RECRYSTALLIZATION MECHANISMS IN WROUGHT MAGNESIUM ALLOYS CONTAINING RARE-EARTH ELEMENTS

From the Faculty of Georesources and Materials Engineering of the RWTH Aachen University

Submitted by

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from New Delhi, India

in respect of the academic degree of

Doctor of Engineering

approved thesis

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Date of the oral examination: 12.12.2016

This thesis is available in electronic format on the university library’s website
To my lovely wife and my beloved parents
ACKNOWLEDGEMENTS

Though only my name appears on the cover of this dissertation, a great many people have contributed to its production. I owe my gratitude to all those people who have made this dissertation possible.

First, I would like to extend my deepest gratitude to my doctoral advisor Prof. Dr. rer. nat. Dr. h.c. Günter Gottstein for providing me an opportunity to pursue my doctoral studies at the Institut für Metallkunde und Metallphysik (IMM) at the RWTH Aachen University. It was an extremely gratifying and cherishing experiencing to explore the world of metal physics during my stay at IMM. I would also like to acknowledge Univ. Prof. Dr.-Ing. Habil. Brita Daniela Zander for carefully reviewing my dissertation.

Secondly, I would be eternally grateful to Dr. –Ing. Talal Al-Samman for his tremendous patience, guidance and generosity during the tenure of this research that helped me mature from a fledgling student to a researcher. Without his constant support and encouragement this research would have been impossible. In particular, I cherish our discussions not only on matters of science but as well as several mundane topics that will always enliven my spirits in the future.

My sincere thanks to Dr.-Ing. Luis A. Barrales-Mora for his insightful comments and constructive criticisms at different stages of my research that were thought-provoking and helped me focus my ideas. Apart from his scientific guidance, I will always value his friendship and the wonderful conversations we shared during these 5 years.

I am grateful to Prof. Dr. rer. nat. Dmitri A. Molodov for his encouragement and practical advice. I am also thankful to him for reading my manuscript, lending his invaluable expertise in helping me understand and enrich my ideas.

My sincere thanks to Mr. Matthias Loeck not only for his technical support but also for being a cherished friend, philosopher and guide during the past 5 years. I would always
treasure our late-night and weekend conversations, we had at IMM, on topics ranging from recrystallization to religion. Many thanks for being like an extended family member to me in Aachen.

My deepest respect to Prof. Dr. Lasar Shvindlerman for his generous guidance and concern since the beginning of my PhD studies.

My heartfelt thanks to Mr. Arndt Ziemons, Mr. David Beckers, Mr. Detlef Fuchs, Mr. Alex Teschner, Mr. Gerhard Schütz, Mr. Nico Poschmann, Mr. Sergej Laiko and Mr. Thomas Burlet for their professional and practical assistance during my research. Special thanks to Dr.-Ing Marco Witte, Dipl.-Ing. Konstantion Molodov, Dipl.-Ing. Thiemo Brüggemann, MSc. Meng Chenlu and Dipl.-Phys. Jann-Erik Brandenburg for their unhindered scientific help regarding texture measurement, analysis with MTEX, mechanical testing and SEM/EBSD measurements. Special thanks to Dipl.-Math. Christian Mießen for his indefatigable assistance with grain growth simulations. Moreover, I would like to acknowledge my dear colleagues Konstantin, Christian Haase and Markus Kühbach for making my stay at IMM scientifically enriching with their stimulating discussions and ideas. Furthermore, I would like to sincerely acknowledge the invaluable contribution of my scientific assistants and students, Zahra, Anand, Carsten, Mohamed, Sebastian, Ming, Aniruddha and Charan for the successful completion of this research.

My sincere thanks to Dr. K.G. Pradeep for his guidance in successfully incorporating atom probe characterization techniques in my research, as well as for his many scientifically beneficial suggestions.

My sincere gratitude to all the past and present colleagues in the institute, many of whom became fast friends and will always remain so. In particular, I would like to thank Chenlu Meng, Christian Haase, Konstantin Molodov, Luis A. Barrales Mora, Matthias Loeck,
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Talal Al-Samman and Thiemo Brüggeman for their memorable company at different stages of my PhD research.

My sincere thanks to my parents for their endless perseverance, patience and strong support that helped me go through every hardship in my life. Their love and belief in my abilities always picked me whenever I have felt down and words cannot suffice my gratitude for their presence in my life. My deepest gratitude to my beautiful wife Charu for her unconditional love and support, which always provided me a deep sense of fulfillment and security. Without her encouragement and understanding I would not have finished this thesis.

Finally, my gratitude towards the almighty divine, my beloved master, for giving us this invaluable gift called ‘life’ and the ability to think and innovate.

Lastly, the financial support of the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged.
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<th>SYMBOL</th>
<th>ABBREVIATION</th>
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<tbody>
<tr>
<td>$\varepsilon_a$</td>
<td>Uniform elongation</td>
</tr>
<tr>
<td>$\varepsilon_f$</td>
<td>Elongation to failure</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stress [MPa]</td>
</tr>
<tr>
<td>1-D/3-D</td>
<td>One-/Three-dimensional</td>
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<tr>
<td>APT</td>
<td>Atom probe tomography</td>
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<tr>
<td>CD</td>
<td>Compression direction</td>
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<tr>
<td>CRSS</td>
<td>Critical resolved shear stress [MPa]</td>
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<tr>
<td>DRX</td>
<td>Dynamic recrystallization</td>
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<tr>
<td>DTN</td>
<td>Deformation twin nucleation</td>
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<tr>
<td>EBSD</td>
<td>Electron back scattered diffraction</td>
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<tr>
<td>$f_{cc}$</td>
<td>Face-centered cubic</td>
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<tr>
<td>GIA-TW</td>
<td>Grain interaction twinning model</td>
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<tr>
<td>GOS</td>
<td>Grain orientation spread [°]</td>
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<tr>
<td>GSFE</td>
<td>Generalized stacking fault energy [mJ/m²]</td>
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<tr>
<td>HAGB</td>
<td>High-angle grain boundary</td>
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<tr>
<td>$h_{cp}$</td>
<td>Hexagonal close-packed</td>
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<tr>
<td>IPC</td>
<td>In-plane compression</td>
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<tr>
<td>IPF</td>
<td>Inverse pole figure</td>
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<td>IQ</td>
<td>Image quality</td>
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<tr>
<td>JMAK</td>
<td>Johnson-Mehl-Avrami-Kolmogorov</td>
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<tr>
<td>LAB</td>
<td>Low angle boundaries</td>
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<tr>
<td>LD</td>
<td>Longitudinal direction</td>
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<tr>
<td>MRD</td>
<td>Multiples of random distribution</td>
</tr>
<tr>
<td>$P_{\text{drag}}$</td>
<td>Solute drag pressure [J/m²]</td>
</tr>
<tr>
<td>$P_{CG}$</td>
<td>Curvature driven grain growth pressure [J/m²]</td>
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<tr>
<td>PSC</td>
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<td>PSN</td>
<td>Particle stimulated nucleation</td>
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<td>RD</td>
<td>Rolling direction</td>
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<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
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<tr>
<td>REE/RE</td>
<td>Rare-earth element/ Rare earth</td>
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<td>SBN</td>
<td>Shear band nucleation</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SF</td>
<td>Schmid factor</td>
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<tr>
<td>TD</td>
<td>Transverse direction</td>
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<tr>
<td>TTC</td>
<td>Through-thickness compression</td>
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<td>TYS/YTS</td>
<td>Tensile yield strength [MPa]</td>
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<td>UTS</td>
<td>Ultimate tensile strength [MPa]</td>
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<td>VPSC</td>
<td>Viscoplastic self-consistent modelling</td>
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CHAPTER 1

INTRODUCTION

The introduction of Magnesium in the world of structural materials can be traced back to as early as the 1930s. The advent of World War II played a pivotal role in revealing the seemingly lucrative properties this metal had to offer. However, post-world war saw the cessation of any prospective growth possible in its usage due to its poor corrosion resistance [1]. The magnesium market then remained mostly untouched; until the 90’s, when impending environmental concerns and overburdening carbon emissions turned the reality upside down. Consequently vehicle lightweighting became the focus and magnesium alloys seemed to be the befitting answer [2]. Fig.1.1a illustrates the impact of weight reduction in automotives upon overall reduction in carbon emissions. Over the past two decades, the pursuit towards achieving lightweight materials in both aerospace and automotive sectors has seen an unprecedented upsurge. The consequent expansion in the usage and application sectors for magnesium alloys is therefore of no surprise.

Magnesium and its alloys offers remarkable potential for light weight construction owing to the low density of magnesium 1.74 g/cm³ that makes them the lightest available constructional metals. Apart from lightness magnesium exhibits numerous other favorable properties such as high specific strength, good machinability, high damping capacity, good castability, and low melting temperature and melting energy [3].
Figure 1.1  a) Impact of vehicle weight reduction on carbon emission reduction, b) Percentage of magnesium used in an average midsized vehicle [4]

The range of applications of magnesium alloys has been mostly confined to liquid and semi-solid molding processes, and sheet-forming processes. A vast majority of all magnesium components (automobile, housings and electric) are produced by die-casting. The die-casting process stands out due to its excellent productivity, and the resulting potential to lower material cost through design strategies. Die-cast magnesium alloys can produce acceptable strength values but the room temperature ductility remains fairly low [5]. In addition, the problem of gas porosity due to splashing during mold filling remains a complex issue, which renders heat treatment to improve the properties difficult [6]. For high-performance structural applications of magnesium alloys it is desirable to develop wrought magnesium products, such as extruded profiles, rolled sheets and forgings, which in contrast to die-cast products possess higher strength and ductility. Nevertheless, industrial usage of wrought magnesium is, however, still far below its expected potential (c.f. Fig. 1.1b) and the
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underlying hindrance lies in the poor room-temperature formability of these materials. On account of such poor formability of wrought alloys the magnesium market remains still dominated by die-casted products.

Magnesium’s hcp structure produces highly inhomogeneous deformation conditions, due to a shortage of independent deformation modes that would accommodate deformation along the c-axis of the magnesium hcp unit cell, unlike fcc metals with their four crystallographically equivalent slip planes, each with three slip directions, providing 12 slip systems, and thus, unconstrained formability [7]. In the case of magnesium, deformation below 498K is limited to only basal and prismatic modes that provide strain accommodation only along the <a> axis. The additional tension twinning is incapable to produce sufficient strain accommodation along the c-axis [8]. Such strong anisotropy in slip activation gives rise to formation of strong textures that manifest into strong yield asymmetry in magnesium and its alloys. Moreover, unlike cubic materials (such as aluminium) recrystallization in magnesium often results in retention and in many cases strengthening of the deformation texture [9]. Improving material formability can be mostly achieved through two classical routes [10],

a) Texture weakening or modification by facilitating evolution of crystallographically softer orientations i.e. those prone to relatively easier slip activation

b) Grain refinement, whereby tensile twinning is inhibited and activation of non-basal slip modes becomes easier.
In particular, the improvement in mechanical response through texture modification has been attracting researchers off late due to the unexplored possibilities it offers, making it the most sought after method of tackling such material behavior.

![Elongation vs. yield strength plot mapping properties of magnesium-RE alloys with respect to other commercially available materials.](image)

The deterministic factors defining a material texture are processing parameters, initial texture and alloy chemistry. It should be noted that processing conditions include both crystallographic deformation and annealing (recrystallization and grain growth) response. While in conventional alloys texture weakening has been made possible to achieve by suitable processing of the materials [11], texture control via modification of alloying chemistry, with a special emphasis on the role of REEs has gained considerable attention during recent times [12-16]. The advantage of dilute additions of REEs to obtain weaker and deformable textures in wrought magnesium
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Alloys have been reported by many researchers, wherein they have proved to act as ideal candidates for designing high performance structural alloys from magnesium as illustrated in Fig. 1.2. However, the interplay between alloying chemistry and processing conditions is still largely not well understood. The work presented here, therefore attempts to further our understanding of the underlying mechanisms related to the evolution of texture and microstructure in REE containing magnesium alloys especially during recrystallization and grain growth. In particular the recrystallization mechanisms that can potentially trigger texture change have been investigated in context with REE additions. The present thesis from here on can thus be classified into 6 chapters.

Chapter 2 elucidates the necessary theoretical concepts pertaining to deformation and annealing behavior in magnesium and its alloys. It further discusses the motivation behind investigating magnesium-REE systems in context with the relevant scientific investigations conducted on these types of alloys. Chapter 3 presents the various experimental techniques implemented during this work and related theoretical background. Production of wrought alloys was achieved by means of different rolling schemes. Mechanical properties were investigated by means of uniaxial tension and plane strain compression tests. Texture and microstructures were investigated using XRD, optical microscope and EBSD analysis. Atomic scale characterization techniques such as 3D-APT were also utilized.

Chapter 4 and 5 discuss the influence of single additions of REEs on the shear-bandning and twinning in binary magnesium-REE alloys. Additionally distinctions between the response of REEs present in form of solutes and precipitates in magnesium are investigated. Furthermore, the impact of REEs on the microstructural
evolution during recrystallization in shear bands and twins, and subsequent grain growth are also addressed.

Chapter 6 investigates the additional role of non-REEs such as Zn and Zr in the presence of REEs. Their contribution in terms of the observed differences in texture and microstructural evolution with respect to their binary counterparts are discussed. Furthermore, the combined influence of texture and REE alloying on the mechanical properties of magnesium is acknowledged.

The aspect of grain boundary segregation characteristics of REEs and its subsequent impact on the texture evolution during recrystallization and grain growth is addressed in Chapter 7. It is shown by means of APT analysis and grain growth simulations that the REE-segregation plays an important role in rendering texture modification in these alloys. Moreover, it is shown that different REEs can exhibit distinct segregation characteristics. Correlations between texture formation and resultant room temperature elongation are drawn. Finally, Chapter 8 outlines the key conclusions derived from the present thesis.
CHAPTER 2

LITERATURE REVIEW

Plastic deformation in Mg and its alloys, due to its low crystal symmetry, is strongly affected by the initial orientation as well as the deformation conditions. Such a behavior severely limits formability of conventional magnesium alloys at ambient temperatures, giving rise to strong plastic anisotropy. The aim of the present chapter is to provide a comprehensive overview of the various crystallographic deformation and annealing mechanisms, with respect to texture and microstructural evolution in magnesium and its alloys. The subject matter is organized in primarily 3 sections. Section 2.1 emphasizes upon the crystallographic and deformation mechanisms commonly observed in magnesium, along with their resultant impact upon material texture. The different recrystallization and grain growth mechanisms prevalent in magnesium, in light of their relative contributions to texture evolution are discussed in Section 2.2. Section 2.3 especially focuses upon the aspect of magnesium alloys with REE additions and their corresponding beneficial effects upon deformation and recrystallization behavior. Finally, the chapter is succinctly summarized in Section 2.4.

2.1 CRYSTALLOGRAPHY AND DEFORMATION BEHAVIOR IN MAGNESIUM AND ITS ALLOYS

The crystal structure displayed by magnesium and its alloys is hcp in nature, wherein the atoms follow an ABABAB… stacking sequence, as shown in Fig. 2.1. This indicates that the layers are stacked alternately in two different ways. The hexagonal unit cell is a parallelepiped with \( a_1, a_2 \) and \( c \) axis as the axes parallel to the edges (c.f. Fig. 2.2). If it is considered in a cluster of 2 unit cells along with 2 halves in the lattice space it produces a hexagonal prism [17].
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**Figure 2.1** Hard sphere model of the stacking sequence in hexagonal closed packed structure

![Hexagonal crystal geometry](image)

**Figure 2.2** Hexagonal crystal geometry – The unit cell is a parallelepiped with edges $a_1$, $a_2$ and $c$ axis

In Fig. 2.2, the coordinates of the atom inside the highlighted parallelepiped are $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$. If observed closely the unit cell in this case is a simple hexagonal with each lattice position associated with atoms at following positions $\left(000; \frac{2}{3}, \frac{1}{3}, \frac{1}{2}\right)$. This type of lattice structure is called a double lattice structure as it is associated with 2 atoms in the primitive unit cell.

In an ideal hcp crystal i.e. where the ratio of $c$-axis to $a$-axis ‘$\gamma$’ is 1.624, each atom has 12 nearest neighbors or a coordination number of 12 (same as in the case of fcc crystal structures). However, depending upon the value of ‘$\gamma$’ the distance of atoms above
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and below may be farther (if ‘γ’ is higher than ideal eg. Zn) or nearer (‘γ’ is lower than ideal eg. Mg) as compared to the coplanar atoms. The distance between the coplanar atoms is equal to the lattice parameter \(a_1 = a_2 = a\), and those above and below are at a distance \(\frac{a(4+3\gamma^2)^{1/2}}{2\sqrt{3}}\) along the \(<20\overline{2}3>\) direction. The number of second nearest neighbours is situated in adjacent close-packed planes at distances \(\frac{a(16+3\gamma^2)^{1/2}}{2\sqrt{3}}\) along 6 of the 12 \(<40\overline{4}3>\) directions. There are 2 third nearest neighbours at a distance \(\gamma\) along \(<0001>\), 6 at distances \(a\sqrt{3}\) along \(<10\overline{1}0>\), and 12 at distances \(\frac{a(28+3\gamma^2)^{1/2}}{2\sqrt{3}}\) [17].

2.1.1 Slip modes in magnesium

Hexagonal crystals structures, due to their low symmetry, often exhibit anisotropic deformation behavior unlike metals with cubic symmetry. Magnesium, in this context, typically suffers from poor formability at ambient temperatures, whereby strain accommodation mechanisms along c-axis are extremely difficult to activate.

Figure 2.3 Different slip systems in magnesium - Basal slip, prismatic slip, 1st and 2nd order pyramidal slip systems

In accordance to von Mises criterion for homogeneous plastic deformation in polycrystalline materials, atleast five independent active deformation modes must be available. Slip in magnesium is potentially feasible on the basal, prismatic, 1st and 2nd order pyramidal slip systems, as shown in Fig. 2.3. However, room temperature deformation of magnesium is sustained primarily by \((0002) < 1\overline{1}20 >\) basal and
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(10\(\bar{1}\)0) < 11\(\bar{2}\)0 > prismatic slip systems, which provide only four independent (2 from each slip system) modes that are able to accommodate strain only along the \(<a> = <11\bar{2}0>/3\) axis. With respect to strain accommodation along c-axis, the only available deformation mode active under tension along the c-axis is the \{10\(\bar{1}\)2\} < 10\(\bar{1}\)1 > extension twinning that contributes as only one-half of a slip mode due to its directional dependence [8].

![Figure 2.4 CRSS dependency of different deformation modes on temperature [18]](image)

On the other hand, when a non-basal slip system (i.e. the shear direction does not lie in the basal plane) with \(<c+a>\) burgers vectors is activated, it alone can provide five independent modes of deformation. However, due to significantly higher associated CRSS i.e. nearly 2 orders of magnitude larger than CRSS for basal slip, its activation becomes highly unlikely during room temperature deformation of Mg [19]. Fig. 2.4 represents the CRSS dependency of different deformation modes on temperature.
2.1.2 **SECOND ORDER PYRAMIDAL** \(< c + a >\) **SLIP: GENERATION MECHANISMS AND MOBILITY**

The \(< c + a >\) deformation mode or the second order pyramidal slip in Mg is described by the slip system viz. (1122) \(< 1123 >\). Being associated with the largest burgers vector given by \(\frac{<11\overline{2}3>}{3}\) and the smallest interplanar spacing, it is regarded as the slip system with the ‘lowest ease of gliding’ i.e. the slip system experiencing the largest Peierls stress. However little is understood about the microscopic mechanisms behind generation and mobility of non-basal dislocation slip. Furthermore, the question as to whether the CRSS for \(< c + a >\) slip depends more upon the dislocation nucleation process or its subsequent mobility demands greater scrutiny [8, 20, 21]. Considering the fact that \(< c + a >\) dislocations are associated with large burgers vectors, it would be expected to exist in a dissociated configuration and comprising of non-planar core structures. Minonishi et al. [22] proposed the following dislocation reaction that gives rise to stacking faults in second order pyramidal slip systems,

\[
b \rightarrow ab + (1 - a)b...
\]

where the Burgers vector is \(b = < c + a >= \frac{<11\overline{2}3>}{3}\) and \(a \approx 1/2\) for symmetric dissociation. In terms of possible nucleation sources of \(< c + a >\) slip, the vicinity of grain boundaries or near incoherent twin boundaries in the grain interiors seem to be the most potent sites. In both cases, it is important to determine whether the source produces the total dislocation in one step (possibly when the stacking fault energy is high) or a partial dislocation with a strip of stacking fault is generate first, followed by generation of another partial dislocation thus forming the total dislocation [20]. Several experimental observations validate such nucleation of \(< c + a >/2\) partial dislocations near and within twin boundaries [23, 24].
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Figure 2.5 Images from a series of diffraction conditions outlines a typical burgers vector analysis of \(<c+a>\) dislocations in conjunction with \(c\) and \(a\) type dislocations [25]

The mechanism of generation of such \(<c+a>\) dislocations is also a subject under continuous investigation. Transmission electron microscopy studies on second order pyramidal dislocations report formation of a glide loop of \(<c+a>\) dislocations in combination with \(<a>\) and \(<c>\) type dislocations [20, 25]. Fig. 2.5 shows a typical
burgers vector analysis for $< c + a >$ dislocation in conjunction with $<c>$ and $<a>$ dislocations. The $< c + a >$ dislocation is unstable in edge orientation but stable in screw orientation. Hence its edge orientation dissociates into $<a>$ and $<c>$ type dislocations. This implies that the association of $<c>$ and $<a>$ dislocations can be also a source of generating $< c + a >$ dislocations. Yoo et. al. [21] provided a possible mechanism for the generation of $< c + a >$ slip based on the formation of attractive junctions between sessile $c$ dislocations on the prismatic plane and the $<a>$ slip dislocations on the basal plane, as shown in Fig. 2.6. The screw component of the basal dislocation first cross slips to the prismatic plane (c.f. Fig. 2.6a). This cross slip event is energetically favored by the elastic interactions between the edge type $<c>$ dislocations and the screw type basal $<a>$ dislocations.

The strength of elastic interaction between an edge and screw component depends upon the parameter $- 1/(1 - \nu)$ [24]. For pure Mg [21, 24], the value of poisson ratio $\nu$ is 0.29, which indicates that the attractive force could be strong enough to pull out the $<a>$ dislocation from the basal plane. In the prismatic plane the screw component of the basal slip intersects with the sessile $<c>$ slip to produce a $< c + a >$ screw dislocation (c.f. Fig.
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2.6b). This \( c + a \) dislocation can then cross slip to the \( \langle 11\bar{2}2 \rangle \) pyramidal planes to generate the \( c + a \) mode of deformation (c.f. Fig. 2.6c). However, the cross slip from prismatic to secondary pyramidal planes is energetically unfavorable in magnesium, even at elevated temperatures [26]. Such an observation contradicts the proposed nucleation mechanism. Furthermore, if the association of \( a \) and \( c \) dislocations is the only means of generating \( c + a \) dislocations, then the number of independent modes of \( c + a \) dislocations should be less than five [8]. This is primarily due to the fact that an independent slip system must have its own independent dislocation source.

Once a glide loop is nucleated, the screw segments may cross-slip from one \( \{11\bar{2}2\} \) plane to another. Thus the \( c + a \) dislocations once emitted from the grain boundaries can be multiplied successively [21]. Atomistic simulation of the dislocation core structure of \( c + a \) edge dislocations [22, 27] on the \( \{11\bar{2}2\} \) pyramidal planes initially predicted them to exist according to the following dislocation reaction,

\[
b \rightarrow \frac{1}{9}[\bar{1}1\bar{2}6] + \frac{1}{9}[44\bar{8}3] \quad (2.2)
\]

In latter works [28, 29], it was found that the second partial dislocation \( \bar{p} = \frac{1}{9}[44\bar{8}3] \) further dissociates to create a basal plane stacking fault, such that,

\[
b \rightarrow \frac{1}{9}[\bar{1}1\bar{2}6] + \frac{1}{9}[1453] + \frac{1}{3}[10\bar{1}0] \quad (2.3)
\]

Experimentally, \( c + a \) dislocations have been observed to be bound to the basal plane in Mg, existing in the following dissociated configuration [24, 30],

\[
b \rightarrow \frac{1}{6}[2023] + \frac{1}{6}[02\bar{2}3] \quad (2.4)
\]

The dissociation shown in Eqn. 2.4 has however not been observed in the atomistic simulations. The screw component of the \( c + a \) dislocations is typically known to dissociate symmetrically as per Eqn. 2.1. Atomistic studies [22, 27] indicate that the screw cores can split on multiples, including combinations of \( \{11\bar{2}2\} \) and first order \( \{10\bar{1}1\} \) pyramidal planes. This suggests a strong feasibility of cross-slip of screw dislocations on pyramidal planes. Moreover, if the stacking fault energies of the \( \{11\bar{2}2\} \)
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and \{10\overline{1}1\} pyramidal planes are in the similar range of values, it is possible that the dislocation dissociation process would depend more upon the overall free energy reduction (\(\Delta G_{\text{reduction}}\)) due to creation of partials given as 
\[
\Delta G_{\text{reduction}} = \Delta G_{\text{total dislocation}} - \Delta G_{\text{partials}},
\]
where \(\Delta G_{\text{total dislocation}}\) is the free energy in the undisassociated state and \(\Delta G_{\text{partials}}\) is sum of the energy of the partial dislocations. In such case, pyramidal slip dissociation could display temperature dependence i.e. at low temperatures dissociation one type of pyramidal plane is favored and it may switch to activate the other one at higher temperatures [21].

2.1.3 Deformation Twinning: Primary Twinning Modes in Mg

Twinning is a shear deformation in which a region of the crystal is transformed into an orientation with mirror symmetry relative to the adjacent parent crystal (matrix), as illustrated in Fig. 2.7. The direction in which the atoms move is referred to as the twinning direction and the mirror plane, common to both twin and matrix is called the twinning plane. In magnesium, mechanical twinning is an important deformation mechanism at low temperatures due to high activation stresses of non-basal slip modes. Deformation twinning is distinguished from crystallographic slip on the basis of the following aspects:

a) Unidirectional nature: Unlike slip, twinning shear is of unidirectional nature. Twinning modes in hexagonal metals are characterized by their ability to produce either tensile or compressive strain along the c-axis, but not both. In case of Mg, the most common tensile twinning mode involves shear on \{10\overline{1}2\}-planes in \(<10\overline{1}1>\) direction and operates under tension along the c-axis. In case of compression twinning that activates only during c-axis compression, the \{10\overline{1}1\}-planes and \{10\overline{1}3\}-planes serve as the twinning planes with respective shears along \(<10\overline{1}2>\) and \(<30\overline{3}2>\) directions [17, 31]. Thus the type of twinning mode activation is strongly limited by the starting texture and the processing technique.
b) **Limited strain accommodating ability**: Deformation twinning typically produce a fixed shear, unlike to crystallographic slip. In magnesium, the maximum tensile strain accommodated by \{10\overline{1}2\} extension twinning is 0.065 [33, 34], provided the entire material volume twins.

c) **Sudden reorientation of matrix**: Twinning is generally associated with a large orientation change, in contrast to gradual orientation change observed during crystallographic slip. Such reorientation can drastically modify the crystallographic texture. Thus, the role of twinning in understanding the evolution of deformation texture in magnesium and its alloys is indispensable. For instance, if a sheet with basal planes oriented normal to the sheet plane is subjected to rolling, deformation twinning would result in reorientation of the basal planes by 86.3° about the \(<11\overline{2}0>\) axis. The new reoriented grains will hence resemble a typical basal rolling textures with basal planes nearly aligned with the sheet plane. Such an orientation will not favorable for further c-axis tension, whereby tension twinning will cease. For other orientations, the twinned grains could further undergo slip and twinning events that were not active in the initial matrix grain. Secondly, the rapid reorientation of the twinned region leads to the twin
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boundaries acting as strong barriers for further dislocation slip, thereby promoting work hardening.

2.1.3.1 Twinning modes and formation mechanisms in Mg

As mentioned earlier, the most commonly observed twinning modes in magnesium (axial ratio \( \gamma < \sqrt{3} \)) is the \{10\text{I}2\}<1011> twinning under tension. This twinning mode is relatively easy to activate, and causes extension in the \( c \)-direction, with the basal planes inside the twin being rotated by 86.3°, as shown in Fig. 2.8a. In the opposite case when compression is normal to the rolling plane and the extrusion direction, \{10\text{I}1\}<10\text{I}2> and \{10\text{I}3\}<30\text{I}2> twinning modes are activated, which produce a favorable compressive strain parallel to the \( c \)-axis, with the basal plane being rotated by 56.2° and 64°, respectively (c.f. Figs. 2.8b and d) [31]. Although the twinning shear of the aforementioned twin types in magnesium is very similar (i.e. 0.129 for \{10\text{I}2\} vs. 0.138 for \{10\text{I}1\} and \{10\text{I}3\}), compression twins are typically much harder to nucleate than extension twins, most likely due to energetic aspects of atomic shuffling [35, 36]. Being less common than extension twins, compression twins in polycrystalline magnesium usually do not produce much texture change during deformation due to their low volume fraction. Additionally, unlike tension twins, they are not prone to twin growth. This is also evident from the morphology of compression twins that is thin and sharp vis-à-vis thick and wavy structure of tension twins. However, compression twins can introduce texture softening within the twinned material, whereby they can decrease the effective work hardening rate as well as the flow stress [37] playing an essential role in the advent of DRX [38]. Compression twins once nucleated often undergo secondary \{10\text{I}2\} tension twinning giving rise to \{10\text{I}1\}–\{10\text{I}2\} or \{10\text{I}3\}–\{10\text{I}2\}, leading to a reorientation of the basal planes by angles of 37.5° and 22° respectively from their original position (c.f. Figs. 2.8c and e).
Figure 2.8 Schematic diagrams showing different twinning modes and associated matrix reorientation: a) \{10\bar{1}2\}, b) \{10\bar{1}1\}, c) \{10\bar{1}1\}--\{10\bar{1}2\}, d) \{10\bar{1}3\} and e) \{10\bar{1}3\}--\{10\bar{1}2\}. [39]
Deformation twinning typically comprises of two steps, namely i) twin nucleation and ii) twin growth. The first dislocation model for \{10\bar{1}2\} twinning was the pole mechanism proposed by Thompson and Millard in 1952 [40], who suggested the following dislocation reaction to form a pole source of twinning,

\[ [0001] \rightarrow \alpha [10\bar{1}1] + [10\bar{1}0] \]...

(2.4)

where \( \alpha \) holds a fractional value ranging between 1/12 and 1/4. However, unlike the pole mechanism of twin nucleation and growth in bcc metals, the one proposed above could only account for growth of twin. Alternatively, Orowan [41] proposed a homogeneous nucleation scheme that was based on the concept of homogeneous lattice shear in the region of high stress concentration, leading to the formation of a twin embryo. In support of Orowan’s proposition, Bell and Cahn [42] ascribed their experimental findings regarding \{10\bar{1}2\} twinning in Zn to the homogeneous nucleation concept. They suggested that the twin nucleation occurred from the stress concentration generated by sessile dislocations arising from the interaction of basal and pyramidal slip. In another study on dislocation free zinc whiskers [43], twin nucleation was observed at the specimen corners and the specimen grips in absence of dislocations, thereby supporting the homogeneous nucleation mechanism. Mendelson [44], on the other hand, proposed that twin nucleation demands non-planar dissociation of slip and hence would originate heterogeneously at preexisting dislocation or interfaces (such as phase/grain boundaries or twin-twin intersection). The heterogeneous twin nucleation mechanism typically involves formation of twin embryo and subsequent glide of zonal dislocations. Zonal dislocations are defined as regions wherein non-homogeneous shear at the twin matrix interfaces is accomplished at the expense of pure atomic shuffling in multilayer twin lamellae. Such a scenario is energetically favorable due to lower nucleation stresses in comparison to a homogeneous shear state i.e. all planes undergoing uniform shear. It must be understood that the process of deformation twinning involves two fundamental processes i.e. atomic shuffling and shearing. While \{10\bar{1}2\} tension twins operate...
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primarily by shuffling mechanisms, its counterpart \{10\bar{1}1\} compression twins are dominated by shearing.

Once nucleated further stress increment promotes twin growth especially in case of \{10\bar{1}2\} tension twins, accompanied by a stress drop. Twin growth, requiring much lower activation stresses, proceed by means of a) thickening process in the direction normal to the twin plane and b) lengthwise growth of the twin. The thickening process is facilitated by the aforementioned mechanism of zonal dislocations [8, 21, 31]. The latter process of length increase of twin depends on the mobility of \{10\bar{1}2\} <10\bar{1}1> twinning dislocations. By contrast, the \{10\bar{1}1\} compression twins that are energetically unfavorable for atomic shuffling tend to form copious bands of parallel, narrow lamellae between 0.1 – 1 \(\mu\)m thick, without displaying a stress drop. The twin bands subsequently strongly interact with pyramidal \(<c+a>\) dislocations, which also explains the consistent stress increase. Longitudinal growth of \{10\bar{1}1\} compression twins is dependent upon the mobility of \{10\bar{1}2\} <10\bar{1}2> twinning dislocations. Shear failure due to slip incompatibility along compression twin boundaries, typically stems from their resistance to growth.

2.1.3.2 Detwinning

In addition to dislocation slip and twinning, untwinning (or detwinning) may occur in a twinned material. Microscopically, detwinning can be characterized by the disappearance of existing twin bands, where twins can disappear or become narrower under reverse loading or unloading, and can reappear under reloading. Keshavarz and Barnett [45], who carried out in-situ investigation of twinning behavior during tensile testing reported such appearance and disappearance of twins during loading and unloading. Fig. 2.9 indicates the microstructure under different loading states. Application of strain of \(\sim5\%\) results in disappearance of twins from grain ‘3’ and formation of new twins in grain ‘2’.
Subsequent unloading leads to reappearance of twins in grain ‘3’ and partial disappearance in grain ‘2’. Additionally, new twins formed in grain ‘6’.

Figure 2.9 Microstructures obtained during in-situ observation of a tensile test in different loading states. Loading direction shown by arrows.[45]

Figure 2.10 Twin volume fraction and microstructural evolution during plastic deformation of Mg-Al-Mn alloy [46]
Further observations of detwinning were made during a compression-tension cyclic loading showing that an extruded magnesium alloy AZ31B has the ability to twin and de-twin through at least 250 cycles [47]. This can be understood by the fact that the initial extrusion texture is not favorable for twinning in tension. However, the grains that have twinned during compression become in optimal orientation to twin again (re-twin or de-twin) during subsequent tensile straining since the basal poles are parallel to the tensile axis after the initial compressive straining. The stress required for detwinning is typically less than that for twinning nucleation, but greater than for twin growth. Due to lower stresses, de-twinning can also initiate during specimen unloading in response to acting residual stresses. Sarker and Chen [46] reported de-twinning while deforming an extruded Mg-Al-Mn (AM30) alloy. The deformation ensued in three steps, beginning with twin formation and decrease strain hardening. With higher twin volume fractions, the strain hardening rose rapidly owing to strong dislocation-twin interactions. These subsequently triggered de-twinning events with led to disappearance of twins. The reduction in twin volume fraction in turn manifested as a regime of low strain hardening. Fig. 2.10 shows the evolution of twin volume fraction and microstructure with increasing plastic strain.

2.1.4 SHEAR BANDS

Shear banding, which are seen as the main manifestation of strain localization and the precursor of damage or failure, often appear during hot rolling or cold rolling of Mg alloys and deteriorate the forming ability, even at high temperature. The flow localization in shear bands has a remarkable influence on deformation mechanisms, recrystallization, and texture. In many cases, the heterogeneous microstructure caused by shear bands cannot be eliminated completely once formed. Therefore, to understand the formation mechanism and microstructure of shear bands is of great importance to improve rolling capability.
Shear bands can be microstructurally described as regions, wherein the crystallographic slip planes inside the band realign themselves along the shear direction. Such reorientation leads to localized plastic instability inside the band, which macroscopically manifests as a strain softening event. They are known to originate from particularly three mechanisms i) clustering of slip bands (especially in materials with high stacking fault energies) [49], ii) localized DRX in the vicinity of grain boundaries, leading to evolution of fine strain free grain clusters that can slip profusely in comparison to the strain hardened matrix [48] and iii) formation of micro-twin band clusters (common in low stacking fault materials) [49]. Among these the latter two mechanisms have been observed in magnesium and are strongly dependent upon the working conditions.

