3Al [23]. These dislocation loops also can retard the movement of the glissile <c + a> dislocation, leading to reduced ductility.

Surprisingly, the <c + a> dislocations that were observed in AZ31 displayed rather different behavior. The dislocations were imaged using the same diffraction vectors as for pure Mg and the WBDF images employing gc = [0002] and ga = [1̅100] are present in Figure 3.6 (e-f). The <c + a> dislocations in AZ31 were observed to align parallel to the basal plane and appeared compact when imaged with gc = [0002], as shown in Figure 3.6 (e). However, contrary to pure Mg, the <c + a> dislocations in AZ31 remain compact with no apparent dissociation or fault fringes even when the basal plane is tilted by 30°, as shown in Figure 3.6 (h). The compact nature of the <c + a> dislocations in AZ31 indicates that
the dissociation on the basal plane is suppressed by the addition of Al and Zn. The suppressed dissociation can be explained by the core transformation model predicted by Wu et al. [15] that the alloying can increase the dissociation energy of <c+a> dislocations on the basal plane. The observation is also consistent with the super jog model that the long and thin loops form on the basal plane, and the growth of the loops can be constrained by the solute atoms or precipitates in AZ31. With the more compact core structure, <c+a> dislocations in AZ31 can be expected to be more mobile than the climb dissociated <c+a> dislocations that are observed in pure Mg, and the increased mobility may be used to explain the higher strain to failure in AZ31. This correlation of alloying, dislocation core modification, and improved mechanical properties points to the role of <c+a> dislocation cores in determining the mobility of <c+a> dislocations and underpins a strategy for Mg alloy design: utilize solute atoms to suppress <c+a> dislocation dissociations (ostensibly by increasing <c+a> dissociation energy) and improve strain to failure and attendant formability. The magnitude of the effect is modest for AZ31, but extension to rare earth (RE) elements like Y, and potentially Ca, holds even greater promise.

It is worth noting that although AZ31 alloy displays improved strain to failure when compared to pure Mg, the amount of the improvement is modest (50%). One striking observation is that the <c+a> dislocations in AZ31 are long and straight and aligned with the basal plane. This observation indicates that although these dislocations did not dissociate on the basal plane, the core might still relax into a nonplanar configuration.
Figure 3.6: [Left Column]: WBDF images of pure Mg with: (a) the basal plane parallel to the incident beam, and (b,c,d) the basal plane systematically tilted 10°, 20°, 30° from the electron beam. [Right Column]: WBDF images of AZ31 taken with the same diffraction conditions.
3.3.3 Dislocation line analysis

One question for \(<c + a>\) dislocations in Mg and Mg alloys is which pyramidal plane is the slip plane of the dislocations. The four dislocations that were marked in Figure 3.6 are analyzed using the projection approach discussed in Section 2.4.2 and the results of the dislocation line vectors are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Plane 1</th>
<th>Plane 2</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0001)</td>
<td>(1112)</td>
<td>Pyramidal II</td>
</tr>
<tr>
<td>(0001)</td>
<td>(1112)</td>
<td>Pyramidal II</td>
</tr>
<tr>
<td>(0001)</td>
<td>(1112)</td>
<td>Pyramidal II</td>
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<td>(0001)</td>
<td>(1112)</td>
<td>Pyramidal II</td>
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<tr>
<td>(0001)</td>
<td>(0111)</td>
<td>Pyramidal I</td>
</tr>
<tr>
<td>(0001)</td>
<td>(1112)</td>
<td>Pyramidal II</td>
</tr>
<tr>
<td>(0001)</td>
<td>(0111)</td>
<td>Pyramidal I</td>
</tr>
<tr>
<td>(0001)</td>
<td>(1212)</td>
<td>Pyramidal II</td>
</tr>
</tbody>
</table>

Determination of the dislocation line directions using the conventional projection approach indicates that the four long straight \(<c + a>\) dislocations in Fig. 4 (a-d) are \([61 54 7 0]\), \([62 56 6 0]\), \([63 55 9 0]\) and \([60 56 4 0]\). Thus, \(<c + a>\) dislocations in pure Mg are close to \(<1\bar{1}00>\) and aligned along the intersection of the basal and pyramidal II plane. The viewing direction is close to \(<1\bar{2}10>\) axis. When viewing the loops that were cut by the two surfaces of TEM foil along a \([1\bar{2}10]\) zone axis, the intersection of the basal plane and the surfaces of TEM foil is in the image plane and the line vector of the intersection is perpendicular to the viewing direction and parallel to a \([10\bar{1}0]\) direction. The SF fringes are parallel to the
surfaces and thus also along \(<10\overline{1}0>\) direction. However, the line vectors of the partials that surround the SF are unknown.

By contrast, dislocations in AZ31 are compact with no apparent dissociation and the line vectors can be determined to have line directions of \([65\ 19\ 46\ 0]\), \([59\ 56\ 3\ 0]\), \([67\ 32\ 34\ 0]\) and \([60\ 5\ 55\ 0]\). Two of the line vectors are close to a \(<1\overline{1}00>\) direction and associated with the intersection of a pyramidal II plane with the basal plane, and the other two are close to \(<1\overline{2}10>\) direction and associated with the intersection of a pyramidal I plane with the basal plane. The observations contradicts the SF configuration suggested by super jog model that the dragged super jog of \(<c+a>\) dislocations on both pyramidal I and II planes will form a loop aligning with the \(<10\overline{1}0>\) direction, the intersection of pyramidal II and basal planes \([12]\). The dislocation line vectors of the \(<c+a>\) dislocations after core transformation are parallel to the intersection of the basal plane and both pyramidal planes, which is not consistent with the super jog model. This is probably attributed to the reason that the dislocations are originally on two pyramidal planes and dissociate onto the basal plane through core transformation. The \(<c+a>\) dislocations after core transformation become sessile and stay at the intersection of the pyramidal planes and the basal plane. If this assumption is true, the \(<c+a>\) dislocations are activated on both pyramidal planes in AZ31.

3.3.4 SF analysis in pure Mg

The widths of SFs increase with tilting angle and scale with the projected area of the basal plane on the image plane, as shown in the top row of Figure 3.7. The compact \(<c+a>\)
dislocation in AZ31 is also shown for comparison. The thickness of each SF (T) follows a simple geometric relationship \( T = t \sin \theta \), where \( t \) is the foil thickness and \( \theta \) is the tilt angle (10-30°), further confirming that the SF lies parallel to the basal plane.

**Figure 3.7:** Magnified images of \(<c+a>\) dislocation 1 of pure Mg (top row) taken in the area highlighted by blue dashed boxes in Figure 3.6 (b-d); and \(<c+a>\) dislocation 1 of AZ31 (bottom row) taken in the area highlighted by red boxes in Figure 3.6 (f-h).

**Table 3.2:** Average thickness of SF versus tilting angle \( \theta \).

<table>
<thead>
<tr>
<th>Tilting angle ( \theta ) (°)</th>
<th>( \sin \theta )</th>
<th>Average thickness of SF (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.174</td>
<td>38.1</td>
</tr>
<tr>
<td>20</td>
<td>0.342</td>
<td>64.5</td>
</tr>
<tr>
<td>30</td>
<td>0.5</td>
<td>82.7</td>
</tr>
</tbody>
</table>

The values of \( \sin \theta \) and the corresponding average thickness of SF for various tilting angles are listed in Table 3.2. Using this relationship between SF thickness and tilting angle and assuming the thickness of foil \( t \) is constant in the foil, the thickness \( t \) can be linearly fitted as the slope while plotting the thickness of SF versus \( \sin \theta \) (Figure 3.8). The linear fitting has an R value of 0.99 and the fitted slope of \( t \) is 165.1 nm.
Figure 3.8: Linear fitting of SF thickness versus \( \sin \theta \) and foil thickness \( t \) is the slope.

The intensity of a SF is a function of the foil thickness \( (t) \), the depth \( (t_f) \) and diffraction conditions including excitation error \( (s) \), extinction distance \( (\xi_g) \) and \( \alpha = \mathbf{g} \cdot \mathbf{R} \ (\mathbf{g} = 1\overline{1}00) \).

The SF intensity is expressed as equation (3.2) [24-26], where \( t' = t_f - t/2 \) and \( s = 0.053 \) nm\(^{-1}\), \( \xi_g = 181 \) nm, which are given in Section 2.4.1.

\[
I_g = \frac{1}{(s \xi_g)^2} \left\{ \sin^2 \left( \pi s t_1 + \frac{\alpha}{2} \right) + \sin^2 \left( \frac{\alpha}{2} \right) - \sin \left( \frac{\alpha}{2} \right) \sin \left( \pi s t + \frac{\alpha}{2} \right) \cos(2\pi t') \right\} 
\]  

(3.2)
Since $\alpha$ is constant for a particular defect and $\mathbf{g}$ vector, and foil thickness ($t$) can be assumed to be constant for a particular sample. Then equation (3.2) becomes

$$I_g \propto \frac{1}{s^2} \{A - B \cos(2\pi t')\}$$  \hspace{1cm} (3.3)

For the SF intensity, the thickness periodicity depends on $s^{-l}$ and the intensity varies as $s^{-2}$. The SF fringes are too close to each other and hard to distinguish when the sample is tilted by 10°, as shown in Figure 3.6 (b). But the SF fringes in Figure 3.6 (c, d) show apparent nine lines, which is in good agreement with the distribution of SF intensity plotted as function of depth ($t_1$) in Figure 3.9.

![Figure 3.9: SF intensity versus depth in the TEM foil.](image-url)
3.4 Summary and conclusions

In summary, \(<\mathbf{c} + \mathbf{a}>\) dislocations were observed in both hot-rolled pure Mg and AZ31 after close-to-\(<\mathbf{c}>\)-axis compression. The presence of Al and Zn in AZ31 was found to suppress the nonconservative dissociation of \(<\mathbf{c} + \mathbf{a}>\) dislocations on the basal plane. The \(<\mathbf{c} + \mathbf{a}>\) dislocations in AZ31 are aligned with the intersection of the basal plane and both pyramidal I and II planes, which indicates the \(<\mathbf{c} + \mathbf{a}>\) dislocations are originally activated on both planes. These experimental findings parallel efforts in MD and DFT simulations that investigated the governing fundamental mechanisms for the improved ductility with alloying and provides a benchmark for these efforts. The compact dislocation cores correlate to increased \(<\mathbf{c} + \mathbf{a}>\) dislocation mobility and improved strain to failure for AZ31 as compared to pure Mg. The potential for using alloying to modify \(<\mathbf{c} + \mathbf{a}>\) dislocation core geometries, in a way that has a transformative effect on \(<\mathbf{c} + \mathbf{a}>\) dislocation mobility, and attendant ductility and formability, is expected to be even more potent in alloy systems (e.g. RE, Ca) that have been shown to have a positive influence in developing more formable Mg alloys.
3.5 References for Chapter 3

CHAPTER 3. UNDISSOCIATED <C+A> DISLOCATION IN AZ31

Chapter 4.
Influence of Rare-earth Alloying on \( <c + a> \) Dislocations in Mg Alloys

As described in the previous chapter, the addition of Al and Zn in the commercial wrought Mg alloy AZ31 has been shown to suppress the dissociation of \( <c + a> \) dislocations and improve the ductility as compared to pure Mg. However, the improvement of mechanical properties (e.g. strain to failure) of AZ31 is still limited. Alloying rare earth (RE) elements with Mg has been shown to dramatically enhance the activity of \( <c + a> \) dislocations and weaken the basal texture, causing a reduction in the overall anisotropy of Mg and providing improved ductility [1]. This chapter contrasts the influence of RE alloying elements on the dislocation behavior with those observed in pure Mg. Single crystal Mg-3Er and pure Mg micropillars were compressed and the two materials present similar deformation behavior. Weak-beam dark field (WBDF) with careful tilting elucidated that the dissociation of \( <c + a> \) dislocations in Mg-3Er alloy is dramatically reduced compared to that of pure Mg. HRSTEM of the dislocation cores for partial \( <c + a> \) and full \( <a> \) dislocations showed that the Er addition has little effect on the core of \( <a> \) dislocations, but it does increase the
dislocation width of partial <c + a> dislocations. This change in dissociation behavior indicates higher dissociation energy and the wider core on pyramidal plane implies less stability on the basal plane, both of which leads to higher mobility of <c + a> dislocations on the pyramidal planes.

4.1 Introduction

To understand the mechanism of RE-induced ductility in Mg alloys, computational and experimental efforts have been undertaken. Sandlöbes et al. performed detailed analysis of the activated dislocations and slip systems via post-mortem TEM and SEM-EBSD based slip band analysis in deformed Mg-Y alloy and concluded that the improved ductility is caused by the high activity of <c + a> dislocations on both pyramidal planes [1]. They also characterized the stacking faults formed by dissociated <c + a> dislocations in Mg-Y and used Ab initio modeling to calculate the I1 stacking fault energy (SFE) of various binary Mg alloy systems; and they concluded that the lower SFE causes the formation of stable stacking faults (SFs) that serve as sources for <c + a> dislocation nucleation [1-3]. However, the reduction of SFE is not always consistent with ductility [4]. And the calculated SFE energy cannot directly explain the spacing of nonconservatively dissociated partial <c + a> dislocations.

Wu et al. employed density function theory (DFT) simulations to calculate the energy change in pyramidal I to II cross slip of <c + a> screw dislocations in Mg alloys with various alloying elements [5, 6]. They found that the addition of RE elements in Mg
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON <C+A> DISLOCATION

decreased the cross-slip barrier of \(<c + a>\) dislocations, promoting cross slip between pyramidal I and II planes. They proposed the activation of cross slip maintains mobile \(<c + a>\) dislocations on pyramidal planes. Evidence for the cross slip of \(<c + a>\) dislocations in Mg-RE alloys has been experimentally shown via TEM observations, where \(<c + a>\) dislocations are connected both on and out of the basal plane [1-3, 5]. Interestingly, the connected \(<c + a>\) dislocations have also been observed in pure Mg [7] and non-RE Mg alloys [8], which might indicate the activation of cross slip. However, the ductility of these materials is not comparable with that of Mg-RE alloys. Moreover, simply aligning dislocation line segments with the edge-on planes in a zone axis does not provide definitive evidence regarding the slip plane of \(<c + a>\) dislocations (e.g. pyramidal plane or basal plane) because TEM images are inherently planar projections of 3-dimensional dislocation structures [9]. Therefore, more detailed experimental work is needed to uncover the influence of RE alloying on dislocation behaviors and deformation mechanism in Mg-RE alloys.

In this chapter, a systematic investigation of Mg-3Er (3 wt.%) was undertaken to better understand \(<c + a>\) dislocations and to determine the influence of RE alloying on their behavior. The addition of Er has been shown to dramatically increase ductility without sacrificing strength and to improve the corrosion resistance in alkaline solutions [10-12]. Moreover, Er has considerable solubility in Mg and easily forms single-phase solid solution Mg alloys. Furthermore, rolled Mg-Er alloys also present weaker texture compared to pure Mg and conventional Er-free Mg alloys. A single crystal, solid solution, binary Mg-RE alloy would be ideal to decouple the influence of grain size, grain boundary, second phase
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON $<\mathbf{c+a}>$ DISLOCATIONS

and texture from the solute effect on dislocation mobility on the strength and ductility. Nevertheless, no single crystal Mg-RE alloy sample has ever been grown successfully, probably due to the high reactivity of the RE elements. In order to isolate the effect of alloying, from grain size and texture on the mechanical behavior and to achieve a single crystal sample in a polycrystalline alloy, compression tests were performed on the single crystalline micropillars fabricated from polycrystalline Mg-3Er and pure Mg samples [13, 14].

The overall morphology of $<\mathbf{c+a}>$ dislocations in Mg-3Er alloy were characterized and compared to those of pure Mg. Detailed tilting and WBDF imaging were performed to visualize the evolution of dislocation morphology. The $<\mathbf{c+a}>$ dislocations were imaged from multiple directions and carefully analyzed. The line vectors of the dislocations were analyzed and compared to the predictions by simulation. In addition, the core structure of $<\mathbf{c+a}>$ dislocations in the Mg-3Er alloy was studied using HRSTEM and the strain field of dislocation cores were carefully measured and modeled.

4.2 Experiments

Both hot-rolled Mg and Mg-3Er alloy sheets were cut using wire electrical discharge machining (EDM) to dimensions of 6 mm x 6 mm x 12 mm. The samples were annealed at 400°C for 24 hours to increase the grain size and to decrease pre-existing dislocation density. The annealed Mg-3Er samples were water quenched to avoid precipitation. The EDM-cut surfaces were mechanically polished with SiC abrasive grinding paper (1200 for
standard ANSI grit or P4000 for European P-grade) under zero load (nominally zero readings on the Allied automated polisher), and finally chemically polished by 5% nitric acid in methanol for 10 minutes to remove residual artifacts on the surface from polishing. The samples were then compressed along the ND to 3% engineering strain to introduce \(<c + a>\) dislocations.

TEM foils were cut parallel to the RD-ND plane from the deformed samples with ND in the plane of the foil using a diamond wire saw with a wire thickness of 0.12 mm. The cut foils had a thickness of 1 mm. To avoid damage, TEM samples were mechanically polished on both sides to a thickness of 150 μm under zero nominal load. Disks of 3 mm in diameter were punched from the polished foil. The disks were then electro-chemically polished with an electrolyte of 5.3 g lithium chloride, 11.16 g magnesium perchlorate, 100 mL 2-butoxyethanol and 500 mL methanol, at -35°C and 100 V, and a hole with thin area was drilled at the center of disc from electro-chemical polishing. The thin area was further thinned to electron transparency using PIIPS in vacuum at liquid nitrogen temperature, 0.2 keV for 30 min. The electro-polishing and PIIPS remove the defects introduced by mechanical polishing and fabricate artifact-free TEM samples. The procedure for TEM sample preparation is shown in Figure 4.1.

EBSD samples were cut using diamond wire saw parallel to the RD-TD plane. The foils were polished on one side using ANSI 1200 grit SiC paper to remove around 400 μm in thickness and then using water-free silica colloidal to mirror-like surface. The surface was subsequently etched with 10% nitric acid in methanol for 20s.
The crystallographic orientation information of the sheets was acquired by electron backscattered detraction (EBSD) and used to generating inverse pole figure (IPF) maps on
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON <C+A> DISLOCATIONS

the surface perpendicular to the ND. A grain with its [0002] axis out-of-plane was located, as highlighted in Figure 4.2. The average misorientation calculated from about 20 random positions inside the grain (marked by black dots in Figure 4.2) was within 2° of the [0001] axis. Numerous micropillars were fabricated using focused ion beam (FIB) annular milling for pillars with dimensions 5 μm diameter, 11 μm length and <1° taper angle. Ten micropillars were compressed using the inSEM microindenter (Nanomechanics Inc.) with a 30 μm diamond flat punch. Four of the pillars were compressed to failure to obtain the full stress-strain curves and the other six were compressed to prescribed 3% strain for FIB lift-out and dislocation characterization.

Figure 4.2: IPF maps of (a) pure Mg and (b) Mg-3Er alloy. The grain with [0001] orientation is highlighted with yellow circles.

TEM foils with the foil normal along a [1120] zone axis were lifted-out from pillars deformed to 3% strain using an Thermo Scientific Helios G4 UC FIB [15-19]. A series of
currents were applied to thin the foil using 30kV voltage to guarantee that the beam damage from each previous step was removed by the lower current. The final step applied 5kV and 80pA to polish the damage from 30kV. The thickness of the lift-out foil after the final step FIB polishing was less than 200 nm. The procedure of FIB lift-out is shown in Figure 4.3.

The FIB prepared thin lamella were then ion polished using a Fischione 1040 NanoMill instrument and a 500 eV Ar-ion beam to remove any implanted Ga from FIB milling [16, 20].