Mechanism (ii) was first reported by Ion et. al [48], who ascribed DRX at magnesium grain boundaries during high temperature deformation to lack of available slip systems. Fig. 2.11 illustrates the mechanism proposed by them. Being favorably oriented for basal slip, the dynamically recrystallized regions in Fig. 2.11a are prone to
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basal slip. However, due to constraints from neighboring grains A and B, shear along AB cannot occur.

Figure 2.12 EBSD Kikuchi band contrast map for pure Mg cold rolled to 30% reduction showing shear band structure and \{10\text{1}2\}\text{-}twins [50]

Figure 2.13 TEM bright-field images of a shear band in deformed Mg 3 wt-% Y; corresponding texture in form of pole figures [51]

With further increase in strain, the bands AB and CD can broaden and merge into a single zone of easy slip (c.f. Fig. 2.11b). The subsequent deformation would then be concentrated in these regions leading to creation of shear zones (c.f. Fig. 2.11c).
The third mechanism was first proposed by Couling and Pashak [52], wherein they observed such bands in cold rolled magnesium alloys that were soft and deformable. They suggested that the shear bands evolved from clustering of compression and double twins. The phenomenon of shear banding via twin clustering has been frequently observed in context with magnesium-REE alloys. Barnett and co-workers [50] reported similar shear banding pathway for cold rolled Mg-Ce alloys (depicted in Fig. 2.12) and termed it as a ‘texture softening’ process. Later investigations using TEM characterization revealed these shear bands comprise of high density of narrow bands with \(\{10\bar{1}1\}\)–\(\{10\bar{1}2\}\) orientation, as shown in Fig. 2.13.

The primary parameters controlling shear banding mechanism are the critical value of strain hardening and favorable arrangement of slip planes for shear band formation. The grain size also affects shear banding. Shear banding is expected to be higher in coarse grained materials. Another parameter is the Zener-Holloman parameter; low Z values reduce the tendency of shear banding. The presence of solutes and particles also favor the tendency of shear banding [49].

2.2 Recrystallization and Grain Growth Mechanisms in Magnesium Alloys

Recrystallization can be defined as a phenomenon of microstructure regeneration that proceeds by nucleation of strain free grains within a deformed matrix and their subsequent growth at the expense of the surrounding matrix until complete impingement. The driving force for recrystallization is provided by the deformation energy stored in the dislocations present in the deformed matrix. Recrystallization may occur post-deformation or during deformation. Post-deformation recrystallization may be due to annealing after cold-deformation (primary static recrystallization) or during cooling of hot-deformed samples (post-DRX). Recrystallization occurring during deformation is also referred to as DRX. Recrystallization phenomenon can also be classified as being discontinuous i.e. initiating locally in the vicinity of special deformation features such as grain boundaries, shear bands,
particles etc. or continuous i.e. occurring homogeneously all throughout the microstructure. The latter is essentially extended recovery.

Figure 2.14 Schematic illustration of a recrystallization nucleus with growth potential in a deformed structure [32].

It must be understood that recrystallization (unlike solidification) ideally does not involve nucleation in a classical sense, but is described by a process of continuous growth; wherein the recrystallized embryo is stable with respect to its surroundings in all stages of growth. This implies that the nuclei are already pre-existing in the deformation substructure. However, the probability of a recrystallized nucleus/embryo to reach a critical size in order to be able to grow depends upon three primary instability criteria [32, 53], illustrated in Fig. 2.14. Firstly, the nucleus must be big enough such that the Gibbs free energy of the nucleus decreases as it grows further, known as the thermodynamic instability criterion. The critical nucleus size to initiate instability is: \[ r_c = \frac{2\gamma}{\rho G b^2}, \]
where \( \gamma \) is the surface energy, \( \rho G b^2 \) is the stored dislocation energy (\( \rho \) is the dislocation density, \( G \) and \( b \) are the shear modulus and burgers vectors). Secondly, the grain boundary of the nucleus has to move in a defined direction, which requires a local imbalance of the driving forces (arising from inhomogeneous dislocation densities, difference in subgrain sizes) that is termed as the mechanical instability criterion. Finally, the nucleus must possess high angle boundaries i.e. its misorientation with respect to its
surroundings is larger than $10^\circ$-$15^\circ$, in order to be mobile throughout the growth process. This is termed as the kinetic instability criterion. Fulfilment of all three criteria is prerequisite for a nucleus to transition into the conventional growth regime.

### 2.2.1 Nucleation Mechanisms during Recrystallization in Magnesium Alloys

Several nucleation mechanisms have been observed in metals, which consequently give rise to different recrystallization textures and microstructures. In Mg alloys, the following mechanisms of nucleation have been proposed.

1. **Grain boundary nucleation**. Locally activated non-basal slip mechanisms in grain mantle regions near the grain boundaries accommodate significant amount of plastic strain leading to nucleation of new fine grains adjacent to the original grain boundaries, as shown in Fig. 2.15 [48]. Conventional wrought alloys generally undergo this type of recrystallization in dynamic cases. Nucleation at grain boundaries is discontinuous in nature and occurs by means of bulging mechanisms. Increasing deformation leads to fluctuations in the grain boundary, leading to formation of serrations and bulges (c.f. Fig. 2.16) that eventually transform into new strain-free grains. Al-Samman et. al. [11], while investigating DRX mechanisms in Mg-Al-Zn (AZ31) alloy reported such bulging phenomenon occurring at boundaries of highly deformed grains creating a necklace structure. The newly formed necklace grains showed misorientations ranging from $5^\circ$ to $20^\circ$. Further necklace formation at the recrystallization front was observed not to occur by repeated bulging but other mechanisms, leading to considerable incoherency between the orientations of the recrystallized and parent orientations. The underlying mechanism was attributed to rotational DRX [54], owing intense localized lattice rotations in the grain boundary regions. Such lattice rotation during deformation typically arises from the formation of subgrains along prior grain boundaries leading to a continuous increase in the misorientation (due to absorption of dislocations) until a HAGB is obtained.
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Figure 2.15 Schematic illustration of deformation and subsequent DRX at grain boundaries [48]

Figure 2.16 (a) Serration or bulging during DRX at grain boundaries leading to (b) fine strain free grains [11]
Moreover, certain orientations showed a higher tendency to undergo rotation. This behavior was correlated to their grain boundary character. Polycrystal grains generally exhibit mixed (tilt/twist) grain boundary character and therefore it has been observed that under external stress grains display concurrent rotational (twist character) and migrational (tilt character) effects. In such cases depending on the grain orientation, the angle between the stress direction and the boundary plane normal will vary resulting in corresponding increase or decrease in degree of grain rotation. Under static annealing cases such events can also occur via migration of high angle boundaries.

(ii) Subgrain boundary migration. The formation of recrystallization nuclei by means of subgrain boundary motion through a deformation zone associated with accumulation of misorientation or coalescence of subgrains, leading to the formation of high angle boundaries [55]. Such nucleation mechanisms are generally continuous in nature accompanied with massive recovery and sub-grain formation. Galiyev et.al [56] reported activation of such recrystallization mechanisms during deformation at lower temperatures (higher Zener (Z) values) in ZK60 alloy. Al-Samman et. al [38] also observed such recovery based recrystallization in magnesium single crystals. The recovery ensues by both rotational and migrational mechanisms depending on dynamic and static cases. Such recrystallization mechanisms generally lead to retention of the deformation texture and occur frequently in case of pure magnesium. Like in the case of grain boundary nucleation mechanism, this mechanism can also be described as a “rotation” recrystallization mechanism (c.f. Fig. 2.17). It requires presence of deformation heterogeneities for the necessary orientation gradients to develop, and the new grains are considered rotated portions of the parent grains.
(iii) **Shear band nucleation (SBN).** There are a variety of shear band types proposed as nucleation sites for recrystallization in magnesium. The relevant ones include kink bands formed in grains poorly oriented for basal slip [48], and twinning-related shear banding taking place in regions undergoing $\{10\bar{1}1\}$ twinning [57] or $\{10\bar{1}1\}$-$\{10\bar{1}2\}$ double twinning [52]. Shear banded microstructures are generally very heterogeneous and show large internal orientation spreads that can account for nucleation of grains with a wide spectrum of orientations (as illustrated in Fig. 2.18), some of which are distinct from the typical deformation texture. SBN of recrystallization has received particular attention in Mg-REE alloys [58, 59].

(iv) **Deformation twinning nucleation (DTN).** Acting as nucleation sites for recrystallization, deformation twins have a significant potential to modify the recrystallization texture owing to the fact that the different variants of primary and secondary twinning induce a large number of rotations associated with new orientations relative to the deformed matrix orientation. Numerous studies have in fact documented this type of recrystallization occurring within deformation twins and
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at twin-twin or twin-grain intersections [38, 39, 60-63]. Fig. 2.19 gives an instance of DRX inside twins in a conventional AZ31 alloy. According to some studies, e.g. [60, 61], the potency of recrystallization nucleation within twins, and thus the contribution to texture depends largely on the twin type (extension or compression) and twin generation (primary or secondary).

**Figure 2.18** TEM micrographs showing nucleation of fine recrystallized grains inside shear bands[64]

(v) *Particle stimulated nucleation (PSN)*. While large densities of very small particles can pin boundaries and retard recrystallization, second phase particles larger than ~ 1 μm in size can actually act as nucleation sites for recrystallization [65], as depicted in Fig 2.20.
Figure 2.19 SE and optical images showing DRX inside twins in AZ31 alloy [11]

Figure 2.20 (a) Deformation zone in the vicinity of particle [65]; (b) Nucleation of fine recrystallized grains near particles [66]
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PSN has been frequently reported in magnesium alloys to provide more randomly oriented nuclei, which gives rise to weaker recrystallization textures [67, 68]. PSN in magnesium is always in competition with other recrystallization mechanisms. Even though its contribution to the recrystallized microstructure (in terms of volume fraction) is generally little, there can be cases where growth of PSN grains could dominate the microstructure and largely affect the overall bulk texture, as shown in [66]. Robson et.al [67] performed extensive studies on the particle effects on recrystallization in conventional magnesium-manganese alloys. They reported that PSN occurred along particle clusters larger than individual coarse particles. The observed behavior was attributed to higher cumulative misorientations along particle clusters than the individual ones. Moreover, the recrystallized grains from PSN had smaller sizes than the grains nucleating from other mechanisms such as HAGB nucleation. The effect of PSN on texture weakening was not quite evident in dynamic cases but on static recrystallization PSN resulted in weak random textures. However, they concluded that the contribution of PSN to final texture is minimal and weak textures observed during static annealing were as a result of strain induced boundary migration mechanisms.

2.2.2 MICROSTRUCTURAL DEVELOPMENT DURING RECRYSTALLIZATION AND GRAIN GROWTH IN CONVENTIONAL MAGNESIUM ALLOYS

Elucidating the texture forming mechanisms during hot working is of particular interest since most commercial Mg alloys are fabricated to semi-finished products by such processing. Hence most investigations present in the literature, on recrystallization and grain growth in wrought magnesium alloys pertain to understanding DRX behavior and related texture evolution. An interesting study was carried out by Barnett [69] on the effect of both dynamic and static recrystallization on the resultant grain size distribution and texture in wrought AZ31 alloy. The study revealed that the DRX kinetics were more dependent upon
the deformation conditions than the initial texture. At higher Z values, DRX did not undergo completion and for lower Z values completely recrystallized microstructures were obtained. The annealing of partially dynamically recrystallized samples resulted in a complex relationship between the Z value and the final grain size. The following observations and related conclusions were proposed:

a) For lower levels of Z, the effect of Z was minor on the microstructure and the final grain size was marginally coarser than the initial dynamically recrystallized grain size. The results indicated that specimens undergoing full DRX, most likely underwent post-DRX grain growth.

Figure 2.21 (a) Blue deformed grains and predominant green recrystallized grains indicating the 30° <0001> misorientation relationship in magnesium, IPF scatter data; (b) grain boundary misorientation distribution with 30° peak [9]
b) For intermediate $Z$ values the coarsest grains were observed. Instances of abnormal grain growth were also seen for this range of $Z$ values. The pre-annealing microstructures were $\sim$80%-95% recrystallized and still comprised of un-dynamically recrystallized regions. Subsequent static annealing thus led to favorable growth of the recrystallized grains lying in the vicinity of still deformed regions, thereby consuming them. Once the recrystallized grains impinge, these newly grown grains with a size advantage continue to grow abnormally.

c) At high $Z$ values, there is a significant amount of un-dynamically recrystallized material prior to annealing and it is likely that these regions undergo static recrystallization on subsequent heat treatment. The final grain size in this case would keep decreasing with increasing $Z$ due to an increase in overall number of nucleation sites.

In terms of texture evolution, the effect of annealing did not affect the deformation texture qualitatively apart from weakening the textures.

Similar observations on texture evolution were made by Cottam et. al. [70], for pure Mg and Mg-Y alloys. They reported that the DRX texture followed on the similar lines as in case of deformation texture, with reduction in intensity. The DRX texture was dependent more on the deformation conditions rather than the special conditions of nucleation or growth. In another study [9] on static recrystallization and DRX behavior in pure Mg and AZ31 alloy, it was observed that static recrystallization does not quite modify the deformation texture other than reducing the overall texture intensity. In terms of texture evolution, the recrystallization process was categorized to be continuous in nature i.e. extended recovery, since the crystallographic texture revealed no qualitative changes from the as deformed one. However, with respect to the microstructural evolution during annealing, recrystallization proceeded discontinuously (by nucleation and growth) resembling that seen in fcc metals. In pure Mg two main basal slip systems were predicted to be active i.e. $<11\overline{2}0>$ (0001) and $<10\overline{1}0>$ (0001) systems, both of which are $30^\circ$ apart and result in a (0001) fiber texture. Due to the 6-fold rotation symmetry exhibited by the basal
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Plane recrystallization related texture changes are very difficult to observe by means of macrotexture analysis. On the other hand, EBSD measurements shown in Fig. 2.21 indeed corroborate the discontinuous nature of recrystallization in magnesium, wherein a $30^\circ < 0001 >$ misorientation relationship between the recrystallized and deformed grains can be observed. Similar findings regarding preferential nucleation of boundaries with $30^\circ < 0001 >$ misorientation relationship with the deformed matrix were previously observed by Lücke and coworkers [71] during recrystallization of pure Mg. However, it could not be predicted whether such preferred orientation was as a result of preferential nucleation i.e. oriented nucleation, or if the preference develops during competitive growth stage i.e. oriented growth.

Jäger et. al [63] performed annealing treatments on rolled commercial AZ31 alloy at temperatures of $200^\circ$ C, $300^\circ$ C and $400^\circ$ C. At $200^\circ$ C, the recrystallization fraction was very low and the predicted nucleation zones were in the vicinity of twins and twin intersections. At $300^\circ$ C, the whole material underwent recrystallization. The recrystallization reached completion within the first 2 minutes of annealing, following which grain growth commenced such that the triple junctions reached closer to the equilibrium arrangement of $120^\circ$. The influence of twins on grain growth was also observed. The grains nucleating at twin boundaries showed greater and more stable growth than others.

Figure 2.22 Twinning behavior at $200^\circ$ C in Mg single crystals [38]
The twin boundaries probably act as preferential sites for nucleation of recrystallization and are hence the first to recrystallize, even at temperatures ~ 150°C - 200°C. Annealing at 400°C leads to development of fully recrystallized microstructure within 60 seconds of holding time. The texture post static recrystallization at 400°C indicated large asymmetrical spreads and much weaker intensities. Unlike the starting basal texture in as-received specimen showing a TD spread, the recrystallized texture showed a predominant RD spread.

In a separate study, Al-Samman and co-workers [38] investigated the DRX behavior in magnesium single crystals, under c-axis compression. It was observed that for deformation at temperatures in the range of 200 °C, the microstructure showed profuse twinning, characterized by primary {10\overline{1}1} and {10\overline{1}3} compression twins that also underwent secondary {10\overline{1}2} tension twinning (c.f. Fig. 2.22a), giving rise to orientations conducive to basal slip (c.f. Fig. 2.22c). Grain boundary maps indicated large fractions of low angle boundaries and high angle boundaries, with misorientation values lying between 80° and 90° (c.f. Fig. 2.22b). These high angle boundaries correspond to the double twinned regions i.e.
the misorientation relationship between the secondary tension twins and primary compression twins. For compression tests conducted at 370 °C, these twinned regions underwent complete recrystallization such that the new grains retained the same c-axis orientation as of their compression twin hosts, misoriented by ~56°±5° from the [0001] direction of the parent grain (c.f. Fig. 2.23a-c). The mechanism of DRX inside the twins followed the continuous recrystallization phenomenon, wherein strong recovery led to formation of high- angle boundaries, thereby generating new strain free grains (c.f. Fig. 2.23d and e). The dynamically recrystallized grains inside the twins further displayed random rotation about their c-axes resulting in fiber spread between [1210] and [0110] axes. Later investigations [72] ascribed the process of DRX in twins to active prismatic slip, leading to simultaneous twin fragmentation and lattice rotation about the c-axes of grains as illustrated in Fig. 2.24.

![Figure 2.24](image)

**Figure 2.24** Schematic illustration of simultaneous slip induced lattice rotation and fragmentation during DRX in compression and double twins [72]

### 2.2.3 Evolution of recrystallization textures: Underlying principles

The recrystallization texture in a metal primarily depends upon, i) the orientation of the new nuclei or sub-grains and ii) the relative rates of nucleation and growth of these
grains. In this respect, there exists two major alternative models that have been known to determine recrystallization texture evolution [53].

Oriented nucleation theory: The oriented nucleation theory proposes that selective orientations can nucleate faster than other orientations and thereby dominate the final orientation distribution. If the fraction of nuclei with the preferred orientations is $A^*$ and the fraction of nuclei with random orientations or other than the preferred ones is $A$, then in for an oriented nucleation scenario, $A^*/A >> 1$. In other words the aforementioned concept is more akin to a ‘grain frequency’ parameter that gives the most frequently occurring nucleus orientation. The drawback of this theory is that it is difficult to predict the orientations that nucleate [53].

Oriented growth theory: Certain recrystallized orientations displaying a special misorientation relationship with respect to the deformed parent will consume the matrix (or grow) faster than others, such as the growth selection corresponding to grain boundaries with $\sim 40^\circ<111>$ observed frequently in fcc metals [73]. Applying the same analogy to hexagonal materials, recrystallized grains showing $30^\circ<0001>$ or $90^\circ<10-10>$ misorientation with the deformed parent are known to grow favorably over others [71]. The oriented growth theory can also be expressed as a ‘grain size’ effect, such that the ratio between the mean grain size of preferred orientation ($D^*$) and the mean grain size corresponding to the non-preferred ones ($D$) is $>> 1$ [53]. Attempts have been made to postulate the underlying mechanisms that result in a case where the criterion, $D^*/D >> 1$ is satisfied. Some of the relevant ones are explained below,

- **Orientation pinning** [74] – A growing grain meets many grain boundaries with varying misorientation values, as illustrated in Fig. 2.25a. If a grain meets a region in deformed material with an orientation similar to its own then it will produce low angle boundaries and hence its mobility will be drastically reduced, thereby impeding its growth. On the other hand, certain orientations might have the
fortune to come across very few orientations similar to their own and hence will relatively grow faster than other grains.

- **Variant inhibition** [75]– Under plane strain deformation conditions the grains deform parallel to the extrusion direction, giving rise to deformed bands of nearly constant orientation stretched along the direction of processing, as shown in Fig. 2.25b. Such microstructure would be described by low angle boundaries between neighboring deformed bands. The grains arising from these deformation texture component will subsequently have a strong inhibition of growth along normal directions and are unable to thicken.

![Figure 2.25 Orientation pinning and variant inhibition][53]

When several nuclei of different orientations grow in a single deformed orientation then the growth rates are dependent on both the misorientation with the deformed matrix and the stored energy. Such a scenario is denoted as competitive growth. On the other hand if the nuclei grow into several deformed grains then the growth rates of the nuclei are a compromise of the varying misorientation with the deformed grains, which is described...
as compromise growth. Both are extreme cases of growth types. In real cases generally the initial growth stage is similar to competitive type and once the nucleus grows out of the deformed grain where it was formed i.e. its diameter equals the smallest dimension of the deformed grain, the growth pattern changes and resembles more to a compromise growth. In realistic cases, it is difficult to distinguish oriented growth from oriented nucleation. Furthermore, the preferred orientation relationship becomes a transient parameter as the grain keeps growing into newer surroundings.

2.3 WROUGHT MAGNESIUM ALLOYS WITH ‘REE’ ADDITIONS: AN OVERVIEW

Modifying the chemical composition of magnesium alloys with special emphasis on REEs has shown numerous indications of improved properties of this class of alloys, such as grain refinement, better formability at low temperatures, and enhanced strength and creep resistance at elevated temperatures. REEs are lanthanide group elements with atomic numbers (Z) from 57 to 71, displaying similar physical and chemical properties. They are categorized into primarily two subgroups viz. Light REs, comprising of all the elements starting from Lanthanum (La, Z=57) till Europium (Eu, Z=63) and, Heavy REs including the rest and additionally Yttrium (Y, Z=39). A conventional thumb rule is that ‘light’ REs generally display low solubilities, whereas the ‘heavy’ REs show large solid solubility in magnesium. The solid solubility of the elements can be exploited by heat treatment, i.e. Mg–Nd alloys have the greatest response to age hardening, followed by Mg–Ce alloys, with Mg–La alloys showing almost no age hardening response due to the low solubility of La in Mg [76].

2.3.1 PHASE TRANSFORMATIONS IN MAGNESIUM-REES

Potentially, in Mg–REE alloys there are many different phases that may form, which are common to all of the REEs, such as the Mg_{12}RE, Mg_{17}RE_{2}, Mg_{3}RE or Mg_{2}RE phases. However, it is not clear which one, or in which form, these phases will nucleate under given solidification conditions. For example, in the Mg–Nd system there is some
conjecture as to whether the Mg_{12}Nd phase is an equilibrium or metastable phase. There is a similar debate about the formation of Mg_{12}La as opposed to Mg_{17}La_{2} in the Mg–La system. Thus in order to understand the effect of REE addition on the mechanical properties and processing of these alloys, it is imperative to acquire some background regarding the phase transformations occurring in these alloys.

For the sake of brevity, the phase transformation of two representative binary Mg-RE alloys will be discussed in this section – one from each sub-group. For an exhaustive data set on the physico-chemical properties of Mg-REEs, the reader is referred to [76].

a) *The Mg-Gd phase diagram:*

Fig. 2.26 represents the equilibrium phase diagram for Mg-Gd binary system. The Mg-Gd phase diagram displays existence of four main binary compounds, Mg₅Gd, Mg₃Gd, Mg₂Gd and MgGd. All these compounds are formed by peritectic reactions. There is a eutectic equilibrium on the Mg side and eutectoid equilibrium connected with two allotropic forms of Gd (β-Gd → α-Gd + MgGd). Mg₅Gd, unlike other Mg-RE
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compounds, is the real composition and its stoichiometric formula is Mg$_{45}$Gd$_{11}$. The eutectic temperature is ~542° C and the composition consists of 40.4 wt.% Gd. The maximum solid solubility of Gd in Mg is ~24 wt.% at 542° C and around 4 wt.% and 6wt.% at 200°C and 300°C, respectively [76].

b) The Mg-Ce phase diagram:

![Mg-Ce phase diagram](image)

**Figure 2.27** Mg-Ce phase diagram [76]

The Mg-Ce phase diagram is characterized by existence of six intermetallic systems viz. Mg$_{12}$Ce, Mg$_{17}$Ce$_2$, Mg$_{41}$Ce$_5$, Mg$_3$Ce, Mg$_2$Ce and MgCe phases, as shown in Fig. 2.27. Apart from Mg$_3$Ce, which is congruently melting compound, all the others are peritectically formed. There are two eutectic transformations one each on the Mg-rich and Ce-rich ends and two eutectoid transformations i.e. decomposition of Mg$_2$Ce $\rightarrow$ $\alpha$-Mg+Mg$_{12}$Ce and decomposition of $\delta$-Ce $\rightarrow$ $\gamma$-Ce + MgCe.

The binary compounds Mg$_3$Ce, Mg$_2$Ce and MgCe are well established in the literature. Mg$_{12}$Ce shows a crystal structure resembling an orthorhombic lattice. The eutectic point at 590°C in the Mg-rich side shows a percentage content of Ce equal to 20.5 wt.% The maximum solid solubility of Ce in Mg, obtained from resistivity
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experiments, has been found to be 0.74 wt.% at 590°C, which further drops to as low as 0.04 wt.% on reducing the temperature to 200°C. The reported solubilities at 300°C and 400°C are 0.06 wt. % and 0.08 wt. % respectively [76].

2.3.2 ROLE OF REES IN TRIGGERING TEXTURE MODIFICATION IN MAGNESIUM ALLOYS

Adding REEs is known to modify textures during deformation and recrystallization of magnesium alloys. However, REE related texture modification during deformation is mostly observed in conjunction with simultaneous softening phenomenon i.e. DRX. Interestingly the first investigations on REE-alloyed magnesium were primarily driven to induce solid solution strengthening and enhance creep resistance of magnesium. The earliest reports on the evolution of weak textures and reduced yield anisotropy in REE alloys dates back to the 1990s when alloys containing additions of Y and REEs such as Nd can develop more random-type textures during extrusion, as opposed to conventional Mg alloys. It was found that a more randomized texture strongly reduces the tension-compression asymmetry, which is an attractive benefit of controlling the texture to enhance formability. The randomized texture observed in such WE alloys (which were heavily alloyed with yttrium and REEs) was ascribed to PSN of recrystallization [68, 77], but the reason for enhanced PSN in combination with REEs was not clarified. However, the relatively low contribution of PSN mechanism (~1%) to the overall texture has often been considered as a negating factor against it being the sole mechanism. Though a recent study did conclude such PSN related texture weakening that was attributed to favorable growth of PSN orientations [66].

Later investigations also showed possibility of altering texture both qualitatively and quantitatively, even for very dilute REE additions (~ 1wt.%). Bohlen et al. investigated six magnesium alloys containing different levels of zinc and REE additions [15]. They reported that the overall texture strength and the basal pole intensity aligned with the sheet normal direction is lower for REE-containing alloys than for conventional
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

alloys. Furthermore they found that the anisotropy of the yield strength was reversed and the planar anisotropy was reduced to $r \sim 1$ in comparison to conventional Mg alloy sheets.

Both aspects were related to texture modification in the Mg–Zn–RE alloys, which placed more grains in favorable orientations for basal slip and extension twinning. In another seminal study conducted by Stanford and Barnett [58], it was found that REE-additions lead to a peculiar texture feature in hot extruded magnesium alloys that was described by the $\langle 11\bar{2}1 \rangle$ directions being parallel to extrusion direction (ED), as shown in Fig. 2.28. The texture feature was coined as ‘RE-texture’. Origin of the RE-texture was attributed to a combined influence of oriented nucleation in shear bands and retarded recrystallization kinetics. On the contrary, texture modification during shear band recrystallization in hot rolled Mg-Zn-Ce (ZE10) alloys [59] was attributed to favorable growth of texture
components rotated by ~45° towards the transverse direction, indicated by the pole figure data in Fig. 2.29.

![Figure 2.29](image)

**Figure 2.29** Shear band recrystallization in hot rolled ZE10 alloy after annealing at 400°C for a) 60s and b) 180s, giving rise to orientations deviated by ~45° towards TD that grow favorably [59]

Another work by Hantzsche et al. [78] attributed the weakening of the magnesium sheet textures with increasing content of Ce, Nd and Y to the appearance of shear bands comprising of compression and double twins, and the restriction of grain growth during subsequent annealing. It is imaginable that nucleation inside compression and double twins, being associated mostly with soft-off basal orientations, could potentially stimulate texture modification during subsequent recrystallization. From the above overview it is clear that the addition of REEs offers an avenue to control the textures of wrought magnesium alloys. In essence the literature suggests, the following key roles of REs in texture weakening of Mg alloys –

i) Modification of the stacking fault energy (SFE) of the Mg matrix

ii) Solute drag or particle pinning effects during deformation and recrystallization.
However, the definite nature of interaction between REEs and deformation and annealing behavior in magnesium alloys is still an obscure area. In this respect, the field demands systematic investigations particularly addressing the following issues:

a) In particular, the critical influence of REE alloying content and the choice of REE need to be understood.

b) Furthermore, how these parameters are influenced by the processing conditions i.e. both crystallographic deformation and annealing treatment requires further investigation.

Lastly, the additional role of non-REEs in aiding REE-related texture modification needs to be acknowledged.

2.4 Summary

The present chapter provides a comprehensive overview regarding the different aspects of deformation and recrystallization behavior in magnesium alloys. Special emphasis was ascribed to the role of REEs in imparting unconventional and favorable textures in wrought magnesium alloys. Furthermore the underlying mechanisms as well as the scope of future investigations to enable suitable alloy design using REEs were also considered.
CHAPTER 3

EXPERIMENTAL TECHNIQUES

This chapter provides an overview of the various experimental methodologies conducted during this work. Section 3.1 outlines the relevant material selection and fabrication procedure. Section 3.2 gives a description of the various processing and material treatment methods implemented in this study. The relevant metallographic techniques are discussed in section 3.3, whereas section 3.4 elaborates on the subsequent analysis techniques used to characterize the material texture and microstructure. Finally, Section 3.5 provides a succinct summary of the entire chapter.

3.1 MATERIAL SELECTION AND PRODUCTION TECHNIQUES

3.1.1 INITIAL MATERIAL

In all the studies, primarily two alloying classes, with single REE additions, were investigated viz. the binary Mg-REE alloys and the quaternary Mg-Zn-Zr-REE alloys. The motivation behind selecting such alloying compositions was to gain a deeper understanding of the individual effects of REEs on material behavior and whether addition of zinc and zirconium are able to further amplify the observed REE-effects.

*Mg-REEs*: Essentially two different REEs viz. cerium (Ce) and gadolinium (Gd) were used as alloying additions. The alloying content was restricted to 1 wt.% so as to maintain the light-weight material advantage, which magnesium offers. The selected elements were categorized on the basis of their solubility, such that the influence of REEs both in the form of solute and precipitate could be determined. While Gd tends to exist primarily as solutes for the aforementioned concentrations, Ce interacts with Mg matrix primarily in the form of secondary phase.

*Mg-Zn-Zr-REEs*: Selected REEs were additionally alloyed with 1wt.% zinc and 0.6wt.% zirconium. Zinc and zirconium are frequently used as alloying additions during
fabrication of wrought magnesium alloys. Both zinc and zirconium act as effective grain refiners. Furthermore, zinc significantly contributes to the mechanical strength increment via solute strengthening effects. Table 3.1 provides an overview of the chemical compositions of the materials used in this study.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Zn(%)</th>
<th>Zr(%)</th>
<th>Ce(%)</th>
<th>Gd(%)</th>
<th>Mg(%)</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Ce</td>
<td>-</td>
<td>-</td>
<td>1.15</td>
<td>-</td>
<td>rest</td>
<td>625 ± 16.1</td>
</tr>
<tr>
<td>Mg-Gd</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.07</td>
<td>rest</td>
<td>720 ± 21.3</td>
</tr>
<tr>
<td>Mg-Zn-Zr-Ce</td>
<td>1.06</td>
<td>0.58</td>
<td>1.01</td>
<td>-</td>
<td>rest</td>
<td>33 ± 3.3</td>
</tr>
<tr>
<td>Mg-Zn-Zr-Gd</td>
<td>0.96</td>
<td>0.57</td>
<td>-</td>
<td>1.04</td>
<td>rest</td>
<td>73 ± 6.9</td>
</tr>
</tbody>
</table>

### 3.1.2 Casting and Homogenization

The alloys were melted using a medium frequency induction furnace under a protective gas atmosphere of Ar/CO₂. Magnesium melt is highly reactive, and therefore, high purity graphite was used as crucible material. The alloys were prepared from high purity Mg, Zn and a Mg-33 wt.% Zr master alloy. The purity of the REEs were in the range of 99.5 - 99.9 wt.%. In case of the quaternaries, Mg (99.93% purity), Zr (in the form of Mg-33%Zr master alloy) and the RE metal are first melted at 700°C. After approximately 10 min Zn is added to the melt and given precisely 1 min to dissolve before casting. During the melting process, the molten metal bath is held under inductive stirring to produce a more homogeneous mix and assist with alloying. In addition, the crucible temperature is carefully controlled to prevent Zn losses. Casting of the molten metal charge is carried out at 700°C into a pre-heated Cu-mould of the size 50 mm x 50 mm x 150 mm, followed by homogenization treatment at 420°C for 20 hours under protective atmosphere, after which the cast billets are air cooled. A graphite cylinder was
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

additionally placed to prevent sublimation and surface oxidation of magnesium. An overview of the as cast grain sizes are given in Table 3.1.

3.2 PROCESSING AND MECHANICAL CHARACTERIZATION METHODS

3.2.1 HOT ROLLING AND STATIC ANNEALING

*Large strain hot rolling and static annealing:* A two-high laboratory rolling mill consisting of cylindrical rolls (c.f. Fig. 3.1) with a diameter of 250 mm and 400 mm length was used. Rolling blocks of dimensions, 60mm x 40mm x 4mm were hot rolled at 450° C (nominal furnace temperature) to 80% thickness reduction (strain rate $\dot{\varepsilon}_h \approx 7s^{-1}$) in a single-rolling pass with subsequent water quenching. The rolling imparted an overall logarithmic true strain of -1.6 ($\varphi_h = \ln(h_1/h_0)$; $h_1$ and $h_0$ final and initial thicknesses). Additional single pass hot rolling schedules at intermediate strains, resulting in 50% thickness reduction ($\varphi_h = -0.7$, $\dot{\varepsilon}_h \approx 3s^{-1}$) were also executed. Post rolling, the specimens were subjected to annealing treatments at 5 different temperatures viz. 250° C, 300° C, 350° C, 400° C and 450° C, for 60 minutes followed by water quenching.

*Unidirectional multi-pass hot rolling and static annealing:* Rolling blocks of dimensions 80 mm x 40 mm x 40 mm were machined from the cast materials and hot
rolled at 450°C (nominal furnace temperature) to a final thickness of 12 mm, imposing a total thickness reduction of 70% in seven passes, amounting to an overall logarithmic true strain $\varphi_t = -1.2$. After every hot-rolling pass, the material was quenched and subjected to inter-pass annealing at 450°C for 15 minutes. Additionally, thickness measurements were made after each pass. Post-rolling, the specimens were subjected to short static annealing so that texture changes were insignificant, yet the microstructure was fully recrystallized and stress relieved. The specimens were rapidly water-quenched after the annealing treatment in order to retain the desired microstructure.

Figure 3.2 (a) DIN 50125 E standard dimension with legend; (b) specimen geometry used in the current investigation; (c) Tensile test set up

3.2.2 Room Temperature Uniaxial Tensile-Tests

Dog-bone shaped tensile specimens with gauge dimensions- 3.56 mm x 0.8mm x 1.5mm, shown in Fig. 3.2, were subjected to tension tests along the rolling direction
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

Tension tests were conducted at room temperature (RT) under an applied true strain rate of $5 \times 10^{-4}$ s$^{-1}$, using a conventional screw-driven testing machine ZWICK. Tensile specimens were strained to failure to determine the maximum ductility (elongation-to-failure; $\varepsilon_f$) and flow strengths (yield stress; TYS, and ultimate tensile stress; UTS). Each test was repeated at least 3 times in order to obtain the average stress-strain values.

### 3.2.3 Room temperature plane strain compression and static annealing

Deformation experiments were carried out in plane strain compression (PSC) at ambient temperature and a constant strain rate of $10^{-2}$ s$^{-1}$. PSC was performed in a channel-die using a conventional screw-driven ZWICK testing machine. Hexagonal boron nitride powder was used as a lubricant to minimize friction between the die surfaces and the specimen. To evaluate the influence of texture on recrystallization and microstructure development during subsequent annealing, channel-die specimens with dimensions of 12 mm (Longitudinal Direction; LD) $\times$ 10 mm (Transverse Direction; TD) $\times$ 4 mm (Compression Direction; CD) were machined from the hot rolled alloys in two different orientations with respect to the PSC loading axis (c.f. Fig. 3.3). TTC Specimens were compressed along the sheet normal direction ‘ND’ (through thickness compression), while IPC specimens were compressed along the sheet rolling direction ‘RD’ (in-plane compression).

**Figure 3.3** (a) Sample orientations with respect to PSC loading axis; (b) Channel-die setup
Deformation was conducted up to ~ 8% and 13% strain for IPC and TTC samples, respectively. The strains were chosen such that the deformed specimens exhibited strongly twinned microstructures. The stress-strain curves were obtained by means of automated measurement of the load and displacement with an average data acquisition frequency of 50 Hz. At least three tests were conducted for each loading orientation and alloy to ensure reproducibility of the stress-strain data. The results presented in this study depict the average flow curves. For the recrystallization study the deformed specimens were annealed at four different temperatures ranging from 300° C to 450° C for one hour followed by water quenching.

3.2.4 VICKERS HARDNESS MEASUREMENTS

Vickers hardness measurements were performed using a Shimadzu HMV micorhardness tester operated with a load of 1N (kgf). Recrystallization kinetics (c.f. Chapter 7) were determined by means of multiple micro-hardness measurements. Atleast 5 hardness measurements were acquired for each annealing time (t). The corresponding recrystallized volume fraction ($X_v$) was subsequently calculated by the following expression,

$$ X_v = \frac{HV_0 - HV(t)}{HV_0 - HV_{final}} \quad \cdots (3.1) $$

where, $HV_0$ and $HV_{final}$ are the initial and the final hardness (after completion of recrystallization) values, $HV(t)$ is the hardness value measured for an intermediate annealing time ‘t’.

Additional static age hardening experiments at 450°C (c.f. section 7.6.3) were also performed by means of sequential micro-hardness measurements for different aging times. Prior to aging, the alloys were solution treated at 560 °C for 14 hrs, followed by
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At least 5 measurements were acquired and the average hardness value was utilized.

3.3 Metallographic analysis

Being a soft and highly reactive metal, metallographic preparation of magnesium is highly prone to scratching and unwanted surface reactions. Hence, the specimen preparation requires immense precaution and care. It is extremely essential to minimize specimen contact with water. Moreover, dry grinding processes are not at all advisable due to the strong oxidizing potential of magnesium.

Spark erosion cutting, in the presence of water as cooling medium, was implemented to produce rectangular specimens from the rolled sheets. This technique offers greater precision and minimizes surface damage. The specimens were subjected to mechanical grinding on rotatory grinding discs with 1200, 2400 and 4000 grit SiC paper. Throughout the process, ethanol was used as a coolant and lubricating medium. After each grinding step, the specimen was subjected to ultrasonic cleaning in ethanol bath. Grinding was performed until no surface deformation lines were visible.

Following grinding, the samples were mechanically polished using three different grades of diamond paste (in ethanol) viz. 3 µm, 1 µm and 0.25 µm. The average polishing duration on each cloth was approximately 5 – 15 minutes (with longer times for finer grades). After each polishing step, the specimen was ultrasonicated for 3-5 minutes. A mixture of alcohol and oil-based medium was used as a lubricant.

3.3.1 Metallography for texture measurement

The specimen dimensions of 20mm x 12mm ensured large surface area coverage, thereby minimizing scattering and background noise effects. The samples were mechanically polished down to 1 µm diamond paste before measurement, since the
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

presence of micro-scale scratches doesn’t significantly affect the quality of results. Measurements were made on the RD-TD plane of the sheet.

3.3.2 **Metallography for Optical Microscopy**

After polishing with diamond paste (down to 0.25 microns), the specimens are subjected to electro polishing in a 5:3 solution of ethanol (125ml) and H₃PO₄ (75ml) for 30 minutes at 1.84-1.93 V under ambient conditions. Polishing was performed under ambient conditions. Post-polishing, the specimen was rinsed using water and subsequently cleaned with ethanol in an ultrasonic bath. The electropolishing produced a scratch free mirror like surface. Acetic Picral and 5%-Nital were used as etchants to reveal the microstructure. Picral produces color etching, demarcating differently oriented regions with different colors. Nital is essentially used to etch grain boundaries. The etching time varied from 5-20 seconds. After etching with Picral, the polished surface revealed a dull golden tint. Optical images were captured on the RD-ND plane of the specimen. Figure 3.4 shows examples of optical microstructures after etching Mg-1Gd with Nital and Acetic Picral.

3.3.3 **Metallography for SEM/EBSD analysis**

Post mechanical polishing, the specimen is subjected to electropolishing in Struers AC2 reagent. The electropolishing conditions vary depending on the alloying composition and are listed in Table 3.2. The binary alloys were polished using Lectro-pol 5, equipped with a polishing stage, at ambient conditions. In case of the quaternary alloys, the electrolyte is cooled down to temperatures ~ -25°C to -30°C so as to suppress any surface reactions. The cooling is achieved by immersing the setup in cooling bath consisting of dry ice in ethanol as a refrigerant (c.f. Fig. 3.5). The electrolyte is maintained under consistent agitation using a magnetic stirrer.
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Figure 3.4 Optical microstructures for Mg-1Gd after etching with (a) 5% Nital and (b) Picral

Table 3.2 Electropolishing parameters for AC2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Voltage (V)</th>
<th>Temp (°C)</th>
<th>Time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Ce</td>
<td>26</td>
<td>R.T.</td>
<td>30</td>
</tr>
<tr>
<td>Mg-Gd</td>
<td>41</td>
<td>R.T.</td>
<td>25</td>
</tr>
<tr>
<td>Mg-Zn-Zr-Ce</td>
<td>29</td>
<td>-25</td>
<td>40-50</td>
</tr>
<tr>
<td>Mg-Zn-Zr-Gd</td>
<td>30</td>
<td>-25</td>
<td>40-45</td>
</tr>
</tbody>
</table>

3.4 MATERIAL CHARACTERIZATION

3.4.1 TEXTURE ANALYSIS

Texture is a collective term for a non-uniform distribution of crystallographic orientations in a polycrystalline aggregate [79].
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

In the current work a distinction is being made between macrotexture, measured by X-ray diffraction, and microtexture which is determined by EBSD technique.

a) Macrotexture measurement by X-ray diffraction (XRD)

Macrotexure measures the volume fraction of a particular family of crystallographic planes with respect to a sample coordinate system. The axes of a sample coordinate system are normally chosen according to important directions associated with the external shape change of the specimen. Those are usually the rolling (RD) or extrusion direction (ED), the normal direction (ND) and the transverse direction (TD). To determine a crystal orientation the sample is rotated systematically around the two angles $\alpha$ and $\beta$, shown in Figure 3.6, so that all lattice planes are brought into the reflection condition described by the Bragg’s law:

$$n \lambda = 2d \{hkl\} \sin \theta \quad (3.2)$$

where $n$: the order of diffraction (usually $n=1$); $\lambda$: wavelength of the x-ray; $d$: interplanar spacing; $\theta$: diffraction angle.

In case of hexagonal symmetry, the interplanar spacing $d$ can be calculated using the lattice parameters $c$ and $a$, and the Miller-Bravais indices $\{hkl\}$ as follows:
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\[ d_{(hkl)} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + k^2 + h.k) + \frac{l^2}{(c/a)^2}}} \quad \ldots (3.3) \]

The texture obtained in this way is an average value for the whole sample volume. A common way to measure macrotexture in a material is by using XRD. Other techniques like neutron or synchrotron diffraction can also be used but they are less common.

XRD pole figure measurements were conducted using a Bruker D8 Advance diffractometer, equipped with a high resolution area detector, operating at 30 kV and 25 mA, using filtered iron radiation and polycapillary focusing optics.

![XRD setup diagram](image)

**Figure 3.6** Schematic showing the principle of texture measurement with XRD.

The measurements were performed on the specimen mid-plane to obtain the bulk texture and avoid any surface effects. A set of six measured pole figures \([\{10\bar{1}0\}, \{0002\}, \{10\bar{1}1\}, \{10\bar{1}2\}, \{11\bar{2}0\} \text{ and } \{10\bar{1}3\}]\) were employed to calculate the orientation distribution function (ODF) using a quantitative texture analysis toolbox MTEX [80].

**b) Microtexture measurement by electron back scattered diffraction (EBSD)**

Electron back scattered diffraction (EBSD) measurements were carried out in order to obtain information related to the microtexture of the specimens. Automated measurements were performed with a High resolution Field Emission Gun scanning...
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electron microscope (HFEG-SEM), LEO-1530 equipped with a field emission gun (operated at an acceleration voltage 20kV) and an HKL-Nordlys II EBSD detector. A working distance of 10 mm and a sample tilt angle of 70° was used. The step width chosen conformed to a ratio of 1:5 between the measurement point dimension and the size of the smallest microstructural feature. The acquired raw EBSD data was subsequently analyzed using MTEX Matlab toolbox and conventional EBSD analysis softwares viz. EDAX-TSL© and HKL©.

The output of an EBSD scan consisted of a list of records containing the (x,y) coordinates of each indexed pattern, a phase indicator, the three Euler angles and a parameter that weights the quality of the acquired pattern (known as image quality, IQ, or band contrast). During post-processing, this information was transformed into images, from which various characteristics related to the crystallography of the sample can be represented according to a certain color code.

3.4.2 MICROSTRUCTURAL ANALYSIS

The microstructural evolution under the different conditions was examined by optical microscopy, SEM and EBSD techniques. Optical microscopy was performed on the etched samples using a Carl Zeiss microscope equipped with a digital camera (Aquinto a4i software) and the grain size and particle analysis was performed using automated image analysis softwares viz. ImageJ and Aquinto a4i analysis.

High resolution SEM was performed on a FEI Helios 600i scanning electron microscope. Chemical characterization of secondary phases was performed by means of energy-dispersive X-ray spectroscopy (EDX).

ATOMIC PROBE CHARACTERIZATION

Atom probe tomography (APT) is a powerful technique which allows for 3D imaging at near-atomic scale and high detection sensitivity. Therefore, APT provides the
opportunity to investigate chemical composition at buried interfaces, giving information regarding solute segregation to defects and grain boundaries. Following the principles of field evaporation, a sharp needle shaped tip of a sample material is desorbed “atom by atom” which are sequentially detected and digitally reconstructed into its near-original shape containing complete chemical information [81, 82].

Figure 3.7 Geometry of a typical atom probe. $V_{\text{tot}}$ is the total accelerating voltage of the system. $V_{\text{ext}}$ is an extraction voltage used with both static and dynamic fields. $V_{\text{pa}}$ is a post-acceleration voltage that can range in value from zero to magnitudes comparable to $V_{\text{ext}}$. $V_p$ is a voltage pulse that is the time-varying component of dynamic fields. L is the flight path length to the center of the detector, and R is the radius of the detector [83]

Under an applied high voltage electric field atoms from a sharp needle-shaped specimen are evaporated and accelerated towards a negatively charged local electrode, as it is illustrated in Fig. 3.7. After passing through the electrode, in-coming ions are collected by a position-sensitive delay line detector. The evaporation process is controlled by the application of high frequency voltage or laser pulses to the base electric field in a way that the required energy for field evaporation is realized only during pulsing. Hence, the time period between pulsing and detection of an ion is synchronized and defined as
the time of flight which is later used for the identification of the initial atomic positions in the sample. Different types of ions are distinguished by means of a time-of-flight mass spectrometer according to their mass-to-charge state ratio.

Finally, three types of information are obtained for each detected ion, namely the x- and y-positions of impact on the detector, the time-of-flight and the mass-to-charge ratio. From such a data collection, the original atomic positions in the investigated tip are reconstructed by reversing the original pathway of ions in the measurement. The reconstructed tip is finally visualized as a 3D tomogram allowing for elemental analysis. The exact pathway of desorbed ions heading towards the detector is determined by the direction of the electric field surrounding the tip-shaped specimen. The modulus of the electric field $E$ on the surface of the tip is approximated by,

$$E = \frac{V}{k_f R} \quad (3.4)$$

where, $V$ is the applied voltage between the tip and electrode, $k_f$ is a geometrical field factor and $R$ is the radius of the tip [82]. Ideally, a tip radius of less than 100 nm is required in order to induce field evaporation of surface atoms. Hence, challenging demands are set to the sample preparation.

The elemental distribution in the bulk and grain boundaries was investigated by APT. APT experiments were performed with a 4th generation local electrode atom probe (LEAP™ 4000X HR, Cameca Instruments), which utilizes a novel energy compensated design consisting of an in-built reflectron system that provides high mass resolution along with wide field of view (up to 250 nm). UV laser source of spot size 355nm was used for the measurements. A laser pulse fraction of 0.15 was applied at a repetition rate of 100 kHz. The tip temperature was maintained at ~60 K. A target evaporation rate of 0.5% was maintained.

Specimen preparation for APT was conducted as per Ref. [84]. Site-specific lift-out of APT tips was performed by means of ion-milling using a dual-beam FIB, with a
Gallium source (Ga\(^+\)). A schematic of the lift-out process is shown in Figure 3.8. The region of interest, for instance a grain boundary (GB) was marked by correlative SEM and EBSD microstructures (c.f. Fig. 3.8(a)). Following which, a protective layer of ~1 μm thick platinum was deposited on the target GB, in order to avoid damage during subsequent Ga\(^+\) ion-milling (c.f. Fig. 3.8(b)). A 20x4x1 μm\(^3\) wedge shaped sample, containing the GB area was lifted out (see Figs. 3.8(c)) and slices of this wedge were mounted and glued over several pre-fabricated Si posts of 2 μm in diameter each using Pt precursor gas.

Figure 3.8 Site-specific APT lift out; grain boundary (GB) identification by correlative EBSD and SE imaging (a); 1 μm platinum precursor coating on the selected GB (b); Lift-out of wedge specimen with GB and deposition on Si coupons (c); Annular milling procedure revealing GB plane trace between grains ‘1’ and ‘2’ (d); Final APT tip after low energy milling (e)
Fig. 3.8(d) shows an SEM image of one of the Si posts with the specimen glued, indicating the grain boundary plane trace between grain 1 and grain 2. Annular milling was subsequently performed in steps of decreasing milling currents, such that the GB area is preserved. Final low-energy (5 keV) Ga\(^+\) ion-milling was carried out to minimize beam damage on the region of interest, whereby APT tips with a radius of curvature \(\sim 30-40\) nm was obtained (Fig. 3.8(e)).

### 3.5 SUMMARY

The present chapter introduced the various experimental processing and characterization techniques implemented in this study. Processing and mechanical characterization of materials primarily involved hot rolling, plane strain compression, uniaxial tension tests and Vickers hardness tests (c.f. Sections 3.1 and 3.2). Material preparation was discussed in detail in Section 3.3. Various microstructural characterization techniques such as XRD, Optical microscopy, SEM, EBSD and 3-D APT measurements were also utilized.
CHAPTER 4

TEXTURE MODIFICATION IN BINARY MAGNESIUM-RE ALLOYS

PART I: ROLE OF SHEAR BANDS

This chapter outlines the large strain hot-rolling treatments performed on two binary Mg-RE alloys, Mg-1wt.% Gd and Mg-1wt.% Ce, subjected to subsequent isochronal static annealing treatments. The results and discussions presented investigate the observed recrystallization and grain growth related microstructure and texture development. A detailed analysis of the material characterization is presented in order to establish concrete correlations between the alloying chemistry and material processing response. Section 4.1 describes the initial material conditions and the processing schedule. Sections 4.2 and 4.3 overviews the results obtained from macro- and meso-scale texture and microstructure characterization performed for the various deformed and annealed states. Section 4.4 discusses, in detail, the observed rolling deformation behavior of Mg-REs and the possible REE related recrystallization and grain growth mechanisms active. The chapter is concluded by a concise summary, outlining the primary highlights of the study, presented in section 4.5.

4.1 INITIAL CONDITIONS

Mg-1wt.% RE (RE= Gd and Ce) alloys were cast and homogenized as per the procedure described in Section 3.1.2. EDX analysis of Mg-1Ce indicated presence of Mg_{12}Ce as secondary phases. The precipitates exhibited either elongated rod-shaped or globular morphologies.

The as-cast material was subsequently processed by means of large strain hot rolling and subsequent isochronal static annealing treatments, as described in section 3.2.1. With a true strain of 1.6 (\( \varphi_h = \ln (h_1/h_0) \); \( h_1 \) and \( h_0 \) are final and initial thicknesses), the single-pass approach enforced severe plastic deformation condition that gave rise to
extensive shear banding. Optical microscopy, XRD and EBSD measurements were carried out on the rolled and annealed specimens.

4.2 XRD Textures and Optical Microstructures

The textures of both alloys in the as-rolled and annealed states are shown in Fig 4.1. In the as-rolled state, both Ce and Gd alloys represented relatively sharp double-peak basal textures. The basal poles were tilted by about ±20° away from the sheet normal direction ND towards the rolling direction RD. Both rolling textures exhibited no significant spread of basal poles in the transverse direction TD. The Gd alloy showed a slightly sharper rolling texture than the other alloy. With respect to the rolling microstructure, both rolled materials exhibited a dense network of shear bands distributed homogeneously throughout the whole RD-ND plane (Fig. 4.2). The shear bands had a wavy nature, probably to maintain strain compatibility, and formed symmetric pairs that were inclined at an angle ±β from the RD, where β ranged from 18° to 28°. The density of shear bands was notably greater in case of Gd alloy than the other alloy. The Ce alloy contained secondary Mg₁₂Ce phases that were preferentially aligned along the shear bands during deformation. After annealing the precipitates were arranged in clusters as ‘stringers’ and as individual particles with a globular morphology (e.g. Fig. 4.2 at 450° C). The particles ranged between very fine particles (<1 µm) that were difficult to quantify and larger ones with sizes between 1 and 5 µm.

The annealing response at 250° C and 300° C showed no significant alteration of texture features for both alloys (c.f. Fig. 4.1). At 250°C the texture intensity remained virtually unaffected. Some increase in this regard was observed at 300°C for both alloys (from 8 to 10 MRD in Mg-1Ce and from 9 to 10 MRD in Mg-1Gd; MRD: multiples of a random distribution).
Figure 4.1 Basal Pole figures for Mg-1Ce and Mg-1Gd alloys at rolled and annealed states.

Figure 4.2 Rolling and annealing optical microstructures (RD-ND plane) of Mg-1Ce (a) and Mg-1Gd (b).

The microstructural evolution during annealing at 250°C showed no visible recrystallization nucleation events for both alloys. However, at 300°C, fine recrystallized grains were observed along shear bands, indicating their importance as nucleation sites (c.f. Fig. 4.2). Although conventional Mg alloys (e.g. AZ31) can readily undergo
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Recrystallization at 200°C [85], the observed delay in recrystallization for the present Mg-RE alloys is rather unsurprising. This behavior has been attributed to the roles of second phase particles (case of Mg-1Ce) and solute segregation to dislocations and grain boundaries (case of Mg-1Gd) as inhibitors of recrystallization [65, 86, 87].

Heat-treatments carried out at 350°C, 400°C and 450°C showed complete recrystallization accompanied by strong texture weakening in both alloys (c.f. Figs. 4.1 and 4.2). For the Ce alloy, no significant change of the basal texture character was observed. The double-peak basal component from the as-rolled state was replaced by a single basal component observed primarily at 400°C and 450°C. By contrast, texture weakening in the Gd alloy was associated with significant texture alteration. New annealing textures with distinct orientations from the typical basal texture were evident. These new orientations were characterized by appreciable tilt of basal poles away from ND (±20°-60°) forming a continuous fiber between TD and RD (outlined pole figures in Fig. 4.1). Increasing the annealing temperature from 350°C to 450°C resulted in slight intensification of the texture from 3 to 4 MRD. With respect to the microstructures, grain growth seemed to be quite restricted in the Ce alloy containing precipitates, whereas in the Gd alloy some grains appeared to have grown at a higher rate relative to their neighbors. By increasing the annealing temperature the growth advantage of selective grains over others became much evident.

4.3 EBSD CHARACTERIZATION

Fig 4.3 presents EBSD orientation maps and local texture data of Mg-1Gd annealed at 300°C. Data presented in Fig. 4.3(a)-(d) correspond to recrystallized regions and in Fig. 4.3(e)-(h) to deformed shear bands remaining from rolling. Recrystallized grains were separated from the deformed structure by defining an average internal misorientation below 1°. The color coding in Figs. 4.3(a) and (e) quantifies the tilt of basal poles (c-axes) away from ND, which is further shown in the corresponding basal
pole figures (single orientation data) (c.f. Figs. 4.3(c) and (g)) and the basal pole tilt distribution diagrams (c.f. Figs. 4.3(d) and (h)). The single orientation data was also represented in the form of recalculated basal pole figures so as to correlate the local texture features with those of the macrotexture. In this regard, the basal pole figures shown in Figs. 4.3(c) and (g) indicate the individual contributions of the recrystallization and deformation orientations to the overall macrotexture, which is a superposition of both. Gray highlighted areas correspond to Kikuchi band contrast data (also known as IQ indexing) and represent the anti-subset of the chosen subset. White areas appearing in Figs. 4.3(a), (b) and (e) show remaining zero solutions (non-indexed EBSD patterns) that, in our case, were assigned to highly deformed regions. Noise reduction was carefully applied to improve the original indexing from 60% to 69% using a minimum of five indexed neighbors. From the results shown in Fig. 4.3 it is evident that the highly deformed shear bands nucleate a wide spectrum of recrystallization orientations. An example of large orientation gradients in the shear bands is given in Fig. 4.3(f) with a cumulative misorientation of ~20°. The (0001) pole figure in Fig. 4.3(c) (single orientation data) shows basal-oriented recrystallized grains highlighted in blue and other “off-basal” grains highlighted in green. It is assumed that these orientations reflect the local deformation texture shown in Fig. 4.3(e) and (g). Basal-oriented grains were characterized by having a maximum spread of 20° from ND. Off-basal grains were considered located between 20° and 50° from ND. Recrystallized grains with spreads larger than 50° (highlighted in orange/red) were evident but were rather less frequent. From the basal pole distribution profile shown in Fig. 4.3(d) it can be seen that the highest fraction of recrystallized grains comprised those with off-basal orientations (frequency peak located between 30° and 35°). The corresponding frequency peak for deformed orientations was located at much lower tilt angles; i.e. between 15° and 20°. Fig. 4.3(b) shows an example of partially impinged recrystallized grains growing in a deformed matrix (shear band). The inverse pole figure representation shows that the
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A similar analysis for the Mg-Ce alloy annealed at 300°C is reproduced in Fig. 4.4. The original indexing for the mapping was 78%. Recrystallization at the shear bands is clearly evident in Fig. 4.4(a). The tilt distribution diagrams for the recrystallized and deformed regions are comparable, unlike Mg-Gd. Both produce a frequency peak between 25° and 30° (c.f. Figs. 4.4(b) and (d)). The recrystallization texture produces a fiber texture feature. However, the degree of spread of the recrystallized off-basal orientations in the single orientation data is considerably lesser than its macrotexture counterpart. The deformed region on the other hand produces relatively higher concentration of basal orientations (c.f. Figs. 4.4 (c) and (d)). The average recrystallized grain size measured at 300°C for both the alloys was nearly similar, with 3.43 µm (SE=0.38 µm) for Mg-Ce and 3.44 µm (SE=0.4 µm) for Mg-Gd.

The EBSD orientation maps in Figs. 4.5(a) and (b) display basal pole tilt mappings (with respect to ND) and local texture data for Mg-1Gd annealed at 350°C and 450°C, respectively. Both mappings show fully recrystallized microstructures that have already undergone grain growth. Both were measured at nearly similar magnifications for a better comparison of the microstructure development and grain size. In case of 450°C an additional larger mapping comprising of 730 grains (at a critical misorientation of 2°) was used to yield statistically sufficient local texture data presented in Fig. 4.5(b). The recalculated EBSD basal pole figures corresponded well with the XRD pole figures reproducing more or less the same unique annealing texture features. The number of detected grains in Fig. 4.5(a) at the same critical misorientation angle was 632.
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Figure 4.3 EBSD orientation maps and local texture data of Mg-1Gd annealed at 300°C; (a) and (e) c-axis orientation maps of recrystallized and deformed regimes of the microstructure superimposed on band contrast maps; (c) and (g) Corresponding basal pole figures showing single orientation data (left) and recalculated contour data (right); (d) and (h) Corresponding basal pole tilt distribution about ND; (b) ND inverse pole figure map showing magnified view of the highlighted area in (a); (f) Example of a cumulative misorientation profile measured in a deformed shear band in (e)
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Figure 4.4 $c$-axis orientation maps with respect to ND and local texture data of Mg-1Ce annealed at 300°C; (a) Recrystallized regions; (c) Deformed regions; (b) and (d) Corresponding basal pole figures and basal pole tilt distributions about ND

The original indexing for both mappings was between 96% and 98%. The color of grains corresponds to a similar color coding as described in Fig. 4.3 for basal and off-basal oriented grains. At 350°C, grains with a basal orientation (depicted in blue) already showed a much diminished occurrence with respect to their off-basal counterparts (depicted in green).
This was particularly evident in the scattered pole figure data shown in Fig. 4.5(a), when compared to the data given in Fig. 4.3(c), i.e. at 300°C where texture modification was not yet observed. The orientations, with $c$-axis tilt angles ranging from 20° to 50° from the ND, are clearly indicative of being the dominant orientation. There is a near disappearance of sharp basal orientations within 5° from ND. The frequency peak was located between 30° and 35° similar to the recrystallized fraction of the microstructure resulting during annealing at 300°C. Increasing the annealing temperature to 450°C resulted in an average grain size of ~40 µm vis-à-vis ~20 µm at 350°C due to accelerated grain growth kinetics. The distribution profile of basal poles as a function of tilt from ND showed a shift in the frequency peak by 5° towards higher angles. The fiber...
orientation located between 30° - 40° seemed to strengthen over other orientations, which showed an obvious relative decrease in frequency including basal orientations within 20° spread from ND. Compared to Fig. 4.5(a) (350°C), the frequency of grains with basal pole tilts larger than 50° (yellow/red orientations) showed an increase. A similar analysis for Mg-1Ce at 450°C is presented in Fig. 4.6(a)-(c). The basal pole tilt distribution in Fig. 4.6(c) shows a maximum at 20-25°. The average grain size measured was 12.5 μm (SE=0.77 μm).

![Figure 4.6](image.png)

Figure 4.6 (a) c-axis orientation maps with respect to ND and (b) local texture data of Mg-1Ce annealed at 450°C and (c) basal pole tilt distribution

4.4 DISCUSSION

4.4.1 SHEAR BANDING PHENOMENON IN PRESENCE OF REs

The rolling conditions produced a state of severe deformation thereby creating a shear banded microstructure. Couling and coworkers [52] were the first to observe such banding effect in certain rolled magnesium alloys and reported that the material inside these bands was soft and readily deformable. This softening behavior makes shear banding energetically favorable at high strains and this phenomenon has been often been referred to in the past as ‘texture softening’ [50] or ‘geometric softening’ [86]. The split
basal texture primarily arises due to alignment of the basal planes inside the shear bands, towards the direction of shear. From a crystallographic perspective the role of basal slip and tensile twinning is evident from the observed basal components in the as-rolled textures. Additional deformation mechanisms that can contribute to similar basal pole splitting in RD are: double twinning and $<c+a>$ pyramidal slip [90].

![Microstructure images](image)

**Figure 4.7** Optical microstructures after 50% rolling reduction for Mg-1Gd (a) and Mg-1Ce (b)

Rolling trials conducted at intermediate strains, wherein a thickness reduction of 50% was achieved, revealed profuse material twinning (c.f. Fig. 4.7), thus indicating that the shear bands possibly originated from clustering of first and second generation twins. Such twinned regions invariably have their basal poles reoriented along the shear direction. The reorientation renders the bands favorable for localized slip and hence gives rise to local work softening and plastic flow. This reorientation is driven by strain compatibility inside the band and is primarily responsible for the inherent heterogeneity of shear bands i.e. end to end (matrix-band-matrix) internal orientation gradient in these bands can be considerably large.

It has been proposed that shear banding in Mg–RE alloys is primarily related to solute effects [86, 91]. With considerably larger atomic radii than magnesium, REEs are expected to exert a much larger solute–dislocation interaction [58, 87], especially
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considering the tendency of solute REEs to form “short range ordering” of RE-RE solute pairs [92, 93]. This not only affects dislocation slip but also retards recovery and recrystallization kinetics, thereby promoting plastic instabilities in the material. A valid argument arises at this juncture regarding the performance of such material with respect to its formability, since localized shear often triggers void nucleation. In comparison to pure Mg, shear banding in Mg–RE alloys shows a much higher density and a more homogeneous distribution. This not only reduces the overall contribution of the usually “hard-oriented” matrix area, but also redistributes the imposed stress and strain due to a considerable increase in the total shear band–matrix interface area per unit volume. Correspondingly, this minimizes the undesirable strain incompatibilities and generates more homogeneous deformation.

Different REEs have naturally different physical and chemical properties, which can be expected to affect the shear banding phenomenon. By comparing the rolled microstructures of the two binary Mg–1Ce and Mg–1Gd alloys, it can be seen that the latter was much more prone to severe shear banding, which can be interpreted on the basis of the following aspects:

a) Solute drag: It has been previously established that the degree of solute drag increases with higher solute concentrations and lower solute diffusivities [94]. The solid solubility of Gd and Ce in magnesium show quite different characteristics, with the first exhibiting a large solubility of 4 at. % (~ 24 wt.%) at 535°C, and the latter displaying a very poor solid solubility of only 0.13 at.% (~0.74 wt.%) at ~590°C [95]. From a different perspective, Gd and Ce have significantly larger atomic weights and sizes than Mg, and are thus expected to have relatively low diffusivity rates. Since Ce will produce negligibly low solute concentrations (being primarily present as a secondary phase), Gd will satisfy both conditions required for exerting stronger solute drag.
b) **Solid solution characteristics**: Both Gd and Mg have a hcp crystal structure and similar electronegativities (Pauling scale). The difference in atomic radii between Gd and Mg is approx. 12.44% \[76\]. Hence, on the basis of the empirical rules for the formation of solid solution, proposed by Hume-Rothery, the Mg-1Gd alloy ought to form a ‘substitutional’ solid solution because the difference in atomic sizes of the two elements is less than 15%. This has already been established in various studies \[96-98\]. Since all lattice sites in a crystal normally lie on close-packed planes, Gd atoms will primarily replace Mg atoms on basal planes, producing a large positive misfit (12.44%) and a strong dislocation-solute interaction. It is assumed that sufficiently high misfit strains can decrease the dislocation width \( w \), and thereby, significantly increase the Peierls stress required for dislocation motion on basal planes, according to the Peierls-Nabarro relationship; \( \tau_p \sim \exp\left(-\frac{w}{b}\right) \). For an edge dislocation: \( w = \frac{d}{1-\nu} \), where \( d \) is the atomic spacing across the slip plane, and \( \nu \) is the Poisson ratio \[99\].

### 4.4.2 Recrystallization and Grain Growth in Presence of REs – Mg-1Gd vs. Mg-1Ce

The shear banded microstructure is very heterogeneous with large internal orientation spreads that can reach 5°/µm. This is possibly caused due to variation in the applied local strain during rolling and the necessity to maintain compatibility with a stiffer matrix. This severe strain heterogeneity in the microstructure prior to annealing can account for nucleation of grains with a wide spectrum of orientations, some of which are distinct from the typical deformation texture. In this regard, it is hence proposed that the observed “Blue” and “Green” recrystallized orientations in Fig. 4.3(a) are the result of plastic heterogeneity. Blue orientations being the ones located in the vicinity of ND are therefore presumed to be associated with less shear strains than Green orientations located further away from ND. EBSD results upon annealing at 350°C (when texture modification first took place) clearly demonstrate that the microstructure and associated
final texture were mainly composed of the off-basal fiber orientation of Green grains, which leads to the conclusion that these grains must have had a growth advantage over the basal-oriented Blue grains that were no more part of the annealing texture.

![c-axes tilts <15°](image)

![c-axes tilts ≥15°](image)

**Figure 4.8** c-axis tilt map for Mg-1Gd at 450°C classified into basal (c-axis tilt < 15°) and off-basal (c-axis tilt ≥ 15°) grains; basal and off-basal average grain sizes are further displayed

At the onset of recrystallization it is not clear which orientation has a higher nucleation rate. Assuming both Blue and Green orientations have equal chances of nucleating the aspect of nucleus growth becomes utterly important. As known, during recrystallization nearly strain-free nuclei develop in a deformed matrix and grow by means of thermally activated grain boundary migration driven by the relative difference in stored dislocation energies between the deformed and recrystallized regions. From that perspective, off-basal nuclei being associated with higher deformation (i.e. higher driving force $p$) should possess a greater migration rate $\nu$ ($\nu = m \ p$; $m$: grain boundary mobility), and thus grow faster than basal-oriented nuclei. When the freely growing grains are not surrounded completely by the deformed matrix (i.e. impingement, cf. Fig. 4.3(a)), further reduction in the systems free energy can only be achieved by reducing the total grain
boundary area. At this stage normal grain growth driven by boundary curvature sets in and the grain size difference criterion (i.e. larger grains will grow while smaller grains will be devoured) provides the statistically larger off-basal grains a significant growth advantage over their competitor basal grains. This is corroborated by the measured volume fractions of Blue (0° - 20° from ND) and Green grains (20° - 50° from ND) from Fig. 4.3(a) being 14% and 33% (of the whole microstructure), respectively. Corresponding lineal intercept measurements of the average grain size of both subsets of grains revealed a value of 3.4 µm (standard error SE = 0.04 µm) for Green grains vis-à-vis 2.7 µm (SE = 0.11 µm) for Blue ones. This slight difference of the average grain size was much increased at higher temperatures. At 450°C the average grain sizes of Blue and Green grain subsets were 30 µm (SE = 2.3 µm) and 41 µm (SE = 1.1 µm), and the area fractions 13% and 85% respectively (c.f. Fig. 4.8). In addition to the size advantage resulting from recrystallization, Green grains have a higher probability of being surrounded by high angle boundaries than Blue grains owing to their much broader orientation fiber (c.f. Figs. 4.5(a) and (b)). Having a higher number of mobile grain boundaries should further add to the favorable growth conditions of off-basal recrystallized grains.

Figure 4.9 Grain size variation with temperature for Mg-1Gd (in green) and Mg-1Ce (in blue) alloy (a); grain boundary pinning at 450°C due to Mg₁₋₂Ce particles.
Considering the Mg-1Ce alloy, the precipitation of secondary Mg\textsubscript{12}Ce phase can play a significant role in influencing the growth kinetics discussed above. Volume fraction measurements of the second phase carried out in the as-cast state, and after rolling and annealing at 400°C, revealed average values of 2.3% (± 0.003) and 5.3% (± 0.014), respectively. Figure 4.9(a) shows the relative grain coarsening rates for Mg-1Gd and Mg-1Ce, suggesting abated grain growth in the latter. During 80% single pass rolling of Mg-1Ce, the second phase precipitates will undergo severe fragmentation accompanied by a decrease in the average particle size (particle refinement) and an increase in the particle volume fraction. Both parameters will increase the Zener drag (pinning) effect on grain boundary migration, which will affect both recrystallization and grain growth during annealing and leads to retention of the basal deformation texture. Even at an elevated annealing temperature of 450°C (~ 0.78 T\textsubscript{m} (K)) the solubility of cerium in magnesium remains negligible and any particle coarsening effect did not seem strong enough to render Zener drag non-effective (c.f. Fig. 4.9(b)). Interestingly, Mg-1Ce alloy became capable of producing unique RE-annealing textures, like the ones shown here for the Mg-1Gd alloy, when 1% Zn and 0.6%Zr were added. Such observed benefits of non-REE additions will be treated in further detail in Chapter 6.

4.5 SUMMARY

The present chapter brings light to the following conclusions:

1) Both REs showed a strong propensity for shear banding along with significant delay in the onset of recrystallization.

2) Recrystallization behavior was predominantly governed by nucleation at shear bands. The nucleation events produced a wide variety of orientations with a fiber character about the sheet normal.

3) The Mg-1Gd alloy showed promising signs of texture modification. The texture change was found to be primarily arising from the deformation-recrystallization
transition. It was found that the contribution of nuclei growth on texture development was significantly dominant. The off-basal orientations showed much advanced growth behavior over the basal orientations, which was also observed during grain growth. Such favorable growth conditions during recrystallization were attributed to inherent deformation heterogeneities inside the shear bands. During grain growth the relative size difference between basal and off-basal recrystallized grains played a significant role.