![Figure 4.3](image)

**Figure 4.3:** Procedure of FIB lift-out TEM foil from the pillar deformed by 3%.

The dislocations were imaged using WBDF on a Tecnai 12 TEM at 100 keV. And the atomic resolution STEM was conducted using a JEOL JEM-ARM200CF instrument fitted with a CEOS ASCOR aberration-corrector and a cold-field emission electron gun. The strain field of dislocation core was analyzed using Gatan DigitalMicrograph software with geometrical phase analysis (GPA) script [21].
4.3 Results and discussion

4.3.1 In situ micro-compression mechanical properties

The engineering stress-strain curves of micro-compression tests on pure Mg (blue) and Mg-3Er alloy (red) [0001]-oriented micropillars are shown in Figure 4.4. The curves of pure Mg start to deviate from the linear elastic region at around 210 MPa, which indicates the onset of plasticity. Strong hardening comprising a series of small strain bursts was then observed. For Mg-3Er, the initial linear region extends to around 280 MPa, which is about 70 MPa higher than that of pure Mg due to solute hardening of Er. The strain hardening rates of Mg-3Er compression is close to that of pure Mg, and the strains to failure of both pure Mg and Mg-3Er are comparable (~10%). Finally, the pillars of both pure Mg and Mg-3Er failed catastrophically and abruptly when they lost stability. Examples of an as-fabricated pillar and a post-compression pillar are shown in Figure 4.5 (a) and (b), respectively. The traces in the failed pillars are all parallel to the basal plane, which means the dominant slip traces come from the basal slip after the instability. No apparent traces of non-basal deformation mechanisms are visible.
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**Figure 4.4:** Engineering stress-strain curve of micro-compression tests, two on pure Mg (blue) and two on Mg-3Er alloy (red).

**Figure 4.5:** Micro-pillar before and after a compression test.
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON <C+A> DISLOCAITON

The high strain hardening is due to the fact that the alignment of the loading direction along the <c>-axis results in a near-zero Schmid factor on the basal plane and suppresses the formation of easy glide basal <a> dislocations and activates only <c + a> dislocations. The Schmid factors of different deformation mechanisms were calculated using \( m = \cos(\phi) \cdot \cos(\theta) \), where \( \phi \) is the angle between the loading direction and the vector normal to the glide plane and \( \theta \) is the angle between loading direction and the glide direction. The Schmid factor of basal <a>, pyramidal I <c + a>, pyramidal II <c + a>, extension twinning and compression twinning are shown graphically in Figure 4.6 (a). Solid and dashed black lines represent the compressive direction on the (1100) and (1120) planes, respectively; and the color areas in between the solid and dashed black lines represent the compressive direction between the two planes. The curves depict the change of Schmid factor of deformation mechanisms with the angle (\( \Phi \)) between the compressive direction and the basal plane increasing from zero (compression along <a>-axis) to 90° (compression along <c>-axis). The shaded region in Figure 4.6 (a) includes all the possibilities of Schmid factor due to the 6-fold symmetry of HCP structure. Due to the asymmetry of deformation mechanisms, <c + a> slip and contraction twinning are activated by <c>-axis compression and extension twinning is activated by <a>-axis compression, the negative Schmid factors are corrected to be zero. The Schmid factor of extension twinning is zero when \( \Phi > 46^\circ \) and contraction twinning and <c + a> slip cannot be activated when \( \Phi < 25^\circ \).
Figure 4.6: (a) Schmid factor and (b) CRSS of different deformation mechanisms in Mg activated by compression along different directions
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON $\langle \mathbf{c}+\mathbf{a} \rangle$ DISLOCATION

The critical values of compressive strength for different compressive directions and deformation mechanisms plotted in Figure 4.6 (b) (the CRSS values from Table 1.1) shows that basal slip is not activated if the misorientation between compressive direction and $\langle \mathbf{c} \rangle$-axis is lower than 2° ($\Phi > 88^\circ$). Therefore, the compression tests on the pillars within 2° off [0001] axis can only activate $\langle \mathbf{c} + \mathbf{a} \rangle$ slip before instability occurs.

To characterize the dislocations in pure Mg and Mg-3Er, TEM was utilized to investigate the post-mortem pillars that were compressed by 3% engineering strain. A $\langle 1120 \rangle$ zone axis was selected and the $\mathbf{g} \cdot \mathbf{b} = 0$ invisibility criteria was utilized to deduce the Burgers vectors [8]. The diffraction vector $\mathbf{g}_c = [0002]$ was used to image $\langle \mathbf{c} \rangle$ dislocations ($\mathbf{b}_{\langle \mathbf{c} \rangle} = [0001]$) and the c-component in $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations ($\mathbf{b}_{\langle \mathbf{c}+\mathbf{a} \rangle} = 1/3[1123]$), but $\langle \mathbf{a} \rangle$ dislocations ($\mathbf{b}_{\langle \mathbf{a} \rangle} = 1/3[1120]$) are invisible. By contrast, for $\mathbf{g}_a = [1\bar{1}00]$ diffraction vectors, $\langle \mathbf{a} \rangle$ dislocations and a-component in $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations are visible but $\langle \mathbf{c} \rangle$ dislocations are invisible. Dislocations that are visible for both $\mathbf{g}_a$ and $\mathbf{g}_c$ are $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations. Representative WBDF micrographs for pure Mg and Mg-3Er are given in Figure 4.7 with diffraction vectors illustrated by yellow arrows. The imaging conditions for pure Mg and Mg-3Er samples were nominally identical. Examples of $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations are highlighted with red dashed lines and the SF fringes in pure Mg was marked with blue arrows. A few out-of-basal segments in Mg-3Er under $\mathbf{g}_c$ condition were circled in yellow, see Figure 4.7 (d).
Figure 4.7: WBDF images of dislocations acquired from longitudinal sections of pillars compressed by 3% strain. Examples of \( <c+a> \) dislocations are highlighted with red dashed lines and the SF fringes in pure Mg was marked with blue arrows. The out-of-basal segments in Mg-3Er are circled in yellow.

The \( <c+a> \) dislocations in pure Mg dissociate on the basal plane with SF fringes observed in Figure 4.7 (a) and long and straight lines in Figure 4.7 (c). The \( <c+a> \) dislocations in Mg-3Er align parallel to the basal plane but show no apparent dissociation, see in Figure
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON $<\mathbf{C+A}>$ DISLOCAITON

4.7 (b) and (d). Interestingly, there exist off-basal dislocation segments in Figure 4.7 (d) and highlighted by yellow circles, but none in Figure 4.7 (b). The presence of contrast in $\mathbf{g}_c$ condition but not in $\mathbf{g}_a$ condition indicates that these segments are pure $<\mathbf{c}>$ instead of cross-slipped $<\mathbf{c} + \mathbf{a}>$. The pure $<\mathbf{c}>$ dislocations can originate from the decomposition of $<\mathbf{c} + \mathbf{a}>$ dislocations into $<\mathbf{c}>$ and $<\mathbf{a}>$ dislocations, and the $<\mathbf{a}>$ dislocations can glide away leaving only the immobile $<\mathbf{c}>$ dislocations [22].

No basal $<\mathbf{a}>$ dislocations were observed in both samples after comparing the contrast images acquired under $\mathbf{g}_a$ and $\mathbf{g}_c$ conditions and ignoring the bright spots of beam damage introduced by FIB cleaning. The absence of basal $<\mathbf{a}>$ dislocations indicates that the alignment of the loading direction along $[0001]$ axis suppressed basal slip.

As discussed in Chapter 3, the undissociated $<\mathbf{c} + \mathbf{a}>$ dislocations may contribute to the improved strain to failure in Mg-3Er. The undissociated $<\mathbf{c} + \mathbf{a}>$ dislocations observed in the lift-out samples and the possible cross-slip process predicted by DFT simulations [5] should lead to decreased strain hardening in Mg-3Er samples. However, no apparent difference in the hardening rate were detected in the micropillars, as shown in Figure 4.4. The equally high strain hardening in the two materials might be related to the size effect of pillar compression [23-27]. The stress-strain curves display a trend of increasing strength with decreasing sample size for single crystal micropillars, and the possible decreased hardening rate introduced by the increased mobility of $<\mathbf{c} + \mathbf{a}>$ dislocations may be overwhelmed by the hardening from the size effect. To overcome the influence of size effect, the diameter of pillars should be larger than 10 μm. However, the time cost of FIB
fabrication increases exponentially with the size of pillars and the number of pillars that can be made from a single grain decreases rapidly with increasing pillar diameter. The dimension of pillars employed in this work was chosen by considering the number of pillars required, the size effect, and the fabrication cost. While the stress-strain curves may be compromised, the micropillars do allow us to introduce and study \(<c+a>\) dislocations.

4.3.2 Suppressed dissociation of \(<c+a>\) dislocation in Mg-3Er

The WBDF micrographs in Figure 4.8 detail the dislocations in polycrystal Mg-3Er samples deformed to 3% strain along ND after annealing at 400°C. Similar to the observation in the lift-out samples from compressed single crystal micropillars, the \(<c+a>\) dislocations are predominantly lying parallel to the basal plane with out-of-basal segments connecting the \(<c+a>\) dislocations on the basal plane, as shown in Figure 4.8 (a). A few out-of-basal segments were also observed in Figure 4.8 (a), but the segments have both \(<c>\) and \(<a>\) components, examples of which were marked with red circles in Figure 4.8 (a) and (b). This indicates that the off-basal segments in the bulk Mg-3Er are \(<c+a>\) dislocations with no decomposition. This observation is different from the pure \(<c>\) off-basal segments in single crystal pillars.

Another feature of \(<c+a>\) dislocations in deformed bulk Mg-3Er sample that is different from the micropillar is the dissociation spacing. When a thin foil prepared from deformed bulk samples was tilted about \(g_a = [1\bar{1}00]\) and away from the \([1\bar{1}20]\) zone axis with the two-beam condition maintained (e.g. the \((1\bar{1}00)\) plane remains parallel to the incident electron beam but the basal plane is inclined at 25° and 45° from the electron beam), the
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON \(<c+a>\) DISLOCATION

\(<c+a>\) dislocations are clearly dissociated on the basal plane with observable SF fringes, but the partial spacing in Mg-3Er (~10 nm) is dramatically narrower than that of pure Mg that was shown in Figure 3.6. It is also worth noting that dissociation is only observed in \(<c+a>\) dislocations, not basal \(<a>\) dislocations. The basal \(<a>\) dislocations are compact even after the foil is tilted 45° off the zone axis.

Figure 4.8: WBDF images of Mg-3Er with: (a) the basal plane parallel to the incident beam, and (b,c,d) the basal plane systematically tilted 10°, 25°, 45° from the electron beam.
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON \(<C+A>\) DISLOCATIONS

The SF loops are sessile with \(1/6<20\overline{2}3>\) Burgers vector that does not lie on the basal plane and can act as obstacles to mobile dislocations. The formation of loops could be from different models but the growth into large loops are mostly from climb-related process. Geng et al. characterized the \(<c+a>\) loops in Mg and proposed that the dislocations loops that are smaller than 100 nm are perfect \(<c+a>\) loops but the larger loops dissociate into two concentric partial dislocations enclosing a SF on the basal plane [28]. They also suggested that a jog can be formed when a gliding screw \(<c+a>\) dislocation on the pyramidal plane is pinned by a less mobile edge dislocation, and the continued motion of the screw \(<c+a>\) dislocation can drag the jog along by climb, resulting in point defects that can coalesce to form dislocation loops. Later, Srivastava et al. employed MD simulation to investigate the process and predicted that the loops with SF introduced by super jog can be formed athermally with several nanometers wide and tens of nanometers long [29]. The prediction of super jog model is consistent with the observation of the SF in width of hundreds of nanometers in pure Mg as shown in Figure 3.6, Figure 3.7 and Figure 4.7, but cannot explain the fact that \(<c+a>\) dislocations are predominantly aligning parallel to the basal plane with none left on the pyramidal planes.

Recently, Wu et al. performed MD simulation and suggested a thermally activated ‘climb-like’ process that the core of edge \(<c+a>\) dislocations can transform from pyramidal plane to the basal plane, forming a sessile configuration of SF surrounded by partial \(<c+a>\) dislocations. This ‘climb-like’ model explains the absence of \(<c+a>\) dislocations on the pyramidal plane but contradicts the observation of the SF width in pure Mg. The addition of Er may unpin the super jog and release the drag effect on screw \(<c+a>\) dislocations, or
it may increase the core transformation energy of edge $\langle c + a \rangle$ dislocations onto the basal plane. Both processes can lead to the improved mobility of $\langle c + a \rangle$ dislocations and contribute to the enhanced ductility in Mg-3Er alloy.

Another point of interest for the $\langle c + a \rangle$ dislocations in Mg-RE alloys is the possible cross-slip behavior. The cross slip is an intermediate process because the initial $\langle c + a \rangle$ dislocations, observed in the post-mortem samples, have dissociated on the basal plane. And if cross slip occurs during loading, the $\langle c + a \rangle$ dislocations could dissociate onto the basal plane from both pyramidal I and II planes. The sessile partial dislocations should lie at the intersection of the basal plane and the active pyramidal planes, and the analysis of line vectors of the dissociated partials in Mg-3Er alloy can be used to determine the active pyramidal slip plane and to analyze the cross-slip behavior of $\langle c + a \rangle$ dislocations.

**Figure 4.9:** A schematic of dislocation lines in Figure 4.8 (b) and (d) colored by black, blue and red for basal $\langle a \rangle$, pyramidal I $\langle c + a \rangle$ and pyramidal II $\langle c + a \rangle$ dislocations.
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON <C+A> DISLOCATIONS

The dislocation line vectors were analyzed using the method described in section 2.4.2, and two incident beams that were tilted 10° and 45° off of the [11̅20] zone axis along g_a. The dislocation lines that appear in Figure 4.8 (b) and (d) were sketched in Figure 4.9 and the g vector of the two images and all the projected lines were quantified using the coordinate shown in Figure 4.9. The basal <a> dislocations are marked in black and the <c + a> dislocations are in red.

For g_a = [1̅100] and an incident beam direction \( \left[ 1 \overline{1} \overline{2} \frac{3 \tan \alpha}{c/a} \right] \), where \( \alpha \) is the tilting angle between the beam direction and [11̅20] zone axis), the (hkil) plane that the dislocation projection lies on, for each incident beam, can be expressed as equation (4.1), where \( \theta \) is the angle between the dislocation line vector and the (1̅100) plane (perpendicular to g_a = 1̅100).

\[
\begin{align*}
    h_i &= -\left(4 \cos^2 \theta + 2 \frac{54 \cos^2 \theta}{\tan^2 \alpha_i}\right) + \sqrt{48 \cos^2 \theta (1 - \cos^2 \theta) \left(1 + \frac{9}{\tan^2 \alpha_i}\right)} \\
    k_i &= 8 \cos^2 \theta - 2 \frac{54 \cos^2 \theta}{\tan^2 \alpha_i} \\
    i_i &= -(h_i + k_i) \\
    l_i &= -\frac{3c \, h_i + k_i}{a \, \tan \alpha_i}
\end{align*}
\]

(4.1)
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON <C+A> DISLOCATION

Table 4.1: Line vector of the dislocations numbered in Figure 4.9 and the two most possible habitat planes with the corresponding error value.

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>i</th>
<th>l</th>
<th>Plane 1</th>
<th>product</th>
<th>Plane 2</th>
<th>product</th>
<th>intersection</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.66</td>
<td>-0.39</td>
<td>-0.27</td>
<td>0.04</td>
<td>(0001)</td>
<td>0.043</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>-0.50</td>
<td>-0.13</td>
<td>0.63</td>
<td>-0.01</td>
<td>(0001)</td>
<td>-0.008</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
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<td>-0.11</td>
<td>0.63</td>
<td>0.00</td>
<td>(0001)</td>
<td>-0.004</td>
<td>(1212)</td>
<td>0.334</td>
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The Miller indices of the dislocation line vectors can be normalized by dividing the value of indices by the vector length $\sqrt{3(h^2 + k^2 + hl + l^2c^2/a^2)}^{1/2}$. If a [uvw] vector is on an (hkil) plane, then we have the product $uh + vk + ti + wl = 0$. The products of the line vector and all the possible slip planes were calculated, and the most probable plane is determined by finding the value of the product closest to zero. The dislocation line vectors and the two most probable planes with the smallest products are shown in Table 4.1. The numbering of the dislocations corresponds to the dislocations in Figure 4.9, which are outlined from Figure 4.8 (b) and (d) with two viewing directions $\alpha_1 = 10^\circ$ and $\alpha_2 = 45^\circ$, respectively.
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON \(<C+A>\) DISLOCATIONS

Most of the \(<c + a>\) dislocations are aligned close to \([10\bar{1}0]\) which is the intersection of the basal plane and the pyramidal II plane, and a few are close to \([1\bar{2}10]\) and associated with pyramidal I plane. Srivastava et al. performed MD simulation of super jog model and predicted the configuration of the dissociated \(<c + a>\) dislocations [29]. If their model is correct, the \(<c + a>\) dislocations on both pyramidal I and II planes would form a loop aligning with the \(<10\bar{1}0>\) direction, the intersection of pyramidal II and basal planes. The prediction captures the behavior of most dissociated \(<c + a>\) dislocations but cannot explain the ones that are parallel to the intersection of the pyramidal I and basal planes. One probability is that the addition of Er changes the dissociation behavior of \(<c + a>\) dislocations and activates the formation of SF that parallel to the intersection with pyramidal I plane. The line vectors that are parallel to the intersections of pyramidal I or II planes may then reflect the original planes that the dislocations are dissociated from, and the \(<c + a>\) dislocations would be predominantly activated on the pyramidal II planes in Mg-Er alloy. The \(<c + a>\) dislocations in pure Mg were believed to glide predominantly on pyramidal I plane, which has been suggested by MD and DFT simulations [30-34] and observed by slip trace analysis [35]. The results of line vector analysis point to the possibility that the addition of Er transfers the dominant slip plane of \(<c + a>\) dislocations from pyramidal I to pyramidal II, which is consistent with the prediction suggested by Ding et al. [30].
4.3.3 Observations of the modified \( <\mathbf{c} + \mathbf{a}> \) dislocation cores in Mg-3Er

To characterize the dislocation core structure of pure Mg and Mg-3Er, HRSTEM HAADF was performed in Lehigh University on behalf of Dr. Christopher Marvel. HAADF provides mass contrast (or Z contrast) and higher atomic number atoms are brighter. HRSTEM HAADF images of pure \( <\mathbf{a}> \) and partial \( <\mathbf{c} + \mathbf{a}> \) dislocations are shown in Figure 4.10 and Figure 4.12. All the atomic-resolution images were acquired using a \([11\bar{2}0]\) zone axis and the Burgers vectors of the dislocations were determined by the Burgers circuit. The strain field of dislocation core was obtained based on a post-processing data analysis technique of the raw data, geometrical phase analysis (GPA), which was first proposed by Hütch et al. [36-38]. The GPA analysis was performed by an open access script in Digital Micrograph (DM, Gatan Inc., USA) developed by Kim et al. [21].

In both pure Mg and the Mg-3Er alloy, the basal \( <\mathbf{a}> \) dislocations were found to have the Burgers vector of \( 1/3(1\bar{1}20) \) with no dissociation observed (see Figure 4.10). We note that the observation of compact \( <\mathbf{a}> \) dislocation cores is at odds with MD predictions that the basal \( <\mathbf{a}> \) dislocation will dissociate to partials with 2-4 nm spacing [39, 40]. The Burgers circuits on the HRSTEM images give a projected Burgers vector of a basal \( <\mathbf{a}> \) dislocation with Burgers vector \( \mathbf{b} = <\mathbf{a}> = 1/3[1\bar{1}20] \) along the viewing direction. Given that the dislocations observed in HRSTEM have the line vector normal to the image plane (parallel to the incident beam), the dislocations observed are projection of the full Burgers vector. However, the in-plane displacements of screw component are negligible compared to those of edge component. As a result, a basal \( <\mathbf{a}> \) dislocation image is a mixed dislocation but
appears as a pure edge dislocation with line vector normal to the image plane and Burgers vector of $b = \sqrt{3}/2<a>$.

Figure 4.10: HRSTEM-HAADF images of a basal $<a>$ dislocation in pure Mg (top) and Mg-3Er (bottom). The viewing direction for both is along the [1120] direction.
Figure 4.11: GPA strain analysis of basal $<a>$ dislocation core in pure Mg (left column) and Mg-3Er (right column).
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON \(<\text{C}+\text{A}>\) DISLOCATION

The displacement that is calculated by GPA technique along \([\bar{1}100]\) direction (x direction as marked in Figure 4.11) is nonzero and the displacement along \([0002]\) direction is negligible (y direction). Therefore, the value of \(\varepsilon_{xx}\) and \(\varepsilon_{xy}\) is non-zero but \(\varepsilon_{yy}\) is negligible (Figure 4.11). The strains are plotted in the range of -0.2 to 0.2 where negative represents compressive strain marked in blue and positive values of tensile strain are marked in red. The strain field is associated with the edge component of a projected full basal \(<\text{a}>\) dislocation with a projected Burgers vector of \(b_x = \sqrt{3}/6(11\bar{2}0)\).

HAADF images of \(<\text{c} + \text{a}>\) dislocation core structures in pure Mg and Mg-3Er are shown in Figure 4.12. The apparent Burgers vector was determined, based on a Burgers circuit. The image of each dislocation core is a projection of a \(\frac{1}{6}(20\bar{2}3)\) partial \(<\text{c} + \text{a}>\) dislocation along the incident beam direction with length of \(\frac{1}{2\sqrt{3}}<\text{a}>\) and \(\frac{1}{2}<\text{c}>\) along the x and y directions. In both pure Mg and Mg-3Er alloy, an \(I_1\) intrinsic SF with the stacking sequence of …ABAB|CBCB…was observed (as shown in Figure 4.12), which corroborates the observations of Geng and Xie [28, 41]. In pure Mg, only one partial can be seen because the complimentary partial dislocation from the experiment resides out of the field of view. Observations of multiple HRSTEM images containing only one partial \(<\text{c} + \text{a}>\) dislocation indicate that the dissociation distance is greater than 100 nm. In Mg-3Er, two partials can be viewed in the same field of view, which indicates the much closer partial spacing in Mg-3Er and points to suppressed dissociation with Er addition.
Figure 4.12: HRSTEM-HAADF images of partial \( \langle c + a \rangle \) dislocation core in pure Mg (top) and Mg-3Er (bottom). The viewing direction is along \([1\bar{1}20]\) zone axis.
Figure 4.13: GPA strain analysis of $\langle c + a \rangle$ dislocation core in pure Mg (left column) and Mg-3Er alloy (right column).
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON $<$C+A$>$ DISLOCATIONS

The strain field measured by GPA is shown in Figure 4.13. The displacements along x direction ([1100]) and y direction ([0002] measured by GPA correspond to the projection of the Burgers vector \( \frac{1}{6} (2 \overline{2} 3) \) along x and y directions with \( b_x = \frac{1}{2\sqrt{3}} \langle a \rangle \) and \( b_y = \frac{1}{2} \langle c \rangle \). The value of \( b_x \) is much smaller than \( b_y \), and thus the contribution of \( b_x \) is negligible compared to that of \( b_y \). For example, the strain filed of \( \varepsilon_{xx} \) is negligible compared to \( \varepsilon_{yy} \), see Figure 4.13 (a)-(d). The presence of the \( b_x \) can slightly rotate the \( \varepsilon_{xy} \), as shown in Figure 4.13 (e) and (f).

![Figure 4.14](image)

**Figure 4.14:** Comparison of \( \varepsilon_{xy} \) profile across the basal \( \langle a \rangle \) and \( \langle c + a \rangle \) dislocations in pure Mg and Mg-3Er alloy

The profiles of \( \varepsilon_{xy} \) across the basal \( \langle a \rangle \) and \( \langle c + a \rangle \) dislocation cores (the line scans are marked as black lines in Figure 4.11 and Figure 4.13) are plotted in Figure 4.14. The strain fields of basal \( \langle a \rangle \) dislocations are identical in pure Mg and Mg-3Er. However, the magnitude of the strain field of the \( \langle c + a \rangle \) partials in Mg-3Er are smaller than that of pure Mg, and the spacing between the positive and negative strain peaks is greater than for pure Mg.
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON $\langle C+A \rangle$ DISLOCATIONS

Mg. This further indicates that the addition of Er influences the core of $\langle c + a \rangle$ dislocations but has little effect on basal $\langle a \rangle$ dislocations. The suppressed dissociation of $\langle c + a \rangle$ dislocations in Mg-3Er that were discussed in section 4.3.2 might be related to a change of the partial dislocation core structure.

To quantify the influence of Er alloying on the dislocation core width, several models can be used, including the isotropic elastic model, anisotropic elastic model, Peierls-Nabarro model and Forman model. Given an edge dislocation with Burgers vector along x direction and extra half plane lying on the y direction, the displacement along x direction $u_x$ and the normal strain $\varepsilon_{xx}$ can be expressed for different models.

The isotropic elastic theory described $u_x$ and $\varepsilon_{xx}$ as [42]

$$u_x = \frac{b}{2\pi} \left[ \tan^{-1} \frac{y}{x} + \frac{xy}{2(1-\nu)(x^2+y^2)} \right]$$  \hspace{1cm} (4.2)

$$\varepsilon_{xx} = \frac{b}{4\pi} \frac{(2\nu-3)x^2y + (2\nu-1)y^3}{[x^2+y^2]^2}$$  \hspace{1cm} (4.3)

where $b$ is the magnitude of the Burgers vector, $\nu$ is Poisson’s ratio.

The anisotropic elastic theory describes $u_x$ and $\varepsilon_{xx}$ as [43]

$$u_x = -\frac{b}{4\pi} \left\{ \tan^{-1} \frac{2xy\lambda \cosh \delta}{x^2 - \lambda^2 y^2} + \frac{C'_{11} - C'_{12}}{2C'_{11}C'_{66} \sinh \delta} \tan^{-1} \frac{2xy\lambda \sinh \delta}{x^2 + \lambda^2 y^2} \right\}$$  \hspace{1cm} (4.4)
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON C+A DISLOCATION

\[ \varepsilon_{xx} = \frac{b}{4\pi} \left\{ \frac{2(y \pm \xi) \lambda \cosh \delta \left[ x^2 + \lambda^2 (y \pm \xi)^2 \right]}{\left[ 2x(y \pm \xi) \lambda \cosh \delta \right]^2 + \left[ x^2 - \lambda^2 (y \pm \xi)^2 \right]^2} + \frac{C'_{11} - C'_{12}^2}{2C'_{11}C'_{66} \cosh \delta} \frac{y \lambda \left[ x^2 - \lambda^2 (y \pm \xi)^2 \right]}{\left[ 2xy \lambda \sinh \delta \right]^2 + \left[ x^2 + \lambda^2 (y \pm \xi)^2 \right]^2} \right\} \] (4.5)

where \( C'_{11}, C'_{12} \) and \( C'_{66} \) are the elastic coefficients in the stiffness tensor with line vector along the z-direction and Burgers vector along the x-direction, \( C'_{11} = \sqrt{C'_{11}C'_{22}} \), \( \cosh 2\delta = \left( \frac{C'_{11}^2 - C'_{12}^2 - 2C'_{11}C'_{66}}{2C'_{11}C'_{66}} \right) / (2C'_{11}C'_{66}) > 0 \), and \( \lambda = (C'_{11}/C'_{22})^{1/4} \).

The Peierls-Nabarro theory described \( u_x \) and \( \varepsilon_{xx} \) as [44]

\[ u_x = -\frac{b}{2\pi} \tan^{-1} \frac{2(1 - \nu)x}{y} \] (4.6)

\[ \varepsilon_{xx} = -\frac{b(1 - \nu)}{\pi} \frac{y}{4(1 - \nu)^2 x^2 + y^2} \] (4.7)

And the Foreman model described \( u_x \) and \( \varepsilon_{xx} \) as [45]

\[ u_x = -\frac{b}{2\pi} \left[ \tan^{-1} \frac{2(1 - \nu)x}{ay} + \frac{2(a - 1)(1 - \nu)xy}{4(1 - \nu)^2 x^2 + a^2 y^2} \right] \] (4.8)

\[ \varepsilon_{xx} = -\frac{b(1 - \nu)}{\pi} \frac{4(1 - \nu)^2 x^2 y + (2a^3 - a^2) y^3}{[4(1 - \nu)^2 x^2 + a^2 y^2]^2} \] (4.9)

where \( a \) is an alterable factor that is related to dislocation core width.
Figure 4.15: Strain maps of a basal $<a>$ dislocation in (a) pure Mg and (b) Mg-3Er measured by GPA, and corresponding strain maps acquired from (c) isotropic elastic, (d) anisotropic elastic, (e) Peierls-Nabarro and (f) Foreman ($a = 4$) models.
### Figure 4.16

Strain maps of a partial $<c + a>$ dislocation in (a) pure Mg and (b) Mg-3Er measured by GPA, and corresponding strain maps acquired from (c) isotropic elastic, (d) anisotropic elastic, (e) Peierls-Nabarro and (f) Foreman ($a = 4$) models.
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The strain fields of basal \(<a>\) and partial \(<c + a>\) dislocations were plotted using the four different models and compared with the experimental results, see Figure 4.15 and Figure 4.16. The contours of the strain maps from the isotropic or anisotropic elastic models are similar, neither of which can describe the strains acquired by GPA. The Peierls-Nabarro and Foreman models can capture some features of the strain field of pure edge dislocation core, but the shapes do not match. The Peierls-Nabarro model is a special case when \(a = 1\) for Foreman model, and the GPA strain maps appear to be in between the Peierls-Nabarro model and Foreman model \((a = 4)\) that the former elongated the strain field and the latter contracts the strain along the extra half plane direction. Therefore, it is reasonable to presume that the Foreman model can be used to simulate the far-field strain around the dislocation measured by GPA [45-48] by fitting the \(a\) factor, which reflects the dislocation core width.

The dislocation width \((w)\) can be calculated by

\[
w = \frac{G b}{2\pi(1 - \nu)p_{\text{max}}} \tag{4.10}
\]

where \(p_{\text{max}}\) is the distribution of Peirels shear stress. \(p_{\text{max}}\) can be determined from the function \(p(\theta)\) which can be expressed as

\[
p(\theta) = \frac{G}{4\pi a^2} \{2(2a - 1) \sin \theta - (a - 1) \sin 2\theta\} \tag{4.11}
\]
where $\theta$ is given by $\cot \frac{\theta}{2} = \frac{2(1-\nu) x}{a - b}$. When $a = 1$, equation (4.11) will be the Peierls-Nabarro model. The cases $a = 1, 2, 3, 4, 5$ are illustrated in Figure 4.17, where the amplitudes of $p_{\text{max}}$ decreases as the width increases (proportional to the alterable factor, $a$).

![Figure 4.17: Curves of shear stress $P$ against distance to the dislocation core ($x/b$)](image)

To evaluate the dislocation width and strain field of dislocations in pure Mg and Mg-3Er, the modeled strain field and experimental results were compared using the sum square difference algorithm. Given two images $J[x, y]$ and $I[x, y]$ with $(x, y) \in N^{N \times M}$, the sum square difference can be expressed as equation 4.3.8 and normalized as equation 4.3.9.
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON $\langle \text{C+A} \rangle$ DISLOCATON

$$S_{sq} = \sum_{(n, m) \in N^{N \times M}} (J[n, m] - I[n, m])^2$$  \hspace{1cm} (4.12)

$$S_{\text{norm}} = \frac{S_{sq}}{\sqrt{\sum J[n, m]^2 \times \sum I[n, m]^2}}$$  \hspace{1cm} (4.13)

The alterable factor $(a)$ can be determined by comparing the experimental images acquired from GPA and the simulated strain maps generated from Foreman model. The most probable values of $a$ are those at which the normalized sum square differences are minimized. The results of this are summarized in Figure 4.18 and the values of $a$ with the corresponding dislocation widths are listed in Table 4.2. The lattice parameters measured from the HRSTEM images are $a = 3.205$ Å, $c = 5.208$ Å for pure Mg and $a = 3.252$ Å, $c = 5.178$ Å for Mg-3Er. The $a$ value and width of the basal $\langle a \rangle$ dislocation are the same in both pure Mg and Mg-3Er, while the partial $\langle c + a \rangle$ dislocation in Mg-3Er is 21% wider than that in pure Mg.

**Table 4.2:** Values of fitted $a$ and corresponding dislocation width $w$ versus Burgers vector $(w/b)$ with $b_{\langle c \rangle} = \sqrt{3}/2\langle a \rangle$ and $b_{\langle c+a \rangle} = 1/2\langle c \rangle$.

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CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON $<c+a>$ DISLOCATIONS

Figure 4.18: The value of normalized sum square difference $S_{norm}$ versus the alterable factor $a$ in Foreman model for $<a>$ and $<c+a>$ dislocations in pure Mg and Mg-3Er.
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Figure 4.19: (a), (b) experimental maps and (c),(d) modeled maps of $\varepsilon_{xx}$ strain at a basal $<\text{a}>$ dislocation core in pure Mg and Mg-3Er. The modeled strain maps employ the $a$ values in Table 4.2.

The magnified experimental $\varepsilon_{xx}$ strain maps of basal $<\text{a}>$ in pure Mg and Mg-3Er are shown in Figure 4.19 (a) and (b). All the strain maps were colored with red for positive strain and blue for negative strain in the same range from -0.2 to 0.2. The orthogonal
CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON <C+A> DISLOCATION

cooridinate is defined with the origin at the dislocation core, as shown in Figure 4.19 (c). In the region of an extra half plane \( (y > 0 \text{ for basal } <a> \text{ and approximately } x < 0 \text{ for partial } <c + a>) \), the strains are negative (compressive) and the lattice is under tensile strain on the other side of the neutral plane \( (y < 0 \text{ for basal } <a> \text{ and } x > 0 \text{ for partial } <c + a>) \). The simulated strain maps acquired from the Forman model are displayed in Figure 4.19 (c) and (d) and were generated using the values of \( a \) listed in Table 4.2. The simulated maps are in very good agreement with experiment in both magnitude and shape. The experimental maps show less symmetry than the simulated maps, likely due to the drift of the sample while acquiring the data and perhaps the twisting caused by the free surfaces of the TEM foil. In addition, the simulated maps have a singularity point at the very center of the contour plots, close to the center of the dislocation core. This is a result of the higher order polynomial terms in the denominator in equation (4.9).

The magnified experimental \( \varepsilon_{yy} \) strain maps of the partial \( <c + a> \) dislocation in pure Mg and Mg-3Er are shown in Figure 4.20 (a) and (b). The simulated strain maps acquired from the Forman model are displayed in Figure 4.20 (c) and (d). The modeled maps applied the values of \( a \) listed in Table 4.2 and the assumption that the Burgers vector is simplified to be \( 0.5\mathbf{c} \) neglecting the projection of partial \( <c + a> \) dislocation on the basal plane. The simulation results are in good agreement with the experimentally obtained strain field of partial \( <c + a> \). The shape of the experiment \( \varepsilon_{yy} \) strain field of partial \( <c + a> \) dislocation in pure Mg has a similar strain contour to the experimental \( \varepsilon_{xx} \) strain of basal \( <a> \) dislocation with the addition of a twist distortion counterclockwise. The widening of the partial \( <c + a> \) dislocation core in Mg-3Er elongates the strain contour along y direction.
and contracts the strain along x direction. In addition, the smaller Burgers vector of the partial $<c + a>$ dislocation results in the lower strain field compared to that of the $\varepsilon_{xx}$.

Figure 4.20: (a), (b) experimental maps and (c),(d) modeled maps of $\varepsilon_{yy}$ strain at a partial $<c + a>$ dislocation core in pure Mg and Mg-3Er. The modeled strain maps employ the $a$ values in Table 4.2.
Figure 4.21: Comparison of angular variation of strain field between Foreman model (solid line) and experiments (dashed line) for \( r = 2b \) (black line) and \( r = 5b \) (red line): (a) pure Mg basal \(<a>\), (b) Mg-3Er basal \(<a>\), (c) pure Mg \(<c+a>\) and (d) Mg-3Er \(<c+a>\) dislocations

To analyze the degree of agreement between the experiment and theory in more detail, we selected two different circles of radius \( r = 2b \) and \( 5b \) from the dislocation core to measure the variation of strain with angle from \(+x\) rotating clockwise, see Figure 4.20 (a). The experimental and theoretical data is plotted with dashed and solid lines respectively, see Figure 4.21. The strain profile of the two circles captures the magnitude and shape of the experimental results very well, which indicates the applicability of Foreman model in describing the strain field of GPA. The good agreement of the modeled and experimental results confirms that the \( a \) values and corresponding dislocation width \( w \) calculated using
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Foreman model are effective representation of the character of the dislocation core for the basal <a> and <c + a> dislocations in both Mg and Mg-3Er alloy.

Another noteworthy fact of Mg-Er alloys that may affect the dislocation core structure and behavior is the reduction of c/a ratio, which is also found in Mg-Li alloys [8, 10, 49]. The c/a ratio of Mg-3Er decreases to 1.592 from 1.625 for pure Mg measured by HRSTEM images. Agnew et al. have suggested that lower c/a ratio allows for the activation of non-basal slip and increase the Peierls resistance of basal slip [8, 49]. However, the change of c/a ratio affects prismatic <a> glide and twinning more than the <c + a> dislocations [50]. The activated prismatic <a> and twinning can also improve ductility and formability and weaken the rolling texture [50], but was not investigated in this study.

The results from the far-field strain fitting confirm the conclusion from the core strain field analysis, that the addition of Er broadens partial <c + a> dislocations but has little influence on basal <a> dislocations. The width of the partial <c + a> dislocation increases and the strain concentration at the partial dislocation cores decreases. However, the partial <c + a> dislocation core spreads out of the basal plane on which dissociation occurs, possibly onto a pyramidal plane. The broader dislocation core alleviates the strain concentration in the lattice around the dislocation and decreases the Peierls stress in the pyramidal plane, which may lead to the more favorable glide on the pyramidal plane compared to pure Mg. Stabilizing <c + a> dislocations on pyramidal planes in Mg-Er alloy would enhance the activity of <c + a> dislocations and improve the ductility and formability of the alloy.
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In addition to the stabilization of <c + a> dislocations on the pyramidal plane, the dissociation of <c + a> dislocations on the basal plane was also observed to be suppressed in Mg-3Er. The suppressed dissociation can reduce glissile-to-sessile core transformation of edge dislocation [22] and reduce the drag effect of SFs for screw <c + a> dislocations [29], thus further improving the mobility of <c + a> dislocations.

4.4 Summary and conclusions

The addition of RE elements in Mg is known to improve the ductility and formability and thought to be related to a change in the behavior of <c + a> dislocations. The <c + a> dislocations in a Mg-3Er alloy were carefully characterized and compared with those in pure Mg. The analysis of <c + a> dislocation morphology reveals that the addition of Er was shown to suppress its nonconservative dissociation on the basal plane, which reduces the obstacles that impede the mobility of <c + a> dislocations. The dislocation core analysis demonstrates that alloying with Er has negligible effect on the basal <a> dislocations but introduces a core spreading of partial <c + a> dislocations on the pyramidal plane, which decreases the strain concentration and enhances the stability of <c + a> dislocations on the pyramidal planes. The suppressed dissociation on the basal plane and stabilized core on the pyramidal plane appear to enhance the mobility of <c + a> dislocations in Mg-3Er and improve the ductility.
4.5 References for Chapter 4

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CHAPTER 4. EFFECT OF RARE-EARTH ELEMENT ON \(<\text{C+A}\)\> DISLOCATION


Chapter 5.
Characterization of Extension Twin Tips in Mg Using TEM

With the overarching goal of increasing the formability and mechanical properties of pure Mg, the previous two chapters focused on understanding the influence of alloying elements on \(<c + a>\) dislocation core structure and its relationship with dislocation behavior and mechanical properties. In addition to \(<c + a>\) slip, deformation twinning, mainly extension twinning, is another prevalent deformation mechanism in Mg. Extension twinning, with low critical activation stress, plays an important role in accommodating deformation of \(<c>\)-axis extension and \(<a>\)-axis compression and in influencing the ductility of Mg. The keys to understand the twinning process is the nucleation, thickening and propagation mechanisms. The twin tip, which is generally the incoherent interface between a twin and its matrix, contains the code for deciphering these mechanisms. In this chapter, experimental characterization of extension twin tips is the focus.
CHAPTER 5. CHARACTERIZATION OF EXTENSION TWIN TIPS

5.1 Introduction

The nucleation and propagation mechanisms of extension twins in HCP materials have garnered great interest in the experimental and computational community [1]. The twin nucleation model was first proposed by Orowan, who considered twins to grow from a lenticular-shaped twin volume of twin shear, multiple crystallographic layers thick [2]. Based on this concept, Yoo and Lee later proposed a homogeneous model using Eshelby’s inclusion solution and considering an eigenstrain[3, 4]. Lebensohn and Tomé investigated the influence of stress state on twin nucleation and suggested that the contribution of hydrostatic pressure is negligible compared to that of resolved shear stress [5]. Although instructive, these homogeneous nucleation models require high stresses for nucleation and that is not consistent with the experimental observations. Because real materials have many defect sites, like dislocations or grain boundaries, capturing heterogeneous nucleation appears to be a more salient modeling approach [6-8]. The dominant heterogeneous nucleation mechanism is believed to be grain boundary (GB) nucleation [9]. Activation of GB nucleation depends largely on the misorientation of the GB and its neighbors. In addition to GB nucleation, twins were also observed to nucleate within grains, which is believed to be related to dislocation dissociation. Thompson and Millard proposed that deformation twins nucleate from the non-planar dissociation of a \(<c\>\) dislocation [10]. Later, Mendelson systematically analyzed the dislocation interaction and formation of twin dislocations, and proposed that twin nucleation can originate from the generation of glissile twin dislocations from the non-planar dissociation reactions including \(<a\>, \(<c + a\>\) or \(<c>\)
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dislocations [11, 12]. In addition to the dislocation reaction models, Wang et al. applied molecular dynamics to simulate the nucleation of extension twins in Mg and proposed that the nucleation is related to the dissociation of partial dislocations with \( \langle 10\overline{1}1 \rangle \) Burgers vector [13, 14]. The wide discrepancies between models and simulation results indicate the complex nature of extension twin nucleation.