4) The Mg-1Ce alloy contrastingly showed negligible texture changes, retaining the deformation texture accompanied with texture weakening. Such a behavior was attributed to the presence of fine distribution of fragmented $\text{Mg}_{12}\text{Ce}$ precipitates, which restricted any growth behavior.
In Chapter 4, the deformation and annealing textures of severely deformed binary Mg-RE alloys were investigated. It was found that the addition of REEs is not always sufficient to impart texture changes during deformation and recrystallization, and the level of recrystallization texture modification depends strongly on the choice of the REE and the annealing temperature. A significant texture change through annealing at temperatures above 300°C was depicted by Mg–1%Gd (wt.) alloy. On the other hand, Mg–1%Ce (wt.) indicated negligible qualitative texture changes, thereby, retaining the deformation texture with moderate drop in texture intensity values for annealing treatments above 300°C. SBN of recrystallization was found to play a critical role in generating a wide spectrum of recrystallization nuclei that displayed a selective growth behavior giving rise to the formation of new annealing textures, as mentioned earlier.

In order to obtain a complete mechanistic understanding of deformation and recrystallization related texture evolution in Mg-REEs, it is necessary to also understand the influence of REE alloying on the formation of twinning and the related recrystallization behavior.

This chapter outlines the twinning behavior observed in Mg-REEs and the corresponding annealing response. The influence of twins on the deformation texture has been described in details by means of both experimental investigations and crystal plasticity simulations. Section 5.1 describes the initial material conditions and the subsequent plane strain compression tests. Sections 5.2 to 5.4 overviews the results obtained from bulk and local texture and microstructure characterization performed for the various deformed and annealed states. Section 5.5 briefly entails the details of the crystal plasticity model employed to simulate plane strain compression and the various
input parameters chosen for the present study. Section 5.6 discusses the twin induced deformation behavior in Mg-REEs and the possible REE related recrystallization and grain growth mechanisms active during annealing treatments. The highlights of the chapters are summarized in Section 5.7.

5.1 INITIAL CONDITIONS

Cast Mg-RE alloys were subjected to multi-pass hot rolling treatment, followed by recrystallization annealing as described in Section 3.2.1. Since different REEs have a different potential for texture modification, different annealing conditions were chosen for each alloy. Thus, Mg-1Ce was annealed at 400°C for 60 mins and Mg-1Gd was annealed at 350°C for 5 mins, both followed by rapid quenching in water. The rolled and annealed sheets were further subjected to room temperature plane strain compression tests as per Section 3.2.2.

Figs. 5.1(a) and (b) display the microstructures and starting textures (corresponding to TTC and IPC) for Mg-1Ce and Mg-1Gd prior to PSC deformation. Both alloys revealed fully recrystallized microstructures with equiaxed grain shape. The measured average grain sizes with the lineal intercept method were 25.1 µm (S.E. = 1.1 µm) for Mg-1Ce and 19.3 µm (S.E. = 0.65 µm) for Mg-1Gd. For the Mg-1Ce alloy the thermomechanical treatment produced a weak basal-type sheet texture (maximum ~ 3 MRD: multiples of random distribution) with an asymmetric broadening of the basal peak towards the sheet transverse direction ‘TD’. On the other hand, the rolled and annealed Mg-1Gd sheet showed a sharper basal-type texture with a tilting of the basal poles from the ND towards the RD.
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Figure 5.1 Optical microstructures after rolling and recrystallization annealing for Mg-1Ce (a) and Mg-1Gd (b); starting XRD textures for PSC deformation for Mg-1Gd (a) and Mg-1Ce (b) are additionally displayed. PSC flow curves for Mg-1Ce (c) and Mg-1Gd (d)

5.2 Plane strain compression flow behavior

Figs. 5.1(c) and (d) show the obtained stress-strain curves for Mg-1Ce and Mg-1Gd specimens for both TTC and IPC modes. The initial ‘non-linearity’ observed in the curves is possibly a result of compliance effects between the compression plate and the sample. The final strain value selected for the IPC samples marked the onset of the typical strain hardening rate increase caused by extension twinning in magnesium [33, 100].
Figure 5.2 Bulk textures and microstructures for Mg-1Ce in IPC (a), Mg-1Gd in IPC (b), Mg-1Gd in TTC (c) and Mg-1Ce in TTC (d)

The corresponding final stress values for both materials were ~ 225 MPa (Mg-1Ce) and ~ 250 MPa (Mg-1Gd). For the TTC samples the final strain chosen between 13% and 14% corresponded to the peak stress of the respective flow curve (~ 440 MPa for Mg-1Ce and ~ 460 MPa for Mg-1Gd). At low deformation strains below 5% the strain hardening
rate for the IPC samples was slightly greater than for the TTC samples for both Mg-1Ce and Mg-1Gd alloys.

5.3 **DEFORMATION AND ANNEALING TEXTURE AND MICROSTRUCTURES**

5.3.1 **IN-PLANE COMPRESSION**

Figures 5.2(a) and (b) show the optical microstructures and XRD bulk textures for Mg-1Ce and Mg-1Gd specimens after PSC deformation at ambient temperature to $\varepsilon = 0.08$ and annealing at 300°C and 450°C for 60 min, respectively. For this loading orientation compression was applied in the RD, almost perpendicular to the c-axis of the crystal (Fig. 5.1(c)). From the (0002) recalculated complete pole figures of the deformed Mg-1Ce specimens it is seen that the basal poles do not remain aligned with the LD but rather rotate towards the CD, in the center of the pole figure (c.f. Fig. 5.2(a)) indicating an emergence of a new basal component. On the other hand, the as-deformed texture for Mg-1Gd (c.f. Fig 5.2(b)) produced maximum texture intensities near LD and secondary components tilted approx. 20-30° away from LD towards CD. Additionally, weaker components tilted towards TD were also indicated by the XRD pole figure. Interestingly, bulk texture measurements for Mg-1Gd. did not reveal a basal component in the pole figures shown in Fig. 5.2(b).

The microstructure of the as-deformed Mg-1Ce material was relatively coarse grained and showed profuse deformation twinning. For the Mg-1Gd material the deformation microstructure seemed more heterogeneous with finer grains and a lower area fraction of deformation twins. Annealing treatments at 300°C and 450°C gave rise to considerable texture and microstructure changes. For the Mg-1Ce material (Fig. 5.2(a)) the annealing textures shown in the pole figures showed a slight increase in intensity and no basal component as compared to the starting texture. At 300°C remnants of the deformation microstructure were still present in the form of twinned grains. The rest of
the annealed microstructure was recovered or recrystallized. The 450°C anneal resulted in a microstructure containing recovered and/or recrystallized grains with fine and coarse grain sizes. The optical micrograph also revealed a considerable increase in the number of large particles (1 – 10 µm) in the microstructure. For the Mg-1Gd material (Fig. 5.2(b)), 300°C and 450°C anneals resulted in texture weakening with the main texture components remaining close to LD (i.e. c-axis more or less aligned with the longitudinal direction of the channel-die). It was also observed that with increasing annealing temperature the texture spread between LD and CD had increased. After annealing at 300°C recrystallization was not evident and the microstructure appeared similar to the one after deformation despite some likely recovery. At 450°C, a heterogeneous annealing microstructure similar to the Mg-1Ce material was observed, with comparable proportions of fine and large grains. Mg-1Gd produced an overall larger grain size due to the absence of second phase particles that could restrict grain growth by Zener pinning.

5.3.2 THROUGH-THICKNESS COMPRESSION

For TTC deformation up to $\varepsilon = -0.13$ the compression axis was parallel to the through thickness of the sheet, and thus virtually parallel to the c-axes of the majority of grains. The TTC texture of the Mg-1Gd material (Fig. 5.2(c)) showed a considerable increase in strength as compared to the initial texture (Fig. 5.1(a)). After annealing, notable texture weakening was observed in the pole figures with a decrease in maximum basal pole intensity to ~8 and ~3 multiples of a random distribution (MRD) at 300°C and 450°C, respectively. With respect to the pronounced weakening of the texture upon the 450°C anneal, it is important to note that for conventional Mg alloy sheets the strong basal texture induced by rolling is usually not randomized by recrystallization and even tends to strengthen during grain growth annealing [9, 101]. The other alloy; Mg-1Ce (Fig. 5.2(d)) showed a much weaker TTC texture (~ 3 MRD) with slight texture modification during subsequent annealing at 300°C. At 450°C the main texture
component with the highest basal pole intensity was clearly rotated away from ND towards the RD by ~35°. Being relatively weak, all Mg-1Ce textures (deformed and annealed) demonstrated a wide spread of basal poles about the maximum intensity.

The optical microstructure upon TTC deformation of the Mg-1Gd alloy revealed what appears to be a highly deformed microstructure despite a low applied deformation strain. This was not observed in case of the Mg1Ce alloy, for which the TTC microstructure seemed less deformed and it was still easy to distinguish individual grains and grain boundaries. Although not clearly visible in the micrographs for the given magnification, deformation twinning was evident in both TTC microstructures. Given the type of loading during TTC most of these twins are expected to be compression and double twins (i.e. secondary tension twins within primary compression twins). The morphological difference between the IPC and the TTC twins can be easily detected by comparing the corresponding optical micrographs (Fig. 5.2(a) vs. Figs. 5.2(c) and (d)). Obviously, the IPC twins with their thick and well-developed feature differ from their TTC counterparts displaying thin lenticular shape etched black in color. The types of these twins will be discussed later in the context of the EBSD results. In terms of annealing microstructure development at 300°C, the microstructure for Mg-1Ce showed a similar development to that seen in the IPC case, with primarily extended recovery based microstructural evolution. For the Mg1Gd alloy, partial recrystallization occurred but the microstructure remained mainly unrecrystallized. Annealing at 450°C produced fully recrystallized microstructures that obviously underwent significant grain growth.

5.4 EBSD CHARACTERIZATION

For statistical orientation analysis of deformed and recrystallized grains and characterization of twin types and fractions EBSD measurements were performed on several deformed and annealed specimens. The aim of the measurements was to
understand the microstructural evolution during deformation, recovery and recrystallization, and grain growth.

5.4.1 EBSD ANALYSIS IPC AND RX ANNEALING

Figs 5.3 and 5.4 show EBSD data obtained for Mg-1Gd after 8% deformation. The original indexing fraction for the raw EBSD data was 54%, which was improved to 70% by careful noise reduction applying a minimum of 5 indexed nearest neighbors. The orientation map in Fig. 5.3(a) is presented in terms of inverse pole figure (IPF) coloring with respect to the compression direction. The characterization of twins in the EBSD map, separately shown in Fig. 5.4(a), was done on the basis of the characteristic misorientation angles and rotation axes (given in minimum angle-axis pairs) of the most frequently observed twin types in Mg alloys, allowing an angular deviation of ± 6°. The identified twins in different colors revealed {10\overline{1}2} extension twins (highlighted in red), {10\overline{1}1} compression twins (blue) as well as {10\overline{1}1} – {10\overline{1}2} double twins (green). Non-indexed areas correlating with high local strains are displayed in black. The IPF map shows two microstructure regimes with very different features: The ‘left’ portion of the map appeared heavily deformed with small, fragmented grains and high density of very small twins, whereas the ‘right’ part of the map comprised a few large deformed matrix grains of the < 10\overline{1}0 > orientation with multiple twins. Tension twinning in the blue-colored parent revealed two twin variants highlighted in ‘red’ and ‘yellow-green’. Tension twins occurring inside the green-colored parent grains with < 11\overline{2}0 > \parallel CD orientation are colored in ‘reddish orange’. Fig. 5.3(b) shows basal pole figures with single orientation scatter data and recalculated contour data, along with the calculated ideal orientations of \{10\overline{1}2\} tensile, \{10\overline{1}1\} compression and \{10\overline{1}1\} – \{10\overline{1}2\} double twins that can form in the matrix during IPC deformation. Although loading in IPC should only induce extension twinning, the other twin types were also considered because their respective orientations seemed to be part of the EBSD deformation texture with
multiple basal and off-basal components. Tensile twin variants originating from the initial matrix orientation with \((\varphi_1, \Phi, \varphi_2) = (90^\circ, 90^\circ, 0^\circ/30^\circ)\) are represented by ‘blue’ dots for parent grains with \(< 10\bar{1}0 > ||CD\) and ‘light green’ dots for different parent grains with\(< 11\bar{2}0 > ||CD\). Compression twin variants that can form in an LD matrix grain are additionally displayed in ‘brown’ and ‘violet’ colors that link each set of compression twin variants to its respective parent orientation. From all the possible secondary twin variants, only those variants are shown that are associated with double twinning (shown in open symbols) with a net reorientation of the basal planes by 38° around a specific \(< 11\bar{2}0 >\) axis. The illustration uses different symbols that link each secondary twin variant to its respective primary twin.

**Figure 5.3** Inverse pole figure (IPF) mapping for Mg-1Gd deformed in IPC (a); (0002) single orientation scatter and recalculated EBSD pole figures with simulated \{10\bar{1}2\} tension, \{10\overline{1}1\} compression and \{10\bar{1}1\}-\{10\bar{1}2\} double twin orientations with respect to compression along RD (b)

On comparison with the calculated twin orientations in the pole figure representation, it can be seen that a superposition of more than one set of twin variants generates an orientation spread between the CD and TD, which explains the experimental texture component residing between the mentioned pole figure axes (c.f. Fig. 5.3(b)).

Fig. 5.4(a) presents an IQ map with highlighted twin boundaries and grains with an orientation spread (GOS) up to 1°.
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Figure 5.4 IQ map for as-deformed Mg-1Gd in IPC with $\{\overline{1}0\overline{1}2\}$ tension twin boundaries in red, $\{10\overline{1}1\}$ compression twin boundaries in blue and $\{10\overline{1}1\}-\{10\overline{1}2\}$ double twin boundaries in green (a); IPF map of highlighted region shown in (a) with highlighted twin boundaries and orientations marked in the pole figure, slip trace analysis in the twin vicinity and experimentally measured twinning shear, measured twin volume fraction (b)

The low GOS regions highlighted in the IQ map indicate numerous instances of fine recovered grains, forming likely from sub-grain boundary migration facilitated by simultaneous slip activity within the compression and double twinned regions. Fig. 5.4(b) displays an IPF map of an area of interest from the IQ map with explicit analysis of present twin types and the resulting orientation changes.

Figures 5.5 and 5.6 show the EBSD data acquired for the Mg-1Gd alloy at partially and fully recrystallized states corresponding to 350°C and 450°C anneals. The original indexing rates were 75% and 91%, respectively. Fig 5.5(a) shows an IPF mapping after annealing at 350 °C, along with corresponding EBSD and bulk texture data. The mapping reveals a partially recrystallized microstructure. The recrystallized grains seem to appear in bands or vein like patterns, whereas un-recrystallized regions consist primarily of large deformed grains (blue) with twinned parts (red) identified as tension twins. The (0002) recalculated pole figure corresponding to the EBSD data reveals two well defined texture components described by a spread of orientations extending from LD towards CD and a
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relatively weaker basal fiber, corresponding to the red tension twinned regions, respectively.

Figure 5.5 IPF mapping of Mg-1Gd in IPC, annealed at 350°C along with XRD and EBSD texture data (a), Recrystallized compression twin band in IPF coloring with unit cell representation and orientation map showing twin-matrix misorientation (b); GOS map for mapping shown in (a) along with GOS demarcation for recrystallized and deformed grains (c); (0002) single orientation scatter for recrystallized and deformed subsets, highlighted region in gray traces the deformation fiber between LD and CD (d)

In comparison with the XRD texture at 350°C, a similar spread of orientations from LD to CD is observed. The basal orientation, visible in the center of the EBSD pole figure does not appear in the bulk texture due to the overall low volume fraction of tension twins. Fig. 5.5(b) shows a magnified view of an area of interest highlighted in Fig. 5.5(a), representing a band of recrystallized grains (shown in IPF coloring). The shown image displays the orientations of the individual grains within the band along with their misorientation relationships with the neighboring, deformed matrix. As seen, the
majority of the recrystallized grains exhibit a boundary misorientation within a range of 56° ± 6° and a misorientation axis close to <1120>, thus suggesting that these recrystallized bands might have originated from {1011} compression twins. Fig. 5.5(c) represents a GOS map of the same measurement shown in Fig. 5.5(a), wherein the recrystallized bands display a GOS value ≤1° [102]. By contrast, unrecrystallized regions including the {1012} tension twins displayed an average GOS value ~5°, with the regions near twin intersections revealing orientation spreads as high as 10° -15°. Fig. 5.5(d) displays the single orientation scatter pole figures for the recrystallized and deformed subsets, demarcated on the basis of the GOS values (c.f. Fig. 5.5(c)), in IPF coloring. The aforementioned texture spread from LD to CD seen in the recalculated pole figures (c.f. Fig. 5.5(a)) nicely correlates with scatter data corresponding to the deformed subset (c.f. Fig. 5.5(d)), forming a prismatic fiber about an axis denoted by $R_{EX_{fiber}}$. Unlike the deformed subset, the recrystallized orientations reveal faint coincidence with the highlighted fiber, with majority of orientations lying outside the periphery of the marked region (shown in gray). The deformed subset additionally indicates a secondary basal component corresponding to the red tension twins.

At 450 °C, the collected EBSD data (c.f. Fig. 5.6) reveals a fully recrystallized microstructure with evidence of significant grain growth. Fig. 5.6(a) represents the microstructure in terms of a SF map for basal slip under compressive loading along CD. For the stress state, a back-stress $\sigma_{TD}=0.5\sigma_{CD}$ was considered. Fig. 5.6(b) plots the grain number fraction as a function of basal slip SF values. The SF values were classified into ‘high’ (>0.3) and ‘low’ (< 0.3) [103] and the corresponding average grain sizes were 95.7 µm (S.E = 0.68 µm) for the ‘high’, and 75 µm (S.E = 0.66 µm) for the ‘low’ SF grains. The average grain size for all the grains was 89.17 µm (S.E = 0.65 µm) and the corresponding grain size distribution is shown in Fig. 5.6(c).
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The orientation scatter data in Fig. 5.6(b) reveals a dominance of the ‘high’ SF grain orientations, evident from a greater density of basal poles inside the highlighted ‘high’ SF region. The recalculated (0002) pole figure shows that the texture components with intensity maxima are associated with these high SF grains. The pole figure also shows a good agreement with XRD macrotexture data. Fig. 5.6(d) shows a GOS map for the same area in Fig. 5.6(a), indicating internal orientation spread values much lower than 1° corresponding well with the measured range of GOS values for recrystallized grains at 350 °C.
EBSD data for the Mg-1Ce alloy in the as-deformed state is depicted in Fig. 5.7. The original indexing fraction was 80%, which was improved to 96% after applying careful cleaning with the noise reduction function explained earlier. Non-indexed regions are displayed in black and from their morphology they most likely correspond to the Mg\textsubscript{12}Ce second phase. Figs. 5.7(a) and (b) show an EBSD microstructure (IPF and SF for basal slip) with the IQ indexing used as the background. (0002) pole figure data is also provided, which seems to correlate well with the macrotexture determined by XRD. Fig. 5.7(c) additionally presents the relative texture contribution of the twinned fraction as opposed to the texture of parent grains.
Figure 5.8 IPF map for Mg-1Ce in IPC, annealed at 300° C along with analysis of twins in individual grains (a); single orientation scatter and (0002) recalculated pole figures (b); Basal SF distribution (c); IPF mapping showing PSN sites and particle-twin nucleation sites (d)

The twin boundaries, outlined in white in Fig. 5.7(b), were identified as \{10\overline{1}2\} tension twin boundaries. From the IPF map it can be seen that the blue parent orientations give rise to mostly red twins that assume a hard orientation characterized by the crystallographic c-axis being almost parallel to the CD. By contrast, the green parent grains produce softer twin orientations depicted in yellow/orange. As a result, the texture resulting from these two twin types have the majority of c-axes tilted by \(~20°\) from the compression axis (c.f. Fig. 5.7(c)). It should be noted that in the current data of Mg-1Ce no instances of compression or double twins were visible.

The annealing microstructures of the Mg-1Ce alloy, as determined by EBSD are reproduced in Fig. 5.8 (300°C) and Fig. 5.9 (450°C). It can be seen from Fig. 5.8 that the microstructural characteristics, unlike the counterpart Mg-1Gd alloy, retain the features
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that were visible in the as-deformed state. Regions of interest highlighted in Fig. 5.8(a) (IPF map) show different \{10\overline{1}2\} twin variants originating from the same parent grains. From the corresponding (0002) pole figures, these twin variants are separated by an angle between 55° and 60°, which corresponds to a characteristic, ideal misorientation relationship of 60°< 10\overline{1}0 > [104]. The microtexture of the annealed sample given in Fig. 5.8(b) showed a broad texture spread with the maximum basal pole density being located between LD and CD. This soft texture gave rise to a high average SF for basal slip of 0.345 (c.f. Fig. 5.8(c)). With respect to recrystallization, Fig. 5.8(d) reveals several nucleation sites of recrystallized grains with random orientations appearing primarily around particles, which is a very well-documented recrystallization mechanism, known as PSN [50, 66].

The EBSD microstructure after 450°C annealing (Fig. 5.9) revealed a fully recrystallized structure with obvious indications of grain growth. Non-indexed regions correlate with the second phase particles and appear distributed more or less uniformly at grain boundaries and within grain interiors. The shown IPF map and corresponding microtexture data (Fig. 5.9(a)) indicate a predominance of off-basal orientations distributed between LD and CD. A secondary basal texture component was also present, in consonance with the textures obtained from XRD. The estimated average grain size (Fig. 5.9(b)) was 54.3 µm (S.E = 0.57 µm). The SF map in Fig. 5.9(c) indicates a further increase in the overall average SF value for basal slip; SF = 0.385 at 450°C vis-à-vis SF = 0.345 at 300°C.

5.4.2 EBSD ANALYSIS AFTER TTC AND RX ANNEALING

Fig. 5.10 displays the EBSD measurement results obtained from Mg-1Gd alloy after deformation and annealing at 300°C. Due to a relatively larger plastic strain induced during through thickness compression, EBSD measurements of the as-deformed conditions rendered very low index fractions and are therefore not presented here.
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Figure 5.9 IPF map for Mg-1Ce in IPC, annealed at 450°C along with single orientation scatter and (0002) recalculated pole figures (a); Grain size distribution for Mg-1Ce at 450°C (b); Basal SF distribution (c)

The original indexing fraction for the displayed data in Fig. 5.10 was 59%, which was improved to 78% after noise reduction. Fig. 5.10(a) shows an IPF map with the IQ indexing used as the background. The microstructure measured was partially recrystallized, consisting for the most part of heavily distorted regions with a low index quality and large orientation gradients. The corresponding microtexture exhibited a single peak basal orientation with appreciable spread in the LD. Recrystallized grains were observed to form at matrix boundaries or within regions that had elongated shapes similar to those of twin bands and were bounded by two matrix grains of identical orientation (Fig. 5.10(b)).
The misorientation data for the recrystallized grains and their adjoining matrix grains shows that even though most of the twin boundaries have lost their character after annealing, the new grains can still be associated in an approximate way with their respective parent compression and double twins.

The other magnified image of selected region “2” is an example of new grains that formed at the initial grain boundaries of deformed regions. The orientations associated with the new grains do not seem to preserve the c-axis orientations of their...
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matrix grain hosts, which mean that their impact on randomizing the deformation texture can be significant once the fraction recrystallized during annealing becomes sufficiently high. Fig. 5.10(c) displays SF distribution for basal slip associated with recrystallized and deformed grains based on the average grain size and GOS value. For recrystallized grains, the data showed a peak at an SF value of 0.48, as compared to a much lower peak value of 0.18 for the deformed grains. To evaluate the role of twinning recrystallization in generating new, soft orientations with high SF for basal slip, Fig. 5.10(d) shows a basal pole figure representation of the 12 \{10\overline{1}1\} primary twins (in closed symbols) and corresponding secondary twin variants that produce a misorientation of 38° from the parent about an axis \langle11\overline{2}0\rangle (in open symbols) during compressive loading of a matrix assuming a basal fiber orientation; \((\varphi_1, \Phi, \varphi_2) = (0°, 0°, 0°/30°)\).

Figure 5.11: IPF mapping of Mg-1Ce in TTC, annealed at 300° C along with single orientation scatter and (0002) recalculated EBSD pole figures (a); Basal SF mapping (b); Analysis of compression and double twin orientations corresponding to regions 1 and 2 (c); PSN evidence seen in TTC mode and corresponding texture in terms of recalculated IPF contouring.
By comparing the calculated twin orientations in the pole figure representation with the experimentally determined orientation distribution of basal poles shown in Fig. 5.10(c) it becomes obvious that the soft orientations, observed mostly for the recrystallized grains, are associated with the primary and secondary twin variants located within the highlighted area in the simulated pole figure representation. It can be further noted that the orientations in the EBSD pole figure of deformed and recrystallized grains correspond to those compression twin variants with a high SF (Fig. 5.10(d)).

Figure 5.12 IQ map showing tension twin boundaries and de-/re-twinned boundaries in red and yellow respectively (a); Misorientation profile across de-/re-twinned boundaries (b); Unit cell representation showing lattice orientations in matrix, twins and de-twinned regions (c)
Similar EBSD measurements presented in Fig. 5.11 were acquired for the Mg-1Ce specimen annealed at 300°C, post TTC deformation. Figs. 5.11(a) and (b) present IPF and basal slip SF maps (IQ index as the background) showing a significant fraction of Mg$_{12}$Ce particles and unrecrystallized extension twins outlined in white. After annealing the sample seemed to have a weak microtexture that can facilitate glide on the basal planes. The calculated average SF for basal slip was 0.38. A few instances of compression and double twinning were seen, for example in regions 1 and 2 (Fig. 5.11(b)). Region 1 depicts two intersecting twins outlined in green (double twin DT1) and blue (compression twin CT2) that in part underwent tension twinning resulting double twin DT2.

The formation of compression twins on the $\{10\bar{1}1\}$ planes of the parent grain P, results in a reorientation of the basal planes by 56º. Out of the six possible $\{10\bar{1}2\}$ secondary twin variants for CT2 and CT (see regions 2), only one variant was observed, which led to double twinning with a net reorientation of the basal planes by 38º around a specific $<12\bar{1}0>$ axis, relative to the parent orientation P.

Fig. 5.11(d) is another example of PSN recrystallization taking place in the vicinity of Mg$_{12}$Ce particles and giving rise to new orientations relative to the matrix orientation (cf. the color coding and the new intensities in Fig. 5.11(d)). It should be noted, that in some parts of the microstructure low angle boundaries (highlighted in yellow) with $<12\bar{1}0>$ misorientation axis and 5º to 9º misorientation angles were related to some extension twins that were partially removed from the microstructure (Figs. 5.12(a)-(c)). This is discussed later in context of a re-twinning (or de-twinning) process during unloading causing reversal of the texture that developed during twinning.
After 450°C annealing, the microstructure of both Mg-1Ce and Mg-1Gd seemed to undergo grain growth after recovery or recrystallization. The EBSD mappings in terms of SF for basal slip revealed that both alloys had a similar texture and microstructure (c.f. Figs. 5.13(a) and (b)). The average grain size for the Mg-1Gd alloy was somewhat higher than that for the Mg-1Ce (~68 µm vs. ~56 µm) due to different grain growth kinetics (c.f. Fig. 5.13). The average SF values for both alloys were quite similar (equal to ~0.36), and the determined microtextures corresponded well with the bulk textures determined by XRD. The textures after grain growth remained more or less basal with asymmetric tilting of the basal poles from the through thickness direction towards the longitudinal and transverse directions of the channel-die.

Figure 5.13 Basal SF map of Mg-1Gd in TTC, annealed at 450°C along with EBSD texture data. Basal SF distribution (a); Basal SF map of Mg-1Ce in TTC, annealed at 450°C along with EBSD texture data. Basal SF distribution (b)
5.5 VPSC MODELLING OF TWINNING INDUCED DEFORMATION BEHAVIOR

The viscoplastic self-consistent (VPSC) model [105] was utilized to simulate the experimentally obtained deformation textures after plane strain compression of both alloys. This was done in order to understand the contribution of twinning and slip modes to the texture development in respect of the loading orientation.

Table 5.1 Relative CRSS, hardening values and twinning parameters implemented in the VPSC model

a) In-plane compression (Modeling parameters)

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<th>$\tau_1$</th>
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b) Through-thickness compression (Modeling parameters)

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<td>Pyramidal $&lt;c+a&gt;$</td>
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<td>60</td>
<td>270</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>{10\bar{1}2} Twin</td>
<td>40</td>
<td>20</td>
<td>160</td>
<td>0</td>
<td>0.1</td>
<td>0.5</td>
</tr>
<tr>
<td>{10\bar{1}1} Twin</td>
<td>60</td>
<td>50</td>
<td>230</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mg-1Ce</th>
<th>$\tau_0$</th>
<th>$\tau_1$</th>
<th>$\theta_0$</th>
<th>$\theta_1$</th>
<th>$A_{nuc}$</th>
<th>$A_{sat}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basal</td>
<td>18</td>
<td>2</td>
<td>260</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyramidal $&lt;c+a&gt;$</td>
<td>11</td>
<td>3</td>
<td>280</td>
<td>0</td>
<td></td>
<td></td>
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<tr>
<td>{10\bar{1}2} Twin</td>
<td>8</td>
<td>1</td>
<td>310</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>{10\bar{1}1} Twin</td>
<td>66</td>
<td>43</td>
<td>710</td>
<td>0</td>
<td>0.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>
A detailed description of the VPSC model can be found in [105, 106] but in summary the viscoplastic formulation of the model describes an inhomogeneous ellipsoidal inclusion (grain) embedded in a homogeneous effective medium that represents the averaged properties of all other grains. Being self-consistent, the model is able to take into account the inherent anisotropy during polycrystal deformation, which makes it advantageous for polycrystal plasticity simulation of low-symmetry crystal structures, such as HCP metals. Additionally, the implementation of different hardening schemes allows accurate prediction of the deformation behavior of hard and soft slip systems, such that the latter can accommodate larger deformation strains during the simulation. This is particularly useful when investigating the influence of alloying elements on the relative activities of different deformation modes during plastic deformation.

In the current study the input texture was obtained by means of discretizing the experimental initial textures, obtained after rolling and annealing, into 8000 grains of the same weight. The discretization procedure was done in MTEX. An inverse rate sensitivity of 20 and an ‘effective’ homogenization scheme ($n_{\text{eff}} = 10$) was used to account for the grain-matrix interaction. This implementation yields a condition between a full constraint Taylor deformation ($n_{\text{eff}} \to 1$) and a non-constraint Sachs deformation condition ($n_{\text{eff}} \to \infty$). Calculations were conducted for ideal plane strain compression with a prescribed strain rate (velocity gradient) of 0.01 s$^{-1}$. The degree of strain increment with each step was chosen as 0.02 von Mises equivalent strain. The allowed deformation modes were $\{0001\} < 11\bar{2}0 >$ basal slip, $\{11\bar{2}2\} < \bar{1}\bar{1}23 >$ pyramidal slip, $\{10\bar{1}2\} < 10\bar{1}1 >$ extension and $\{10\bar{1}1\} < 10\bar{1}2 >$ compression twinning. $\{1\bar{1}00\} < 11\bar{2}0 >$ prismatic slip was not considered in the simulations due to its hard activation during through thickness deformation and the lateral constraints imposed by the channel-die walls during in-plane deformation. In addition, secondary $\{10\bar{1}2\}$ extension twinning was chosen in combination with $\{10\bar{1}1\}$ compression twinning, which allows the model to
activate it once a grain is already reoriented by primary compression twinning. Since compression and double twinning were experimentally observed, such implementation in the model is very helpful to assess their role in the deformation texture evolution.

A modified Voce empirical hardening scheme was employed for each individual deformation mode in individual grains. The Voce hardening equation is characterized by the evolution of threshold stress with accumulated shear strain in each grain, and is given as,

$$\tilde{t}^s = \tau_0^s + (\tau_1^s + \theta_1^s \Gamma) \left\{ 1 - \exp \left( -\frac{\theta_0^s \Gamma}{\tau_1^s} \right) \right\} \ldots (5.1)$$

where, $\tau_0^s, \tau_1^s, \theta_0^s$ and $\theta_1^s$ are the initial CRSS, scaling stress for work hardening, initial hardening rate and the hardening rate at the final strain for a deformation mode ‘s’ (slip + twin), respectively. $\Gamma$ is the accumulated shear in a grain. For simplicity, $\theta_1^s$ was assumed to be zero for all deformation modes. Basal slip was chosen as a reference deformation mode. The parameters for the other deformation modes were then correspondingly adjusted relative to the reference mode, i.e. basal slip. Table 5.1 outlines the relative CRSS and hardening parameters for each deformation mode used in the present study. Latent hardening was assumed to be equivalent to self-hardening for all deformation modes. Reorientation of grains by twinning was done by the predominant twin reorientation (PTR) scheme [105] defined implicitly in the model. The PTR scheme reorients the grain if the volume fraction of twins ($f_{\text{grain}}$) in a particular grain exceeds a certain threshold fraction ($f_{\text{threshold}}$) given as,

$$f_{\text{threshold}} = A^{\text{nuc}} + A^{\text{sat}} \left( \frac{f_{\text{eff}}}{f_{\text{tot}}} \right) \ldots (5.2)$$

where, $A^{\text{nuc}}$ and $A^{\text{sat}}$ are input parameters describing the minimum threshold fraction for reorienting a grain by twinning and the maximum threshold volume fraction the twin covers in the grain. Thus the total volume fraction of twins in a twinned grain would be equivalent to $A^{\text{nuc}} + A^{\text{sat}}$. $f_{\text{eff}}$ and $f_{\text{tot}}$ denote the effective twin volume fraction
(volume fraction of already reoriented grains) and the accumulated twin volume fraction (same as the experimentally measured twin volume fraction) for the twinning system ‘t’.

Fig. 5.14 represents the simulated textures along with the corresponding slip mode activities and evolution of twin volume fractions with increasing strain, obtained from the VPSC model. The simulated textures show a reasonable agreement with the experimental textures. A more detailed discussion regarding the physical significance of the simulation results will be presented in the forthcoming section.

![Image of VPSC simulations showing slip and twin activities, twin volume fractions and volume fraction of primary and secondary twinning events for Mg-1Gd in TTC (a) and IPC (b), Mg-1Ce in TTC (c) and IPC (d)]
5.6 DISCUSSION

In order to achieve a mechanistic understanding of the rare-earth related texture modification phenomenon in REE-containing Mg sheets, it is important to understand the twinning response under various loading conditions that trigger different twin types, and determine whether twinning recrystallization during annealing treatments contributes in some part to the RE-texture modification effect seen after shear band recrystallization of the same materials investigated in Chapter 4. The results presented have revealed that the two alloys have different deformation characteristics at ambient temperature and low strains, which influence their microstructure development during subsequent annealing. In the following, the results are discussed in terms of observed and simulated deformation modes during TTC and IPC loading, and the mechanisms of texture formation during recrystallization and grain growth annealing.