By comparison, the propagation of extension twins has better consensus in the community. It is commonly accepted that the propagation of deformation twins in Mg is attributed to the glide of twin dislocations on the twin plane \( \{10\overline{1}2\} \), along the twinning direction \( \langle 10\overline{1}1 \rangle \), activated by the combination of shear stress and atomic shuffling [15, 16]. The piling-up of twin dislocations can readily form pairs of basal-prismatic (BP) and prismatic-basal (PB) interfaces [17-21]. The BP interfaces describes the boundary that aligns the basal plane of the twinned region and the prismatic plane of the matrix, or the converse as prismatic-basal (PB) interfaces [22, 23]. The misorientation between the basal plane of the twin and prismatic plane of the matrix is low (4°) and the twinned region is reoriented 86° along \( \langle 11\overline{2}0 \rangle \) direction, and the formation energy of a BP/PB boundary is low (164 mJ m\(^{-2}\)) [18]. Twin dislocations are predicted to slip on coherent \( \{10\overline{1}2\} \) boundaries and cross-slip onto the BP/PB boundaries [23] or to glide on coherent \( \{10\overline{1}2\} \) boundaries sequentially to move the BP/PB interfaces [17], either of which facilitates the twin propagation. In addition to the twin dislocation glide model, Li and Ma [24] proposed a shuffle-dominated twin propagation process that twin dislocations nucleate separately at each local point on the twin boundary. Even though the twin dislocation glide model has
been widely accepted while the shuffling model has been called into question [25], more solid experimental observations should be performed to support either process.

Twin propagation can also be accomplished by the interaction of basal \( \langle a \rangle \) dislocations in the matrix with coherent twin boundaries. Yoo and Wei [26] proposed that two basal \( \langle a \rangle \) dislocations (e.g. with Burgers vectors \( 1/3[1\bar{2}10] \) and \( 1/3[\bar{2}110] \)) can glide to a coherent twin plane \( \{10\bar{1}2\} \) and react to form a \( \langle c + a \rangle \) dislocation and a residual dislocation at the interface [27-29]. The residual dislocation can be stabilized to form a twin dislocation at the twin boundary and facilitate the growth and propagation of extension twin. Recently, the reaction was experimentally observed by Wang et al. [28] in their in-situ extension test on a single crystal Mg specimen. However, the characterization was only performed on the dislocations at a coherent twin boundary on the twin side. The possible dislocation interactions at the twin tip was not investigated.

In addition to the propagation of an extension twin in a grain, extension twinning in polycrystalline Mg can also propagate transgranularly to form the adjoining twin pairs (ATPs). In polycrystalline Mg, extension twins can propagate through a grain. The twin tips that terminate at the GB generate forward stress and can lead to the formation of a new twin in the neighboring grain immediately in front of the first twin tip [21]. The ATPs in Mg have been systematically investigated in the literature both experimentally and computationally [30-35], but the influence of twin size at the early stage of twin tip – GB has not been considered.
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The twin tip is the boundary between the region that has been twinned and the region that is to be twinned, and thus contains the information of twin propagation for post-mortem characterization. In this chapter, the following points related to the tips of extension twins in Mg have been addressed: i) characterization of the morphology and elastic strain field around a twin tip that terminates inside a grain; ii) interaction between a propagating twin tip and surrounding dislocations; and iii) the influence that terminating a twin tip at a GB has on both the twinned and neighboring grains.

5.2 Experiment

Hot-rolled pure Mg samples were cut using wire EDM to 3 mm x 3 mm x 6 mm, prisms oriented with the longitudinal direction parallel to the rolling direction (RD). After machining, the samples were annealed for 3 hours at 300°C in vacuum to reduce the dislocation density from rolling and to homogenize the microstructure. The four longitudinal faces of as-annealed samples were mechanical polished using SiC abrasive grinding paper (1200 for standard ANSI grit or P4000 for European P-grade) under zero nominal load (read from the force meter in an Allied automated polisher) and then chemical polished with 5% nitric acid in methanol to remove the recast layer from EDM and oxide layer from annealing. The microstructure of annealed pure Mg has been described in Figure 3.1. The samples were compressed along the RD at a strain rate of $10^{-4}$ s$^{-1}$. Three samples were compressed to failure to obtain the stress-strain curves, with the detail of testing outlined in Section 2.2.1, and others were deformed to 2% and prepared for post-mortem TEM characterization.
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TEM foils were cut perpendicular to the compressive direction (parallel to the TD-ND plane) using a diamond wire saw (diameter 0.12 mm). After specimens were sectioned, they were mechanically polished using SiC abrasive grinding paper (1200 for standard ANSI grit and P4000 for European P-grad) under zero load and twinjet electropolished using an electrolyte of 5.3 g lithium chloride, 11.16 g magnesium perchlorate, 100 mL 2-butoxyethanol and 500 mL methanol at -35°C and 100 V. A precision ion polishing system (PIPS) was used at 0.2 keV in vacuum at liquid nitrogen temperature for 30 minutes to achieve electron transparency. A Thermo Scientific TF30 TEM equipped with ACOM and TOPSPIN, was utilized to characterize the twin morphology and to map the elastic strain field around the twin tip. Weak-beam dark field (WBDF) imaging technique was employed to image dislocations around the twin tip.

5.3 Results and discussion

5.3.1 Morphology of extension twin tip

The stress-strain response from compressing pure Mg along the ND (red) and the RD (blue) are shown in Figure 5.1. The ND compression showed a high yield point at 75 MPa followed by strong strain hardening. In addition, the ND showed low strain to failure, likely attributed to the low activity of \(<c + a>\) dislocations resulting from the dislocation core transformation, discussed in Chapters 3 and 4. In contrast, the RD compression stress-strain response displayed a slightly lower yield point (70 MPa), which is likely due to the activation of extension twins [36]. In the initial plastic region (1-7% strain) the RD
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compression displayed a plateau in the stress-strain response and low strain hardening. After all the grains are twinned and reoriented 86° to the matrix, approximately 6% strain was accommodated by extension twinning [37]. The twinned grains reorient the crystallographic c-axis close to the loading direction. As a result, \(<c+a>\) slip dominates plastic deformation after all the grains are twinned (~7% engineering strain), and high hardening reappears again. It is worth noting that the strain hardening of twinned sample appears to be a little lower than for ND loading. This lower hardening rate has been attributed to the fact that the twinned texture is not as strong as the basal texture in the as-rolled samples [38, 39].

![Stress-strain curve](image)

**Figure 5.1:** Stress-strain curves of compression tests for pure Mg conducted along the ND (red) and RD (blue) directions.
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To experimentally observe twin tip, two compression tests were terminated at 2% engineering strain to introduce a relatively low density of deformation twins with limited twin growth. TEM foils were extracted from the deformed specimens and several intragranular extension twin lamellas were identified for further characterization. We note that most of the twins observed in the TEM specimens nucleated at the GB and then propagated across the grain reaching the opposing GB, even though the samples were compressed to only 2%. The parallel twin lamellae observed in Figure 5.2 suggest that the twins have the same variant. The twins are in lenticular shaped and 1-2 μm long. The size of these twins is dramatically smaller than the twins that propagate across the grains, which indicates that the twins are at the early stage of propagation with limited growth.

![Figure 5.2: Bright field images of intragranular extension twins in pure Mg](image)

Figure 5.2: Bright field images of intragranular extension twins in pure Mg
The morphology of each twin lamellae in Mg is related to the twin dislocation induced nucleation and propagation mechanisms of extension twins. The 3d structure of extension twins investigated by Liu et al. showed that the forward (along $\langle 1\bar{1}0\bar{1} \rangle$ direction) and lateral propagation (perpendicular to $\langle 1\bar{1}0\bar{1} \rangle$ in the twin plane) of extension twin is easier than the normal growth [40]. Moreover, the lateral expansion is faster than forward propagation, which is attributed to the reason that the screw component in the lateral interfaces has a lower barrier than the edge component of the forward interface, and it moves faster. As a result, the extension twins are likely to form a lenticular shape with the length in lateral direction larger than the width in forward direction and significantly larger than the thickness in the normal direction at the early stage of propagation before the forward direction growing to the opposing GB. The twin lamellas observed in Figure 5.2 are twins cut by the TEM foil on the forward-normal plane with the twin tips pointing at the forward directions ($\langle 1\bar{1}0\bar{1} \rangle$).

To characterize the morphology of twin tips at higher resolution, HRTEM was performed focusing on twin tip 4 in Figure 5.2 with the specimen tilted to a $\langle 11\bar{2}0 \rangle$ zone axis. The HRTEM micrograph in Figure 5.3 shows that the twin tip is sharp in nature. Variable contrast can be observed, which is associated with the formation of dislocations that are marked as dashed yellow lines. The dislocations lie on the basal plane, and interestingly, the dislocation density on the top side of the twin tip is higher than it is on the bottom side. In addition, the twin boundaries at the twin tip are not sharp but were observed to have a width of around 2 nm.
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Figure 5.3: HRTEM morphology of extension twin tip, with yellow dashed lines represent dislocations and solid yellow lines the twin boundary.

The HRTEM image of the region marked with dashed red box in Figure 5.3 is shown in Figure 5.4. The twin boundary close to the twin tip is 5-10 atomic layers wide. This expanded twin boundary structure at the twin tip is similar to what has been reported by Sun et al., whose HRTEM micrograph showed a twin boundary width of several layers of
atoms [23]. The wavy and band-like structure of the twin boundary at the twin tip indicates a non-planar, 3D morphology of the twin boundary. Liu et al. also observed the 3D morphology and propagation of twin boundaries during in situ compression, and surprisingly, some of the twin boundary segments were observed to be sharp BP/PB interfaces when the TEM foil was sufficiently thin (< 90 nm) [41]. This suggests that multiple layers overlap the BP/PB interfaces at the twin boundary region and form the 3D structure of twin boundary.

The formation of one layer of the boundary with the BP/PB steps is metastable even though the energy is reported to be low [18]. It is reasonable to assume that the stacking of layers of BP/PB comprising the twin boundary along the lateral direction staggers the sequence of atoms. The staggered layers of twin boundaries with BP/PB interfaces provide a 3D path for the motion of twin dislocations that the atoms can be shuffled from the interface on one layer to that on the other, which may be more energetically favorable. And the multiple staggered layers of twin boundaries with BP/PB interfaces stack to form a broadened twin boundary.
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Figure 5.4: HRTEM image of twin boundary at twin tip acquired from the region marked by red dashed box in Figure 5.3.

WBDF was used to characterize the dislocations at twin tip 4. The dislocations that are imaged using $\mathbf{g}_a = [\overline{1}00]$ but invisible under $\mathbf{g}_c = [0002]$ (Figure 5.5) are basal $<a>$ dislocations. Lines of basal $<a>$ dislocations were emitted from the twin tips and observed in the matrix near the tips. No dislocations are observed on the twin boundaries. The
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formation of extension twins introduces a shear of the lattice in the twinned region. The coherent twin boundary has no elastic strain, but the twin tip where the twin boundary deviates from the coherent twin plane can generate a significant stress concentration. However, the stress concentration appears to be released by the emission of basal $<a>$ dislocations [15, 42].

![Figure 5.5: WBDF images of basal $<a>$ dislocations at twin tip 4: (a) was imaged using $g = [0002]$ with $<c>$ and $<c + a>$ dislocations visible; (b) was imaged using $g = [1100]$ with $<a>$ and $<c + a>$ dislocations visible. The majority of dislocations were only observed in (b) and are $<a>$ dislocations.](image)

The right tips of the three extension twins in Figure 5.2 were carefully characterized, as shown in Figure 5.6. It is interesting that the basal dislocations were found to be emitted from the same side of the twin tips. After carefully compare the two sides of the twin tips, the top sides of the twin tips are closer to the coherent $\{10\overline{1}2\}$ plane (see Figure 5.6 (e)).
Figure 5.6: \(<a>\) dislocations emitting from extension twin tips and sketch of asymmetric twin tip: (a), (b), (c) correspond to twin tips 1, 4 and 5 in Figure 5.2, (d) the diffraction pattern acquired from matrix and (e) schematic diagram illustrates the RSS-induced asymmetry of twin tip.
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The asymmetric twin tip can be attributed to the resolved shear stress on the twin boundary, as shown in Figure 5.6 (e). The resolved shear stress glides the twin dislocations to the left on the $C_2$ boundary and to the right on the $C_1$ boundary. When the twin dislocations glide towards the twin tip, basal $\langle a \rangle$ dislocations can be emitted from the BP interface into the matrix. Meanwhile, a step would be generated on the other side of the twin tip, deviating the boundary from the coherent twin plane. The incoherent twin boundary on the other side can be stabilized to form a BP/PB interface via local atomic shuffling and cause the asymmetry.

5.3.2 Elastic Strain concentration at lenticular twin tips

The NBED-TOPSPIN technique was applied to measure and map the elastic strain concentration at the twin tip. Both the twin and the matrix are oriented with a $\langle 11 \bar{2}0 \rangle$ zone axis parallel to the incident beam. The twin plane $\{1\bar{1}02\}$ is edge on to minimize the influence of twin boundary inclination on the elastic strain field. All the maps are 400 nm x 400 nm and were gathered with an acquisition step size of 1 nm. The orientation information was confirmed by comparing the diffraction pattern of each pixel with the simulated database, and elastic strain maps were calculated by comparing the diffraction patterns with a reference pattern that was acquired from an unstrained area. More details of the orientation and strain mapping using NBED technique are given in Section 2.3.5.

The virtual bright field micrograph of the twin tip 4 in Figure 5.2 is reconstructed by placing a virtual aperture over the incident beam, as shown in Figure 5.7 (a), and the IPF image is shown in Figure 5.7 (b). The boundaries highlighted in red have a misorientation
angle of 86.3° rotated along (11\bar{2}0) direction, which indicates extension twin boundaries. The associated diffraction patterns from the twin and matrix are displayed in Figure 5.7 (c) and (d), respectively. The measured misorientation angle of 86° from the diffraction patterns further confirms the nature of extension twin.

Figure 5.7: (a) Virtual bright field and (b) IPF image of the twin tip 4 reconstructed from the NBED ACOM technique, and diffraction patterns acquired from (c) twin and (d) matrix.
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The two-dimensional elastic strains of twin tip 4 are mapped in Figure 5.8 with the x-axis along the normal direction (perpendicular to the twin plane) and the y-axis along the forward direction (⟨10̅1̅⟩ in the matrix). The matrix is selected as the area of interest and by comparing the pixel diffraction patterns with the reference and enforcing a correlation for less than 0.2. The elastic strain was found to be within ± 1%. Concentrated positive $\varepsilon_{xx}$ was detected at the twin tip and associated with a line of basal $\langle a \rangle$ dislocations.

Figure 5.8: (a) $\varepsilon_{xx}$, (b) $\varepsilon_{yy}$ and (c) $\varepsilon_{xy}$ maps of twin tip 4 measured by NBED-TOPSPIN with (d) x-axis along normal direction and y axis along forward direction (⟨10̅1̅⟩).
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The strain at the twin tip was quantitatively measured using a line scan across the area of interest, as shown in Figure 5.9. Each point on the line scan profile was calculated by averaging the strain value of 50 pixels perpendicular to the line scan direction. The normal components of the elastic strain (Figures 5.7 (a) and (b)) at a twin tip measured by NBED TOPSPIN was quantified to be 0.4%. Using the stiffness tensor for pure Mg (Table A1.1), the corresponding stress level was measured to be approximately 200 MPa, which is lower than the value that was predicted using the elastic models like the dislocation array model [43] and the ellipsoidal model [44]. This indicates that the residual stress generated by a twin tip is significantly released by plastic deformation in the matrix, e.g. the motion of basal \(<a>\) dislocations.

To justify the quantification of strain measurement, the strain sensitivity of the NBED-TOPSPIN measurements needs to be evaluated. The sensitivity of strain measurement varies with different material system and the status of acquisition systems. One reliable approach for estimating the strain sensitivity is to quantify the strain level in a nominally strain-free area and measure the background noise of strain measurement [45]. The value of \(\varepsilon_{xy}\) is close to zero and the profile of \(\varepsilon_{xy}\) can be used to estimate the background noise of strain measurement. The fluctuations in the \(\varepsilon_{xy}\) profile fall within ±0.02%, and thus the sensitivity of the NBED-TOPSPIN strain measurements for this Mg sample is 0.02%. Therefore, the elastic strain measurements with values higher than 0.02% is reliable. The strain concentration at the twin tip (0.4%) and the strain around the basal \(<a>\) dislocations (0.2%-0.6%) are an order of magnitude larger than the sensitivity. The measured strains are reliable.
Figure 5.9: Strain profiles of the line scans at the twin tip in Mg acquired by averaging the points perpendicular to the scanning direction.
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5.3.3 Interaction between dislocation and propagating twin tip

As discussed in the previous section, when intragranular extension twins are small in size (1-2 μm), the strain concentration at the twin tips can be released by the formation of basal <a> dislocations. When the extension twins continue to grow, the strain concentration that accumulates at the twin tip can activate a high density of dislocations around the extension twin. Figure 5.10 displays a sharp twin tip of an extension twin with a length of ~20 μm, which is approximately ten times longer than the twin tips shown in Figure 5.2. The bright-field TEM image was acquired with the specimen tilted to a (1120) zone axis. The multiple beam condition makes both basal <a> and <c + a> dislocations visible. The twin tip is asymmetric with the top side closer to the coherent {1012} plane, and an orientation map of the twin, tip acquired by NBED-ACOM, is shown in Figure 5.10 (c).

A very high density of dislocations was observed in front of and on both sides of the twin tip. The dislocations are extremely localized around the twin and slightly more dislocations were observed in the matrix than in the twin. The dislocations appear to be distributed in a band with a width of ~2 μm, but this width is likely determined by the top and bottom surface of the thin foil. The dislocation density in the matrix away from the band is much lower. A magnified image of the twin tip (Figure 5.10 (b)) indicates that the dislocations are predominantly lying on the basal plane. Surprisingly, a line of dislocations was observed to be emitting from the front of the twin tips on multiple micrographs, which is aligned roughly along the ⟨1011⟩ direction in the matrix.
Figure 5.10: (a) Bright-field image of a twin tip acquired when the specimen was tilted to a (11\overline{2}0) zone axis. (b) Magnified image of the dislocations at the twin tip. (c) IPF image of the twin tip acquired by NBED-ACOM illustrates the nature of extension twin. The twin boundary is marked with yellow line in the bright-field images and with a red line in the IPF image. A line of dislocations emitting from the twin tip are circled in red, and were seen on multiple micrographs.
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Figure 5.11: Bright-field images of two extension twins with different variants with the sample tilted to a (1120) zone axis.

The twins that stop in a grain surrounded by a very high density of dislocations was commonly observed in the samples that were compressed by 2% along the RD. Another example of two extension twin lamellas with different variants are shown in Figure 5.11. The twin tips are asymmetric, with the coherent and incoherent sides marked by red and yellow dashed lines, respectively. Bands of dislocations approximately 1 μm in width
surround both twins; and a line of dislocations emitting from the twin tip align with the (10$\overline{1}$1) direction on the twin plane.

To investigate the characters of the dislocations that localize around the extension twins, the dislocations at the twin tip and at the coherent boundary far away from the twin tip were characterized using WBDF. The dislocations at the coherent twin boundary in Figure 5.11 were imaged with two diffraction conditions, as shown in Figure 5.12. The Burgers vectors of the dislocations were determined using the $g \cdot b = 0$ invisibility criteria. The diffraction vector $g_c = [0002]$ was used to image $<c>$ dislocations ($b_{<c>} = [0001]$) and the $c$-component in $<c+a>$ dislocations ($b_{<c+a>} = 1/3[11\overline{2}3]$), but $<a>$ dislocations ($b_{<a>} = 1/3[11\overline{2}0]$) are invisible. By contrast, for $g_a = [1\overline{1}00]$ diffraction vectors, $<a>$ dislocations and $a$-component in $<c+a>$ dislocations are visible but $<c>$ dislocations are invisible. Dislocations that are visible for both $g_a$ and $g_c$ are $<c+a>$ dislocations. When the matrix was tilted to $g_a$ condition, the twin has an 86° rotation along the beam direction, which is close to the $g_c$ two beam condition, as shown in Figure 5.12 (a). Similarly, when the matrix was tilted to $g_c$ condition, the twin is close to $g_a$ condition (Figure 5.12 (b)). The $<c+a>$ dislocations appear to be long and straight under $g_c$ condition. Dissociation into stacking fault loops in both the twin and matrix were observed for the $g_a$ condition. The configuration of $<c+a>$ dislocations echo the observations in Chapters 3 and 4.

We note that the as-annealed samples have low dislocation density before compression, as shown in Figure 3.3; and RD compression was specifically employed to suppress $<c+a>$ slip and to activate extension twinning. This means that the formation of the high density
of \(<c + a>\) dislocations near the twin boundaries and at the twin tips is generated by the propagation of the extension twins.

The formation of \(<c + a>\) dislocations at the twin boundaries can be explained by the interaction of basal dislocation in the matrix and twin boundaries. The \(<a>\) dislocations in the matrix are categorized into groups with respect to the \((1\overline{1}02)\) twin plane: those with the \(1/3[1\overline{1}20]\) Burgers vector parallel to the interface and zone axis, and those with \(1/3[1\overline{2}10]\) and \(1/3[\overline{2}110]\) Burgers vectors that are \(60^\circ\) to the intersection line of the basal plane and twinning plane. The two \(<a>\) dislocations of the second category glide on a basal plane in

**Figure 5.12:** WBDF images of \(<c + a>\) dislocations at a coherent twin boundary.
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the matrix and can react to produce a \(<c + a>\) dislocation on the prismatic plane in the twin and a residual dislocation at the interface by [27-29]:

\[
2 \times [\mathbf{a}]_M = [\mathbf{c} + \mathbf{a}]_t + \mathbf{b}_r
\]  

(5.1)

where \([\mathbf{a}]_M\) is the two basal \(<a>\) dislocations in the matrix, \([\mathbf{c} + \mathbf{a}]_t\) is a \(<c + a>\) dislocation formed in the twin and \(\mathbf{b}_r\) is a residual dislocation at the interface [26, 46]. The residual dislocation can be stabilized to form a twin dislocation at the twin boundary and promote the growth and propagation of extension twin. Fan et al. simulated this interaction using discrete dislocation dynamics and suggested a two-step interaction. The first dislocation arrives at the twin boundary and decomposes into a half \(<c + a>\) dislocation and a twinning dislocation; the half \(<c + a>\) repulses the following dislocations in the matrix moving to the twin boundary and the twinning dislocation glides away. With increasing stress acting on the new leading incident dislocations to overcome this repulsive stress, a second dislocation would reach the twin boundary and decompose to another half \(<c + a>\) dislocation and a twinning dislocation. An integrated \(<c + a>\) dislocation can subsequently be emitted into the twinned crystal from the twin boundary. However, in addition to the \(<c + a>\) dislocations in the twin, higher density of \(<c + a>\) dislocations were observed on the matrix side, which cannot be directly explained by the model. The \(<c + a>\) dislocations in the matrix may result from the reaction between the basal \(<a>\) dislocation in the twin and the twin boundary. The \(<c + a>\) dislocations in the matrix become sessile after dissociation on the basal plane and line up at the twin boundary to form a dislocation wall around the twin. The sessile \(<c + a>\) dislocation walls will retard the thickening of extension twin.
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Figure 5.13: Bright-field images of dislocations at the twin tip under multiple two beam conditions.

The dislocations at the twin tip were also characterized in bright field, see Figure 5.13. The four micrographs correspond to the visibility of the dislocations near to \{11\bar{2}0\} zone axis, \(g_a = [1\bar{1}00]\), \(g = [1\bar{1}01]\) and \(g_c = [0002]\). The Burgers vector can be determined using \(g_a\) and \(g_c\) conditions, and all three \(<a>\), \(<c>\) and \(<c + a>\) dislocations can also be observed using \(g = [1\bar{1}01]\). The long and straight dislocations that are visible in all images are \(<c + a>\) dislocations. The \(<c + a>\) dislocations dissociate on the basal plane and generate stacking faults, and the stacking fault fringes are shown in Figure 5.13 (c). The line of dislocations that are emitted from the twin tip and aligned with the twin plane (marked by
red circle in Figure 5.13) have different contrasts at \( \mathbf{g}_a \) and \( \mathbf{g}_c \) two-beam conditions. This difference in visibility reveals that the line emitting from the tip contains both \(<a>\) and \(<c + a>\) dislocations.

The presence of a high density of \(<c + a>\) dislocations at the twin tip of the matrix does not support this dislocation interaction hypothesis since no TB was yet formed in this region. Moreover, the higher dislocation density in the matrix cannot be explained by the model of basal \(<a>\) dislocation-twin boundary interaction. The observations point to the fact that the formation of \(<c + a>\) dislocations in the matrix is not simply the consequence of dislocation-twin boundary interaction but might be related to a dislocation reaction at the twin tip.

The formation of \(<c + a>\) dislocations at the twin tip is related to the twin dislocation reaction. The nucleation and propagation of twins can be accomplished by the formation and pile-up of twin dislocation dipoles in a grain [47]. The twin tip for the model can be schematically described in Figure 5.14 [7, 10-12, 48]. The high density of twin dislocations at the twin tip generates a strain concentration that can be released by emission of basal \(<a>\) dislocations at the early stage of propagation. The twins continue to grow and a high density of twinning dislocations accumulate at the twin tip. The twin dislocations can react to generate matrix \(<c + a>\) glide by the following reaction:

\[
\langle 1\bar{1}0\bar{1} \rangle_t = \frac{1}{3}\langle 1\bar{2}10 \rangle_M + \frac{1}{3}\langle 2\bar{1}1\bar{3} \rangle_M \tag{5.2}
\]
Figure 5.14: Schematic diagram of extension twin tip: (a) low magnification illustrates the gradient of twin dislocation density with higher density closer to the twin tip and (b) the BP/PB configuration of the twin dislocations.

A twin dislocation \( \mathbf{b} = \langle 1\overline{1}0\overline{1}\rangle_t \) decomposes to a basal \( \langle a \rangle \) dislocation \( \mathbf{b} = 1/3\langle \overline{1}210\rangle_M \) and a \( \langle c+a \rangle \) dislocation \( \mathbf{b} = 1/3\langle 2\overline{1}3\rangle_M \) in the matrix. This reaction is not energetically favorable. However, it could occur under the influence of the stress concentration at the twin tip. The basal \( \langle a \rangle \) dislocations can glide in the matrix, and the \( \langle c+a \rangle \) dislocations can dissociate on the basal plane. The sessile dissociated \( \langle c+a \rangle \) dislocations line up at the twin tip and may inhibit the propagation of extension twins.

The stress concentration at the twin tip may rearrange the dislocations in the matrix to form a low-angle grain boundary in front of the twin tip [47]. The low-angle grain boundary contains both \( \langle c+a \rangle \) and \( \langle a \rangle \) dislocations from the twin dislocation reaction. These dislocations can coalesce to form a twin embryo according to the reverse reaction of (5.2). A macroscopic twin could then evolve when such twin nuclei grow into each other under
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an applied stress. As a result, a thin extension twin is formed in its own forest of dissociated $<\mathbf{c} + \mathbf{a}>$ dislocations. This process was observed at the tip of $\{11\bar{2}1\}$ twins in Co [46] and $\{10\bar{1}2\}$ twins in Zn [22].

5.3.4 Interaction between GB and terminating twin tip

The previous two sections discussed the morphology and interaction of intragranular twin tips. The twins that continue to grow will eventually terminate at the opposing GB. The interaction between the twin tip and the GB can generate forward stress and lead to the formation of a new twin in the neighboring grain. The two connected twins in the neighboring grains are referred to as adjoining twin pairs [21, 30-35]. The stress concentration in the neighboring grain that generates the adjoining twin pairs have been simulated using crystal plasticity [31, 49-52] and measured by high-resolution EBSD [53]. The twins that were simulated or characterized were in micron sized polycrystals and have grown to generate high stress concentrations in the neighboring grains. The characterization of the twin tip-GB interaction and the measurement of strain generated from the interaction needs the guidance of TEM.

One example of a twin tip that terminates at a GB is shown in Figure 5.15. The thickness of the twin tip is about 120 nm, which is below the spatial resolution of the EBSD-based IPF map and dramatically thinner than the twins observed in EBSD. This implies that this image was taken in the early stage of the interaction between the twin tip and the GB. The thickness of the twin tip is also significantly thinner than the set-up values for crystal
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plasticity simulation (e.g. ~3 μm [49]). No adjoining twins were observed in the neighboring grain in front of the twin tip. Instead, dislocations were detected.

Figure 5.15: Bright field image of a twin that terminates at a GB.

Figure 5.16: IPF image of the grain with twin tip and the neighbor grain and the corresponding misorientation of the GB.
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The IPF map of the grains acquired from NBED-ACOM are shown in Figure 5.16, where the extension twin boundary is highlighted in red and the grain boundary is marked with a black line. The IPF map confirms that no adjoining twin is formed in the neighboring grain. A line scan across the GB measured the misorientation angle to be $28^\circ$.

To measure the strain concentration at the twin tip - GB junction, the NBED-TOPSPIN technique was applied. The virtual bright field images, x-axes of strain analysis, coefficient correlation maps, and three in-plane strain components of the top and bottom grains in Figure 5.15 are shown in Figure 5.17 and Figure 5.18, respectively. The grain of interest was tilted to a $[11\bar{2}0]$ zone axis to acquire the maximum number of diffraction spots (Figure 5.17 and Figure 5.18 (b)), and the grain shows dark contrast in the virtual bright field image, as shown in Figure 5.17 and Figure 5.18 (a). For both grains, the direction parallel to the twin plane was selected as the x-axis and the normal as the y-axis as the coordinate for strain display, see Figure 5.17 and Figure 5.18 (b). The coefficient correlation maps in Figure 5.17 and Figure 5.18 (c) show the index quality in the map in which the defects (boundaries or dislocations) have lower value for coefficient correlation and exhibit dark lines. In the grain boundary and twin boundary region, the expanded width instead of a sharp line observed in the coefficient correlation maps implies the inclination of the boundaries. The borders of the inclined GBs in the grain of interest were marked by black dashed lines in the strain maps, as shown in Figure 5.17 and Figure 5.18 (d-f).
Figure 5.17: (a) Virtual bright field image, (b) diffraction patterns of the two grains. (c) correlation coefficient map and (d-f) strain maps when the top grain is tilted to one [1120] zone axis.
Figure 5.18: (a) Virtual bright field image, (b) diffraction patterns of the two grains. (c) correlation coefficient map and (d-f) strain maps when the bottom grain is tilted to one $[\overline{1}120]$ zone axis.
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In the strain maps for grain 1 (Figure 5.17), a local strain concentration can be detected at the twin tip - GB junction. However, the strain concentration area falls within the region of inclined boundaries, which contain the overlapped diffraction pattern from both the matrix of the grain 1 and the twin in grain 2 and can introduce an artificial elastic strain. After excluding the contribution of inclined boundaries, the strain in the neighboring grain in front of the twin tip is negligible. The strains detected in grain 1 are aligned with the dislocations; the contrast of dislocations can be seen in the correlation coefficient map in Figure 5.17 (c). This indicates that the shear strain generated from the twin tip in the neighboring grain was absorbed by emission of dislocations.

Elastic strain maps in the bottom grain also show stain concentration at the overlapped regions of the inclined GB (Figure 5.18 (d) and (2)). Ignoring the overlapped regions, the strains are aligned with the dislocation lines in Figure 5.18 (c). The higher density of dislocations around the twin tip – GB junction in the bottom grain elucidates the fact that dislocations can also be activated at the junction to release back stress in the twinned grain.

The formation of adjoining twins in the neighboring grain generated by twin tip-GB interactions is predicted to be determined by two main factors, the misorientation angle and the local elastic stress/strain concentration. The misorientation angle of the GB determines the alignment of the Schmid factor of the twinned and neighboring grains. Xin et al. [35] and Kumar et al. [31] calculated the Schmid factor representing the alignment of incoming and outcoming twin vectors in the two neighbor grains and found that there is a cutoff angle of the GB misorientation above which twin transmission is rare. The cutoff
angle for Mg is about 50°. The GB misorientation (28°) measured in Figure 5.16 falls within the range for the formation of an adjoining twin. However, no transmitted twin was observed in the neighboring grain.

The second factor that controls the adjoining twin formation process is the local elastic stress/strain concentration at the twin tip – GB junction. The simulation results predicted that a positive twin plane resolved shear stress concentration develops in the neighboring grain in front of the twin tip and favors the formation of an adjoining twin [31]. The formation of a twin in the neighboring grain have been suggested to relax the back stress locally at the twin tip and may facilitate the local twin thickening at the GB even when the dislocation slip systems have been considered for plastic deformation accommodation [49]. However, little strain concentration produced by the twin tip-GB interaction was detected. The strain was released by the formation of dislocations.

At the early stage of twin tip – GB interaction when the twin tip is small, the transmitted and back stresses, formed at the junction in the neighboring grain and twinned grain, can be dissipated by the formation of dislocations. The lack of stress concentration results in the absence of an adjoining twin. Continued straining leads to the thickening of the twin and exhausts the dislocations in the neighboring grain. Strain may then accumulate in front of the twin tip and nucleate adjoining twins. Therefore, in addition to the determinants of GB misorientation and stress concentration, a third factor, critical size of the twin tip, may be required to activate the adjoining twin in the neighboring grain in front of the twin tip.
Figure 5.19: Propagation process of an extension twin.

Taken altogether, the propagation of extension twins occurs in two stages. The first stage is intragranular propagation and the second stage is the formation of adjoining twin pairs, see Figure 5.19. The intragranular propagation stage starts from the nucleation of a twin that occurs mainly at a GB with the right misorientation and geometry, and sometimes inside a grain, as shown in Figure 5.19 (a). Strain concentrations at small twin tips can be mitigated by the formation of easy-glide basal \(<a>\) dislocations in the matrix. As the twin grows (Figure 5.19 (b)), twin dislocations accumulate at the twin tip. The reaction of twin
dislocations generates basal $<\mathbf{a}>$ and $<\mathbf{c} + \mathbf{a}>$ dislocations in the matrix and releases the elastic strain concentration. The dissociated $<\mathbf{c} + \mathbf{a}>$ dislocations on the basal plane impedes the thickening of the twin, while the reverse reaction of the basal $<\mathbf{a}>$ and $<\mathbf{c} + \mathbf{a}>$ dislocations can nucleate twin embryos in front of the twin tip and promote the forward propagation of the twin to form a thin and sharp configuration.

**Figure 5.20:** IPF map of a Mg sample that is compressed along the RD by 2% illustrates high density of adjoining twin pairs.
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The second stage of the twin propagation involves the intergranular formation of adjoining twin pairs. The twin continues to propagate in the grain until it terminates at the opposing GB with a misorientation angle < 50°. The local stress concentration at the GB generated from the twinning shear can be dissipated by the formation of dislocations in the neighboring grain, as shown in Figure 5.19 (c). The thickness of the twin tip increases with continued straining, and at some critical point the higher stress concentration in the neighboring grain cannot be released by dislocation glide, resulting in the nucleation of adjoining twin pairs. The newly nucleated twin in the neighboring grain will experience stage I from the beginning and propagate the twin transgranularly. An example of the adjoining twin pairs in a hot-rolled Mg that was compressed along the RD by 2% is shown in the IPF map in Figure 5.20. The twinned regions (predominantly extension twins) are presented as red lamellae and show large numbers of adjoining twin pairs.

5.4 Summary and conclusions

In summary, extension twin tips in Mg were systematically analyzed, including the morphology of twin tips, the elastic strain concentration and the interaction of twin tips with dislocations and GBs. Based on our results and analysis, the following key observations can be made:

1. The nucleation and propagation of extension twins are attributed to the motion of the incoherent twin dislocation (e.g. BP/PB interfaces) connecting the coherent {1102} boundaries. The resolved shear stress on the twin boundary results in the asymmetric
mobility of the twin dislocations on the two sides of a twin tip and leads to the asymmetric morphology of the twin tip.

2. Intragranular twin tips generates elastic strain concentration at the twin tip but the strain is released by the formation of basal $<$a$>$ dislocations.

3. A very high density of dislocations was observed to localize around the twin boundaries both in the twin and the matrix. The interaction of a basal $<$a$>$ dislocation and twin boundary results in a $<$c + a$>$ dislocation and a residual dislocation on the twin plane, which facilitates the thickening of an extension twin. The propagating extension twin leads to the formation of low angle boundaries of $<$c + a$>$ and $<$a$>$ dislocations, which may react to form dislocations with $$(1\bar{1}01)$$ direction and aid the twin growth. The alternate formation of $<$c + a$>$ and $<$a$>$ dislocations at the twin tip and the twin embryos from dislocation reaction causes the twin propagation to form a shape of thin and sharp lamella.

4. Twin tips that terminate at a GB can develop elastic strain in the neighboring grain and back stress in the twinned grain. These strain concentrations can also be released by formation of dislocations in either grain. A critical size of the twin tips is required to generate a high enough stress concentration to nucleate an adjoining twin in the neighboring grain.
5.5 References for Chapter 5

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Chapter 6.
Investigation of Texture Weakening in Mg-Ca Alloy

Dislocation slip and deformation twinning play critical roles in determining the mechanical behavior of Mg. However, texture introduced by processing can be more significant in practical applications. Strong basal texture can be formed in pure Mg and commercial Mg alloys. The addition of rare earth (RE) and Ca has been shown to weaken the rolling texture intrinsically and by annealing [1]. In this chapter, we characterized deformation texture in pure Mg and Mg-0.1Ca after hot rolling and the texture evolution during annealing by electron backscatter diffraction (EBSD); investigated the different dislocation and grain boundary (GB) structures in Mg-0.1Ca alloy with TEM; and analyzed the influence of the modified microstructure after Ca addition on static recrystallization (SRX) and texture weakening. Careful TEM tilting experiments revealed that the addition of Ca enhances \( \langle c + a \rangle \) dislocation activity by suppressing dissociation and decomposition simultaneously, and that the activated \( \langle c + a \rangle \) dislocations decrease rolling texture by reducing the anisotropy of slip. High-angle annular dark field (HAADF) equipped with energy-
dispersive X-ray spectroscopy (EDX) revealed that Ca segregates to high angle grain boundaries (HAGBs), which retards the GB mobility, and that the low-mobility GBs activate the nucleation of (static recrystallization) SRX inside deformed grains with high misorientation with respect to the main texture; and the probability of more uniform GB energy versus misorientation after segregation enables the growth of SRX-ed grains with more random orientation. The effect of GB segregation on both nucleation and growth of SRX grains weakens the texture during annealing.