5.6.1 TWINSING BEHAVIOR AND VARIANT SELECTION IN Mg-REs

5.6.1.1 SOLID SOLUTION MAGNESIUM-GADOLINIUM ALLOY

(A) IPC MODE

Loading this alloy sheet in IPC resulted in little extension twinning despite the fact that compression was applied parallel to the basal direction of grains, as per the initial sheet texture after rolling and annealing. Usually for pure Mg or AZ31 Mg alloy, compression loading normal to the $c$-axis reveals prolific $\{10\bar{1}2\}$ twinning after small increments of strain, and twin reorientation results in a characteristic 86° reorientation of the basal pole to an orientation nearly aligned with the loading axis [107]. Such drastic change in the crystallographic orientation was not observed in the IPC bulk texture determined by XRD, where most of the grains had their $c$-axes aligned with LD with a spread of about 20° about TD and CD. On comparison with the EBSD orientation maps and microtextures displayed in Figs. 5.3 and 5.4, it can be seen that different types of deformation twinning occurred. Characterized by their misorientation angles and rotation
axes, these twins were identified as \{10\overline{1}2\} extension, \{10\overline{1}1\} compression and \{10\overline{1}2\}-\{10\overline{1}1\} double twins. All twin types appeared with a thin and elongated lenticular structure. Inside many twinned grains of a large size, more than one set of twins of different orientations were detected. Although a given grain could theoretically twin on any of the six \{10\overline{1}2\} planes, only those twins nucleate where the resolved shear stress on the habit plane and in the shear direction exceeds a critical value [50, 107]. Thus it appears that two extension twin variants (red and green) formed in particular matrix grains because their resolved shear stresses exceeded the critical value. Intuitively, it can be expected that the twin variant with the highest SF will be selected first, which is a rule that has been observed to be obeyed in numerous studies of extension twinning in Mg alloys [108]. For compression in the \langle 10\overline{1}0 \rangle direction, activated twinning is generally dominated by one variant pair with an ideal SF value of 0.499 that consumes most of the microstructure before the other, lower SF twins are nucleated. However, in the current work, a different variant selection behavior was observed. Twinned matrix grains revealed the presence of both high (red) and low (green) SF twins in ‘comparable’ volume fractions. Figs. 5.3 and 5.4 show examples, where the low SF twins (SF= 0.24) are even of larger size, and thus occupy a larger portion of the matrix grain than the high SF twins. It should be noted, that this behavior is not entirely a ‘non-Schmid’ behavior that applies particularly to the formation of compression and double twins [109] in Mg alloys since the high SF twins were ‘not’ absent. They did appear along with their counterparts with lower SF’s but their volume fraction was much ‘lower’ than would be expected. Extension twins corresponding to the ‘green’ matrix were almost exclusively high SF variants with SF=0.437. The formation of multiple twin variants with different orientations has a favorable effect on the formability because it prevents the formation of a strong basal texture component and facilitates glide on the basal planes inside respective twins.
The observed variant selection behavior can be explained on the basis of local stress inhomogeneities resulting from the development of internal stresses, which when superimposed on the macroscopic applied stress, can either reduce or increase the effective local stress. In our experiments, it is important to consider the influence of the lateral constraint stress, arising from the channel-die walls, on both the global and local stress states, and the resultant net stresses that take part in promoting the activation of low SF twins. For plane strain compression in a channel die setup, a fixed constraint stress, $\sigma_{22}$ relative to the compression stress, $\sigma_{33}$ is usually assumed. From fcc single crystal deformation studies [110], the stress ratio $\alpha = \sigma_{22}/\sigma_{33}$ was found to strongly depend on the crystal orientation and strain amount. For (110) compression plane, the stress ratio was close to zero when the [001] direction was parallel to the LD (expansion direction). By varying the expansion direction in this plane, the value of $\alpha$ was found to change. For extension along the [111] $\alpha$ was close to unity, and for [110] it was 0.5, which corresponds to an isotropic stress state. In the current study, a local variation of $\alpha$ in different grains as a function of their orientation may influence the theoretical SF values for the activation of different twin variants. It is also important to consider that with increasing deformation strain, the value of $\alpha$ can significantly vary for some grain orientations more than others.

For a stress ratio of zero (no constraint stresses), the SF values of high and low SF variants correspond to 0.499 and 0.12 for extension twinning inside $<10\overline{1}0>$ ||$CD$ oriented grains, which clearly favors the activation of one twin variants, viz. the ‘red’ twins in Fig. 5.4(a). The fact that low SF twins were also evident in the deformation microstructure suggests that the value of stress ratio, $\alpha$ is not zero, which is also a realistic assumption in case of polycrystals. For a completely isotropic or randomly textured material, the assumption is that $\sigma_{22} = 0.5 (\sigma_{33} - \sigma_{11})$. With no stress in the LD during plane strain deformation, $\alpha$ becomes equal to 0.5, which increases the SF value for low SF twins to 0.312. This indicates a clear trend to diverge from the Schmid rule with
increasing constraint stresses. For moderately textured materials and low deformation strains (as in the current case), it is reasonable to assume values of $\alpha$ between 0.2 and 0.4, which lead to SF values of 0.24 to 0.29 for the low SF twin variants. The SF values for the high SF variants remain 0.499 irrespective of $\alpha$.

Another factor influencing the Schmid rule for twin variant selection in hexagonal materials is the development of high internal back-stresses induced by the accommodation strains associated with twin formation. When a twin forms at a grain boundary, the associated shear can be accommodated by slip or twinning in the adjoining neighboring grain [103]. The accommodation strains imposed on the neighboring grains by twinning can be readily calculated from the twinning shear $s$ by rotating its displacement tensor into the crystallographic reference frame of the neighboring grain [103]. Potential twin variants that require little or no difficult accommodation in the neighboring grains are found to form more easily, even if their SF’s are relatively low. Conversely, the nucleation of twins that require a large accommodation work (e.g. prismatic slip) in the neighboring grain, will be rather difficult even if the calculated SF’s are relatively high. While this criterion for the variant selection applies mostly to compression and double twins in magnesium, it was recently shown that the ‘nucleation’ of primary extension twins do follow the Schmid law but the ‘growth’ of these twins is controlled by the accommodation strain [103]. This would explain the prominence of the low SF extension twins displayed in Figs. 5.3 and 5.4. If these twins require the least accommodation work in the adjacent grains they would grow more quickly than the other twins associated with the high SF’s. In fact, slip trace analysis in the vicinity of ‘green’- twinned regions associated with low SF’s revealed obvious sets of parallel lines coinciding with slip on the (0002) basal plane (c.f. Fig. 5.4(b)). Slip lines corresponding to $\{10\bar{1}0\}$ prismatic planes were comparatively much less observed due to the CRSS of prismatic slip being at least an order of magnitude higher than that of basal slip at ambient temperature. The experimentally measured shear parallel to one of the basal slip
burgers vectors, induced by tension twinning was found to be $\gamma_{\text{twin shea}} = 0.125$ (c.f. Fig. 5.4(b)), which correlates well with the theoretical twin shear given by $S^t = \left(\frac{c}{a}\right)^2 - \frac{3}{\left(\frac{c}{a}\right)^2}$ [8]. For magnesium with $c/a = 1.624$, $S^t = 0.129$.

Despite the fact that most of the grains were initially favorably oriented for extension twinning in IPC, considerable amount of {10\overline{1}1} compression and {10\overline{1}2} – {10\overline{1}2} double twins were detected from the EBSD measurements, producing soft grain orientations lying between LD and CD in the (0002) pole figure. This ‘anomaly’ can arise from the aforementioned lateral stresses exerting compressive forces on the material. Given that the initial prismatic texture deviated from an ideal $<0001>||$LD orientation, grains with basal poles closer to TD can experience a compression stress component along their $c$-axes, and hence, compression twinning becomes feasible.

(B) TTC MODE

Deformation of the Mg-1Gd alloy in TTC seemed to induce a relatively high proportion of compression and double twins, in comparison to conventional magnesium alloys deformed under similar conditions. Since it was difficult to obtain reliable EBSD measurements of the as-deformed condition it was not possible to quantify the actual fraction of these twins. However, the measurement obtained after annealing at 300°C for 60 min still revealed prevalent compression and double twins that were also associated with the formation of new recrystallized grains (Fig. 5.10(b)). This observed twinning recrystallization might have taken place during deformation by means of progressive rotation of subgrains formed inside the twins, as was reported in [72] for Mg single crystals deformed at room temperature. It could have also occurred during annealing by means of classical discontinuous recrystallization. The single orientation data of the respective mapped area revealed a broad orientation scatter in the LD (Fig. 5.10(c)) that seems to coincide well with compression twin variants of ‘high’ SF values and their corresponding double twins (Fig. 5.10(d)). The orientation scatter in the recrystallized
regions was relatively more widespread in comparison to the deformed fractions of the microstructure, highlighting the role of twinning recrystallization in the overall texture development. The formation of compression and double twins during deformation is important for creating new orientations that persist during recrystallization nucleation and become quantitatively influential upon the formation of new grains. In conventional magnesium alloys, compression and double twinning recrystallization is not common due to significantly larger amount of work required to nucleate compression twins that is likely to produce catastrophic shear localization followed by cracking. In the present case, assuming an easier nucleation of compression twins accompanied by non-basal slip the reported outcome can be quite expected.

Deformation twin formation consists of twin nucleation and propagation. Most twinning studies in hexagonal materials are concerned only with twin propagation given its role in the hardening response and texture evolution during plastic deformation. However, the fact that twin nucleation precedes twin propagation makes it equally important to understand the aspects of twin nucleation. While the exact mechanisms of twin formation in magnesium are still in debate, there is a general agreement that twin nucleation takes place at the grain boundaries rather than inside the grain, and that dislocation pile-ups constitute a plausible twin nucleation mechanism [8, 31]. This renders twin nucleation strongly dependent on the local stress state and the atomic structure of the grain boundary. Recent molecular dynamics (MD) simulations have shown that the interaction of pre-existing grain boundary dislocations with incoming lattice dislocations or pile-up dislocations transforms the grain boundary defects into twinning partials that coalesce and form a stable twin nucleus [111, 112].

To interpret the difficulty of compression twin formation in magnesium it is necessary to focus on the associated rate-controlling processes, such as atomic shuffling and simultaneous shear, i.e. glide of twinning dislocations during twin formation. Recent atomistic simulation studies on the above two aspects during \{10\bar{1}2\} tension and \{10\bar{1}1\}...
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Compression twinning revealed that in the latter, twin formation was accomplished primarily by glide of twinning dislocations rather than shuffling. The activity of atomic shuffling was lower for \{10\bar{1}1\} twinning than for \{10\bar{1}2\} twinning, which was attributed to a much higher activation energy required for atomic shuffling in case of compression twinning [35, 36]. Additional molecular dynamics studies [113] have revealed that for tension twinning the Burgers vector associated with a twinning partial is nearly $1/12$ of the Burgers vector of a basal dislocation, which implies that the dislocation energy ($\propto b^2$) associated with a tension twin can be more or less considered negligible. This also explains the low stresses required to nucleate and grow tension twins in pure magnesium. On the other hand for compression twinning, the Burgers vector of the twinning partials accommodating the same shear is almost 10 times larger than that for tension twin partials [114]. Thus, even though both \{10\bar{1}1\} and \{10\bar{1}2\} modes produce similar characteristic shears ($\varepsilon_{\text{compression}} = 0.137$ vis-à-vis $\varepsilon_{\text{tension}} = 0.129$), formation of the former is mostly driven by shear while the latter is shuffle dominated. Since the degree of shear accommodation at the compression twin boundaries is considerably large, void nucleation due to shear localization often becomes a subsequent phenomenon [115]. On the basis of these perspectives, the observed unequivocal nucleation of tension and compression twins in the current work is rather unexpected and ought to be related to RE solute effects altering the twinning propensity.

Solute REEs have been known from first-principles studies to considerably lower the generalized stacking fault energies ($\gamma_{\text{GSFE}}$) associated with the basal planes in magnesium [35, 116, 117], which has important implications for the movement of dislocations and the plasticity in general. The two commonly observed intrinsic basal stacking faults, the ‘growth’ fault $I_1$ (…ABABCBCB… stacking sequence) and the ‘deformation’ fault $I_2$ (…ABABCACA… stacking sequence) can be considered as intrinsic sessile and glissile faults, respectively, which can be generated by shear deformation on the basal planes in the $<10\bar{1}0>$ directions [118, 119].
particularly important ductility parameter in hcp metals, and can be structurally described by dissociation of a $\frac{1}{2} < 1 1 2 0 >$ perfect basal dislocation into two Shockley partial dislocations ($\frac{1}{3} < 1 0 1 0 > + \frac{1}{3} < 0 1 1 0 >$). The variation of $\gamma_{GSFE}$ as a function of relative shear displacement involves two main parameters, namely the stable ($\gamma_{stable}$) and unstable ($\gamma_{unstable}$) stacking fault energies corresponding to the local minimum and the local maximum in the GSFE curve, respectively. While a lower $\gamma_{stable}$ physically signifies greater stability of an existing stacking fault structure, a reduced $\gamma_{unstable}$ results in easier generation of stacking faults i.e. lesser energy is expended to initiate shear between adjacent atomic planes. It is proposed that solute REEs in general could stabilize existing twin and/or stacking faults by segregating to the dislocation cores of dissociated partials (Suzuki effect), thereby lowering $\gamma_{stable}$. On the other hand, a decrease in $\gamma_{unstable}$ could be possibly triggered by the formation of point or zonal defects [120] that are likely to form owing to the strong ‘clustering’ tendency of solute Gd atoms.

A higher density of sessile growth faults would be ideal for enhanced dislocation generation. Sandlöbes et al [120] proposed that such growth faults give rise to planar defect structures not only on basal planes but also on prismatic and pyramidal planes. Experimental TEM observations by Li and co-workers [121, 122] revealed an interaction between pyramidal dislocation cores and basal stacking faults in pure magnesium, which was seen to generate $\{1 0 1 1\}$ pyramidal stacking faults by the glide of these dislocations. Considering the influence of Gd solute segregation, such dislocation-stacking fault interactions would be further intensified, resulting in formation of pyramidal faults that facilitate compression twin nucleation at considerably lower stresses.

From a different perspective, lowering the intrinsic deformation fault energy would increase the separation distance $R$ between dissociated basal partials since $\gamma \propto 1/ R$. Correspondingly, this would affect the kinetic process of partial dislocation motion, thereby retarding cross-slip and climb, which in turn, substantially reduces the mobility of basal dislocations. Moreover, the aforementioned Suzuki effects (segregation of solute
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atoms to stacking faults) could further restrict dislocation motion leading to dislocation pile-ups on the basal planes, and thus to significant strengthening of basal slip. In such cases, activation of deformation modes out of the basal plane would become obviously favorable. These important effects would not only facilitate compression twin nucleation but also accommodate the elastic strain energies at twin-matrix interfaces, thus preventing shear localization and premature failure. Analogously, a reduction of stable and unstable twin fault energies in the presence of solute Gd atoms could be in part responsible for the observed invariant tension twinning behavior, since the overall elastic strain energies generated during twin nucleation and propagation would be much lower in comparison to pure magnesium. Furthermore, it is quite likely that solute REEs with their significantly large sizes may considerably increase the activation energies of atomic shuffling during tension twinning that may additionally contribute to the aforementioned effect.

5.6.1.2 Precipitate containing magnesium-cerium alloy

The twinning response of Mg-1Ce in the IPC mode, exhibited strong variant selection indicated by the dominance of high SF twins (SF ≈ 0.43 -0.49). Cerium existing primarily as a secondary phase will not be expected to display significant solute-related effects as compared to gadolinium in the Mg-1Gd alloy. However, precipitate/twin interactions can also influence the twinning behavior of the material in various ways: a) Particles contribute to the local stress fluctuations in the microstructure, and thereby to twin nucleation at the grain boundaries; b) precipitates can have a significant impact on twin growth, critically depending on precipitate shape, type, size and habit plane. For example: (i) Large semi-coherent / incoherent precipitates can arrest twin growth completely, triggering additional nucleation of new twins; (ii) intermediate-sized semi-coherent precipitates are generally expected to be engulfed by twins, subsequently undergoing rigid body rotation with no shearing; (iii) for fine coherent precipitates, twins
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements are able to both engulf and shear the precipitates simultaneously [123]. The average size of precipitates in the Mg-1Ce (> 5 µm) clearly applies to the first case (i) that inhibits twin growth by pinning the twin boundaries (c.f. Figs. 5.8(d), 5.15(a) and (b)).

Deformation in the TTC mode appeared to activate several twinning modes including extension twinning, yet the twin fraction remained comparatively lower than that in the IPC mode (~16 ± 1.8% vs. ~23 ± 4.7%). Considering that twins are essentially stacking faults bounded by twinning partials pulled together by the twin fault energy, and since the stacking fault energy varies inversely with the area of fault, twin growth should be a favorable outcome in order to reduce the overall system energy. In the presence of precipitates, the overall interfacial energy increases due to additional precipitate-matrix accommodation strains. Fig. 5.15(a) shows a schematic of the stress field around a particle inside a grain. The particle-matrix accommodation strains, as mentioned before would necessitate the formation of geometrically necessary dislocations (GNDs). The shape change assumed by shearing of the particle would then be compensated by prismatic dislocation loops. These dislocations have been categorized into two types: Vacancy dislocation loops or V-Loops (originating at the dilated regions of the interface) and Interstitial dislocation loops or I-Loops (originating at the compressed regions of the particle matrix interface). With increasing deformation strain, the degree of compensation and subsequently the density of prismatic loops will increase. The number of prismatic dislocation loops per particle can then be mathematically expressed by means of [124] as,

\[ N_{GND} = \frac{K \times d_{\text{particle}} \times \epsilon_{\text{shear}}}{b_{\text{basal}}} \]...

(5.3)

Where, \(d_{\text{particle}}\) is the particle radius (measured value ~ 6.6 µm (S.E = 0.49)); \(b_{\text{basal}}\) is the magnitude of Burgers vector for basal slip \(\frac{1}{3} < 1120 >\); \(K\) is a constant depending on the particle shape, and \(\epsilon_{\text{shear}}\) is the extent of particle shear, which depends on the applied stresses. For large particles and greater local shear corresponding to higher deformation strains, the number of dislocations around particles would be high. The
higher the number of GNDs generated in the vicinity of the particle-matrix interface, the larger is the exerted back stress on the twin boundary dislocations interacting with particles, which means a greater restriction of twin growth. The increased stress concentration at the particle-twin interface is then often relaxed by the nucleation of twin embryos, and their coalescence to form stable twin nuclei. Based on the previous notion, the impact nature of precipitates on twin formation is apparently contradictory, i.e. even though the Ce-containing precipitates in this study seemed to suppress twin growth, they appeared to simultaneously stimulate twin nucleation.

In case of IPC, the particle-twin interaction can be expected to nucleate extension twins, schematically illustrated in Fig. 5.15(a). Analogously, deformation in TTC can be expected to form both extension (nucleated at lower strains inside grains deviating from the basal orientation) and compression twins (nucleating at higher strains in basal oriented grains) associated with particle-twin interfaces. Fig. 5.15(b) illustrates a compression twin nucleating in a basal oriented grain, near a twin-particle interface. Due to the directional dependence of twinning (i.e. on the sign of the applied stress), the relaxation of internal residual stresses at grain boundaries and in the vicinity of particles can sometimes lead to full or partial disappearance of twins (Fig. 5.15(c)). Generally, during deformation twinning, the twinned regions undergo stress relaxation, whereby local stresses are concentrated at neighboring grain or phase boundaries [125]. This is a typical load transfer mechanism frequently seen in composites and polycrystalline metals, wherein the soft-ductile regions relax by plastic deformation and the majority of the stresses are borne by the rigid zones in the material (harder secondary phases in composites or hard oriented grains in metals).

In the case of a particle-containing microstructure (Mg-1Ce), the residual stress fields around the particles could be instrumental in imposing a reverse shear on the existing twins during unloading, leading to twin reversal (detwinning) [126, 127]. Such pseudo-elastic behavior would be expected to be more pronounced for weaker textures,
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wherein grains assume diverse orientations resulting in large differences between the local and global mechanical response. The reversal of twinning dislocations shown schematically in Fig. 5.15(c) indicates such stress reversal or ‘push back’ effect. On the other hand, the aforementioned residual stresses could also contribute to ‘re-twinning’ during unloading, such that the twinned region would twin again by a different variant rotating the parent twin into an orientation close to the initial matrix orientation.

Figure 5.15 Illustration along with optical microstructures showing tension twin nucleation at particle-twin interface in Mg-1Ce (a); Illustration along with optical microstructures showing compression twin nucleation at particle-twin interface in Mg-1Ce (b); Schematic of de-twinning in Mg-1Ce
In such cases, the re-twinning event can be associated with the same misorientation axis of the primary twin but with the ‘opposite’ twin plane resulting in a configuration, wherein the re-twinned region would have a misorientation from the parent by $\sim 7^\circ < 11\bar{2}0 >$. The experimentally calculated misorientation values between select twins and their parent grains in Figs. 5.12(a) and (b) corroborate the aforementioned theoretical arguments.

### 5.6.2 VPSC Modeling

In order to gain further insight on the various deformation modes responsible for the observed texture and microstructural evolution during TTC and IPC, polycrystal plasticity simulations were carried out. Fig. 5.14(a) represents the VPSC simulation results for Mg-1Gd deformed in TTC mode. The model prediction of the texture evolution after 14% strain showed reasonable accuracy, displaying similar texture characteristics and texture strength, as compared with the corresponding experimental texture shown in Fig. 5.2. The slip mode activities are represented as a cumulative stacked column plot. As depicted in Fig. 1a the starting texture fed into the model was of basal-type with nearly $30^\circ$ scatter about the sheet plane normal and the loading axis during TTC. From the calculated slip activities, the incipient deformation was primarily accommodated by basal slip, accompanied by $\{10\bar{1}2\}$ extension and $\{10\bar{1}1\}$ compression twinning. At 2% strain compression twinning was suddenly rendered as important as basal slip, and the activation of extension twinning was significantly decreased. This was changed at strains of 4% and higher, which witnessed an increasing activation of extension twinning that is in part attributed to secondary twinning in compression twins giving rise to $\{10\bar{1}1\} - \{10\bar{1}2\}$ double twins. The predominant deformation mode in terms of activation frequency remained basal slip. At higher strains between 8% and 14%, the model seemed to additionally activate $\langle c+a \rangle$ pyramidal slip as a secondary slip mechanism. The prediction of twin volume fraction with respect to increasing strain
showed relatively higher values for compression twinning in comparison to extension twinning. Furthermore, the calculated volume fractions of compression and extension twins beyond 4% strain showed a similar rate of increase. Interestingly, the onset of secondary twinning was also seen within a similar strain regime, showing a comparable rate of increase with the primary twin volume fraction that most likely indicates the onset of double twinning, i.e. the model activates secondary extension twins inside grains reoriented by primary compression twins.

The final volume fraction of \([10\bar{1}1]\) twins predicted by the model is ~65% and that of \([10\bar{1}2]\) twins ~57%. With respect to primary twins (both compression and extension) and secondary twins (only extension), the predicted volume fractions were ~85% and ~37%, respectively.

For IPC deformation of Mg-1Gd (Fig. 5.14(b)), the predicted plane strain deformation texture at 8% strain was associated with a very high activation of \(<c+a>\) pyramidal slip that is known to always cause splitting of the basal texture about TD. Prismatic slip was not considered because of the effect of the lateral constraints that suppress its activation. The initial low activity of basal slip was also not unexpected when considering the starting texture with the basal planes aligned almost parallel to the loading axis CD. Pyramidal slip activity is supposed to reorient the \([11\bar{2}3]\) plane of a crystal such that it aligns with the compression plane, which would simultaneously lead to rotation of the basal poles towards the CD. Such change of initial orientation would result in favorable SFs for basal slip and both compression and extension twin modes. This was indeed observed in the simulations as a function of strain increment (Fig. 5.14(b)). The calculated twin volume fractions at each deformation strain showed higher values for \([10\bar{1}1]\) twins than \([10\bar{1}2]\) twins. These were ~24% vis-à-vis ~13% at the final strain of 8%. With respect to primary and secondary twinning, the activated twin modes were almost exclusively first generation twins. The overall volume fraction of double twins was around 1% when the final strain was reached. From EBSD
measurements at 8% strain, the estimated area fraction of extension twins was approx. 8%, which does not correlate perfectly with the predicted value but lies within a reasonable agreement range. This can be for the most part attributed to the difficulty of obtaining accurate estimation of the twin area fraction during EBSD measurements due to high local shears and excessive twin clustering. This argument also applies to the other twins modes. The activation of hard deformation modes, such as \{10\bar{1}1\} compression twinning and \langle c+a \rangle pyramidal slip in the Mg-1Gd alloy could be highly feasible considering the aforementioned influence of solute REEs on the intrinsic stacking fault energies of Mg.

TTC simulations of Mg-1Ce (Fig. 5.14(c)), revealed strong activation of basal and pyramidal \langle c+a \rangle slip. \{10\bar{1}1\} compression twinning was assigned a much higher activation stress value relative to \langle c+a \rangle slip because of its very low fraction in the final microstructure (c.f. Fig. 5.2(d)). The calculated twin volume fractions thus revealed a much higher density of tension twins as opposed to compression twins, which can be interpreted by the almost random starting texture and the relative ease of extension twin formation. Therefore, secondary twinning events were significantly lower as compared to its counterpart Gd-containing alloy. The simulated tension and compression twin volume fractions at the final strain were \sim 14\% and \sim 5\%.

For IPC simulations on Mg-1Ce, the results again revealed a dominant activation of \langle c+a \rangle pyramidal slip accompanied by a secondary contribution of basal slip (Fig. 5.14(d)). Similar to the previous case, compression twins were not observed during the microstructural analysis of this alloy after 8\% of deformation, and thus, their contribution was not considered in the simulations. As seen in Fig. 5.14(d), the deformation initiates with a high activity of extension twinning, which abruptly wanes with increasing strain levels. The respective twin volume fraction showed a rapid increase up to \sim 14\% at a strain of 2\%, after which extension twinning was obviously almost exhausted, since
further increase in twin volume fraction as a function of strain increment was very sluggish.

5.6.3 **Dynamic Recovery and Recrystallization Mechanisms**

5.6.3.1 **Magnesium-Gadolinium**

The deformation microstructure of the Mg-1Gd alloy revealed instances of fine, strain-free grains inside compression and double twins, seen during channel die compression (Fig. 5.4(a), IPC) or after annealing (Fig. 5.5(b), IPC and Fig. 5.10(b), TTC). Fig. 5.16(a) reveals further evidence regarding the appearance of new grains inside \{10\bar{1}1\} compression twin bands that are highlighted in Fig. 5.16(b) by their characteristic boundary misorientation of \(57^\circ\) about \(< 11\bar{2}0 >\). As discussed in previous studies [72], this ‘twinning recrystallization’ mechanism is based on extensive dynamic recovery, and characterized by progressive reorientation of subgrains formed during deformation until their boundary misorientations become sufficiently large (\(\sim 15^\circ\)) to be considered as low angle boundaries. The formation of subgrains can be related to the ease of dislocation slip in the compression and double-twinned areas that have a high SF for basal and prismatic slip. This favorable condition of easy glide can increasingly generate more dislocations, which would preferably accumulate at the twin boundaries. Dislocation pileups at these boundaries could trigger dislocation rearrangement mechanisms, such as cross-slip that would give rise to cell walls and subgrain boundaries (polygonization). Such areas are indicated in Fig. 5.16(c) by very low GOS values lower than 1°. Another contributing factor to preferred subgrain formation in compression and double twins is their energetic reluctance to twin growth throughout deformation (unlike \{10\bar{1}2\} twins), which retains a limited mean free slip distance for dislocations inside the twins. Contrary to grown extension twins, having a much shorter slip length and more rapid dislocation generation conjoins compression and double twins with high dislocation densities. The
aforementioned non-planar movement of dislocations during recovery is essential for the formation of a three-dimensional dislocation structure.

The microstructures after annealing at 300°C and 350°C exhibited similar characteristics for both compression modes. In addition to unrecrystallized extension twins and retained deformation structure, the microstructures of the annealed specimens were also characterized by a number of recrystallized compression and double twin bands bounded by matrix areas with the same orientation (Fig. 5.5(a) for IPC and Fig. 5.10(b) for TTC).

**Figure 5.16** DRX in compression and double twins shown in IPF map of as-deformed Mg-1Gd in IPC (a); Corresponding unit cell representation with highlighted twin boundaries (b); GOS map (c); Single orientation scatter and recalculated pole figures showing a ‘prismatic fiber’ evolving in compression and double twins due to DRX (d)
Since such recrystallized bands were also sighted in the deformed state at room temperature (Fig. 5.16(a)), it remains unclear whether compression and double twinning recrystallization proceeds solely by means of ‘slip-aided’ dynamic recovery (as explained above) or also by nucleation at the ‘high-angle’ twin boundaries and subsequent nucleus growth by HAGB migration that concurrently removes the deformation structure inside the twins. This mechanism is not unlikely, considering that the observed recrystallized bands upon annealing show some grain boundary bulging and grain boundary serration, which are common features of this recrystallization mechanism.

Quantitative EBSD analysis of the recrystallized grain orientations within the twin bands in the as deformed state revealed that these orientations produce a continuous fiber in the basal pole figure connecting both LD components that correspond to the initial matrix orientation in IPC loading (c.f. Fig. 5.16(d)). Interestingly, each group of recrystallized grains within a twin band shared almost the same c-axis alignment among each other, which corresponded also to the same c-axis alignment of their compression or double-twin host (c.f. Fig. 5.16(b)). Additionally, the a-axis orientation of the grains was found to form a prismatic fiber texture component (c.f. Fig. 5.16(d)). Molodov et al. [72] suggested the development of those specific orientation fibers to arise from active ‘prismatic slip’ inside compression and double twins, which induces twin fragmentation and rotates the grains around the c-axis of their parent twin. By correlating these results with the ones obtained upon annealing, the above-mentioned microstructurally key features of slip-induced twin recrystallization do not seem to hold for annealing twin recrystallization. This can be clearly assessed from Fig. 5.5(b) by the arbitrary orientations of new grains associated with fragmented compression and double-twins, which also explains why all recrystallization orientations within these twins fail to perfectly reside on the ‘twin recrystallization’ fiber indicated in Fig. 5.16(d) and drawn in Fig. 5.5(d) for comparison purposes. Based on these findings, it is proposed that twin recrystallization in the investigated alloy has the ability to proceed through a
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A discontinuous process during static annealing (SRX) comprising nucleation and growth by HAGB migration or a continuous process during deformation (DRX) involving extensive recovery and reorientation of subgrains.

The onset of recrystallization in IPC deformed specimens was not observed until 350°C anneal. The annealing microstructure constituted large matrix grains (only of the \( <10\bar{1}0 > \) orientation) comprising extension twins with a basal orientation (c.f. Fig. 5.5(a)). In pure magnesium and conventional magnesium alloys of the AZ or AM series containing little precipitates, the extensive growth capability of \( \{10\bar{1}2\} \) twinning is one of the predominant features of this twinning mode [128]. While extension twins can easily grow during deformation and compensate the internal stresses, compression and double twins remain rather thin and undergo DRX instead. In the present study, extension twins were not liable to twin growth during deformation (strain induced) nor during annealing (thermally activated). Such retarded twin growth kinetics is believed to arise out of either twin boundary pinning by solute pairs/clusters of large Gd atoms [93, 129] during deformation or due to thermally driven Gd-solute segregation to twin boundaries [92, 130] during annealing treatment.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) measurements conducted by Nie and coworkers [130] on dilute binary Mg-Gd alloys revealed a strong tendency to periodic segregation of Gd atoms at fully coherent twin boundaries during static annealing. The Gd atoms were observed to align in between Mg atoms at the dilated regions of the boundary. Such segregation events not only retard static recovery but also lower the elastic strain energies associated with the twin boundaries, thereby significantly reducing their boundary mobilities. Unlike the hard-oriented ‘red’-colored twins that were left unrecrystallized upon annealing, other \( \{10\bar{1}2\} \) twins of softer orientations (c.f. Figs. 5.4(a) and (b)) were no longer present in the annealing microstructure at 350°C. Those twins were capable of undergoing sufficient dislocation glide, and thus accommodate greater plastic strain energy that would render their recrystallization easier than their hard-oriented
counterparts. However, considering the above mentioned impurity drag influence on the mobility of grain and twin boundaries; it is likely that the driving pressures for recrystallization might be insufficient to render free growth of the recrystallized regions to consume the entire deformation matrix. At 450°C, the recrystallized grains are provided with sufficient thermal activation to overcome the solute drag effect, exhibiting unhindered growth at the expense of the deformation microstructure and the remnant extension twins. The high frequency and larger grain sizes of high SF off-basal grains (Fig. 5.6) indicate the preferential growth of orientations arising from compression and double twins during recrystallization and grain growth stages.

Nucleation of recrystallization in TTC deformed specimens took place at 300°C and fully recrystallized microstructures were obtained readily at 350°C (not shown here). The underlying difference in the recrystallization kinetics between the two loading modes possibly arises from the difference in the final deformation strains (13% for TTC vis-à-vis 8% for IPC), which usually determines the available driving force for recrystallization. Additionally, the larger activation of compression and double twinning in the TTC mode leading to higher volume fraction of these twins relative to IPC loading would produce a higher density of nucleation sites (c.f. Fig. 5.10, 5.14(a) and (b)). This increases the nucleation rate of recrystallization leading to more rapid grain impingement and earlier onset of curvature-driven grain growth. A larger average grain size obtained upon 450°C annealing of IPC samples (~89 µm) in comparison to the TTC counterparts (~69 µm) further suggest a higher nucleation density in the latter. Grain growth in both cases increases the spread of off-basal orientations leading to effective texture weakening (c.f. Figs. 5.6 and 5.13(a)).

5.6.3.2 Magnesium-Cerium

Due to a very weak starting texture, significant extension twinning was observed in both deformation modes. For IPC deformation, annealing at 300°C retained a weak
texture, and the annealing microstructure resembled that of 8% IPC. Previously formed extension twins of basal and off-basal orientations were still present upon annealing. The fact that the soft-oriented twins were also unrecrystallized suggests that they did not attain sufficient stored energy for recrystallization at this temperature. It can be therefore proposed that the low deformed regions in Fig. 5.8 formed subgrains during recovery that proceeds more slowly throughout the annealing process to give rise to a complete recrystallization of the microstructure. Nucleation of discontinuous recrystallization at 300°C was solely observed at second phase particles and particle-twin interfaces, giving rise to random orientations that are well distributed within the spread of the deformation texture. In the presence of large particles and almost solute-free matrix, these PSN orientations can grow and consume adjacent twinned areas. At 450°C, the thermal activation energy is considered sufficient enough to promote twin recrystallization and further PSN to result in a fully recrystallized, twin-free microstructure, and still a very weak, favorable texture. The final grain size recorded for this alloy upon annealing at 450°C was ~55 µm, which is significantly lower than the one for the Mg-1Gd alloy annealed at this temperature (~ 89 µm). It is proposed that such a difference arises mostly from the different recrystallization mechanisms featured in both alloys. Boundary pinning contributions are also important but were not considered in this study due to the large average particle size present.

With respect to the TTC-mode, apart from recovery of tension twins and PSN, nucleation of recrystallization inside compression and double twins was also observed. However, due to the low volume fraction of these twins in this alloy, the nucleation density from these regions was considerably small. The relative difference in grain size between Mg-1Gd (~68 µm) and Mg-1Ce (~56 µm) was considerably smaller in the TTC mode as opposed to the IPC mode. The underlying reason could be attributed to the relatively higher nucleation density, as stated earlier, for the TTC mode in Mg-1Gd.
5.7 SUMMARY

The following conclusions can be drawn from the present chapter:

1) Twinning behavior and related recrystallization is strongly dependent on the choice of RE.

2) Deformation of Mg-1Gd in IPC led to evolution of sharp ‘prismatic fiber’ texture and a complete absence of basal texture. Contrarily Mg-1Ce, loaded in IPC, resulted in development of weak basal component. While Mg-1Gd exhibited competitive nucleation of tension and compression twins, Mg-1Ce displayed predominantly tension twinning. Slip assisted DRX inside compression and double twins were witnessed in Mg-1Gd, giving rise to recrystallized grains with their c-axes aligned to the host twin orientation.

3) TTC deformation leads to evolution of a strong split basal texture in Mg-1Gd, whereas Mg-1Ce produced a weak basal texture accompanied by a large off-basal spread. Mg-1Gd showed profuse compression and double twinning, forming banded structures. On the other hand, Mg-1Ce primarily activated tension twins along with extremely low volume fractions of compression and double twins. Deformation associated twin growth was restricted due to presence of particles, which at higher strains triggered de-twinning or re-twinning events.

4) Static annealing resulted in strong texture weakening, yet preserving the deformation features.

5) Onset of recrystallization in Mg-1Gd was observed to initiate discontinuously inside compression and double twins by means of high angle boundary formation, whereby arbitrary orientations were generated. Onset of grain growth was not observed until 450° C annealing, due to impending impurity drag effects. Grain growth promoted favorable growth of recrystallization orientations originating
inside compression and double twins at the expense of the parent grains and basal tension twins.

6) Mg-1Ce displayed extended recovery based twin recrystallization along with discontinuous recrystallization in the vicinity of particles. Uninhibited grain growth was witnessed at 450° C, characterized by growth of PSN orientations and twins.
CHAPTER 6

REE RELATED TEXTURE MODIFICATION IN PRESENCE OF NON-REEs

The studies presented in chapters 4 and 5 indicate the favorable effects of REE addition on texture modification in binary magnesium-rare earth alloys. However, the results further imply that the level of texture modification achieved is strongly dependent on (i) the choice of REE and (ii) the processing parameters. Modified textures show either a decrease in texture intensity up to a random level or display new orientations viz. ‘RE-texture’ components, which depart from the standard sheet texture. In both cases, the orientations are characteristically ‘soft’ i.e. conducive to subsequent basal slip. Additionally, it is observed that texture modification is primarily recrystallization induced, arising either from shear-bands, twins or particles.

Another invaluable parameter deciding the degree of RE-texture modification is additional role of non-REEs. In numerous cases, the favorable influence of non-REE additions on texture and ductility in Mg-REEs has been observed, as exemplified in section 2.3.2. However, the underlying interactions are little known. The present chapter will investigate the concomitant role of non-REE additions in augmenting texture modification in Mg-REEs. In this context, the following questions will be addressed:

a) How does the addition of Zn and Zr succeed in triggering or enhancing RE-texture modification effect? Moreover, how do they interact with both solute and precipitate REE additions?

b) Is such an effect subject to the choice of processing conditions? (e.g. deformation history and annealing temperature)
In order to understand the recrystallization mechanisms in Mg-REEs in the additional presence of non-REEs, quaternary Mg-1Zn-0.6Zr-1Gd and Mg-1Zn-0.6Zr-1Ce alloys were fabricated and subjected to the same treatment as described in section 4.1. The results revealed that the addition of “non-REEs”, like Zn and Zr can in fact impart qualitative texture changes in Mg–1Ce alloy, rendering Ce an “effective” RE-texture modifier. Furthermore, for the Mg–1Gd alloy, which was already seen as a befitting material for generating unique and soft textures through annealing treatments, the addition of Zn and Zr appeared to lower the transition temperature for the observed texture modification in the binary alloy. The forthcoming sections compare the rolled binary alloys from chapter 4 with their more complex counterparts with Zn and Zr in terms of texture, microstructure and resulting mechanical response in tension at ambient temperature (c.f Sections 6.1 to 6.4). The aim is to understand the concept of how the addition of Zn and Zr succeed in triggering or magnifying the RE-texture modification effect, and how this influences the fundamentals of deformation, recrystallization and grain growth (c.f. Section 6.5). The overall conclusions are presented in Section 6.6.

6.1 ROLLING TREATMENT – TEXTURE AND MICROSTRUCTURES

Two alloys, with compositions: Mg-1Zn-1Ce-0.6Zr and Mg-1Zn-1Gd-0.6Zr were cast and subjected to hot-rolling treatment (80% total thickness reduction in one pass at 400°C) as per the procedure described in Section 4.1.

The as-rolled and annealing textures for Mg-1Zn-1Ce-0.6Zr and Mg-1Zn-1Gd-0.6Zr alloys are displayed in Fig. 6.1(a). The rolling treatment produced a double peak basal texture in both alloys, with the basal poles of maximum intensities being tilted away from the sheet normal (ND), by approximately ± 20° towards the rolling direction (RD). The distribution of peak intensities about the ND was asymmetric. In terms of texture strength, the MRD (multiples of a random distribution) values for both alloys were quite different. During rolling deformation the Gd-containing alloy seemed to develop a much
weaker texture than the other alloy. For easier comparison, the respective textures of the counterpart binary alloys are shown in Fig. 6.1(b).

Optical microscopy in the RD-ND plane of both rolled alloys revealed high density of shear bands (Fig. 6.2). The shear bands appeared like sharp straight lines traversing homogeneously throughout the microstructure in the form of symmetric pairs, inclined at an angle of \( \pm \beta \) from the RD, where \( \beta \) ranged from 18° to 28°. The individual shear band thickness was much finer than the resolution limit of optical microscopy. In addition, second phase precipitates of different compositions, shapes and sizes were evident.
Figure 6.2 Optical microstructures for Mg-Zn-Zr-Ce and Mg-Zn-Zr-Gd along with respective 2-D average grain diameter. Inset SEM image (at higher magnification) for as-rolled Mg-Zn-Zr-Ce
In Fig. 6.3(a), ternary Mg-Zn-Ce particles with rod-shaped morphologies were primarily observed at the grain boundaries, whereas other Mg-Zr precipitates (with some traces of Zn) appeared as clusters in the matrix. It is noted that some “brighter” regions of the Mg matrix have shown a high Zr concentration (cf. Fig. 6.3(a)) that is most likely arising from extremely fine Zr and/or Zr-rich particles (<< 1 µm) that are difficult to quantify [131]. As known, zirconium is highly insoluble in magnesium, and therefore it is very prone to form dispersoids during casting. For the Gd-alloy (c.f. Fig. 6.3(b)), second phase particles were limited to Zr-rich compounds, which are characteristic of Zr-refined multicomponent magnesium alloys [132]. Gd seemed to be mostly in solid solution.

![Figure 6.3 Precipitate characterization and EDS analysis for a) Mg-Zn-Zr-Ce and b) Mg-Zn-Zr-Gd](image)

### 6.2 Static Annealing Treatment

#### 6.2.1 XRD Textures and Optical Microstructures

The annealing response at 250°C (see Fig. 6.1(a)) showed no significant alteration in the texture features for both alloys. However, the variation in the texture intensity showed opposing trends for both alloys, with the texture strength increasing in the Gd-alloy and decreasing for the Ce-alloy. Increasing the annealing temperature to 300°C led to a quite different texture response for the Gd-alloy, wherein the rolling basal texture was replaced by a more random texture, with new orientation peaks, primarily tilted
towards the TD. By contrast, the Ce-alloy retained its rolling texture but additionally produced a discernible TD spread, with negligible change in the texture strength. Heat treatments performed at 350°C and above led to significant rolling texture modification for both quaternary alloys and binary Mg-1Gd alloy, but not for the Mg-1Ce binary alloy (cf. Fig. 6.1(b)). The annealing textures for both quaternary alloys are outlined in Fig. 6.1(a) and those for the binaries are shown in Fig. 6.1(b). A direct comparison between the annealing textures at 350°C and 400°C in Fig. 6.1(a) reveals that the Ce-containing alloy still had a basal texture component at ND that seemed to disappear at a “high enough” annealing temperature of 450°C. For the Gd-alloy, this texture component was already absent at annealing temperatures above 300°C. All the new textures seemed to share a common feature characterized by an off-basal orientation distribution about the ND forming a continuous fiber connecting TD and RD. The position of maximum texture intensity seemed to shift between TD and RD depending on the chemical composition and the annealing temperature.

With respect to microstructural evolution during annealing (Fig. 6.2), the onset of recrystallization was not observed until 300°C. At 300°C, extremely fine, new grains were visible along the shear bands, indicating their importance as nucleation sites (SBN of recrystallization). Additional observations were made of new grains appearing close to second phase particles (PSN of recrystallization) upon annealing at 300°C and 350°C for the Ce-alloy and the Gd-alloy, respectively. Despite annealing at quite elevated temperatures of 400°C and 450°C grain growth was restricted in both alloys, unlike to what has been observed in the binary Mg-1Gd alloy (c.f. Section 4.2).

6.2.2 EBSD ANALYSIS

Fig. 6.4 displays EBSD IQ maps (used as the background) and corresponding local texture data (recalculated pole figures) for the Mg-1Zn-1Gd-0.6Zr alloy for selected annealed states.
Figure 6.4 EBSD analysis (IQ maps and recalculated pole figures) for Mg-Zn-Zr-Gd at 300°C, 350°C and 450°C, with corresponding key legend. The percentage values account for relative contribution from recrystallized (larger grains in ‘white’ and smaller grains in ‘blue’) and deformed regions.

The IQ map, at 300°C, is classified into recrystallized and deformed grains, highlighted in green and gray, respectively. Due to significant substructure formation in the microstructure during rolling, a visual distinction between recrystallized and deformed regions at this annealing condition was fairly difficult. Recrystallized grains were thus selected on the basis of two criteria: the maximum in-grain misorientation for a recrystallized grain must not exceed 2° and a recrystallized grain must be associated with only high angle boundaries (>15°) [133, 134]. Furthermore, recrystallized grains displaying internal substructures were deselected manually. The measured recrystallized...
fraction was 54% and the average recrystallized grain size was 2.4 µm (Standard Error (SE) = 0.6). Unlike the EBSD texture of deformed grains, the recrystallization texture was more or less devoid of a strong basal orientation. Superposition of both deformation and recrystallization textures showed good agreement with the corresponding X-ray bulk texture shown in Fig. 6.1(a).

At 350°C, the percentage of recrystallized area increased to 93%. Recrystallized grains were divided into two groups (data subsets) based on the average grain size of the recrystallized fraction of the microstructure (deformed grains excluded): (a) ‘white’ grains larger than 3.6 µm and (b) ‘blue’ grains smaller than 3.6 µm (Fig. 6.4). The ‘white’ grains accounted for ~71% of the recrystallized microstructure, and the ‘blue’ ones for ~22%. The respective EBSD textures shared a similar fiber characteristic about ND, yet depicted discernible differences regarding the position of the orientation peaks and the strength of the basal orientation, which was still a main feature of the deformation texture.

At 450°C, a bimodal nature of grain size distribution was clearly evident, with clusters of small grains being surrounded by coarser ones. The average grain size measured was 7.8 µm (SE=0.5). In analogy to 350°C, ‘white’ grains with a grain size larger than 7.8 µm constituted ~69% of the fully recrystallized microstructure, and exhibited a similar texture to the one at 350°C, yet with much less orientations in the center of the pole figure. ‘Blue’ grains on the other hand accounted for ~31% of the microstructure and revealed a similar orientation distribution to the one at 350°C with orientation peaks tilted towards RD and TD. The excellent agreement between EBSD recrystallization textures and X-ray bulk textures indicates that the latter resulted primarily from recrystallization.
The other alloy (Mg-1Zn-1Ce-0.6Zr) was subjected to a similar analysis presented in Fig 6.5. At 300°C, the recrystallized area (55% of the total microstructure) with an average grain size of 2.2 µm (SE=0.7) primarily produced an RD-split basal texture, which was qualitatively different from the corresponding recrystallization texture of its counterpart Gd-alloy (cf. Fig. 6.4). At 350°C, the average recrystallized grain size was 3.8 µm (SE= 0.6). The recrystallization textures of ‘white’ (75%) and ‘blue’ (16%) grains were essentially similar, and differed from the recrystallization texture at 300°C by showing a double RD-TD spread rather than a single RD spread. At 450°C, the average
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Grain size of the fully recrystallized microstructure came to 5.3 µm (SE=0.6). The two groups of smaller and larger grains were now showing appreciable variation in their EBSD textures. ‘Blue’ grains (< 5.3 µm) revealed an RD-TD double split texture, very similar to the one observed at 350°C for both grain classes. ‘White’ grains (> 5.3 µm), consuming 70% of the recrystallized microstructure showed a rather different texture, characterized by an obvious decrease in the basal pole intensity in the center of the (0002) pole figure, and an increase in the intensity of the RD-TD split orientations (c.f. Fig. 6.5).

6.3 Tension tests at ambient temperatures

6.3.1 Deformation response and mechanical properties

Tensile tests till failure were conducted along the RD for both the multi component Mg-Zn-Zr-RE alloys investigated in this study and their binary counterparts reported in Chapter 4. Fig. 6.6 represents typical true stress-strain curves for all four alloys in their rolled and annealed states. Table 6.1 gives the corresponding mechanical properties, listed in terms of uniform elongation; εu, elongation to failure; εf, ultimate tensile strength; UTS and tensile yield strength; TYS. A comparison between top and bottom diagrams in Fig. 6.6 demonstrates the impact of non-RE additions on the flow behavior and the resulting mechanical properties, whereas a comparison between right and left diagrams depicts the role of chosen RE. For the binary alloys (Fig. 6.6(a) and (b)), significant differences in strength and ductility were first observed at annealing temperatures of 350°C and above. The Mg-1Ce alloy displayed no significant improvement in the ductility response with its maximum elongation reaching 17% after annealing at 450°C, whereas the Mg-1Gd alloy produced a maximum elongation of ~30% for annealing temperatures between 350°C – 450°C. At lower annealing temperatures (250°C – 300°C) both alloys produced higher ultimate tensile strength values than the rolled states but displayed very low elongations. Table 6.1 reports higher yield strength values (0.1% offset yield point) for Mg-1Ce than Mg-1Gd.
Figure 6.6 Tensile flow curves at room temperature for different rolled-annealed states of a) Mg-Ce, b) Mg-Gd, c) Mg-Zn-Zr-Ce and d) Mg-Zn-Zr-Gd. The highlighted region represents the typically observed elongation range for conventional Mg-alloys at room temperature.

The mechanical behavior of the binary alloys demonstrated tremendous enhancement in strength and ductility by the addition of Zn and Zr (Fig. 6.6(c) and (d)). The quaternary alloys exhibited significant rise in the yield strength and ultimate tensile strength values, in comparison to their binary counterparts. The elongation values showed a considerable increase, particularly for the Ce-containing alloy, upon annealing at 300°C and above.
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Table 6.1 Mechanical properties, listed in terms of uniform elongation; $\varepsilon_u$, elongation to failure; $\varepsilon_d$, ultimate tensile strength; UTS and tensile yield strength; TYS.

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<th>Treatment</th>
<th>$\varepsilon_u$ (%)</th>
<th>$\varepsilon_d$ (%)</th>
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<th>TYS$_u$ ± TYS$_u$ (MPa)</th>
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<th>$\varepsilon_d$ (%)</th>
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<td>274 ± 2.5</td>
<td>192.5 ± 2.5</td>
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<tr>
<td>300 °C</td>
<td>11.9</td>
<td>12.8</td>
<td>276.4 ± 3.3</td>
<td>176 ± 2.7</td>
</tr>
<tr>
<td>350 °C</td>
<td>25.2</td>
<td>29</td>
<td>268 ± 2.4</td>
<td>169.6 ± 1.5</td>
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<tr>
<td>400 °C</td>
<td>29.7</td>
<td>32.6</td>
<td>263.6 ± 2.5</td>
<td>155 ± 1.7</td>
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<tr>
<td>450 °C</td>
<td>29.3</td>
<td>31.8</td>
<td>264 ± 2.9</td>
<td>135.7 ± 0.4</td>
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<table>
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<tr>
<th>Treatment</th>
<th>$\varepsilon_u$ (%)</th>
<th>$\varepsilon_d$ (%)</th>
<th>UTS$_u$ ± UTS$_u$ (MPa)</th>
<th>TYS$_u$ ± TYS$_u$ (MPa)</th>
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<tbody>
<tr>
<td>Rolled</td>
<td>4.3</td>
<td>4.8</td>
<td>173.3 ± 4</td>
<td>138.2 ± 1.7</td>
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<tr>
<td>250 °C</td>
<td>3.3</td>
<td>3.4</td>
<td>194.2 ± 5.9</td>
<td>129.3 ± 4.9</td>
</tr>
<tr>
<td>300 °C</td>
<td>3.8</td>
<td>4.2</td>
<td>225 ± 2.6</td>
<td>124.5 ± 1.4</td>
</tr>
<tr>
<td>350 °C</td>
<td>24.5</td>
<td>29.7</td>
<td>240 ± 2.2</td>
<td>111 ± 4.8</td>
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<tr>
<td>400 °C</td>
<td>24.9</td>
<td>29.6</td>
<td>184.9 ± 2.5</td>
<td>71.3 ± 3.4</td>
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<tr>
<td>450 °C</td>
<td>26.7</td>
<td>29.6</td>
<td>220.6 ± 2.9</td>
<td>70.4 ± 2.4</td>
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<table>
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<th>Treatment</th>
<th>$\varepsilon_u$ (%)</th>
<th>$\varepsilon_d$ (%)</th>
<th>UTS$_u$ ± UTS$_u$ (MPa)</th>
<th>TYS$_u$ ± TYS$_u$ (MPa)</th>
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<tr>
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<td>5.3</td>
<td>7.1</td>
<td>168.5 ± 3</td>
<td>146 ± 5.5</td>
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<tr>
<td>250 °C</td>
<td>2.6</td>
<td>2.7</td>
<td>205.5 ± 7</td>
<td>134 ± 2.5</td>
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<tr>
<td>300 °C</td>
<td>3.1</td>
<td>3.3</td>
<td>212.7 ± 4.7</td>
<td>124.6 ± 1.5</td>
</tr>
<tr>
<td>350 °C</td>
<td>11.8</td>
<td>11.9</td>
<td>197.6 ± 4.2</td>
<td>106 ± 4.7</td>
</tr>
<tr>
<td>400 °C</td>
<td>14.1</td>
<td>14.9</td>
<td>203.1 ± 2.6</td>
<td>101.5 ± 1.6</td>
</tr>
<tr>
<td>450 °C</td>
<td>15.2</td>
<td>16.9</td>
<td>203.3 ± 4.4</td>
<td>99 ± 2.1</td>
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</table>

* mean ($\overline{x}$) and standard deviation ($\Delta$) calculated over 3 measured stress-strain curves

Fig. 6.7(a) clearly indicates an obvious trend of increasing elongation with decreasing texture intensity. The best ductility response for both alloys was observed for annealing treatment at 400°C, at which the Gd alloy achieved an outstanding maximum elongation of ~ 40% (c.f. Table 6.1). Figs. 6.7(a) and (b) represent the variation of maximum elongation and ultimate tensile strength as a function of basal pole intensity and annealing temperature.
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

Figure 6.7 a) Elongation to failure as a function of basal pole intensity (left) and b) the variation of elongation to failure (dashed lines) and ultimate tensile strength (dash-dot-dashed lines) as a function of annealing temperature (right)

6.3.2 Texture and Microstructural Characterization

Fig. 6.8 represents post-mortem textural and microstructural analysis for the specimens displaying the highest tensile elongations (cf. Fig. 6.6). Fig. 6.8(a) depicts optical micrographs of the tensile specimens at their respective failure strains. The binary alloys exhibited some evidence of deformation twinning, mostly observed in coarse grains. Few instances of void nucleation at twin-twin intersections were also visible (marked by arrows in Fig. 6.8(a)). For the quaternary alloys, twinning seemed to be more or less impeded, as indicated by the optical micrographs. Tensile deformation at ambient temperature seemed to refine the annealing microstructure (with grain size measurements yielding values of 2.5 µm (SE = 0.7) for the Gd alloy and 3.2 µm (S.E = 0.7) for the Ce-alloy). Fig. 6.8(b) shows EBSD orientation maps represented in terms of basal pole tilt from ND. Noise reduction was performed up to a minimum of 5 indexed neighbors for each mapping. Corresponding EBSD basal pole figures (scatter and contour data) are given in Fig. 6.8(c). It is shown that in case of the binary alloys, tensile deformation produced primarily basal textures, with frequency peaks of basal pole tilt between 25° - 30° (Fig. 6.8(c)).
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

Figure 6.8 a) Optical micrographs post-tensile tests for the four alloys (Mg-Gd, Mg-Ce, Mg-Zn-Zr-Gd and Mg-Zn-Zr-Ce), b) Corresponding basal pole tilt maps, c) Single orientation scatter and recalculated pole figures, d) basal pole tilt distribution histograms

Table 6.2 CRSS ratios used in the GIA-TW model

<table>
<thead>
<tr>
<th>Alloy Name</th>
<th>$r_{py&lt;\alpha}$</th>
<th>$r_{py&lt;\alpha}$</th>
<th>$r_{py&lt;\alpha+a}$</th>
<th>$r_{etw&lt;n&gt;/r_{etw&lt;g}&gt;}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Ce</td>
<td>--</td>
<td>100</td>
<td>70</td>
<td>0.5/0.25</td>
</tr>
<tr>
<td>Mg-Gd</td>
<td>--</td>
<td>--</td>
<td>70</td>
<td>--</td>
</tr>
<tr>
<td>Mg-Zn-Zr-Ce</td>
<td>1</td>
<td>0.9</td>
<td>1.7</td>
<td>--</td>
</tr>
<tr>
<td>Mg-Zn-Zr-Gd</td>
<td>0.9</td>
<td>0.7</td>
<td>4</td>
<td>--</td>
</tr>
</tbody>
</table>

$r_t = \frac{r_t}{r_{basal}}$; (pr: Prismatic, py: Pyramidal, etw: Tensile twin, n : nucleation & g: growth)

This was particularly striking for the Gd-alloy since its annealing texture was off-basal in nature. The tensile textures of the quaternary alloys showed generally little variation from the corresponding annealing textures. For the quaternary Gd-alloy, it was particularly evident that the texture spread in TD became more prevalent than the spread in RD, which is also the tensile direction. The position of peak orientations was basically
unchanged in comparison to the annealing texture (Fig. 6.8(d)) but there were much more orientations on the TD-ND fiber.

6.4 Texture Evolution Prediction Using a Grain-Interaction Model

To investigate the underlying deformation mechanisms a grain interaction model (GIA-TW) was used to simulate the experimental textures for the specimens showing the best ductility response during tension at ambient temperature (c.f. Table 6.2). Details of the GIA-TW model can be found in [135]. The respective starting experimental textures (Fig. 1) were discretized into 4000 grains of the same weight and used as input to the model. The average initial grain dimensions were defined as 20µm x 20µm x 20µm and the grains were assumed to be of equiaxed nature. The model simulated the deformation of the material under uniaxial tension for an imposed strain rate of $5 \times 10^{-4}$ s$^{-1}$, up to select strain levels, equal to the recorded failure strains. Hardening effects due to both slip and twinning were not considered in predicting the texture development. The only parameters that were varied in the simulation were the CRSSs of the deformation modes, which were given as multiples of the reference deformation mode; basal slip. The CRSS values were considered the same for all equivalent systems in one deformation mode. The allowed deformation modes were $(0002)(11\bar{2}0)$ basal slip, $(1\bar{1}00)(1\bar{1}2\bar{0})$ prismatic slip, $(1\bar{1}01)(1\bar{1}2\bar{0}) <α>$ pyramidal slip, $(1\bar{1}22)(\bar{1}\bar{1}23) <c+a>$ pyramidal slip and $(10\bar{1}2)(\bar{1}011)$ tension twinning (with two different CRSSs for nucleation and growth).

Fig. 6.9 represents the simulated pole figures along with the corresponding slip mode activities, obtained from the GIA-TW model. The simulated textures show a reasonable agreement with the experimentally obtained EBSD textures (c.f. Fig. 6.8(c)). The corresponding deformation modes and their relative CRSS ratios are given in Table 6.2. The individual slip mode activities indicate the relative contribution from different slip and twinning modes to the simulated texture development, which will be discussed in detail in the following section.
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6.5 DISCUSSION

6.5.1 INFLUENCE OF ‘NON-REES’ ON SHEAR BANDING

The addition of Zn and Zr to the binary Mg-1Ce and Mg-1Gd alloys seemed to magnify the tendency of the material to shear banding. Rolling trials conducted at intermediate strains, revealed profuse material twinning in both case (c.f. Fig. 6.10). Moreover, like in the case of the binaries (c.f. section 4.4.1), the Gd alloy once again revealed a relatively higher density of shear bands compared to the Ce alloy. It is proposed that this is as a result of additional interactions caused due to the zinc solute atoms. The atomic radius is 0.134 nm for Zn, 0.160 nm for Mg, and 0.180 nm for Gd. As opposed to Gd, Zn substitutional solute atoms will cause a somewhat larger but negative misfit (16.25%). Having both elements in the solid solution will produce strong compression and extension strain fields. Therefore, it is probable that individual Gd and Zn atoms will tend to segregate to each other in order to minimize the elastic strain energy of the solid solution. Based upon atomic size and weight effects, Zn can be
expected to have a much higher diffusivity rate than Gd. Under sufficient thermal activation, it is hence conceivable that both elements could form solute pairs or even clusters of multiple pairs. For the current study, this tenable process could likely occur during homogenization treatment at 450°C prior to rolling, and would subsequently produce effective obstacles to dislocation motion on slip planes. Similar observations can be found in the literature on such co-segregation of Zn and RE solutes in Mg alloys to form dimers, and the resulting hindrance towards dislocation glide and enhanced creep resistance of the material [136-138].

The observation regarding shear banding during rolling being highly promoted in the quaternary alloys, as opposed to their binary counterparts could be thus elucidated by a hypothesis that solute pairs or solute clusters of large REE atoms and small Zn atoms have a stronger dislocation-solute interaction (pinning effect) than individual REE atoms. It is noted that even if some REEs in a binary Mg-RE solid solution manage to form ‘short range ordering’ of REE-REE solute pairs [129], the aforementioned pinning effect would still be more profound for multi-component solid solutions with additional ‘non-REE’ atoms. The difference between the shear band densities of the alloys with respect to the REEs can be likely attributed to the poor solid solubility of Ce, whereby the co-segregation of Zn and Ce atoms could lead to precipitation of Mg-Zn-Ce phase observed.

Figure 6.10 Heavily twinned as-rolled microstructures after 50% rolling reduction
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

in Fig. 6.3(a), thereby reducing the overall solute content, and the associated pinning effects on dislocation glide.

6.5.2 Recrystallization and grain growth texture development

Mg and its commercial alloys commonly undergo recrystallization at $T \sim 0.5T_m$ [11]. In the present study, onset of recrystallization was delayed to $T \sim 0.6T_m$. Retardation of recrystallization kinetics in Mg alloys containing REEs has been often attributed to drag effects on grain boundaries by secondary phases and solute segregates, as mentioned previously in section 4.2. The current results have demonstrated that recrystallization has led to the nucleation of new grain orientations relative to the deformation texture, and resulted in a significant texture weakening. These new orientations were not randomly distributed, and depicted a characteristic tilt around the sheet plane normal forming a continuous fiber between RD and TD. Nucleation of recrystallization in the investigated alloys was primarily associated with shear bands. These have exhibited very large internal misorientation gradients, ranging between $5^\circ$ - $10^\circ/\mu$m. Such high distortions can generate a wide orientation spectrum for recrystallization nucleation, similar to that observed in the binary alloys (c.f. Chapter 4). The deformation/recrystallization texture transition for the investigated alloys, where a significant alteration of the annealing texture was detected, has shown different characteristics. For the binary Mg-1Ce alloy annealing texture modification was purely quantitative. Qualitative alteration was achieved when Zn and Zr were additionally alloyed. For the Gd containing alloys, new annealing textures were detected in both cases, with and without Zn and Zr. However, the latter case seemed to trigger the texture transition at a lower temperature (cf. Fig. 6.1). The following discussion will treat the aforementioned texture response in each alloy system and point out the underlying mechanisms.
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

Figure 6.11 Schematic illustration of proposed SBN mechanism.

(i) Gd-containing alloys: To obtain a better insight into the observed recrystallization texture modification in the investigated Mg-1Gd and Mg-1Zn-1Zr-0.6Gd alloys, it is crucial to determine the role of shear bands in the recrystallization process. Fig. 6.11 depicts a simplistic illustration of the SBN mechanism of recrystallization. Shear bands are usually sites of high strain energy and orientation gradient (Fig. 6.11(a)). Accordingly, recrystallization nucleation at shear bands results in nucleation of grains with various orientations, including ones with distinct orientations from the deformation texture (Fig. 6.11(b)). As is generally known, the crystallographic texture resulting from
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

Recrystallization is determined by the orientation of the nuclei, and any selective nature of the growth process. Selective growth can obviously lead to one type of nuclei eclipsing another (Fig. 6.11(c)), and by that determine, which orientation(s) would appear in the final recrystallized microstructure. In the current investigation, the growth process of recrystallization nuclei in the shear bands would depend upon the following criteria:

a) The driving force provided by stored strain energy.

b) Percentage of high angle boundaries of evolving subgrains.

c) Solute drag effects.

While the first two factors will accelerate the recrystallization process via increasing the driving pressure and grain boundary mobility, needed to grow at the expense of the surrounding matrix, the third parameter will be responsible for retarding the recrystallization rate. During annealing treatments, it is quite likely that the proposed solute-pairs/clusters (cf. section 6.5.1) will exert solute pinning effects on grain boundary migration, thus affecting nucleus growth. With respect to recrystallization growth behavior of Mg-1Gd (c.f. Chapter 4), we reported that in terms of driving pressure and growth rate ‘off-basal’ nuclei posed a clear advantage over ‘basal’ ones. In the presence of strong solute pinning, oriented growth should become more evident, since only those nuclei with large enough driving pressure and mobility will have a chance of growing into new grains in the recrystallized microstructure. In this regard, the role of annealing temperature is important. At 300°C, basal-oriented grains were a major part of the final annealing microstructure of the Mg-1Gd alloy despite their aforementioned growth disadvantage. This can be attributed to (a) weaker solute drag effects, and (b) comparatively lower shear band density. The observed relative difference in the fraction of HAGBs in Mg-1Gd and Mg-1Zn-0.6Zr-1Gd at 300°C (Table 6.3) is most likely a result of different solute drag pressure between the two alloys.
Recrystallization mechanisms in wrought Mg alloys containing rare-earth elements

Table 6.3 HAGB percentage values for Mg-1Gd and Mg-1Zn-0.6Zr-1Gd

<table>
<thead>
<tr>
<th>Alloy</th>
<th>No. of grains measured</th>
<th>H.A.G.B fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-1Gd</td>
<td>4947</td>
<td>63.2</td>
</tr>
<tr>
<td>Mg-1Zn-0.6Zr-1Gd</td>
<td>6842</td>
<td>31</td>
</tr>
</tbody>
</table>

The aspect of shear band density is also important because it affects the strain distribution in the microstructure. Low shear banding frequency in the Mg-1Gd alloy will increase the average local strain sustained in each shear band, which implies greater stored strain energy to overcome solute drag. Consequently, growth of basal-oriented nuclei will become easier relative to the counterpart quaternary alloy.

Increasing the annealing temperature to 350°C resulted in additional nucleation events in the vicinity of precipitated Mg-Zr clusters (Mg-1Zn-0.6Zr-1Gd alloy). Recrystallized grains associated with PSN were much smaller than other new grains resulting from SBN (c.f. Fig. 6.12). The EBSD results at 350°C in Fig. 6.4 presented a classification of ‘large’ and ‘small’ grains, aiming to evaluate the contribution of each nucleation mechanism to the recrystallization texture. Interestingly, while both grain groups seemed to contribute to the off-basal texture fiber component in the (0002) pole figure, basal orientations appeared to pertain only to the group of small grains. This observation agrees with the general concept of PSN giving rise to ‘random-oriented’ recrystallization nuclei, including ones with close orientations to the deformation basal texture. However, the predominance of off-basal grains as the vast majority of the final annealing microstructure is clear indication that this group of orientations, resulting from both PSN and SBN are generally associated with a higher growth rate, determined by the driving force and grain boundary mobility.
At 450°C, the EBSD microstructure in Fig. 6.12 (Kikuchi band contrast) shows appreciable grain growth with a bimodal nature of grain size distribution. In Fig. 6.4, the corresponding group of ‘small’ grains (primarily associated with precipitates) appeared to retain its broad texture spread characteristics. The other group of larger grains has also maintained their off-basal orientation fiber with intensity peaks close to RD and TD. Grain growth, occurring after recrystallization is terminated, seems to provide the ‘statistically larger’ grains with a new growth advantage over smaller grains. Driven by the boundary curvature, large grains will coarsen further and small grains will be consumed in order to minimize the interfacial energy. Thus, the role of grain growth during annealing at elevated temperatures is to sustain the recrystallization texture.

(ii) Ce-containing alloys: The annealing texture response of the quaternary Ce alloy with respect to its binary counterpart at 350°C and above was remarkably contrasting (cf. Fig. 6.1). It is proposed that the solubility and the precipitation characteristics of the two alloys strongly influence the delicate interplay between particle
pinning and particle stimulated recrystallization, which dictates the evolution of the recrystallization texture. Table 6.4 provides a general characterization of precipitates present in both alloys. With respect to recrystallization, precipitates can hence be categorized as (a) Zr-rich (haloes) and fine Mg-Zn-Ce particles (<1 μm) that contribute towards Zener pinning, and (b) Mg-Zr clusters and large Mg-Zn-Ce precipitates (>1 μm), which promote recrystallization [65]. Due to substantially low solubility of Ce in Mg, the effect of solute drag on recrystallization at lower annealing temperatures can be neglected. The observed delay in the onset of recrystallization is instead explained on the basis of particle pinning, whereby at lower annealing temperatures the driving force for nucleus growth cannot overcome the pinning effect. Fig. 6.13(a) presents the average size and area fraction of second phase particles at different processing conditions for the Mg-1Zn-0.6Zr-1Ce alloy. As evident, there is a consistent decrease in both parameters from the as-rolled state to the 450°C annealed state. Prior investigations conducted by Aaron and Kotler [139] have established that the overall dissolution rates of spherical precipitates are relatively higher than needle or plate-like precipitates. Moreover, smaller spheres were observed to dissolve faster than coarser ones due to lower interfacial area and higher diffusive fluxes. It is thus proposed that the dissolution rate of the finer (<1 μm) precipitates will be rather fast. This implies that during annealing the effect of Zener pinning should decrease, which renders recrystallization possible. From Fig. 6.1 (X-ray bulk textures) and Fig. 6.5 (EBSD microtextures) it is evident that the presence of basal orientations falls back with increasing annealing temperature, i.e. with decreasing particle pinning effect.

Annealing temperatures of 350°C and 400°C were apparently sufficient enough to result in favorable growth of the off-basal shear band nuclei. Yet, particle pinning seemed still capable of restricting their growth to the extent that basal orientations were not completely diminished.
Raising the temperature to 450°C witnessed a complete disappearance of basal orientations (cf. Fig. 6.1), and led to accelerated dissolution kinetics of precipitates. As shown in Fig. 6.13(a), the measured area fraction of particles decreased by 50% relative to the initial state. Fig. 6.13(b) and (c) further indicate a more or less consistent average particle diameter, and an increase in the mean spacing between particles. Such tendencies agree with the assumption made earlier that coarse precipitates tend to retain in the microstructure and finer ones dissolve into the matrix. The maximum solubility of Zr in Mg at 450°C is ~0.5 wt. %, as compared to ~0.04 wt. % at 300°C (Fig. 6.13(d)) [140]. An increased solubility at higher annealing temperatures could very likely promote (a)
dissolution of free-Zr particles into the matrix, and (b) their subsequent diffusion to the
thermodynamically more stable Mg-Zr clusters. This will cause an increase in the local
solute content of their whereabouts, prompting the previously dissolved Zr particles to
redeposit on their surface, a behavior resembling ‘Ostwald ripening’.

Table 6.4 Precipitate classification on the basis of size, distribution and thermodynamic stability in the
investigated Mg-Zn-Zr-RE alloys

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Ce-alloy</th>
<th>Gd-alloy</th>
<th>Thermodynamic stability</th>
<th>Size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-Zr</td>
<td>Yes</td>
<td>Yes</td>
<td>stable</td>
<td>&gt;1</td>
</tr>
<tr>
<td>Zr-rich*</td>
<td>Yes</td>
<td>Yes</td>
<td>metastable</td>
<td>&lt;&lt;1</td>
</tr>
<tr>
<td>Mg-Zn-(Ce,Gd)</td>
<td>Yes</td>
<td>No</td>
<td>metastable</td>
<td>&lt;1 &amp; 1-10</td>
</tr>
</tbody>
</table>

* Solubility of Zr in Mg $\rightarrow$ 0.04 wt.% at 300°C vs. 0.5 wt.% at 450°C

Since the Mg-Zr phase is thermodynamically stable at 450°C, the observed
reduction of the total particle fraction could arise mainly from dissolution of the ‘fine’
metastable Mg-Zn-Ce phase. Sanjari et al. [141] have recently established that the
solubility of Ce in Mg-1wt.%Zn-1wt.%Ce increases to 0.0932 wt.% at 450°C, as
compared to 0.00066 wt.% - 0.02 wt.% between 300°C and 400°C. An overall reduction
of fine particles and a concomitant increase in the Ce solute content in solid solution will
result in a similar recrystallization behavior to the one witnessed in the counterpart alloy
containing Gd. Large grains pertaining to shear band nuclei with large strain energy and
growth advantage exhibit off-basal orientations close to RD and TD, while smaller grains
pertaining mostly to PSN nuclei (with no particular growth advantage) show more or less
a random orientation distribution (Fig. 6.5). With significant reduction of fine particle
fraction, PSN occurs readily at the Mg-Zr clusters and the ‘coarse’ Mg-Zn-Ce precipitates.
For the binary Mg-1Ce alloy, Mg$_{12}$Ce is the only class of precipitates that is usually present. Our investigations have shown that high strain rolling resulted in severe fragmentation of this phase, whereby the occurrence of PSN became very unlikely. The absence of bimodal size distribution of second phase particles renders the aforementioned process of particle coarsening during annealing difficult. As a result the pinning effect of Mg$_{12}$Ce particles will continue even at elevated annealing temperatures, thereby resulting in qualitatively negligible texture modification.