6.1 Introduction

The weakened recrystallization texture in single phase Mg alloys with RE or Ca was originally proposed to be related to dynamic recrystallization (DRX), including shear band induced nucleation (SBIN) [2, 3] and deformation twin induced nucleation (DTIN) [4-6]. Basu et al. [2] and Stanford et al. [3] interpreted the effect of shear bands as being limited to texture weakening. More uniformly distributed shear bands in Mg-RE alloys are thought to act as favorable sites for nucleation of more randomly oriented grains. However, uniformly distributed shear bands are also observed in RE-free alloys with strong texture [7, 8]. Molodov et al. [4] and Beer et al. [9] reported preferable recrystallization nucleation sites at deformation twins, but growth of recrystallized grains is constrained by twin size and the effect of DTIN on texture weakening is limited. Furthermore, non-basal dislocations have been discussed as one of the reasons for texture weakening during DRX [10-12]. Sandlöbes et al. [13] proposed that RE alloying decreases stacking fault energy (SFE) and activated $I_1$ stacking faults, which serve as sources of non-basal dislocation
nucleation. Wu [14] predicted that RE addition (as well as Ca and Mn) decreases the energy barrier of non-basal dislocation cross-slip and maintains the mobility of non-basal dislocations. The increase in mobility of non-basal dislocations alleviate the anisotropy of Mg alloys and may weaken the forming texture.

In addition to DRX, static recrystallization (SRX) was later reported to influence texture [1]. Bhattacharyya et al. [15] reported that texture in AZ31 Mg alloy remains constant at lower annealing temperatures and shows a steady increase at higher temperature. The basal texture strengthening with grain growth is hypothesized to be attributed to the anisotropic grain boundary (GB) energy and mobility of HCP Mg. By contrast, in Mg-0.1Ca alloy, even though strong basal texture can be formed after hot rolling, weaker texture can be attained by annealing [1, 16]. The weaker texture in the Mg-Ca alloy is believed to be related to the GB segregation of solute atoms. The segregated solute atoms are reported to introduce solute drag effect on GB mobility and weaken the texture during annealing [1]. However, Robson et al. applied Langmuir-McClean and Cahn–Lücke–Stüwe models to investigate the solute drag effect of various RE and other elements, and predicted that the solute drag effect is insufficient to strongly retard SRX under typical annealing conditions but that it can suppress DRX by any mechanism requiring boundary migration [17, 18]. It was also hypothesized that the GB energy of decorated GBs are less sensitive to misorientation, which result in weaker texture by leveling out the differences in GB energies encountered in traditional Mg alloys, and thus promoting equal growth and nucleation opportunities [19-21].
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In summary, the weaker texture with addition of Ca and RE elements has been attributed to recrystallization, which is thought to be affected by twinning, shear banding, non-basal dislocation motion and GB segregation. In this chapter, we combined TEM-based automated crystal orientation mapping (ACOM) with traditional electron backscattered diffraction (EBSD) to characterize the microstructure of pure Mg and Mg-0.1Ca and investigated the effect of non-basal dislocations and GB segregation on texture weakening.

6.2 Experiments

Pure Mg and Mg-0.1Ca (at%) were hot rolled at 500°C with 50% thickness reduction and samples perpendicular to the normal direction (ND) and the transverse direction (TD) were cut using wire electrical discharge machining (EDM). The TD and ND pure Mg samples were annealed at 300°C for 1, 3, 5, 7, 10, 15, 30 min, and the Mg-0.1Ca samples were heat treated at 300°C for 5, 10, 15, 30, 60 and 120 min due to lower recrystallization rate after Ca alloying. All the samples were metallographically prepared with SiC paper and 50nm diameter water-free silica suspension. The mirror-like surfaces were subsequently cleaned by argon ion beam milling using a Fischione Model 1060 Ion Mill. TEM specimens of TD samples were mechanically polished under nominally zero load to 150 µm, electro-chemically polished with 10% nitric acid in methanol at -50 ºC, and subsequently further thinned to electron transparency using a precision ion polishing system (PIPS) at liquid nitrogen temperature and low voltage to avoid beam damage.
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EBSD was performed using a FEI scanning electron microscope (SEM, Thermo Scientific Helios G4 UC) equipped with an EDAX EBSD detector. After annealing, all the samples were quenched in cold water and polished using SiC and colloidal suspension as discussed in the previous paragraph. EBSD scans of all the as rolled and annealed samples were performed in 3 random areas of 1 x 1 mm using step size 1 µm. The EBSD results were analyzed with TSL OIM 8 software, which provides information including grain size and orientation (inverse pole figure maps, IPF), texture strength (pole figures, PF), grain size distributions, GB misorientation distributions, recrystallization fraction and boundary misorientations. The grain orientation spread (GOS) in each grain is determined by calculating the average misorientation (angle) between all points sampled within the grain. This operation is performed by computing the average (macroscopic) grain orientation and then by calculating the average deviation between the macroscopic grain orientation and the (microscopic) crystal orientations of each point within the grain. The threshold GOS of dynamically recrystallized grains is typically 1° – 2° [19].

TEM imaging and ACOM mapping were conducted using a Thermo Scientific TF30 microscope equipped with a NanoMEGAS ASTAR system operating at 300 kV. Grain size and morphology were observed using conventional bright-field (BF) and dislocations were imaged with weak beam dark field (WBDF). In order to observe and identify the misorientation of sub-grains and recrystallized grains, TEM-based ACOM was applied to obtain two-dimensional orientation maps with nanoscale resolution [22]. This technique relies on obtaining an array of diffraction patterns by rastering a focused probe across the specimen and indexing the patterns to obtain a full 2D orientation dataset, which inherently
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contains information about grain size and GB character [23-25]. A small parallel beam was obtained by using small condenser aperture (30 μm) and large spot size (spot size 9). The probe size limits the spatial resolution of the orientation maps, and a nominal probe size of 1.5 nm was used in all experiments with a 10 nm step size between points. A small convergence angle reduces the size of the spots in the diffraction pattern, which is required to reliably index the patterns obtained at each point. A camera length of 13.5 cm was used to generate diffraction patterns with small, sharp spots that were sufficiently separated. Beam precession (0.5°) was applied to increase the number of spots and, hence, the reliability of diffraction pattern indexing [22]. The ACOM results were analyzed using the MapViewer and TSL OIM 8 software. For all grains considered, the orientation results were compared with the raw diffraction patterns to ensure that the patterns were not produced by overlapping grains.

High resolution scanning transmission electron microscopy (HRSTEM, Joel ARM 200) equipped with EDX was applied to quantify the GB segregation of Ca. The TEM sample for STEM-EDX was prepared by FIB lift-out with low kV thinning to minimize beam damage, and subsequently cleaned by nanoMill at liquid nitrogen temperature to remove the damage layer from FIB. The grain boundary was imaged using HAADF and the composition information was provided by the EDX spectra. The nanoMill and high resolution HAADF with EDX analysis were performed in Lehigh with the assistance of Dr. Christopher Marvel.
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6.3 Results

6.3.1 Microstructure evolution during SRX

The IPF maps of ND and TD from as-rolled and annealed pure Mg and Mg-0.1Ca with corresponding insets of PFs are shown in Figure 6.1 to Figure 6.6. All the IPF maps are colored identically and the intensity of all PFs are normalized, as shown in the IPF and PF color legends in Fig. 1. Both the as-rolled Mg and Mg-0.1Ca maps present strong basal texture with crystallographic \( <c> \)-axis nearly parallel to the rolling ND. To evaluate the microstructure evolution with SRX, the recrystallized grains are highlighted using GOS < \( 2^\circ \) threshold (See Figure 6.2), which indicates small average deviation of orientation and low dislocation density within the grains.

The texture intensity of as-rolled Mg-0.1Ca (10.9–11.2 mrd) is lower than that of pure Mg (14.1–14.3 mrd), see Figure 6.1. Notably, the PF of Mg-0.1Ca alloy has a spread towards the rolling direction (see Figure 6.1 (c)), in accordance with previous observations in literature [15]. For both samples, the texture of recrystallized regions is weaker than overall texture (Figure 6.2). In pure Mg, the grain sizes of both TD and ND are uniformly distributed and growing rapidly with annealing time. The recrystallization is progressed homogeneously, and no obvious preferable sites are observed (see Figure 6.3 and Figure 6.4). In Mg-0.1Ca alloy, bimodal grain size is observed with extra-large deformed grains and smaller DRX-ed grains (Figure 6.5). The large deformed grains vanish with annealing.
time and eventually the material is composed of relatively uniaxial and uniform recrystallized grains, see Figure 6.6.

Figure 6.1: IPF maps of as-rolled ND and TD from pure Mg and Mg0.1Ca and corresponding (0002) PFs show basal texture after hot rolling. The PF color is normalized as shown color bar the maximum intensity of the PFs is labelled in each case.
Figure 6.2: IPF maps of recrystallized regions in as-rolled ND and TD from pure Mg and Mg0.1Ca and corresponding (0002) PFs show basal texture after hot rolling.
Figure 6.3: IPF and PF maps of the whole and recrystallized ND surface for annealed pure Mg.
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Figure 6.4: IPF and PF maps of the whole and recrystallized TD surface for annealed pure Mg.
Figure 6.5: IPF and PF maps of the whole and recrystallized TD surface for annealed Mg-0.1Ca.
Figure 6.6: IPF and PF maps of the whole and recrystallized TD surface for annealed Mg-0.1Ca.
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The recrystallization kinetics in Figure 6.7 (a) illustrates the area fraction of recrystallized materials as a function of log(time). The curve of Mg-0.1Ca has characteristic sigmoidal form and shows an apparent incubation time, which is followed by an increasing rate of recrystallization, a linear region, and finally a decreasing rate of recrystallization. This shape of the curves indicates discontinuous recrystallization. By contrast, no apparent incubation stage is observed in pure Mg with SRX starts immediately upon annealing.

Figure 6.7: (a) Recrystallized area fraction evolution with log annealing time, (b) evolution of the maximum intensity from PF, (c) linear fitting of maximum PF intensity with recrystallized fraction and (d) grain size evolution with annealing time. The data of pure Mg is in blue and that of Mg-0.1Ca alloy is in red, and the overall data is in solid lines and the recrystallized data in dashed lines.
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The texture evolution of pure Mg and Mg-0.1Ca with annealing time is shown in Figure 6.7 (b). The overall texture of pure Mg increases continuously with annealing time and reaches a plateau after 15min heat treatment, which indicates the completion of recrystallization, as shown in Figure 6.7 (a). The texture of the recrystallized area shares the same trend of strengthening with annealing but is consistently lower than overall texture. Figure 6.7 (c) shows that the maximum PF intensity linearly decreases with recrystallization fraction. Meanwhile, the grain size of the recrystallized regions in pure Mg displays a rapid increase after annealing over the original 15 min and remains constant afterwards, as shown in Figure 6.7 (d). The coincidence of texture evolution and grain growth indicates that the growth of continuously recrystallized grains increases the texture in pure Mg [15].

The texture evolution and grain growth behavior of Mg-0.1Ca varies from that of pure Mg. Contrary to the strengthened texture in pure Mg, the overall texture is weakened linearly with recrystallized fraction, as shown in Figure 6.7 (c), and the texture evolution rate is obviously lower than that of pure Mg, which is displayed in Figure 6.7 (a). The recrystallized texture decreases fast during the incubation time and evolves continuously weaker with SRX. The grain size fluctuates dramatically in Mg-0.1Ca alloy due to the existence of extra-large deformed grains. The grain size of recrystallized region remains constant during the incubation stage and subsequently increases slowly with annealing time. The misalignment between the rate of texture weakening and grain growth indicates that mechanisms other than growth of recrystallized grains may be responsible for the texture weakening of Mg-0.1Ca.
6.3.2 Sub-grains and recrystallized grains

To uncover the mechanism that controls the texture weakening in Mg-0.1Ca, TEM was employed to characterize the microstructure of recrystallized and deformed regions. As shown in BF TEM images in Figure 6.8, both as-rolled pure Mg and Mg-0.1Ca appear to have submicron grains that are significantly smaller than the statistical results from EBSD. Interestingly, a large proportion of boundaries are along the ND. The EBSD orientation information of deformed and recrystallized regions of the TEM samples from 1min-annealed pure Mg (a and b respectively) and 10 min-annealed Mg-0.1Ca (c and d respectively) are shown in Figure 6.9. Examples of deformed and recrystallized regions are highlighted by red and blue boxes individually. To distinguish the sub-grains from recrystallized grains, ACOM is applied to illustrate detailed information.
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Figure 6.9: IPF maps of thin areas in (a) 1 min-annealed pure Mg and (c) 10 min-annealed Mg-0.1Ca alloy TEM foils with ND and RD marked by white arrows; and the corresponding recrystallized regions in (b) and (d) respectively.

The ACOM maps acquired from deformed and recrystallized regions in pure Mg sample with incident electron beam along rolling TD are shown in Figure 6.10. The high angle grain boundaries (HAGBs, misorientation > 15°) are highlighted with black lines and LAGBs (2 – 15°) with red lines. The BF images illustrates sub-grain structure in the recovered grain (right) and cell structure in non-recovered grain (left), as shown in Figure 6.10 a. The GB bulges from right to left due to higher stored energy in the non-recovered grain (see Figure 6.10 a and b). Recrystallized grains can be formed at the bulging GBs, the examples of which are shown in Figure 6.10 d and e. The misorientation between [0001] crystallographic direction and the rolling ND is mapped in Figure 6.10 c and f with red to blue representing misorientation angles ranging from 0° to 90°. The dominant red color in the misorientation maps of both deformed and recrystallized regions indicates that neither recovery nor recrystallization has obvious effect on texture weakening.
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Figure 6.10: BF TEM images of (a) deformed region and (d) recrystallized region pure Mg, the area of which are marked with blue and red respectively in Figure 6.9 a; (b, e) ACOM maps of the same area of interest with HAGBs marked with black lines and LAGBs in red; and (c, f) the maps of misorientation between crystallographic [0001]-axis of grains and rolling ND, in which red to blue indicates increasing misorientation angle between [0001] and ND.

The IPF maps of Mg-0.1Ca acquired from ACOM are shown in Figure 6.11. In the grains from the deformed region, besides the straight and parallel-to-[0001] LAGBs detected in pure Mg, inclined boundaries connecting the [0001] boundaries are observed (Figure 6.11 b). In the recrystallized region, submicron recrystallized grains are formed inside a large grain with no apparent bulging effect observed (see Figure 6.11 d and e). This indicates a different nucleation mechanism of recrystallization in Mg-0.1Ca compared to that of pure Mg. Moreover, although the grain in the deformed region aligns its [0001] direction along
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the ND (Figure 6.11 c), the recrystallized grains have noticeable misorientation of <c>-axis off ND (Figure 6.11 f), which appears to be related to the change in recrystallization nucleation mechanism.

Figure 6.11: BF-TEM images, corresponding ACOM maps and the maps of misorientation between crystallographic <c>-axis of grains and ND of (a, b, c) deformed region and (d, e, f) recrystallized region in Mg-0.1Ca alloy. Both regions correspond to the blue and red box marked in Figure 6.9 c.

6.3.3 <c + a> dislocations

To underline the mechanisms that result in LAGBs with various morphologies in Mg-0.1Ca and pure Mg, the dislocations comprising the boundaries highlighted by blue and red boxes
respectively in Figure 6.10 and Figure 6.11 were imaged using WBDF. For both Mg-0.1Ca alloy and pure Mg, one (11\(\bar{2}\)0) zone axis was selected, and the \(g \cdot b = 0\) invisibility criteria was utilized to deduce the Burgers vectors [26]. The diffraction vector \(g_c = [0002]\) was used for imaging \(<c>\) component of \(<c + a>\) dislocations (Figure 6.12 a and c). Under this diffraction condition, the Burgers vectors of \(<a>\) dislocations (\(<a> = 1/3[11\bar{2}0]\)) satisfy the invisibility criteria. When we apply \(g_a = [\bar{1}00]\) to investigate the dislocations in the same area (Figure 6.12 b and d), \(<a>\) dislocations and a-component of \(<c + a>\) dislocations appear with the \(<c>\) dislocations invisible. The dislocations that are visible in both \(g_a\) and \(g_c\) conditions are deduced to be \(<c + a>\) dislocations. All the images were acquired when the specimen was tilted 20° away from [11\(\bar{2}\)0] zone axis with the corresponding two-beam condition maintained. The diffraction vectors are demonstrated with yellow arrows.

It is illustrated in Figure 6.12 a and b that the \(<c + a>\) dislocations in pure Mg appear long and straight and parallel to the basal plane under \(g_c\) condition and can be seen to dissociate on the basal plane under \(g_a\) condition. One example of the dissociated \(<c + a>\) dislocations in pure Mg is highlighted by the yellow dashed box. This phenomenon has previously been reported in literature [27-30]. It is worth noting that dislocations appear to be terminated at the LAGBs in pure Mg. Segments of dislocations with \(<c>\) components are aligned with the LAGBs along the [0001] direction, an example of which is highlighted with a blue dashed line. But no \(<a>\) component of the dislocation can be observed under \(g_a\) conditions. This means the dislocations trapped at the LAGB are pure \(<c>\) dislocations, which is formed from the decomposition of \(<c + a>\) dislocations. Since the straight LAGBs in pure Mg are composed of basal \(<a>\) dislocations, which can be indicated by the appearance of
dislocation contrast under $g_a$ condition, the $<a>$ dislocations that decomposed from $<c+a>$ dislocations may react with the LAGBs and leave the $<c>$ dislocation behind along the LAGB.

![WBDF images](image)

**Figure 6.12:** WBDF images with (a) $g_c = [0002]$ and (b) $g_a = [1\bar{1}00]$ in 1min-annealed pure Mg and images with (c) $g_c = [0002]$ and (d) $g_a = [1\bar{1}00]$ in 10min-annealed Mg-0.1Ca alloy. The $g$ vectors applied for imaging are marked with yellow arrows; examples of dissociated $<c+a>$ dislocations in pure Mg are emphasized by yellow dashed boxes; $<c+a>$ LAGB is highlighted with red box; and examples of trapped pure $<c>$ or $<c+a>$ dislocation is shown as blue dashed lines.

The behavior of $<c+a>$ dislocations in Mg-0.1Ca varies from that of pure Mg. Firstly, the non-basal dislocations indicate no obvious dissociation under identical $g_a$ condition to pure Mg, as shown in Figure 6.12 d, which concurs with our observation in AZ31 alloy in our previous work [31]. Secondly, even though the $<c+a>$ dislocations in Mg-0.1Ca are also
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trapped at the LAGBs, the constrained dislocations can be contrasted under \( g_a \) condition, which means the \( <c+a> \) character is maintained in Mg-0.1Ca instead of pure \( <c> \) in pure Mg. This can be attributed to the addition of dilute Ca that inhibits the decomposition of \( <c+a> \) dislocations. As a result, the two glissile-to-sessile transformation of \( <c+a> \) dislocations in pure Mg, dissociation and decomposition, are both suppressed by Ca alloying, which leads to an increase in the mobility of \( <c+a> \) dislocations in Mg-0.1Ca. One of the outcomes from the improved mobility of \( <c+a> \) dislocation is that higher density of cross-slip features can be observed (see the out-of-basal \( <c> \) components in Figure 6.12 c). The other is the possibility of forming \( <c+a> \) LAGBs, which is highlighted by the red boxes in Figure 6.12 b and d. The \( <c+a> \) LAGB is well aligned with the inclined and crinkled boundaries in Figure 6.11 b.

6.3.4 Grain boundary segregation

The HAADF image of a grain boundary from 10 min-annealed Mg-0.1Ca sample is shown in Figure 6.13 a. The HAADF technique provides Z-contrast images, which means that heavier elements exhibit brighter contrast. Ca has a higher atomic number than Mg and the increased contrast at the GB area can be attributed to the segregation of Ca. To confirm the composition at the GB, the integrated EDX spectra of the GB (marked with a red box in Figure 6.13 a) and the grains on both sides (marked with black boxes in Figure 6.13 a) were acquired and normalized for comparison. A Ca peak can be observed in the GB spectrum, while the Ga peak can be attributed to ion implantation during FIB preparation.
Figure 6.13: (a) STEM-HAADF map of a grain boundary in Mg-0.1Ca alloy and (b) integrated EDX spectra of the grain boundary region and two neighbor grains.