### 6.5.3 Deformation Mode Activation and Simulated Texture Development During Tension

The effect of recrystallization texture transition on the ductility of the material was clearly evident, with Mg-1Gd, Mg-1Zn-0.6Zr-1Ce and Mg-1Zn-0.6Zr-1Gd reporting excellent maximum tensile elongation values ranging between ~ 30% - 40%. Polycrystal plasticity texture simulations provided useful insight into the deformation mechanisms that could have given rise to the experimentally measured tensile textures shown in Fig. 6.8.

The deformation mode activity for Mg-1Ce indicated strong activation of basal slip along with some {10\(\bar{1}2\)} tensile twinning, resulting in a basal deformation texture, similar to the one measured by EBSD. Considering the corresponding starting texture resulting from annealing at 450°C, activation of the aforementioned deformation modes is plausible, and it seems that addition of cerium alone does not display much potency of activating other slip modes. After some straining the model activated pyramidal slip modes. Yet, their relative activities remained negligible in comparison to basal slip (Fig. 6.9(a)).

The deformation behavior of Mg-1Zn-0.6Zr-1Ce was very different (Fig. 6.9(c)). The imposed tensile strain was mostly accommodated by ‘pyramidal <a>-slip’, along with comparably less contributions from basal, prismatic and pyramidal <c+a>-slip
modes. The relative contribution of the latter two modes increased with increasing strain, whereas the activity of basal slip decreased consistently. Looking at the starting texture, all of the aforementioned slip systems have a similar probability of activation, in terms of SF. In a conventional Mg alloy, the most preferred slip mode in such a case would have been basal slip due to its relatively much lower CRSS. For the Mg-1Zn-0.6Zr-1Gd alloy the deformation mode activity showed similar trends of preferential pyramidal $\langle a \rangle$-slip activation throughout the simulation. Basal and prismatic slip modes were also important to some extent (Fig. 6.9(d)).

Assuming that the demonstrated relative ‘hardening and softening’ of basal and pyramidal $\langle a \rangle$-slip modes takes place in experiments, it would be most likely a solute-related phenomenon. The effect of solute pairs or clusters on impeding basal slip has been elucidated in sections 4.4.1 and 6.5.1. Moreover, the role of solute REEs in decreasing unstable stacking fault energies, thereby promoting nucleation of non-basal slip modes has been also reported in literature (e.g. [35]). It is also noted that the finer grain size in the Zr-refined alloys will effectively inhibit mechanical twinning [65] (Fig. 6.9).

Interestingly, although the chosen Mg-1Gd alloy possessed a ‘modified’ annealing texture prior to the tensile experiments, its texture development during tension showed a recurrence of basal-like sheet texture with some TD spread (Fig. 6.8). By comparison to its counterpart quaternary alloy, the lack of pyramidal $\langle a \rangle$ and prismatic slip mode activation in the simulation is attributed in reality to weaker dislocation-solute interactions (c.f. sections 4.4.1 and 6.5.1). The contribution of these two slip modes is important for maintaining the TD-spread character of the modified annealing texture. Even though, compression and double twinning were not considered in the texture simulations, they might still have contributed to the experimental texture development during tension.
6.6 **SUMMARY**

The present chapter can be summarized as follows,

1) Influence of REEs on shear banding is amplified in the presence of additional 'non-REEs', wherein 'REE-non-REE' pairing/clustering intensify such solute-dislocation interactions.

2) Nucleation of recrystallization initiated inside shear bands and near particles. SBN produced a diversity of orientations with varying stored energies, whereas particle stimulated recrystallization resulted in nucleation of 'random' orientations.

3) Texture modification in Mg-1Zn-0.6Zr-1Gd is primarily dictated by oriented growth characteristics during recrystallization, wherein the growth is restricted to those nuclei with sufficient stored energies and grain boundary mobilities that are successfully able to break free of any existing solute atmosphere. In that respect, the off-basal orientations originating from shear bands, associated with much larger stored energies and neighboring misorientation, show favorable growth. On the other hand, the PSN orientations and the basal-oriented shear band nuclei show more or less no distinct growth advantage, accounting for a minor fraction of the overall recrystallized microstructure.

4) In contrast to Mg-1Gd, reduction in the texture transition temperature exhibited by its quaternary counterpart is attributed to a greater extent of solute drag and higher shear band frequency.

5) With respect to recrystallization texture modification in Mg-1Zn-0.6Zr-1Ce or the lack thereof in Mg-1Ce alloy, the respective dissolution and precipitation kinetics of the added alloying elements plays a significant role. Contrary to Mg-1Ce, it’s more complex counterpart exhibits reverse precipitation and simultaneous instances of particle coarsening, resulting in a competition between particle pinning and particle stimulated recrystallization events.
6) The addition of 'non-REEs' further augmented the REE-related ductility enhancement, resulting from activation of non-basal deformation modes. A remarkable ductility enhancement of ~40% elongation to failure was exhibited by Mg-1Zn-0.6Zr-1Gd alloy upon large-strain rolling and subsequent recrystallization annealing at 400°C.
ROLE OF IMPURITY SEGREGATION AT GRAIN BOUNDARIES ON TEXTURE MODIFICATION IN BINARY MAGNESIUM-RE ALLOYS

Our findings related to texture evolution in dilute binary Mg-RE alloys during recrystallization and grain growth, with single REE additions, suggest that the degree of observed texture modification strongly depends upon the material processing technique and the choice of REE addition. It was found that recrystallization in shear bands [102, 142], twins [143] and in the vicinity of particles [66, 142, 143] are typically the most potent means of modifying texture in magnesium. With respect to the influence of the type of REE-addition, significant texture changes were displayed by solute based Mg-1wt.%Gd on recrystallization and grain growth unlike its counterpart precipitate based Mg-1Ce alloy that revealed none or negligible deviation from the basal deformation texture (c.f. Chapter 4). While the observed texture changes in the former alloy was attributed to favorable growth of off-basal orientations over the grains oriented basally, the lack of REE-induced texture modification in the latter alloy was primarily attributed to the detrimental role of secondary Mg₁₂Ce phases, which were fine enough to pin grain boundaries and thereby restricting any growth related evolution of the crystallographically soft non-basal orientations.

Numerous studies [92, 93, 117, 142, 144-148] attribute such drastic RE-texture modification during recrystallization and grain growth to arise from the tendency of solute based REEs to segregate at stacking faults and grain boundaries. In particular such segregation behavior displayed by solute REEs is frequently known to inhibit DRX, whereby they significantly change the DRX mechanism and the subsequent recrystallization texture [70]. DRX in extruded Mg-RE alloys have been known to result in strong texture modification and randomization, unlike pure Mg and conventional alloys where the DRX texture often closely follows the orientation of the deformed grains.
that are primarily basal in nature [58, 70]. While REE-segregation near stacking faults can alter stacking fault energies, thereby influencing recovery and recrystallization processes [117, 142, 143]; the presence of solute REEs in grain boundaries can significantly modify the recrystallization and grain growth behavior with respect to an overall retardation of recrystallization kinetics and changing relative boundary mobilities [16, 145]. Such retardation of annealing kinetics not only triggers formation of deformation heterogeneities, such as shear bands or compression twins, but also facilitates nucleation of less common orientations that would be absent during recrystallization in conventional alloys [145]. Although there have been quite a few arguable theories on how RE elements might affect the development of recrystallization and grain growth textures in Mg-RE alloys, the principal mechanisms on how RE orientations nucleate in the deformation microstructure and subsequently grow during recrystallization are still not fully understood and remain subject to greater scrutiny. In purview of the afore-mentioned theories, the present work is an attempt to further extend our understanding of the REE-related recrystallization and grain growth, especially with respect to solid solution Mg-RE alloys. The current work will hence address the following questions,

1) Does different solute REEs exhibit distinctive tendencies of segregation at grain boundaries and what is their resultant influence upon the overall recrystallization and grain growth behavior?

2) Is there a correlation between segregation characteristics of different REE-solutes to the associated texture evolution during recrystallization and grain growth and whether it impacts the overall material ductility?

This chapter documents the texture and microstructure evolution during shear band recrystallization and grain growth in binary Mg-1Dy and Mg-1Gd alloys. Both Gd and Dy are solute based REEs exhibiting similar size (Dy ~179 pm vis-à-vis Gd ~180
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pm) and weight (Dy ~164 u vis-à-vis Gd~157 u) characteristics. Attempts to establish a
definite correlation between RE-solute segregation behavior at grain boundaries and
corresponding recrystallization and grain growth behavior in the two binary alloys by
means of atomic, mesoscale and macroscale characterization are presented in Sections 7.1
to 7.3. Subsequently the suggested mechanisms are correlated with the respective texture
evolution and are described in sections 7.4 and 7.6. Finally, the manuscript also considers
the overall impact of solute segregation and related texture modification on the
consequent room temperature ductility in both alloys (c.f. section 7.5 and 7.6). The
overall conclusions are summarized in section 7.7.

7.1 XRD Textures and Optical Microstructures

Fig. 7.1 shows the bulk textures and optical microstructures for Mg-1Gd
(reproduced from Chapter 4) and Mg-1Dy alloys for rolled and annealed states. Both
produced split basal rolling textures, with ~±15° splitting along the RD. The basal peaks
display asymmetry in terms of texture intensities. Microstructurally, both alloys reveal
massive shear banding, with no remnants of the initial microstructure.

Annealing at 300° C induces negligible changes in the texture features, apart from
a massive drop in the texture intensity values witnessed in the case of Mg-1Dy. On the
other hand, Mg-1Gd retains its texture strength after annealing at 300° C. Increasing the
temperature to 350°C led to a drastic texture transition in Mg-1Gd, highlighted by a
complete disappearance of basal component. On the other hand texture evolution in Mg-
1Dy after 350°C anneal indicated no changes both qualitatively and quantitatively.
Subsequent annealing at higher temperatures (400° C and 450° C) retain the qualitative
features in Mg-1Gd accompanied by slight strengthening of the off-basal peaks, while the
texture components in Mg-1Dy show increased off-basal spreads and weakening of basal
component.
Optical microstructures after annealing at 300°C for 60 min revealed onset of recrystallization inside the shear bands in both alloys, depicted by formation of fine recrystallized grains displaying a banded morphology. Annealing at 350°C resulted in complete recrystallization in both alloys, with Mg-1Dy showing relatively finer grain sizes than its counterpart Gd alloy. Anneals performed at 400°C and 450°C led to massive grain growth in Mg-1Dy in comparison with Mg-1Gd, which revealed a bimodal grain size distribution comprising of large grains surrounded by clusters of small grains.
7.2 EBSD CHARACTERIZATION, GRAIN DISTRIBUTION AND SIZE ANALYSIS

Figure 7.2 IPF mappings and mean grain sizes of a) Mg-1Dy and b) Mg-1Gd after annealing at 350°C; c) EBSD pole figures of Mg-1Dy and Mg-1Gd, annealed at 350°C; d) Normalized grain size distribution for Mg-1Dy and Mg-1Gd, annealed at 350°C

Figs. 7.2(a) and (b) present the inverse pole figure (IPF) orientation maps for Mg-1Dy and Mg-1Gd at 350°C. The mean recrystallized grain sizes corresponding to Mg-1Dy and Mg-1Gd were measured as 9.1 µm (S.E. = 0.53) and 23 µm (S.E. = 0.47) respectively. The chosen sample size for grain size measurements for Mg-1Dy and Mg-1Gd were ~9000 and ~3000 grains (obtained from multiple mappings), respectively. Both microstructures reveal similar spatial distribution of grains, described by numerous small grain clusters in the vicinity of larger ones. In Mg-1Gd the contribution of the basal oriented grains (in red) was considerably lower and most of them were associated with the smaller grain sizes, whereas such a distinction was difficult to establish for Mg-1Dy. Fig. 7.2(c) presents the recalculated EBSD (0002) pole figures for both the alloys. The
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Microtexture data shows excellent agreement with the bulk textures shown in Fig. 7.1. Fig. 7.2(d) represents the normalized grain size distribution for both Dy and Gd alloys. The normalized grain size parameter is expressed as a ratio of the individual grain size to the mean grain size value. Both distributions follow a log normal behavior. The longer tail seen in Mg-1Dy in comparison with Mg-1Gd indicates larger variation of grain sizes. The largest grain in Mg-1Dy is nearly 5 times the mean grain size, whereas the ratio between the largest and the mean grain size in Mg-1Gd is ~4.

Figs. 7.3(a) and (b) display the IPF mappings for Mg-1Dy and Mg-1Gd after annealing at 450°C for 60 min. The mappings indicate significant differences in the topology of grains. While in the case of Mg-1Dy, the distribution is spatially random with most grains assuming large grain sizes; the arrangement of grains in Mg-1Gd seems to maintain the grain topology observed in 350°C i.e. small grain clusters in the vicinity of considerably larger grains. As in the case of 350°C, majority of the larger grains in Mg-1Gd were associated to the off-basal orientations, while the smaller ones were mostly that of basal type. The average grain sizes (measured over ~2000 grains) for Mg-1Dy and Mg-1Gd were 75 µm (S.E. = 0.62) and 38.9 µm (S.E. = 0.67), respectively. The relative difference in the grain sizes for basal and off-basal orientations measured for Mg-1Gd and Mg-1Dy, defined as $\Delta d_{rel} (%) = \left( \frac{d_{off-basal} - d_{basal}}{d_{basal}} \right) \times 100$; were 34% and 17% respectively. The EBSD recalculated (0002) pole figures shown in Fig. 7.3(c) show reasonably good agreement with the bulk textures, further corroborating the statistical validity of the orientation data set.

Fig. 7.3(d) displays the grain size distribution for both alloys at 450°C. A longer tail of the distribution in case of Mg-1Gd in comparison with Mg-1Dy indicates retention of most of the recrystallized orientations in the Mg-1Gd microstructure after annealing at 450°C. Typically the width of grain size distribution scales inversely with decreasing grain number density i.e. the right hand tail of distribution shortens with decreasing grain
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number density. The ratio between the largest and the mean grain size values are ~5 for Mg-1Gd and ~ 3.5 for Mg-1Dy.

Figure 7.3 IPF mappings and mean grain sizes of a) Mg-1Dy and b) Mg-1Gd after annealing at 450°C; c) EBSD pole figures of Mg-1Dy and Mg-1Gd, annealed at 450°C; d) Normalized grain size distribution for Mg-1Dy and Mg-1Gd, annealed at 450°C; e) Experimentally measured relative frequencies of the number of grain interfaces for Mg-1Gd and Mg-1Dy, after annealing at 450°C.

Fig. 7.3(e) presents the relative frequencies of number of grain faces i.e. next neighbors in 2D, extracted from the EBSD datasets corresponding to Mg-1Gd and Mg-
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1Dy alloys obtained after annealing at 450°C for one hour. The distribution corresponding to Mg-1Gd is significantly broad, indicating presence of grains with number of neighbors ranging from 3 to 20 in the present sample. On the other hand, Mg-1Dy revealed a much narrow distribution with the number of grain interfaces lying between 4 and 14. Whereas the grain metrics [149] have an important contribution to the driving force of a particular grain during grain growth, the topology (i.e. number of faces) remains the decisive factor for the determination of a grain’s curvature [150]. For this reason, it is suggested that grains in the Mg-1Gd alloy have a larger growth potential after recrystallization.

The mean grain size variation with increasing annealing temperature for Mg-1Gd and Mg-1Dy alloys is shown in Fig. 7.4. The plot depicts considerably higher grain coarsening rates for Mg-1Dy, varying parabolically with increasing temperature as compared to Mg-1Gd that shows a linear increase with temperature. Comparing the mean grain sizes up till 350°C, the values corresponding to Mg-1Gd are larger than those of Mg-1Dy. At higher annealing temperatures (above 350°C), the trend reverses with the mean grain sizes reported for Mg-1Dy being considerably larger than those observed for Mg-1Gd.
indicating onset of much faster grain growth kinetics in Mg-1Dy at higher annealing temperatures.

7.3 **Three Dimensional Atom Probe Tomography (APT) Characterization**

In order to correlate the texture evolution with respect to the degree of solute-grain boundary interaction in Mg-1Gd and Mg-1Dy, elemental analysis at random HAGBs were performed using APT measurements. The microstructures obtained after 350°C anneals were investigated due to the drastic differences observed in the relative texture evolution trends in the two alloys. Since the magnitude of segregation can very likely vary for different grain boundaries (owing to changing grain boundary character), multiple HAGBs were measured in order to obtain reasonable consistency in the segregation characteristics. The results presented here are thus representative datasets resembling the overall statistical trends in the two alloys.

Fig. 7.5 shows the 3-D spatial elemental distribution of Gd at and around a random HAGB in Mg-1Gd alloy after an hour annealing at 350°C. A volume of 155 x 120 x 118 nm$^3$ was measured from an area containing a HAGB (c.f. Fig. 3.8). The measured dataset comprised of a total of 41 million atoms. Fig. 7.5(a) defines the Gd atomic distribution at the grain boundary in terms of a 2at.% Gd iso-concentration surface. In order to obtain a 1-D concentration depth profile across the grain boundary, a cylindrical region of interest (ROI) defined by a depth, ‘h’ = 70 nm and radius, ‘r’ = 10 nm was oriented normal to the grain boundary plane as shown in Fig. 7.5(b). The ROI coordinates are further displayed in Fig. 7.5(b). The concentration-depth profile plot is shown in Fig. 7.5(c), with zones classified as bulk and grain boundaries. A bin width of 1.5 nm was chosen. The concentration depth profile reveals a strong segregation behavior of Gd atoms over a distance of ~15nm across the grain boundary, with the peak Gd concentration reaching ~ 5at. %. The measured bulk composition (99.76 at.% Mg and 0.24 at.% Gd (~1.1 wt. %)) shows reasonable agreement with chemical composition shown in Table 3.1. Fig. 7.5(d) shows an SEM image of the atom probe tip prior to final
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low energy (5 kV) annular milling step. The image contrast clearly demarcates the boundary highlighted by the dashed white line between grain 1 and 2. The marked region in red corresponds approximately to the area of measurement in the atom probe. Fig. 7.5(d) also shows a 2D contour plot depicting the planar Gd atomic density in the region of APT measurement. A relatively higher Gd concentration highlights the grain boundary.

Figure 7.5 a) 2 at.% Gd iso-concentration surface at and around a random high angle grain boundary in Mg-1wt.%Gd (0.22 at.% Gd) after annealing at 350°C, b) cylindrical region of interest (ROI) across the grain boundary, c) 1-D concentration profile across the grain boundary indicating a Gd-concentration spike at the grain boundary, d) SEM image of the APT tip prior to final step of milling and 2-D contour plot showing planar atomic density of Gd.

Fig. 7.6 shows the APT reconstruction of Mg-1Dy alloy after annealing at 350°C for 60 min. A total volume of ~ 320x150x134 nm$^3$, comprising 130 million atoms was measured. The bulk composition was measured as 99.69 at.% Mg and 0.31 at.% Dy, showing slightly higher values than the expected ~1wt.% (~0.19 at.%). Fig. 7.6(a) shows
a 2D contour plot depicting the planar atomic density of Mg atoms, revealing the grain boundary running normal to the plane of measurement. The grain boundary plane can be also detected from the visible difference in milling tendencies of grains ‘1’ and ‘2’ as well as from the observed image contrast in the SE image of the tip prior to the low energy annular milling procedure shown in Fig. 7.6(a) (as inset). The area highlighted in red in Fig. 7.6(a) indicates the area of measurement. Fig. 7.6(b) shows the individual 3-D elemental maps for Mg and Dy. In both cases evidences of elemental segregation is not distinctive enough to highlight the grain boundary location. Fig. 7.6(d) shows the 1-D concentration-depth profile, with a bin width of 1.5 nm, for the defined cylindrical ROI in Fig. 7.6(a), with a depth ‘h’ = 70nm and radius ‘r’ = 10 nm. The peak Dy concentration is measured as ~1.04 at.%, indicating much weaker grain boundary segregation behavior in comparison to Gd.

**Figure 7.6** (a) 2D contour plot of the planar atomic density of Mg atoms with inset SE image of the APT tip, showing the grain boundary running along the z-axis, (b) 3D-elemental distribution of Mg and Dy elements, (c) 1-D concentration profile measured along the cylindrical region of interest shown in (a)
7.4 Grain growth simulations

To elucidate the impact of grain boundary segregation on microstructure and texture development, computer simulations of grain growth were utilized. Different models can be utilized for this task, namely, network [151-153], Monte-Carlo [154, 155], phase-field [156, 157] and more recently level-set [158, 159] models. Due to its excellent computational stability and good description of the physics of grain growth, a level-set model was used in the present work. The utilized level-set model is available as an open source program\(^1\) and was modified for the present application. This model is capable of considering anisotropic grain boundary energies and mobilities as well as the effect of finite triple junction mobilities in 2D [159].

The essential idea of the level-set algorithm is to describe an interface \(\Gamma\) by the zero level-set of an implicit real valued function \(\Phi(t, x)\) and can be expressed by the following level-set function,

\[
\Gamma := \{ x \in \Omega \mid \Phi(0, x) = 0 \} \ldots (7.1)
\]

where \(\Omega\) is the computational domain. For numerical advantages the level-set function \(\Phi(t, x)\) is restricted to fulfill

\[
|\Phi(t, x)| = 1 \ldots (7.2)
\]

The aforementioned expression is called a signed distance function and its zero contour line represents the entire GB of a certain grain. The algorithm of the model is briefly presented in the following,

1. Initialization of input microstructure: The algorithm initializes a signed distance function to each grain in the microstructure, which represents the entire grain as well as the grain boundary, during the evolution algorithm.

\(^1\) https://github.com/GraGLeS/GraGLeS2D
2. Computation of grain growth: The computation obeys an iterative procedure, comprising of primarily 3 sequential steps that processes the signed distance function representing each grain individually. These steps have been described below,

a) Predictor step: Grain boundary motion is computed on the basis of the mean curvature flow for individual grains. The motion is subsequently altered in order to consider interfacial anisotropy effects such as grain boundary energies, grain boundary mobilities and triple junction mobilities.

b) Corrector step: In order to restore the topological integrity of the microstructure, the grain boundary motion is further corrected by removing free spaces and overlaps between neighboring grains.

c) Re-distancing: Since the level-set function resulting from the Corrector step does not fulfill the conditions imposed in Eq. 3.2., it has to be re-initialized as signed distance function to its zero level set.

This dividing strategy enables the application of grain growth computation on parallel computer architecture. For a more detailed explanation the reader is referred to [158, 159]. For the simulations, microstructures obtained by means of orientation microscopy (EBSD) were discretized and used as input. The resolution was set to 20 grid points per grain in each direction. In order to obtain input data with similar grain size distribution and grain number densities for both alloys, the microstructure obtained after annealing Mg-1Dy at 350°C for 60 mins was adopted as the initial network, whereas in case of Mg-1Gd a starting network corresponding to annealing treatment at 450°C for 4 mins was chosen. The grain boundary migration was mathematically calculated from,

\[ v_n = \mu \gamma_{GB}(\theta) \kappa \quad (7.3) \]
where $\mu$ is the grain boundary mobility, $\kappa$ is the grain boundary curvature and $\gamma_{GB}(\theta)$ is the misorientation angle ($\theta$) dependent grain boundary energy. Misorientation angle ($\theta$) dependent grain boundary energies ($\gamma_{GB}$) were determined by means of the Read-Shockley expression, given as,

$$
\gamma_{GB}(\theta) = \begin{cases} 
\frac{\theta}{15^\circ} \left(1 - \ln \left| \frac{\theta}{15^\circ} \right| \right) & \text{for } \theta \leq 15^\circ \\
\frac{\theta}{15^\circ} & \text{for } \theta > 15^\circ
\end{cases} \quad \text{...(7.4)}
$$

Grain growth simulations for Mg-1Dy considered only the effect of different grain boundary energies on the growth rate, with all mobilities assigned a value, $\mu = 1$. In case of Mg-1Gd, anisotropy in grain growth due to solute drag effects was introduced by considering different grain boundary mobilities, such that the mobility values for grain boundary segments were scaled with respect to the relative grain size difference between adjacent grains. For numerical reasons GB energies and GB mobilities were normalized to the interval (0, 1]. Thus, the mobilities were further weighted by the maximum grain size value by means of the following expression:

$$
\mu_{ij} = \frac{|d_i - d_j|}{d_{max}} \quad \text{...(7.5)}
$$

where $\mu_{ij}$ is the mobility of grain boundary segment between grains ‘i’ and ‘j’, $d_i$ and $d_j$ are the grain diameters of neighboring grains ‘i’ and ‘j’; $d_{max}$ is the grain diameter of the largest grain in the microstructure at a particular time step. The obtained values were subsequently ranged between 0.29 and 1, such that the values below 0.29 were clamped to the lower bound in order to restrict the maximum permissible mobility difference between the fast and slow moving grains in the network. The lower bound value of 0.29 was chosen such that it maintains the experimentally calculated ratio between the coarsening rates of the largest grain (with $\mu_H = 1$) in the microstructure to the mean grain coarsening rate, yielding a value of ~ 3.4.

The temporal changes in the topology of grains in the simulated microstructures were tracked by means of internal simulation time steps that were described as a function of
the rate of coarsening of the mean grain size. The simulated outputs were subsequently correlated with the experimental microstructures corresponding to conditions where the observed grain growth was of similar magnitudes. A more detailed discussion regarding the physical significance of the simulation results will be presented in the section 7.6.2.

**Figure 7.7** Uniaxial tensile curves for a) Mg-1Dy and b) Mg-1Gd (reproduced from Fig. 6.6) for different rolled and annealed states, c) Elongation to failure at different rolled and annealed conditions for both alloys d) UTS values at different rolled and annealed conditions for both alloys

### 7.5 Room temperature tensile tests

Figs. 7.7(a) and (b) show the room temperature tensile stress-strain curves for the two alloys corresponding to as-rolled and annealed conditions. The stress-strain data for Mg-1Gd is derived from Chapter 6. Fig. 7.7(c) shows the variation of mean elongation values with respect to different annealing temperatures for Mg-1Gd and Mg-1Dy. Fig. 7.7(d) displays the relative ultimate tensile strength (UTS) values and corresponding grain sizes for both alloys at different annealing conditions. The best mechanical response
in both alloys is observed for annealing treatment corresponding to 350°C (c.f. Figs. 7.7(a)-(c)), wherein elongation to failure values of Mg-1Gd are ~ 30% vis-à-vis Mg-1Dy displaying elongation values of ~25%. The trends indicate the considerable impact of alloying chemistry as well as the resultant texture on the ambient formability.

7.6 DISCUSSION

The results in the present study reveal marked differences in the recrystallization and grain growth behavior in two solute based Mg-REE alloys viz. Mg-1Dy and Mg-1Gd. While recrystallization texture modification in Mg-1Gd was highlighted by sudden appearance of new soft off-basal orientations, the texture changes in Mg-1Dy during recrystallization and grain growth exhibited a gradual evolution leading to weakening of the initial deformation texture. It is proposed that such distinctive behavior is strongly influenced by the differential role of solute segregation during recrystallization and grain growth. The current section would hence discuss in detail the relative solute segregation tendencies in Mg-1Gd and Mg-1Dy in context with their respective potencies to modify recrystallization textures in magnesium.

7.6.1 GRAIN BOUNDARY SEGREGATION BEHAVIOR IN Mg-1Gd AND Mg-1Dy

APT results indicated greater tendency of grain boundary segregation for Gd solute atoms than Dy atoms, which subsequently manifest in form of higher solute drag in the former. The measured solute concentration at random HAGBs in Mg-1Gd reached as high as ~ 5.2 at. % in comparison with measured grain boundary Dy concentrations of ~1 at.%.

In physical terms the ease of transporting a solute atom to the boundary must primarily depend upon the (i) free energy of segregation ($\Delta G_{\text{seg}}$), which describes the interaction energy between the solute and the boundary, and (ii) the ease of diffusivity ($\Delta G_{\text{diff}}$) of the solute atom from bulk to the grain boundary. Considering that Gd and Dy display similar size and weight characteristics, it would be reasonable to assume that both
REs must possess similar diffusivities. Under such circumstances, the differential segregation tendencies would be strongly dependent upon the respective free energies of segregation. The extent to which a solute segregates at a grain boundary at equilibrium could be classically expressed by means of the Langmuir-Maclean adsorption model [160] for binary systems, given as,

$$X_{GB} / (1- X_{GB}) = \{X_{MAT} / (1- X_{MAT})\} \times \exp(-\Delta G_{seg} / RT) \ldots (7.6)$$

where, $X_{GB}$ is the grain boundary solute concentration and $X_{MAT}$ is the bulk concentration. $R$ and $T$ have their usual meanings and $\Delta G_{seg}$ is the free energy of segregation (per mole of solute). Eqn. 7.6 can be hence used to calculate equilibrium grain boundary segregation energies for both Gd and Dy in random magnesium high angle boundary, on the basis of the experimentally obtained bulk and grain boundary chemical compositions obtained from APT analysis. Fig. 7.8 shows the variation of free energy of segregation in Mg-1Gd and Mg-1Dy as a function of distance from the grain boundary. The calculations reveal that the segregation energies at the core of the HAGBs (shown by red arrows in Fig. 7.8) can reach sufficiently high negatives values of $\Delta G_{seg}^{Gd} = -17.1 \text{ kJ.K}^{-1}\text{mol}^{-1}$ for Gd atoms vis-à-vis $\Delta G_{seg}^{Dy} = -6.3 \text{ kJ.K}^{-1}\text{mol}^{-1}$ for segregation of Dy atoms. More negative segregation energies indicate a greater tendency of segregation.

The free energy of grain boundary segregation, $\Delta G_{seg}$ depends upon various parameters such as change in elastic strain energy on moving a solute from matrix to grain boundary, chemical enthalpy change associated with solute diffusion to boundaries, anharmonic and vibrational entropies [161]. However, for misfits larger than 10% i.e. in the case of Gd in Mg (~12.44%) and Dy in Mg (~11.8%) [76], the contribution from the elastic strain energy term dominates. The elastic strain energy contribution describes the total change in misfit strain energy when all the solute atoms are transported from the
bulk to the grain boundaries. Thus higher the elastic misfit, greater would be the favorability towards segregation at the grain boundaries.

Figure 7.8 Experimental calculated variation of free energy of grain boundary segregation of Gd and Dy across random high angle grain boundaries for Mg-1Gd and Mg-1Dy.

Comparing, only the atomic misfits of Gd and Dy with respect to Mg, such high difference in elastic strain energies cannot be explained. Theoretical estimates of grain boundary segregation energies [148] on the basis of atomic misfits yields comparable values for Gd ($\Delta G_{seg}^{Gd}(Theoret.) \approx -6 \text{ kJ.K}^{-1}\text{mol}^{-1}$) vis-à-vis Dy with $\Delta G_{seg}^{Dy}(Theoret.) \approx -4 \text{ kJ.K}^{-1}\text{mol}^{-1}$, which are in complete contradiction to the trends observed in the current work. A possible correlation could be then ascribed to the impact of local atomic arrangements displayed by Gd and Dy in magnesium, which can strongly influence the segregation behavior. The formation of a binary solid solution is contingent to sum of energy of ‘mixing’ and ‘ordering’ energy (also known as ‘exchange’ energy) [32]. The enthalpy of mixing or formation energy of a random solid solution: $\Delta E_{mix}$ is
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usually defined as a difference between the energy of a random state of the alloy and the concentration weighted average of the energies of the alloy components.

On the other hand, the ordering energy ($\Delta E_{\text{order}}$) is described in terms of the pair effective interactions in the binary alloy, given by the following expression,

$$\Delta E_{\text{ordering}} = 2\Delta E_{AB}^n (T) - \Delta E_{AA}^n (T) - \Delta E_{BB}^n (T) ... (7.7)$$

where, $\Delta E_{ij}(T)$ are the binding energies for AB-, AA- and BB- bonds in an binary alloy AB; n and m refer to site indices. While the mixing enthalpy ($\Delta E_{\text{mix}}$) is configuration independent, the ordering energy ($\Delta E_{\text{order}}$) accounts for the configuration dependent contribution. The sign of $\Delta E_{\text{order}}$ bears witness to the nature of bonding between solute and solvent atoms. For an ideal (conforming to Raoult’s law) solution, $\Delta E_{\text{order}}$ becomes zero i.e. the arrangement of atoms is independent of the binding energies. If $\Delta E_{\text{order}} < 0$ i.e. the random solid solution formation is associated with heat release, then the number of AB pairs increase, favoring local short- or long-range ordering by means of ‘uphill’ diffusion. In the case of $\Delta E_{\text{order}} > 0$, formation of AB bonds becomes energetically unfavorable, whereby separation of the solid solution into clusters enriched and depleted with solutes would be expected. Pahlman and Smith [162] experimentally derived standard free energies of formation in solid magnesium-REE phases from vapor pressures measurements. The reported standard free energy of formation in pure solid state (assuming unit activities) for Mg-Gd and Mg-Dy phases at 673 K (400° C), were -17.4 kJ.mol$^{-1}$ and -12 kJ.mol$^{-1}$, respectively. Moreover, the binding energies for Mg-Mg, Gd-Gd and Dy-Dy diatoms at the 673K (calculated from Ref. [163]) are -16 kJ.mol$^{-1}$, -207 kJ.mol$^{-1}$ and -75 kJ.mol$^{-1}$ respectively. Substituting the aforementioned values in expression (2), we obtain $\Delta E_{\text{order}} (\text{Mg} - \text{Gd}) \sim -257.8 \text{kJ.mol}^{-1}$ vis-à-vis $\Delta E_{\text{order}} (\text{Mg} - \text{Dy}) \sim -115 \text{kJ.mol}^{-1}$. Larger negative deviations in the ordering energy in the case of Mg-Gd alloy as compared with Mg-Dy alloy indicates a greater tendency towards formation of local short range ordering in the former case.
A more pronounced short range ordering in the case of Mg-Gd would lead to formation of Gd clusters, thereby generating sufficiently large lattice strains to promote segregation at grain boundaries. Such short range order clustering effect in Mg-Gd alloys is not a novel observation and has been previously reported [92, 93, 145, 146]. HAADF-STEM investigations by Bugnet et al. [92] on Mg-0.28at.%Gd alloys revealed formation of ordered fcc-Gd phases in magnesium grain boundaries, wherein the Gd-content was reported to be as high as 50 at.%. Thermodynamically, the formation of intermetallic Mg$_x$Gd (x=1,2,3 or 5) phases accompany a structural transformation from hexagonal to cubic crystal symmetry with increasing Gd concentration, such that the crystal structure pertaining to MgGd phase is face-centered cubic in nature [76]. It would be worthwhile to mention here that the maximum solid solubility of Gd in Mg at temperatures ranging from 300° C to 400° C varies from ~6 wt.% - 10.4 wt.% in comparison with ~14 wt.% - 17.8 wt.% for Dy in Mg. The observed differences in solid solubility limits in the two Mg-RE alloys could be most likely attributed to a significantly higher short range ordering tendency in Mg-Gd, since the solid solubility of an alloying element is known to scale inversely with the observed extent of clustering and segregation [161].