6.4 Discussion

6.4.1 Effect of non-basal dislocations on rolling texture and recrystallization nucleation

The deformation texture is determined by the active deformation mechanisms in a material, and the dominant deformation mechanism in Mg is basal $<\mathbf{a}>$ slip [32], which results in the strong basal texture after rolling [33]. There are other dislocation slip systems in Mg, and one of the most significant involves $<\mathbf{c} + \mathbf{a}>$ dislocations. However, the CRSS of $<\mathbf{c} + \mathbf{a}>$ dislocations is substantially higher than that of basal $<\mathbf{a}>$ [34]. Wu et al. predicted that the difficulty of $<\mathbf{c} + \mathbf{a}>$ glide should be attributed to the decomposition and dissociation behavior [35]. The $<\mathbf{c} + \mathbf{a}>$ dislocations have $\mathbf{b}_{c+a} = 1/3<1\bar{1}23>$ Burgers vector, and the dislocations can either decompose to a pure $<\mathbf{a}>$ dislocation ($\mathbf{b}_{\mathbf{a}} = 1/3<1\bar{1}20>$) with a pure
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\(<c>\) dislocation \((b_c = [0001])\) or dissociate on the basal plane as two non-basal partials by
\[\frac{1}{3}<11\bar{2}3> = \frac{1}{6}<20\bar{2}3> + \frac{1}{6}<02-23>\]. In both cases, the \(<c + a>\) dislocations transform from glissile to sessile and can no longer accommodate deformation. We note that both the decomposition and dissociation are suppressed in the Mg-0.1Ca samples and the mobility of \(<c + a>\) dislocations is improved. The active \(<c + a>\) dislocations in Mg-0.1Ca may be hypothesized to decrease the anisotropy and contribution to the weaker texture after DRX during hot rolling. However, the possibility that the initial texture contributes to some degree is not ruled out.

The activated \(<c + a>\) dislocations in Mg-0.1Ca can facilitate recrystallization nucleation from sub-grains. The \(<c + a>\) dislocations can react with the basal \(<a>\) LAGBs. In pure Mg, the \(<a>\) components of the \(<c + a>\) dislocations terminating at \(<a>\) comprising sub-grain boundaries seems to be annihilated by the boundaries, which keeps the \(<c>\) component trapped in place (See Figure 6.12 a and b). The immobile residual \(<c>\) dislocations in Mg [35] can pin the LAGBs. On the other hand, the \(<c + a>\) dislocations in Mg-0.1Ca alloy appears to be penetrating the LAGBs (See Figure 6.12 c & d), which is ascribed to higher stability and mobility of \(<c + a>\) dislocation. Therefore, it is reasonable to assume that the mobile \(<c + a>\) dislocations impede the LAGBs less than the sessile \(<c>\) dislocations in pure Mg. The weaker interaction between \(<c + a>\) dislocations and basal \(<a>\) LAGBs should lead to higher mobility of sub-grain boundaries in Mg-0.1Ca, and the higher mobility of sub-grain boundaries should expedite the nucleation of recrystallized grains [36].
6.4.2 Effect of GB segregation on boundary mobility

Mg-0.1Ca alloy displays significantly lower SRX and grain growth rate during annealing, which may arise from the GB segregation [1]. The GB segregation in Mg-0.1Ca alloy can decrease boundary mobility (M) by solute drag [37]. The recrystallization rate (v) and grain growth rate (ˇG) are determined by the velocity of HAGBs, v = ˇG = M · P, where P is the driving pressure (generally taken to be a function of dislocation density) for recrystallization or driving force on the boundaries (function of boundary energy and curvature) for grain growth. According to the CSL model, solute atoms can introduce a drag pressure [37]:

\[ P_d = \frac{\alpha VC_0}{1 + \beta^2 V^2} \]  

(6.1)

where \( V \) is the boundary migration velocity, \( C_0 \) the solute concentration and \( \alpha \) and \( \beta \) are constant.

\[ P = P_0 + P_d = \frac{V}{M} + \frac{\alpha VC_0}{1 + \beta^2 V^2} \]  

(6.2)

For low velocity and low driving force, when \( V \ll 1/\beta \),

\[ P = \left( \frac{1}{M} + \alpha C_0 \right) V \]  

(6.3)
For simplified GB profile

$$\alpha = \frac{N_v (kT)^2}{E_0 D} \left( \sinh \frac{E_0}{kT} - \frac{E_0}{kT} \right)$$

(6.4)

where $N_v$ is the number of atoms per unit volume, $E_0$ the difference in interactive energy between GB and matrix, $k$ Boltzmann constant, $T$ temperature, $D$ bulk diffusion coefficient of solute and $\delta$ width of GB.

In the case of low velocity, the effective mobility $M_{\text{eff}}$:

$$\frac{1}{M_{\text{eff}}} = \frac{1}{M} + \alpha C_0$$

(6.5)

To evaluate the influence of Ca solute on the mobility, we calculated the value of $\alpha$ to be approximately $2.33 \times 10^{12}$ Jsm$^{-4}$ by applying $D=3.61 \times 10^{-17}$ m$^2$s$^{-1}$, $E_0=-12$kJmol$^{-1}$ and $T=573$K. The values of coefficients are roughly estimated from those of Y [17, 38, 39] due to the similarity between Ca and Y [40]. Thus, the second term in equation (6.5) is in the $10^{19}$ order of magnitude (using $C_0=10^{-3}$). The mobility of GBs in pure Mg is in the range $10^{-8} \sim 10^{-9}$m$^4$J$^{-1}$s$^{-1}$, and consequently $M_{\text{eff}}$ is approximately $10^{-18} \sim 10^{-19}$m$^4$J$^{-1}$s$^{-1}$, which is about ten orders of magnitude lower than that of segregation-free boundaries.

No apparent solute segregation was observed at either LAGB or dislocation cores, and the content of Ca in the matrix was extremely low. Thus, we conclude that the influence of Ca solute on LAGB is limited. The mobility of LAGB in pure metals is slightly lower than, or
6.4.3 Texture weakening mechanism during SRX

The texture weakening of Mg-0.1Ca alloy and the texture strengthening of pure Mg are both linearly related to SRX. The shift in texture evolution in Mg-0.1Ca is controlled by the change in SRX behavior, which includes nucleation and growth during recrystallization.

Strain-induced grain boundary migration (SIBM) is the main mechanism of nucleation in pure Mg during recrystallization, which can be indicated by the bulging effect and recrystallized grains in Figure 6.10. A characteristic feature of SIBM nucleation mechanism is that the new grains will likely have similar orientations to the old grains from which they have grown [36]. As a result, the decrease in texture of recrystallized grains after SRX is not as significant. In Mg-0.1Ca alloy, the driving force of boundary migration in Mg-0.1Ca from stored energy is largely balanced by the solute drag pressure from segregation, and SIBM mechanism is difficult to activate. Large proportion of stored energy is released by the formation and growth of sub-grains. The sub-grain growth mechanism can be clued by the reduced fraction of LAGB (Figure 6.14 a) and the increased proportion of HAGB during SRX. The orientation of the recrystallized grains from sub-grain growth is determined by the misorientation gradient of the mother grain. Due to the non-uniform deformation in deformed grains in Mg-0.1Ca, the deformation concentrated
area (e.g. shear band or twin) incorporates higher misorientation gradient [2, 5], and the accumulation of misorientation with sub-grain growth capacitates the formation of recrystallized grains with large misorientation to the original grain (see Figure 6.11 f).

Figure 6.14: (a) Misorientation distribution of HAGBs in pure Mg (solid lines) and Mg-0.1Ca alloy (dashed lines) annealed at 300°C for different times; (b) HAGB content evolution in pure Mg and Mg-0.1Ca alloy with annealing time.

It is worth noting that HAGB content is a method of determining the transition between discontinuous recrystallization and continuous recrystallization [42]. As shown in Figure 6.14 a, in pure Mg, no significant change in the percentage of HAGBs during annealing indicates continuous recrystallization is dominant and an obvious increase of HAGB content in Mg-0.1Ca implies discontinuous recrystallization.

As to the influence of grain growth on texture evolution, it has been predicted that the existence of a high GB energy barrier in pure Mg retards the formation of non-basal texture during annealing [15, 43], whilst GB segregation of RE or Ca elements can level out the grain boundary energy differences and randomize the annealing texture by equalizing the
possibility of growth of grains with large misorientations to the dominant texture [1, 19, 20]. No direct evidence can support this hypothesis as of now, but one indirect proof in Figure 6.14 b can be used to indicate the change of GB energy and mobility: the misorientation distribution of HAGBs in Mg-0.1Ca alloy grows flatter with annealing time compared to that of pure Mg. Pure Mg contains a significant number of boundaries with ~30° misorientation about the <0001> direction and this boundary type persists throughout the annealing treatment. In Mg-0.1Ca alloy, however, the ~30° is obviously weaker than for pure Mg, and instead a larger proportion of higher angle (>50°) boundaries are developed with increasing annealing time. The more uniform HAGB misorientation distribution indicates weaker anisotropy of GB (mobility and energy) with Ca solute segregation in Mg-0.1Ca. The more isotropic GB enables the growth of the recrystallized grains that nucleate inside the deformed grains surrounded by HAGBs with high misorientation to the main texture. As a result, the texture is being weakened with the growth of recrystallized grains during annealing.

Therefore, Ca solute segregation at GBs triggers a new nucleation and growth behavior of SRX-ed grains during annealing and results in the weaker texture. The SRX and texture weakening process is hypothesized as follows. In the first stage at the beginning of SRX (the incubation stage in Figure 6.7 a, annealing for <10 min), nucleation of SRX-ed grains concurs with the growth of DRX-ed grains. However, SRX-ed grains nucleate at a higher rate due to the dramatically decreased mobility of HAGB. The new grains are small with relatively random orientation (see Figure 6.11 e and f), which leads to the rapidly decreasing texture (Figure 6.7 b) with no apparent grain growth in the recrystallized region
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(Figure 6.7 d). In the second stage (10-120 min), the driving force for recrystallization nucleation rate decreases with the consumption of stored energy, and subsequently the growth of nucleated grains becomes dominant. The driving force of GB mobility in this stage is still the difference in stored energy of neighboring grains. The deformed grains with higher stored energy are gradually replaced by recrystallized grains but at a low rate due to pinning caused by GB segregation. This process causes the slow but consistent weakening of texture with rapid increase in recrystallized volume fraction. The last stage occurs when SRX is completed, and the texture and grain size remain constant with annealing time at 300°C for Mg-0.1Ca alloy. The schematic process of the texture strengthening in pure Mg and weakening in Mg-0.1Ca during SRX is shown in Figure 6.15.

Figure 6.15: Schematic processes of texture strengthening in pure Mg and texture weakening in Mg-0.1Ca during SRX
6.5 Summary and Conclusions

In this work, we performed detailed microscopic characterization on dislocation and GB segregation and analyzed their effects on texture change during rolling and annealing in pure Mg and Mg-0.1Ca alloy. The key findings can be concluded as follows:

(1) The rolling texture of Mg-0.1Ca is weaker than that of pure Mg. The texture of pure Mg is strengthened with annealing time and that of Mg-0.1Ca is weakened.

(2) Ca alloying in Mg were found to suppress both the dissociation and decomposition, and increase the stability and mobility of $<c+a>$ dislocations. The mobile $<c+a>$ dislocations mitigate the anisotropy of Mg and weaken the rolling texture. The activated $<c+a>$ dislocations can also form LAGBs and unlock the immobile basal $<a>$ LAGBs. Both effects may facilitate recovery and SRX nucleation inside deformed grains.

(3) The texture strengthening during SRX in pure Mg is attributed to the SIBM nucleation and the anisotropic GB energy. The former results in nucleation of grains with orientation close to the dominant texture while the latter leads to the preferable growth of grains with basal texture.

(4) Ca solute segregation at HAGB in Mg-0.1Ca retards the mobility by solute drag effect. The impeded HAGB restrains the SIBM and activates recrystallization nucleation in deformation concentrated areas inside the grains. The nucleated grains show high misorientation off the dominant rolling texture. The GB segregation also levels out the GB energy difference versus misorientation and enables the growth of SRX-ed grains with relatively random orientation. As a result, the texture is weakened during SRX.
6.6 References for Chapter 6

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Chapter 7.  
Summary of the Thesis and Future Directions

The primary focus of the work involved two non-basal deformation mechanisms, $\langle c + a \rangle$ slip and extension twinning. The effect of alloying elements on the $\langle c + a \rangle$ dislocation core structure and behavior was investigated. The characterization of extension twin tips within grains and at grain boundaries revealed dislocations that reduced the strain concentration at twin tips and illustrated a previously unreported mechanism for twin propagation. The texture weakening mechanisms in Mg-Ca alloy were also systematically investigated. The overarching goal of the research presented in this dissertation was to elucidate the governing deformation mechanisms in Mg and Mg alloys and to develop the understanding need to develop more ductile and formable Mg alloys.

7.1 Review of key findings

$\langle c + a \rangle$ dislocations were introduced by compression along the ND of hot-rolled pure Mg and the commercial wrought Mg alloy, AZ31. Careful tilting experiments and WBDF electron microscopy observations were performed to contrast and analyze the $\langle c + a \rangle$
dislocations in Mg and AZ31. The character and core structures of $<c + a>$ dislocations in AZ31 and Mg were systematically analyzed. The results can be summarized as follows:

- $<c + a>$ dislocations were observed in both hot-rolled pure Mg and AZ31 after close-to-$<c>$-axis compression. $<c + a>$ dislocations were observed to be nonconservatively dissociated on the basal plane in pure Mg, but the presence of Al and Zn in AZ31 was found to suppress the dissociation of $<c + a>$ dislocations on the basal plane.

- The compact dislocation cores correlate to increased $<c + a>$ dislocation mobility and improved strain to failure for AZ31 as compared to pure Mg.

- The thickness of the observed SFs (T) followed a simple geometric relationship with respect to the sample thickness (t) and titling angle, $T = t \sin \theta$, confirming that the dissociation of $<c + a>$ dislocations are on the basal plane.

- The analysis of $<c + a>$ dislocations in AZ31 reveals that the dislocations lie at the intersection of the basal plane and both pyramidal planes, which suggests that the $<c + a>$ dislocations on both pyramidal planes are originally activated.

In addition to AZ31, the $<c + a>$ dislocations in a Mg-Re alloy, Mg-3Er, were systematically analyzed to determine why RE elements have such a positive effect on ductility. The influence of Er addition on the mechanical behavior of single crystalline Mg-3Er was evaluated through micro-pillar compression and subsequent TEM analysis. The dislocation line vectors were systematically calculated to analyze the resident pyramidal planes of the $<c + a>$ dislocations. Moreover, the dislocation cores of $<c + a>$ dislocations
in both Mg-3Er and pure Mg were imaged with HRSTEM. The results can be summarized as follows:

- The stress-strain curves of the in-situ micro-pillars compression of Mg-3Er displayed similar deformation behavior to pure Mg. Post-mortem characterization with TEM revealed that the enhanced ductility of the Mg-3Er alloy may be attributed to the increased mobility of \(<c+a>\) dislocations.

- The dissociation of \(<c+a>\) dislocations in Mg-3Er alloy was observed to be suppressed with the spacing of dissociated partials on the basal plane significantly smaller than for pure Mg. The more compact core facilitates the motion of \(<c+a>\) dislocations and improves the ductility.

- The addition of Er has negligible effect on the core of basal \(<a>\) dislocations was found to spread the core of partial \(<c+a>\) dislocations along the out-of-basal plane direction.

- The Er alloying decreases the energetic favorability of basal dissociation and improves the stability of \(<c+a>\) dislocations on pyramidal planes. The \(<c+a>\) dislocations that are maintained on the pyramidal planes can accommodate plastic deformation and enhance the ductility of Mg-Er alloy.

Another dominant deformation mechanism in Mg, extension twinning, was investigated. Observations of twin tips were made to study the nucleation and propagation mechanisms of extension twins in pure Mg. The morphology of the tips, strain concentration at the twin
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tip and the interaction between twins and dislocations and grain boundary were analyzed. The results can be summarized as follows:

- The nucleation and propagation of extension twins can be attributed to the motion of incoherent twin boundaries (e.g. BP/PB interfaces) that connect the coherent \{1\bar{1}02\} boundaries. The resolved shear stress on the twin boundary results in the asymmetric mobility of twin dislocations and leads to an asymmetric morphology of the twin tip.

- Twin tips that terminate inside a grain are known to generate a strain concentration at the twin tip, but this strain was observed to be released by the formation of numerous basal \(<a>\) dislocations.

- The twin boundary and twin tip were also observed to create and interact with dislocations in the matrix. The interaction of a basal \(<a>\) dislocation and the twin boundary results in a \(<c+a>\) dislocation and a residual dislocation on the twin plane and actuates the thickening of extension twin. The propagating extension twin also leads to the formation of low angle boundaries of \(<c+a>\) and \(<a>\) dislocations, which may react to form dislocation with \(\langle 1\bar{1}01\rangle\) direction and aid the twin growth. The alternate formation of \(<c+a>\) and \(<a>\) dislocations at the twin tip and the twin embryos from dislocation reactions causes the formation of thin twin in the matrix consistently close to the \(\langle 1\bar{1}01\rangle\) direction.

- The twin tip that terminates at a GB can develop elastic stress in the neighboring grain and back stress in the twinned grain. These strain concentrations were also observed to be released by formation of dislocations in both grains.
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In addition to the deformation mechanisms of dislocation slip and twinning, the mechanisms of texture weakening in Mg-0.1Ca alloy was investigated. I performed detailed microscopic characterization on dislocation and GB segregation and analyzed their effects on texture formation during rolling and annealing of pure Mg and Mg-0.1Ca. The key findings can be concluded as follows:

- The rolling texture of Mg-0.1Ca is weaker than that of pure Mg. The texture of pure Mg is strengthened with annealing time and that of Mg-0.1Ca is weakened.

- Ca alloying in Mg suppresses both the dissociation and the decomposition of \(<c + a>\) dislocations, and therefore increases their stability and mobility. The mobile \(<c + a>\) dislocations reduce the anisotropy of Mg and weaken the rolling texture. The activated \(<c + a>\) dislocations can also form low-angle grain boundaries and increase the mobility of basal \(<a>\) low-angle grain boundaries. Both effects promote recovery and static recrystallization of deformed grains.

- The texture strengthening during SRX in pure Mg is associated with strain-induced boundary migration nucleation and the prefered growth of textured grains that results from the anisotropic grain boundary energy.

- Ca solute segregation at grain boundaries in Mg-0.1Ca appears to retard the mobility by solute drag. The impeded grain boundaries inhibit stain-induced boundary migration and promotes in-grain recrystallization. The nucleated grains show high misorientation off the dominant rolling texture. The grain boundary segregation also levels out the variability of grain boundary and enables the growth
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of static recrystallized grains with relatively random orientation. As a result, the texture is weakened during SRX.

Taken as a whole, the experimental investigations performed in this study advanced the understanding of the influence of alloying elements on the structure and behavior of \(<c + a>\) dislocations in Mg, the propagation mechanisms of extension twinning and the role of texture weakening mechanisms in Mg-0.1Ca.

7.2 Future directions

The results and conclusions presented in this dissertation help advance the understanding of deformation mechanisms and provide a knowledge of the improved ductility and weakened texture in Mg alloys. The findings also motivate future investigates that could be undertaken to promote a more fundamental understanding of the influence of alloying on deformation mechanisms and its effect on mechanical properties of Mg. Key areas of focus are discussed as follows:

7.2.1 In-situ characterization of \(<c + a>\) dislocations

All the dislocations that were characterized in this dissertation were observed post-mortem. To investigate the dynamics of \(<c + a>\) dislocation motion, in-situ TEM test can be performed. The dissociation behavior that transforms the glissile \(<c + a>\) dislocation to sessile partials on the basal plane is a thermally activated process and may be spontaneously stimulated at room temperature. This means that the dissociation of \(<c + a>\)
dislocation may not be a dynamic process during deformation but a stabilization result after unloading. The combination of in-situ TEM tensile testing and tomography has been carried out to study \(<c + a>\) dislocation motion and morphology in pure Mg nano-pillars [1], and no apparent dissociation of the dislocations were observed. The addition of RE elements has been predicted to lower the barrier for pyramidal cross-slip [2]. The in-situ test and tomography technique can also be applied to investigate the influence of the alloying elements on the behavior of \(<c + a>\) dislocations, such as suppressed dissociation and cross slip between pyramidal planes.

7.2.2 \(<c + a>\) dislocations activated by a-axis extension

All the \(<c + a>\) dislocations in the thesis were introduced by \(<c>-axis\) compression of single crystal or close-to-\(<c>-axis\) (ND) compression. This type of loading is most favorable for the activation of \(<c + a>\) dislocations. However, in the practical application of wrought Mg, such as extruded bars or rolled plate, the loading mode is generally tension along the a-axis. In this case, both \(<c + a>\) dislocations and prismatic \(<a>\) dislocations could be activated to accommodate the plastic deformation [3, 4], and the ductility of the Mg product is determined by the mobility of both types of slip. The influence of prismatic \(<a>\) dislocations makes the activation of \(<c + a>\) dislocations more complicated. To more comprehensively evaluate the effect of alloying elements on the ductility of Mg, the characterization of the relative mobility of prismatic \(<a>\) and \(<c + a>\) dislocations would be needed.
CHAPTER 7. SUMMARY OF THE THESIS AND FUTURE DIRECTIONS

7.2.3 Influence of alloying elements on deformation twinning

In this thesis, the twin tips of Mg were characterized with no consideration of the influence from alloying elements. The addition of RE can affect not only the behavior of dislocations, but also the activation of twinning. The RE alloying may change the CRSS for twin nucleation. For example, Stanford et al. [5] reported that the addition of Y decreases the CRSS for compression twinning and increases the difficulty for extension twinning. One possibility of the modified CRSS for twinning is the segregation of alloying atoms at the twin boundary [6], but the periodic segregation of alloying atoms can only be realized by post-loading annealing. How the solute atoms segregate at the twin boundary during deformation is still to be investigated. To evaluate the influence of solute atoms on twinning-induced mechanical properties, single crystal bulk samples or micro-pillars can be fabricated and compressed along a-axis [7]. To elucidate the solute atom – twin boundary interaction, in-situ tension along \(<c>\)-axis or compression along a-axis can be performed on TEM thin foil [8]. The step loading along with high-resolution HAADF can be applied to characterize the possible segregation of solute atoms. Moreover, the twin-dislocation interaction, twin-twin interaction can also be characterized using this technique.

7.2.4 In-situ characterization of SRX

The texture weakening in Mg-0.1Ca is shown to be related to the SRX and the texture strengthening in pure Mg is determined by anisotropic grain growth. To better characterize the texture evolution introduced by Ca or RE elements, in-situ EBSD and synchrotron
experiments should be performed [9-11]. The texture, GB character and grain size of recrystallized and non-recrystallized grains could be acquired in the as-rolled or deformed sample, and then the maps of the same area of the sample could be obtained while the sample is being annealed in-situ [12]. Alternatively, ex-situ characterization may also be applicable if the polished surface can be carefully maintained with the sample being annealed in oil at elevated temperature for a series of times and oil quenching.
7.3 References for Chapter 7

Appendix 1.

Analysis of Near-core Strain Field Using Anisotropic Peierls-Nabarro Model

The strain field of the dislocation core can be described by Peierls-Nabarro (PN) model, which is used for dislocations with planar cores. The concept of PN model is to spread the displacement dislocation over the glide plane. The strain field of dislocations in an isotropic material can be written in the classical PN model as:

\[ \varepsilon_{xx} = -\frac{b}{4\pi} \left[ \frac{2(y \pm \xi)}{x^2 + (y \pm \xi)^2} + \frac{y[x^2 - (y \pm \xi)^2]}{(1 - \nu)[x^2 + (y \pm \xi)^2]^{2}} \right] \]

\[ \varepsilon_{yy} = \frac{b}{4\pi} \left[ \frac{2\nu y \pm (2\nu - 1)\xi}{(1 - \nu)[x^2 + (y \pm \xi)^2]} + \frac{(x^2 - y^2 + \xi^2)(y \pm \xi)}{(1 - \nu)[x^2 + (y \pm \xi)^2]^{2}} \right] \quad (A1.1) \]

\[ \varepsilon_{xy} = \frac{b}{4\pi} \left[ \frac{x}{(1 - \nu)[x^2 + (y \pm \xi)^2]} - \frac{2xy(y \pm \xi)}{(1 - \nu)[x^2 + (y \pm \xi)^2]^{2}} \right] \]
APPENDIX 1. STRAIN FIELD ANALYSIS BY ANISOTROPIC P-N MODEL

where \( \nu \) is Poisson’s ration, \( b \) is the magnitude of the Burgers vector and \( \xi \) is the half width of the dislocation core. If the anisotropy of HCP Mg is considered, equation 4.3.2 can be written as the following:

\[
\varepsilon_{xx} = \frac{b}{4\pi} \left\{ \frac{2(y \pm \xi)\lambda \cosh \delta \left[ x^2 + \lambda^2(y \pm \xi)^2 \right]}{[2x(y \pm \xi)\lambda \cosh \delta]^2 + \left[ x^2 - \lambda^2(y \pm \xi)^2 \right]^2} + \frac{C_{11}''^2 - C_{12}''^2}{2C_{11}'' C_{66}'' \cosh \delta} \frac{y\lambda \left[ x^2 - \lambda^2(y \pm \xi)^2 \right]}{[2xy\lambda \sinh \delta]^2 + \left[ x^2 + \lambda^2(y \pm \xi)^2 \right]^2} \right\}
\]

\[
\varepsilon_{yy} = \frac{b}{4\pi} \left\{ \frac{\lambda(C_{11}'' - C_{12}'' \lambda)(y \pm \xi)[x^2 + \lambda^2(y \pm \xi)^2] \lambda^2 + 2x^2 y\lambda^2 \sinh^2 \delta}{[2xy\lambda \sinh \delta]^2 + \left[ x^2 + \lambda^2(y \pm \xi)^2 \right]^2} \right\}
\]

\[
\varepsilon_{xy} = -\frac{b}{8\pi} \left\{ \frac{2x[x^2 + \lambda^2(y \pm \xi)^2] \lambda \cosh \delta}{[2x(y \pm \xi)\lambda \cosh \delta]^2 + \left[ x^2 - \lambda^2(y \pm \xi)^2 \right]^2} + \frac{C_{11}''^2 - C_{12}''^2}{2C_{11}'' C_{66}'' \cosh \delta} \frac{x[x^2 + \lambda^2(\xi^2 - y^2)] \lambda}{[2xy\lambda \sinh \delta]^2 + \left[ x^2 + \lambda^2(y \pm \xi)^2 \right]^2} \right\}
\]

where \( C_{11}'' \), \( C_{12}'' \) and \( C_{66}'' \) are the elastic coefficients in the stiffness tensor with line vector along the \( z \)-direction and Burgers vector along the \( x \)-direction, \( C_{11}'' = \sqrt{C_{11}'' C_{22}''} \), \( \cosh 2\delta = \left( \frac{C_{11}''^2 - C_{12}''^2 - 2C_{11}'' C_{66}''}{2C_{11}'' C_{66}''} \right) > 0 \), and \( \lambda = (C_{11}''/C_{22}'')^{1/4} \). The stiffness tensor coefficients for in Mg are shown in Table A1.1.
APPENDIX 1. STRAIN FIELD ANALYSIS BY ANISOTROPIC P-N MODEL

Table A1.1: Coefficient values for basal \(<a>\) dislocations in Mg

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>(C'_{11})</th>
<th>(C'_{12})</th>
<th>(C'_{22})</th>
<th>(C'_{66})</th>
<th>(\lambda)</th>
<th>(\cosh 2\delta)</th>
<th>(\sinh 2\delta)</th>
<th>(\cosh \delta)</th>
<th>(\sinh \delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(&lt;a&gt;)</td>
<td>59.75</td>
<td>21.7</td>
<td>61.7</td>
<td>16.39</td>
<td>0.992</td>
<td>1.258</td>
<td>0.764</td>
<td>1.063</td>
<td>0.359</td>
</tr>
<tr>
<td>Partial (&lt;c + a&gt;)</td>
<td>61.7</td>
<td>21.7</td>
<td>59.75</td>
<td>16.39</td>
<td>1.008</td>
<td>1.258</td>
<td>0.764</td>
<td>1.063</td>
<td>0.359</td>
</tr>
</tbody>
</table>

The half width of the dislocation core (\(\xi\)) can be calculated using equation (A1.2) with the values reported in Table A1.1 and compared with the experimental results in Figure 4.14.

The half width of the dislocation core values are calculated for the basal \(<a>\) and partial \(<c + a>\) dislocations in pure Mg and Mg-3Er alloy and are listed in Table A1.2. It is worth noting that the fitted Burgers vector is consistently 87.7±1.6% of the theoretical value in average, which is acceptable due to the systematic error from experiment. And the \(c/a\) of pure Mg is close to the theoretical value [1-3] and that of Mg-3Er is similar to that measured by high resolution image. The addition of Er decreases the \(c/a\) ratio of Mg, which accords the results in literature [4-6]. However, the width of dislocations fitted using the strain profile across dislocation core is two order of magnitude lower than that of classical theory [7-9]. This is probably ascribed to the significant strain concentration acquired from the GPA approach at the dislocation core area. To evaluate the dislocation core width getting rid of the singularity at the close-to-core area, the far field strain analysis can be a better option.

Table A1.2: Dislocation width and effective Burgers vector of basal \(<a>\) and \(<c + a>\) dislocations, where \(\xi\) is the half width of the dislocation core, \(w\) is the width of the dislocation and \(b\) is the fitted Burgers vector.

<table>
<thead>
<tr>
<th></th>
<th>(\xi) (nm)</th>
<th>(w) (nm)</th>
<th>(b) (nm)</th>
<th>lattice parameter (nm)</th>
<th>(w/b_x)</th>
<th>(c/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (&lt;a&gt;)</td>
<td>0.0052</td>
<td>0.0104</td>
<td>0.240</td>
<td>(a = 0.277)</td>
<td>0.0433</td>
<td>1.635</td>
</tr>
<tr>
<td>Mg (&lt;c + a&gt;)</td>
<td>0.0039</td>
<td>0.0078</td>
<td>0.227</td>
<td>(c = 0.453)</td>
<td>0.0344</td>
<td></td>
</tr>
<tr>
<td>Mg03Er (&lt;a&gt;)</td>
<td>0.0055</td>
<td>0.0110</td>
<td>0.250</td>
<td>(a = 0.288)</td>
<td>0.0440</td>
<td>1.570</td>
</tr>
<tr>
<td>Mg-3Er (&lt;c + a&gt;)</td>
<td>0.0083</td>
<td>0.0166</td>
<td>0.226</td>
<td>(c = 0.453)</td>
<td>0.0735</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX 1. STRAIN FIELD ANALYSIS BY ANISOTROPIC P-N MODEL

References for Appendix 1

Appendix 2.
Contraction Twin Tip Analysis

In addition to extension twin lamella in Mg samples, contraction twins were characterized in the as-rolled Mg-0.1Ca alloy. The contraction twins observed in TEM are in lenticular shape inside the parent grain, which is similar to that of extension twin, as depicted in Figure A2.1. The misorientation of the twin lamella boundary is uniform (55°), as seen in Figure A2.1 (c) and (d), which confirms that it is contraction twin.

Double twinning occurs with a tension twin forming on the original contraction twin, and the misorientation angle transfers from 55° to 39° (see Figure A2.2). The misorientation of double twin boundary is 86°, which is the misorientation for extension twin. The irregular twin shapes illustrated in Figure A2.2 can be attributed to the fact that high density of dislocations in twinned regions can be pinned by other dislocations at the interior of parent grains, and further deformation may cause the twins transform into sub-grains with wavy boundaries [1-3]. The formation and growth of sub-grains can also result in the gradual misorientation deviation off 55° with distance from the double twin boundary, as shown in Figure A2.2 (c) and (e).
APPENDIX 2. CONTRACTION TWIN TIP ANALYSIS

Figure A2.1: Contraction twin in as-rolled Mg-0.1Ca alloy.

Figure A2.2: Double twinning in as-rolled Mg-0.1Ca alloy.
References for Appendix 2

Appendix 3.
Matlab Codes for Dislocation Line Vector Calculation

To calculate the line vectors of straight dislocations, at least two bright field or weak beam dark field images were acquired using the [1\overline{1}00] g vector with two different titling angles off the [1\overline{1}20] zone axis. The higher the angle between the two incident beams, the more accurate the calculated line vector will be. The g vector and projected plane in the two images were measured using the orthogonal coordinate with x-axis pointing to the right direction and y-axis to the up direction. After the g vectors and projected plane vectors were acquired in both two images, the line vector of the dislocations and the most possible resident plane can be calculated by the Matlab code as below:

```matlab
clear
clc
angle1 = 10/180*pi; % angle between the 1st incident beam and [1\overline{1}20] zone axis
angle2 = 58/180*pi; % angle between the 2nd incident beam and [1\overline{1}20] zone axis
x_1100 = 1; % the \overline{1}00 g vector in 1st ZA image
```
APPENDIX 3. CODE FOR DISLOCATION LINE VECTOR CALCULATION

\[ y_{1100} = 0.16; \]
\[ l_{1100} = \sqrt{x_{1100}^2+y_{1100}^2}; \]
\[ x_1 = [x_1, x_2, x_3, \ldots]; \quad \% \text{x values of line vector in the image of the 1st incident beam} \]
\[ y_1 = [y_1, y_2, y_3, \ldots]; \quad \% \text{y values of line vector in the image of the 1st incident beam} \]
\[ x_{1010} = 1; \quad \% \text{the 1100 g vector in image of the 2nd beam, mostly same as the 1st image} \]
\[ y_{1010} = 0.16; \]
\[ l_{1010} = \sqrt{x_{1010}^2+y_{1010}^2}; \]
\[ x_2 = [x_1, x_2, x_3]; \quad \% \text{x values of line vector in the image of the 2nd incident beam} \]
\[ y_2 = [y_1, y_2, y_3]; \quad \% \text{y values of line vector in the image of the 2nd incident beam} \]

\[ \theta_{\text{cos}} = \text{zeros(length}(x_2),2); \quad \% \text{cosine of angle between line vector and the g plane} \]
\[ m = \theta_{\text{cos}}; \]
\[ \text{for } i = 1:\text{length}(x_2) \]
\[ \quad \text{for } j = 1:2 \]
\[ \quad \quad \text{if } j == 1 \]
\[ \quad \quad \quad \theta_{\text{cos}}(i,j) = \frac{(x_1(i) * (-y_{1100}) + y_1(i) * x_{1100})}{\sqrt{x_1(i)^2+y_1(i)^2}}/l_{1100}; \]
\[ \quad \quad \text{elseif } j == 2 \]
\[ \quad \quad \quad \theta_{\text{cos}}(i,j) = \frac{(x_2(i) * (-y_{1010}) + y_2(i) * x_{1100})}{\sqrt{x_2(i)^2+y_2(i)^2}}/l_{1010}; \]
\[ \quad \text{end} \]
\[ \quad m(i,j) = \theta_{\text{cos}}(i,j)^2; \]
\[ \text{end} \]
\[ \text{end} \]

\[ \text{beam} = [1,1,-2,3*\tan(\text{angle1})/1.624;1,1,-2,3*\tan(\text{angle2})/1.624]; \quad \% \text{incident beam vectors} \]
\[ n = [\tan(\text{angle1})^2;\tan(\text{angle2})^2]; \]
\[ \text{p\_proj} = \text{zeros(length}(x_2),4,2); \quad \% \text{the two projected planes for two incident beams} \]
\[ \text{for } i = 1:\text{length}(x_1) \]
\[ \quad \text{for } j = 1:2 \]
\[ \quad \quad p\_\text{proj}(i,1,j) = -(4*m(i,j)^2+54*m(i,j)/n(j))+\sqrt{48*m(i,j)*(1-m(i,j))*(1+9/n(j))}; \]
APPENDIX 3. CODE FOR DISLOCATION LINE VECTOR CALCULATION

\[
p_{\text{proj}}(i,2,j) = 8*m(i,j)-2+6*m(i,j)/n(j)*9;
\]

\[
p_{\text{proj}}(i,3,j) = -(p_{\text{proj}}(i,1,j) \cdot p_{\text{proj}}(i,2,j));
\]

\[
p_{\text{proj}}(i,4,j) = 3/\text{beam}(j,4)*(p_{\text{proj}}(i,1,j)+p_{\text{proj}}(i,2,j));
\]

\[
d = \text{zeros}(\text{length}(x_1),4); \quad \% \text{d}(i,1) \to \text{d}(i,4) \text{ represents the line direction of dislocation } [hkil]
\]

for i = 1:length(x_1)

\[
d(i,1)=(p_{\text{proj}}(i,1,2)+2*p_{\text{proj}}(i,2,2))*p_{\text{proj}}(i,4,1)-(p_{\text{proj}}(i,1,1)+2*p_{\text{proj}}(i,2,1))*p_{\text{proj}}(i,4,2);
\]

\[
d(i,2)=(p_{\text{proj}}(i,2,1)+2*p_{\text{proj}}(i,1,1))*p_{\text{proj}}(i,4,2)-(p_{\text{proj}}(i,2,2)+2*p_{\text{proj}}(i,1,2))*p_{\text{proj}}(i,4,1);
\]

\[
d(i,3) = -(d(i,1) + d(i,2));
\]

\[
d(i,4) = 3*(p_{\text{proj}}(i,1,1) \cdot p_{\text{proj}}(i,2,2) - p_{\text{proj}}(i,1,2) \cdot p_{\text{proj}}(i,2,1));
\]

\[
l = \text{sqrt}(3*(d(i,1)^2 + d(i,2)^2 + d(i,1)*d(i,2)) + d(i,4)^2 * 1.624^2);
\]

\[
d(i,1) = d(i,1)/l; \quad \% \text{normalized direction indices}
\]

\[
d(i,2) = d(i,2)/l;
\]

\[
d(i,3) = d(i,3)/l;
\]

\[
d(i,4) = d(i,4)/l;
\]

end

plane = [1,0,-1,1;1,-1,0,1;0,1,-1,1;1,0,1,1;-1,1,0,1;0,-1,1,1; \% pyramidal I planes
1,1,-2,2;1,-2,1,2;-2,1,1,2;-1,1,2,2;-1,2,1,2; \% pyramidal II planes
0,0,0,1; \% basal plane
1,0,-1,0;1,-1,0,0;0,1,-1,0;-1,0,1,0;-1,1,0,0;0,-1,1,0]; \% prismatic planes

error_pd = \text{zeros}(\text{length}(x_1),\text{length(plane(:,1))}); \% \text{values of line vector } [hkil] \text{ planes (hkil)}

slip_p = \text{zeros}(\text{length}(x_1),4); \% most possible resident plane with error_pd closest to 0

error = \text{zeros}(\text{length}(x_1),1); \% error of the most possible resident plane

for i = 1:length(x_1)
APPENDIX 3. CODE FOR DISLOCATION LINE VECTOR CALCULATION

```matlab
error_pd(i,:) = (plane*d(i,:))';
t = 1e8;
c = 0;
for j = 1:length(error_pd(1,:))
    if t > abs(error_pd(i,j))
        t = abs(error_pd(i,j));
        c = j;
    end
end
slip_p(i,:) = plane(c,:);
error(i) = error_pd(i,c);
end
slip_p
error
```
Luoning Ma as born in Anshan, China in 1989 and went to study in Beihang University (BUAA) in Beijing, China in 2008. He completed an honor’s research thesis titled, ‘Repair and Life Extension of a Post-service Turbine Blade Made of Ni-base Superalloy by Hot Isostatic Pressing and Rejuvenation Heat Treatment’ in Professor Zheng Zhang’s group that focuses on Failure Analysis and Prevention of Engineering Materials, and in 2012, he earned a Bachelor of Engineering in Materials Science and Engineering. Thereafter, he joined Professor Zheng Zhang’s group and completed the graduate program to obtain a Master of Science in Material Science in 2015 by completing an honor’s research thesis titled, ‘Characterization and Repair of Cracks in a Post-service Turbine Vane Made of Co-base Superalloy’. He then joined the Department of Mechanical Engineering at Johns Hopkins University in September 2015 for his doctoral studies under the advisement of Professor Kevin J. Hemker. In May 2017, he earned a Master of Science in Engineering in Mechanical Engineering and continued fulfilling the requirements for a Doctor of Philosophy degree in Mechanical Engineering to completion in March 2020.