7.6.2 Recrystallization and grain growth behavior in Mg-1Gd and Mg-1Dy

(i) Recrystallization behavior at medium annealing temperatures: 300° C – 350° C

The microstructural characterization results (c.f. Fig. 7.1) indicate that nucleation of recrystallization occurred discontinuously inside shear bands. Shear bands can be assumed as microstructural regions with large orientation gradients, composed of arrays of crystallites separated by diffused low angle boundaries, commonly referred to as dislocation cell boundaries [53]. During the onset of recrystallization, these crystallites tend to coalesce with the neighboring cells, thereby producing sub-grains/embryos of relatively larger sizes and higher misorientations. Such sub-grain formation is most likely
expected to occur by means of in-situ low angle boundary migration [65]. Sub-grains thus formed will be of varying orientations depending on the degree of local accumulated shear strain. The probability of these sub-grains to become potential high angle boundary nuclei is denoted by the ‘primary’ growth stage, which typically depends upon the presence of high local stored energy and large orientation gradients. The rate of boundary migration ‘v’ in such a case can be classically expressed as,

\[ v = \mu \cdot P \ldots (7.8) \]

where \( \mu \) is the grain boundary mobility and P is the driving pressure for recrystallization. As the sub-grains grow into the neighboring deformed regions, the solute atoms in the vicinity will attach to the grain boundaries. Depending on the tendency of solute atoms to segregate at the boundaries, the solute concentration at the boundaries will increase proportionately. In light of the APT results it is proposed that Gd atoms will tend to segregate to the magnesium boundaries significantly strongly in comparison with Dy atoms. Increasing solute levels at the boundary would directly retard the boundary mobility ‘\( \mu \)’, manifesting as back driving pressure or solute drag effect during recrystallization. By means of the Cahn-Lücke-Stüwe approach [94, 164, 165], the change in mobility due to presence of impurities at the boundaries could be approximated as,

\[ \mu_{imp} = \frac{D}{nkT \cdot c} \ldots (7.9) \]

where D is the solute diffusivity rate to the grain boundaries; n is the number of impurity atom sites per unit area of boundary; c is the solute concentration at the boundaries and k and T hold their usual meanings. Equation 3 indicates that with progressive increase in solute concentration at the boundaries, their motion becomes more and more sluggish, such that certain sub-grains growing in relatively less deformed regions inside the shear bands (those assuming basal or near basal orientations) may cease to transform into a high angle boundary nuclei. On the other hand, the off-basal orientations being associated with areas of higher plastic deformation and orientation gradients would be favored over
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the basal ones. Fig. 7.9(a) represents the recrystallization kinetics curves for Mg-1Gd and Mg-1Dy for annealing at 325°C. The aforementioned ‘primary’ growth of sub-grains into nuclei stage typically appears as an incubation period in the recrystallization kinetics curve, as highlighted in Fig. 7.9(a). Longer incubation times observed in Mg-1Gd compared with Mg-1Dy for annealing treatments at 325°C, directly correlates with the higher solute segregation and subsequent drag effects in the former, whereby sub-grain growth would be more retarded. The experimentally measured JMAK exponents indicate values of 1.1 for Mg-1Gd and 1 for Mg-1Dy (c.f. Fig. 7.9(b)), indicating nucleation to be site-saturated.

Following primary growth, the ones that successfully overcome solute pinning and reach a critical nuclei size would then exhibit a sharp increase in the rate of coarsening due to the onset of ‘conventional’ growth regime. The linear region in the JMAK curve highlights the ‘conventional’ growth stage. Once the recrystallized grains impinge, the growth rate decreases sharply, marking the transition from recrystallization growth to curvature driven grain growth (being ~ 2 orders of magnitude smaller than driving pressures for recrystallization). The measured grain sizes at 325°C, just after impingement (99% recrystallized volume fraction) shows relatively larger mean grain sizes in Mg-1Gd (5.16 µm ± 2 µm) in comparison with Mg-1Dy (3.5 µm ± 1.1 µm). For

Figure 7.9 a) JMAK recrystallization kinetics for Mg-1Gd and Mg-1Dy at 325°C, highlighting the onset of impingement, b) Avrami exponent calculation from Fig. 7.9(a).
site saturated nucleation, the nucleation density ($N$) can be typically correlated to the final recrystallized grain size ($D_{\text{rex}}$) by the following expression,

$$D_{\text{rex}} \propto N^{-\frac{1}{3}} \ldots (7.10)$$

On the basis of aforementioned proportionality, it is obvious that Mg-1Gd would be associated with lower nucleation densities in comparison with Mg-1Dy, which is most likely attributed to retarded nucleation kinetics due to solute pinning in the former. Physically, it can be imagined that lower nucleation densities would indicate recrystallized grains traversing relatively larger distances before meeting each other, whereby higher grain sizes are obtained on recrystallization completion. This observation is further corroborated from the recrystallization kinetics measurements at 325° C (c.f. Fig. 7.9(a)), wherein onset of impingement is delayed and observed at relatively higher recrystallized volume fractions ($X_V = 92\%$) in Mg-1Gd vis-à-vis Mg-1Dy ($X_V = 87\%$).

For annealing treatments performed at 350°C, the aforementioned differences are further amplified i.e. increased thermal activation accelerates nucleation and growth in Mg-1Dy, whereas in Mg-1Gd the impending solute drag is further enhanced due to higher solute diffusivities resulting in even more retarded nucleation behavior. The resulting microstructures thus reveal even greater mean grain size differences between Mg-1Gd (~23 µm) and Mg-1Dy (~9.1 µm). Solute diffusivity data for Gd in Mg at 350°C, calculated from [166] indicate values in the order of $\sim 10^{-16}$ m$^2$/s (indicating an order of magnitude increase from diffusivities at 300° C, which is $\sim 10^{-17}$ m$^2$/s), which becomes comparable to self-diffusion rates in polycrystalline Mg at 350° C i.e. $\sim 8 \times 10^{-16}$ m$^2$/s, calculated from [167]. Easier solute diffusivities would further augment grain boundary pinning by solutes during recrystallization growth. It must be understood that while nucleation density varies inversely with the cube of the final grain size, the growth rate ($D_{\text{rex}} = \dot{G} \Delta t$) varies linearly with the grain size parameter ($D_{\text{rex}}$). Hence a stronger influence of nucleation density on the final grain size would be an expected outcome.
With respect to texture evolution on increasing the annealing temperature from 300°C to 350°C, the drastic deviation in the texture response of Mg-1Gd in terms of absence of the basal component, in comparison with Mg-1Dy can thus be attributed to an increased solute pinning in the former alloy. Under stronger solute drag, the nucleation density significantly declines in Mg-1Gd permitting growth of primarily off-basal orientations that are associated with larger driving pressures, as illustrated in Chapters 4 and 6. On the other hand, Mg-1Dy with significantly lower drag would initiate higher number of nuclei orientations, thereby permitting both basal and off-basal orientations to grow.

**Figure 7.10** a) IPF mapping and mean grain size (~9600 grains) of Mg-1Gd after annealing at 450°C for 4 mins, b) EBSD recalculated (0002) pole figures, c) Normalized grain size distribution of Mg-1Gd after annealing at 450°C for 4 mins

**(II) Grain growth at high annealing temperatures: 450°C**

Fig. 7.10 shows the microstructure and texture for Mg-1Gd annealed at 450°C for 4 minutes, depicting complete impingement along with indications of early stages of grain growth. At higher annealing temperatures (~450°C), thermal activation becomes sufficiently large to overcome solute drag effects impeding recrystallization growth in Mg-1Gd. Fig. 7.10(a) displays the EBSD orientation mapping for the specimen annealed
at 450°C for 3 minutes, comprising of ~9600 grains, in IPF coloring. Fig. 7.10(b) shows the recalculated (0002) pole figure for the annealed microstructure. Figs. 7.10(a) and (b) indicate presence of both basal and off-basal orientations after completion of recrystallization. The measured average grain size is reported as 7.8 µm (S.E. = 0.52), which is considerably lower than the average grain size values reported at 350°C, indicating higher nucleation densities during annealing at 450°C. The annealing microstructure in Fig. 7.10(a) evinces certain anomalously large grains originating amidst clusters of much smaller grains. The observations are well reproduced in the grain size distribution trends shown in Fig. 7.10(c), wherein a longer tail on the right hand side of the distribution depicts presence of grains significantly larger than the mean grain size (~7 times larger). For longer duration anneals (~60 minutes), solute Gd atoms would have sufficient time to diffuse from the grain interiors to the grain boundaries, whereby re-establishing a solute atmosphere at the boundaries becomes a strong likelihood. Solute diffusivities of Gd atoms in magnesium at 450°C, calculated from [166], are of order of ~3*10^{-15} m²/s, displaying a ~30 fold increase over the diffusivities rates measured at 350°C. Increased solute diffusivities can be expected to result in a transient stage wherein curvature driven grain growth and solute drag behave as competing processes. In such a scenario, grain boundaries with a large enough driving force would be able to break free of solutes while the others remain loaded with solutes. This represents a transition from a loaded to a free zone once the driving force exceeds a critical value $P_{drag}$ [94, 164, 165]. This would explain the local appearance of anomalously large grains surrounded by clusters of much smaller grains (c.f. Mg-1Gd at 450°C in Fig. 7.1). The driving pressure ($P_{GG}$) on the grain boundary segment shared by grains 'i' and 'j' during curvature driven grain growth can be mathematically expressed as [168],

$$P_{GG} = \gamma_{GB} \left( \frac{1}{r_i} - \frac{1}{r_j} \right) \ldots (7.11)$$
where $\gamma_{GB}$ is the misorientation dependent grain boundary energy; $r_i$ and $r_j$ are the equivalent grain radii for grains ‘$i$’ and ‘$j$’.

Figure 7.11 (a)-(d) Temporal evolution of abnormal grain growth in Mg-1Gd using the level set modelling, (e) simulated microstructures, acquired at different time intervals, overlaid upon one another to indicate the difference between the growth rates of the large grains and the mean coarsening rate.
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Figure 7.12  a) – c) Grain growth simulations under anisotropic and isotropic growth conditions in Mg-1Gd compared with the experimental microstructure after annealing at 450°C for 1 hr; d) – f) Grain growth simulations under anisotropic and isotropic growth conditions in Mg-1Dy compared with the experimental microstructure after annealing at 450°C for 1 hr

It is proposed that the grains, subjected to a supercritical driving force ($P_{GG} > P_{drag}$) i.e. the ones that are relatively larger than their neighborhood grains and comprise of greater than six interfaces in 2D, will be able to overcome solute pinning and exhibit rapid free growth. By contrast, the remaining grains experiencing sub-critical driving ($P_{GG} \leq P_{drag}$) pressures will be strongly retarded due to solute drag, thereby migrating at much slower speeds. Such selective growth phenomenon will however vary depending on the neighboring grains. Fig. 7.11 illustrates the temporal evolution of grain topology during selective grain growth under solute drag. Figs. 7.11(a)-(d) shows the evolution of a growing grain that experiences a supercritical driving force, whereby it is able to grow abnormally larger than the neighboring grains. Depending on the local topology of the microstructure, the average value of the radii of its new neighbor grains can be either smaller or larger than that of its previous neighbors. Correspondingly the new driving force for the grain can be either supercritical or subcritical, which implies that not all grains that have eroded their neighbor grains will retain their growth advantage. Only
those grains that have the fortune to meet smaller grains again will be subjected to supercritical driving forces and rapidly grow further, as highlighted in Fig. 7.11(e). As expected of a grain growth process, the growth advantage of large grains will be limited by the temporal evolution of spatial arrangement and size distribution of the grains in the microstructure. The grains that undergo the aforementioned process repeatedly may grow anomalously large in comparison to others (c.f. Fig. 7.11(e)). The presence of grains ~5 times larger than the mean grain area in Mg-1Gd after annealing for one hour is indicative of such a behavior.

Grain growth simulations were performed on Mg-1Gd, utilizing the EBSD data after 450°C anneal for 4 minutes as an input microstructure (c.f. Fig. 7.10(a)). Figs. 7.12(a) and (b) display the simulated microstructures and the experimentally obtained data after annealing at 450°C for one hour. The simulated microstructures mimic the same degree of coarsening that is observed experimentally, after an hour annealing i.e.
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from a mean grain size of 7.8 µm to 38.9 µm. The grain boundaries in Fig. 7.12(a) are color coded with respect to their grain boundary migration rates, derived from the product of normalized grain boundary energies and assigned mobility values. To model solute drag in Mg-1Gd alloy, anisotropic growth conditions were imposed such that a growth advantage is assigned to larger grains (with higher number of interfaces) as described in section 7.4. These grains hence can assume boundary migration velocities nearly 3-4 times the mean coarsening rate, which is depicted by the velocities of grain boundaries shown in blue. The simulated grain topology in Fig. 7.12(a) shows reasonably good qualitative agreement with the experimental data (c.f. Fig. 7.12(b)). For the sake of comparison, isotropic growth conditions (considering only the effect of grain boundary energies) were also implemented on the same starting network in Mg-1Gd. Fig. 7.12(c) represents the simulated results under isotropic grain growth, indicating that the large grains observed initially (c.f. Fig. 7.10(a)) would lose their advantage under such assumptions. These results further strengthen the argument that grain growth behavior in Mg-1Gd indeed displays abnormal characteristics.

It is well known that the 30°<0001> grain boundaries that lie close to the Σ13 coincident site lattice grain boundaries are most frequently observed in pure magnesium and its alloys [169, 170]. In the present case, experimentally measured grain boundary misorientation distribution in Mg-1Gd at 350°C and 450°C showed no visible preference of the aforementioned special boundaries. Grain growth simulations, wherein grains boundaries with a 30°<0001> (± 4°) misorientation relationship were assigned higher mobilites did not display any selective growth tendencies, thus substantiating that the observed abnormal grain growth in Mg-1Gd cannot be attributed to faster migration of special boundaries. These trends most likely indicate that segregation of Gd solutes to grain boundaries significantly alter the structure as well as the mobility of grain
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boundaries. A more detailed outlook regarding these aspects will be addressed in a separate study.

Figs. 7.13(a) and (b) represent the grain number fraction with respect to the number of 2D-interfaces and the simulated texture evolution results for Mg-1Gd. It can be seen that the starting microstructure of Mg-1Gd comprises of grains with as many as 26 neighbors, which reduces to a maximum of 19 neighbors after annealing for one hour. However, the overall spread of the distribution does not undergo significant tapering. More importantly the left end of the distribution remains unchanged after one hour annealing thus signifying a delayed shrinkage of the grains described by less than six interfaces, whereby the larger grains have an opportunity of retaining their growth advantage. The distribution of the number of neighbors obtained from the simulations resonates well with those determined from the experimental microstructures for Mg-1Gd after annealing at 450°C for 60 mins (c.f. Fig. 7.3(e)), further validating the implemented simulation approach. The simulated textures obtained after grain growth agree reasonably with the bulk textures of Mg-1Gd annealed at 450°C for 60 minutes (c.f. Fig. 7.12(b)), indicating that the larger grains with a migration advantage correspond primarily to the off-basal orientations.

Annealing treatments performed for very long durations further confirm such anomalous grain growth tendencies in Mg-1Gd. Figs. 7.14(a), (c) and (d) show the optical and simulated microstructures; and grain size distribution corresponding to Mg-1Gd after annealing at 450°C for 1230 minutes. The microstructure shows an abnormally large grain (~ 0.6 mm in size) surrounded by significantly smaller grains (c.f. Fig. 7.14(a) and (c)). The mean grain size measured over ~1360 grains was 118 µm (S.E. = 0.63). The grain size distribution displays a marginal increase in the right tail of the distribution (from 4.9 after 60min anneal to 5.2 times the mean grain size) and the maximum grain number fraction from ~20% after 60 min anneal to ~22% after 1230 min anneal (c.f. Fig. 7.14(d)). Longer tail indicates presence of selective grains that grow faster than the mean
coarsening rate of the grains i.e. discontinuous growth tendencies. Comparing the experimental and simulated microstructures, it seems the topological evolution tends more towards a normal grain growth behavior in the latter. Even though the large grains continue to hold their size advantage, they begin losing interfaces over longer annealing times with the max grain faces decreasing from 19 to 13 due to simultaneous coarsening of local microstructure. On the other hand, the minimum interface number remains unchanged on comparing the simulated microstructures corresponding to 60 mins (Fig. 7.13(a)) and 1230 mins (Fig. 7.14(e)) anneals, depicting typical abnormal grain growth tendencies. These observations indicate that the grains without any advantage i.e. those dragged by solutes, will also exhibit coarsening but at much slower rates (~ 3-4 times slower than the large ones).

**Figure 7.14**  a) Optical image of Mg-1Gd after annealing at 450°C for 1230 mins, b) corresponding EDX analysis showing presence of Mg$_5$Gd phases, c) simulated grain growth microstructures corresponding to annealing time of 1230 mins, d) normalized experimental grain size distribution, e) simulated grain number frequency plot, f) simulated and experimental bulk texture data for annealing at 450°C for 1230 mins

Fig. 7.14(a) also indicates presence of fine precipitates both in grain interiors and at the grain boundaries, which were identified as Mg$_5$Gd phases by means EDX analysis (c.f. Fig. 7.14(b)). It must be understood, with progressive grain coarsening the average
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grain boundary length per unit area consistently decreases. This directly correlates to an increased solute concentration at the grain boundaries. Considering the tendency of clustering exhibited by solute Gd atoms, it is likely that the solute distribution at the boundaries would be inhomogeneous in nature, such that certain regions would be enriched more with impurity atoms in comparison with other sections of the grain boundaries. Longer annealing times would then promote local solute partitioning by means of diffusion along grain boundaries, whereby the enriched regions would be further enriched at the expense of purifying neighboring grain boundary sections.

The rate of coarsening of the large solute clusters of size $R'$ is typically dependent upon the solute diffusivities ($D$), interfacial energy of the solute cluster-matrix interface ($\gamma_{\text{sol}}$) and annealing duration ($t_{\text{anneal}}$), expressed as,

$$R^3 \sim \gamma_{\text{sol}} D t_{\text{anneal}} \cdots (7.12)$$

Such localized solute aggregation at the grain boundaries could in some cases lead to local solute concentration levels exceeding the solubility limit of Gd in Mg at $450^\circ\text{C}$ (~14 wt.%), whereby the solute clusters would tend to precipitate out as $\text{Mg}_5\text{Gd}$ phases. Depending on the particle size, these may act as either effective pinning agents (when < 1 µm) or in some cases can be too coarse for enforcing Zener drag. On the other hand, precipitation in the bulk far away from grain boundaries could be ascribed to grain boundary excess solute concentration originating from the overall reduction in grain boundary area. As the larger grains consume the neighboring smaller ones, the additional solute atoms would tend to attach themselves with the moving boundaries. During this process, certain segments of the grain boundary could become saturated enough to be unable to accommodate further solutes. These excess solute clusters that are subsequently left behind by the migrating grain boundary would be prone to coarsening over time by means of bulk diffusion processes and precipitating out as secondary phases. Such dynamic precipitation would facilitate the larger grains in maintaining their size and
growth advantage, despite simultaneous coarsening of other grains in the network over time, thereby sustaining the abnormal grain growth characteristics. Fig. 7.14(f) shows a good agreement between the simulated textures vis-à-vis bulk textures, indicating that the orientations corresponding to the larger grains present in the microstructure during earlier annealing times (at 4mins and 60 mins) are still preserved.

With respect to Mg-1Dy, negligible solute drag pressures would further propel grain coarsening rates at higher thermal activation. Increasing the annealing temperature from 350° C to 450° C shows ~ 8-9 fold increase in grain size of Mg-1Dy, whereas the microstructural coarsening for Mg-1Gd in the same temperature range is only by a factor of 2 (c.f. Fig. 7.4). Unlike Mg-1Gd, the grain size distributions obtained for Mg-1Dy at 350° C and 450°C (c.f. Figs. 7.2 and 7.3) indicates shrinking of right tail of the distribution on increasing the annealing temperature. Such an observation typically corresponds to a case where the microstructure exhibits normal grain growth behavior, described by the unrestrained shrinkage and subsequent disappearance of the smaller grains leading to uniform grain coarsening. This leads to a shift of the mean grain size value more towards the right end of the distribution.

Fig. 7.11(d) represents the simulated microstructure corresponding to a starting network of Mg-1Dy annealed at 350°C for one hour (c.f. Fig. 7.2(a)). The simulated data assumes only the contribution of grain boundary energies so as to ensure an isotropic growth behavior. The starting microstructure was hence subjected to ~64 fold areal coarsening. The simulation results showed good topological agreement with the experimental microstructural data obtained for Mg-1Dy after one hour annealing at 450°C (c.f. Fig. 7.12(e)). Further proof of the predicted growth behavior is evinced from the microstructure simulation results assuming anisotropic grain growth behavior (c.f. Fig. 7.12(f)), which contradicts (in terms of grain topology) the experimentally observed microstructural evolution seen for Mg-1Dy. Figs. 7.13(c) and (d) show the grain number fraction with respect to number of interfaces and the texture evolution results. As obvious
for normal grain growth behavior, most grains lose interfaces such that distribution narrows down from both ends (c.f. fig. 7.13(c)). The maximum number of interfaces after one hour annealing reduces from 16 to 12, while the minimum increases from 2 to 4. On comparison with the distribution of number of grain faces obtained experimentally for Mg-1Dy after annealing for one hour at 450°C (c.f. Fig. 7.3(e)), the simulated trends duplicate the expected behavior extremely well. The agreement between the simulated and experimental textures (c.f. Fig. 7.13(d)) further validates the assumed grain growth behavior in Mg-1Dy. The increased texture spread during grain growth in Mg-1Dy, can be attributed to a higher nucleation density in comparison with Mg-1Gd, whereby a much greater diversity of orientations are present in the microstructure prior to grain growth. Additionally the initial size advantage of the off-basal grains originating from regions of higher stored energy may also contribute to the increased orientation spread.

### 7.6.3 Influence of RE-alloying on ambient deformation characteristics

Figs. 7.7(c) and 7.7(d) indicate that Mg-1Gd shows superior UTS values along with higher elongations (c.f. Fig. 7.7(c)) in comparison with Mg-1Dy thus evading the typical “strength-ductility trade off” effect. Moreover, UTS values for both alloys display an anomalous increase from 400°C to 450°C annealed states. While Mg-1Dy shows a slight increase in the mean UTS from 189.2 MPa after annealing at 400°C to 196 MPa corresponding to 450°C anneal, Mg-1Gd shows a significantly larger UTS increment from 184.9 MPa (for specimens annealed at 400° C) to 220.6 MPa (for annealing condition of 450°C). Intuitively, a coarser microstructure would comprise a lower grain boundary area density, thereby leading to a reduction in the strain hardening rate and subsequent lowering of UTS. The observed increase in UTS values, despite grain coarsening, most likely alludes to contribution from additional hardening effects.
Figure 7.15 Age hardening response of Mg-1Gd and Mg-1Dy at 450°C, the peak hardness value is observed after aging duration of 60 mins. Mg-1Gd shows greater hardenability than Mg-1Dy.

Fig. 7.15 represents the static age hardening response for both alloys at 450°C. The results evince the Mg-1Gd possess a greater hardenability potential in comparison with Mg-1Dy. Interestingly in both cases, the peak hardness at 450°C is observed after aging duration of 60 mins that coincides with the annealing time. The room temperature stress-strain curves corresponding to specimens annealed at 450°C indicated higher UTS values for Mg-1Gd as compared to Mg-1Dy with the difference \( \Delta UTS = 24.4 \text{ MPa} \). Comparing this with the strength differential \( \Delta \sigma \) calculated from the peak hardness values of Mg-1Gd and Mg-1Dy using the expression [171, 172]: \( \Delta \sigma (\text{MPa}) = 0.33 \times \frac{\Delta Hv}{\text{mm}^2} \), yields a value of 22.9 MPa. The values suggest the beneficial influence of precipitation hardening on the resultant mechanical behavior, especially in case of Mg-
1Gd. Further investigations correlating the clustering kinetics and underlying mechanisms in Mg-1Gd are underway.

7.7 Summary

Grain boundary segregation behavior is successfully correlated with microstructural evolution during recrystallization and grain growth in Mg-1Gd and Mg-1Dy alloys. The following conclusions are drawn,

1) Onset of recrystallization in Mg-1Gd is characterized by drastic texture modification, which is further amplified during grain growth. By contrast, Mg-1Dy shows a gradual texture evolution highlighted by consistent weakening and increasing texture spread for higher annealing temperatures.

2) Gd shows significantly stronger solute segregation tendencies in comparison with Dy. The calculated minimum free energies of segregation at random HAGBs in magnesium, for Gd and Dy are $-17.1 \text{kJ.K}^{-1}.\text{mol}^{-1}$ and $-6.3 \text{kJ.K}^{-1}.\text{mol}^{-1}$, respectively.

3) Mg-1Dy exhibits higher nucleation densities in comparison with Mg-1Gd, due to stronger solute pinning effects in the latter. Enhanced solute drag in Mg-1Gd significantly amplifies the growth advantage assumed by the off-basal grains over the basal orientations during recrystallization. On the other hand, recrystallization growth in Mg-1Dy fails to display any distinctive favorable growth characteristics.

4) The off-basal orientations in Mg-1Gd, being associated with larger sizes and more neighbors, can break free of solute atmospheres during grain growth at higher annealing temperatures (450° C) and subsequently display abnormal growth.
behavior. Annealing for very long times, results in segregation induced dynamic precipitation in the large grains, thereby sustaining the abnormal grain growth characteristics.

5) In contrast, grain growth in Mg-1Dy converges to an isotropic grain growth behavior. The texture spread at 450° C is attributed to a larger nucleation density and the initial size advantage of the off-basal grains originating from regions of higher stored energy.

6) The influence of alloying chemistry and texture on the resultant room temperature mechanical properties indicates a significant impact of atomic scale REE-clustering/segregation effects. Texture modification and simultaneous precipitation hardening effects in Mg-1Gd not only improves the room temperature elongation values but also the UTS values, despite grain coarsening.
CHAPTER 8

GENERAL CONCLUSIONS

The present work addressed critical issues with respect to the influence of single REE additions on the deformation, recrystallization and grain growth behavior in magnesium. It is shown that the extent of texture modification observed in magnesium alloys containing REEs is contingent upon the following important criteria:

- The processing parameters, encompassing crystallographic deformation, recrystallization, grain growth and phase transformation mechanisms
- The choice of REE-addition on the basis of their interaction with the matrix i.e. as solutes or second phase, or due to differential segregation characteristics of solute based REEs
- The additional influence of non-RE elements triggers or amplifies annealing texture modification in Mg-RE alloys

Moreover, the role of texture on the subsequent room-temperature ductility improvement in dilute Mg-RE alloys was also addressed.

8.1 IMPACT OF MATERIAL PROCESSING

Differential processing routes were implemented in order to generate shear banded and twinned microstructures. Shear bands were predicted to arise from clustering of compression and double twins that were observed in a banded morphology at lower rolling strains. Static recrystallization inside shear bands resulted in nucleation of diverse orientations owing to the presence of large orientation gradients. Shear band recrystallization in Mg-1Gd saw preferential growth of off-basal orientations that appeared in regions of larger local plastic strains. Grain growth sustained the observed growth advantage of the off-basal grains. Large strain hot rolling of Mg-1Ce resulted in
severe fragmentation of Mg$_{12}$Ce phases, which subsequently pinned growth during recrystallization and grain growth.

Mechanical behavior of binary magnesium-RE alloys under controlled plane strain compression at ambient temperatures gave rise to twinned microstructures. While the deformation behavior of Mg-1Ce was quite conventional with much stronger propensity for tension twinning (irrespective of the loading direction), twinning in Mg-1Gd indicated quite anomalous tendencies with unequivocal nucleation of both tension and compression twins in IPC and profuse compression and double twinning for the TTC deformation. Compression and double twins being orientationally soft for basal slip subsequently underwent intense basal and prismatic slip giving rise to ‘prismatic’ type fiber texture. The prismatic slip resulted in strong lattice rotations about the c-axis, leading to simultaneous fragmentation of the twins and triggering dynamic recovery mechanisms. Deformation in Mg-1Ce indicated interesting interactions between the secondary Mg$_{12}$Ce phases and the twins. The particles arrested twin growth and acted as sites for further twin nucleation. At higher stresses in TTC deformation, the twin-particle intersections were also able to nucleate compression twins. Post-mortem analysis of the as-deformed microstructures also showed un-twinned regions that were proposed to arise from either de-/re-twinning. During unloading the particle twin intersections with act as zones of high stress concentration exerting back stresses, whereby they could activate de-twinning (by reversal of atomic shuffling) or re-twin the already twinned region along the same misorientation axis. VPSC simulations modelling the texture evolution during deformation additionally indicated that a significant contribution of second order pyramidal $<c+a>$ slip is necessary to attain the textures obtained experimentally.

Recrystallization in twins (c.f. Chapter 5) also depicted unique characteristics especially in case of Mg-1Gd solid solution. Contrary to the prismatic fiber obtained during DRX of twins, static annealing initiated grain boundary nucleation mechanisms in twins highlighted by typical bulging of twin boundaries. The corresponding recrystallized
orientations no longer obey the prismatic fiber observed in the as deformed condition, giving rise to arbitrary orientations that result in severe texture weakening phenomenon. It must be noted that such difference in recrystallization texture evolution in dynamic and static conditions seems peculiar to solute Mg-RE alloys, since in conventional alloys static annealing seems to strengthen the already existing deformation texture. In case of Mg-1Ce alloy, static annealing was described by extended recovery mechanisms occurring inside tension twins. Additional role of PSN was evident in the Mg-1Ce alloy that gave rise to random orientations. Growth during recrystallization and grain growth favored growth of orientations with high SF for basal slip i.e. crystallographically soft orientations originating from twins and near particles.

8.2 Choice of Rare-earth Element

Investigations with different REEs as alloying addition clearly reveal the significant role of the choice of REE addition for the desired texture modification. The distinctive nature of REEs strongly depends upon their individual physico-chemical properties. Juxtaposing the solid solution Mg-1Gd alloy with the precipitate based Mg-1Ce alloy clearly indicated the beneficial role of solute REEs as potential texture modifiers. While Gd addition strongly altered the overall deformation and annealing response, thereby giving rise unconventional textures; the lack there of in the Ce containing alloy was attributed to the detrimental effect of Mg$_{12}$Ce phases. Segregation of Gd to linear and planar defects i.e. dislocations, stacking faults and grain boundaries, was attributed as the primary cause behind such distinctive response exhibited by Mg-1Gd alloy.

Chapter 7 compared two solid solution Mg-RE alloys with respect to their influence upon recrystallization and grain growth behavior. Like in the case of Mg-1Gd and Mg-1Ce, it was shown that different solute REEs can also show varied response depending on their individual segregation tendencies. Gd solute atoms revealed strong
tendency of clustering and segregation in comparison to Dy atoms. Such clustering effects of Gd arising from more negative ordering energies, was found to be the fundamental cause behind enhanced solute drag effects at the grain boundaries as well as improved age hardening response in the binary Mg-1Gd alloy. These atomic scale mechanisms greatly determine the macro-texture evolution and bulk scale mechanical properties in these alloys. It was shown that the combined influence of annealing texture modification and precipitation hardening phenomenon in Mg-1Gd could help evade the classical “strength-ductility trade-off” effect.

![Graph showing true stress vs true strain for REE containing Mg alloys](image)

**Figure 8.1** Uniaxial tensile curves for REE containing magnesium alloys depicting the typical range of observed ductility values

### 8.3 Triggering REE related texture modification by adding non-REEs

Comparisons drawn between the binary Mg-RE alloys and quaternary Mg-Zn-Zr-RE alloys showed that Zn and Zr can indeed amplify the REE-induced texture modification tendencies. Density of shear bands in both alloys increased on addition of
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non-REEs. Adding Zn and Zr to the Mg-1Ce stimulates texture modification. A more diverse particle size and shape distribution was attributed for the observed texture change, which enabled complex interaction of PSN and zener pinning effects in the quaternary Ce-alloy. On the other hand, texture modification effects in the Gd alloy were enhanced by addition of non-REEs. The transition from deformation to recrystallization texture was achieved at relatively lower annealing temperatures than its corresponding binary counterpart. The strengthening in texture modification in the Gd alloy was attributed to higher density of shear bands and stronger solute drag effects.

The overall impact of alloying and texture on mechanical properties was significant, with room temperature elongation values reaching as high as ~40% in the quaternary Gd alloy. Fig. 8.1 succinctly summarizes the beneficial role of REE alloying on the ambient formability of magnesium alloys.
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ABSTRACT

Modifying the chemical composition of magnesium alloys with special emphasis on rare earth (RE) elements has shown numerous indications of improved properties of this class of alloys, such as possibility of grain refinement, better formability at low temperatures, and enhanced strength and creep resistance at elevated temperatures. In particular, has been their ability in facilitating formation of less-common and unconventional sheet and extrusion textures. However, such texture modification in RE elements containing Mg alloys has been associated primarily with changes in the recrystallization texture, as opposed to changes in the deformation texture. What has been and still remains subject to greater scrutiny and investigation are the primary underlying physical mechanisms that are associated with RE-influence over recrystallization and grain growth behavior, whereby such significant texture modification is realized.

The present work investigated in detail the influence of dilute additions of RE-elements upon deformation, recrystallization and grain growth behavior under varying processing conditions involving large strain hot rolling, plane strain compression and uniaxial tension tests. Comparisons were drawn between solid solution Mg-1Gd alloy and precipitate based Mg-1Ce alloy. Recrystallization inside shear bands, deformation twins and near particles was analyzed with context to texture formation features in the presence of rare-earths. By means of in-depth characterization ranging from atomic to bulk scales, the overall role of RE elements on the microstructure and texture development was understood.

Shear banding in magnesium was enhanced in the presence of RE element additions. With respect to deformation twinning, addition of solute Gd triggered activation of \{10\bar{1}1\} compression and \{10\bar{1}1\}–\{10\bar{1}2\} double twins in conjunction with \{10\bar{1}2\} tension twinning. While dynamic recrystallization was severely retarded during the large strain rolling treatment, deformation under plane strain compression witnessed slip
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assisted dynamic recovery inside twins. Solute rare-earths indicated a significantly larger potency of texture modification during annealing, as opposed to precipitate based Mg-RE alloys. Texture modification during recrystallization and grain growth was attributed to selective growth behavior stemming from segregation of RE atoms at the grain boundaries, whereby off-basal orientations assumed a growth advantage over their basal counterparts. The results indicated that not all RE elements behave in a similar fashion and the choice of RE element is critical for the desired texture modification.

Adding non-RE elements (Zn and Zr) amplified the texture modification effects in the solute Mg-1Gd alloy, while Mg-1Ce, in the additional presence of non-RE elements, started exhibiting modified off-basal textures. The enhancement in texture modification was attributed to a larger solute drag in the Gd containing alloy and an intricate interaction of particle nucleation and Zener pinning effects in the Ce containing alloy. The resultant impact on the room temperature ductility was significant with the quaternary alloys revealing total elongation values as high as 34 -40%.

Atom probe tomography investigations performed on two solute based RE-alloys viz. Mg-1Gd and Mg-1Dy, further highlighted that the aforementioned influence of the choice of RE element also holds valid when considering two elements showing similar interaction with matrix i.e. both are in solid solution. It was shown that the segregation tendencies are not just contingent to solubility limits of RE elements but strongly depend upon other factors such as clustering/ordering and phase formation energies. It was suggested that the greater tendency of clustering/ordering shown by Gd facilitates much stronger segregation to the grain boundaries, whereby the impact on texture evolution mechanisms during annealing is substantial.


Die Scherbandbildung wurde im Allgemeinen durch RE-Zugabe verstärkt. Zwillingsbildung, in Form von \{10\overline{1}1\} Druckzwillingen und \{10\overline{1}1\}–\{10\overline{1}2\} Zwillingen in Verbindung mit \{10\overline{1}2\} Zugzwillingen, wurde durch gelöstes Gd begünstigt. Des

Weitere Zugabe von nicht RE-Elementen (Zn und Zr) verstärkte die Texturentwicklung in der Mg-1Gd-Legierung (reiner Mischkristall), wohingegen sich in der mit Zn/Zr versetzten Mg-1Ce-Legierung (ausscheidungsbasiert) modifizierte, nicht basale Texturen ausbildeten. Diese Texturmodifikationen konnten durch eine verstärkte rücktreibende Kraft auf die Korngrenzen durch Fremdatome in der Mg-1Gd-Legierung und durch komplexe Wechselwirkungen zwischen Keimbildung an Partikeln und dem Zener-Effekt in der Mg-1Ce-Legierung erklärt werden. Daraus resultierte ein bemerkenswerter Einfluss auf die Verformbarkeit bei Raumtemperatur, so dass die quaternären Legierungen eine Gesamtdehnung von 34-40% aufwiesen.

Zusätzlich wurden an zwei Legierungen, Mg-1Gd und Mg-1Dy, Untersuchungen unter Verwendung der Atomsonde durchgeführt, welche die Erkenntnis bestätigten, dass die Wahl der RE-Elemente einen starken Einfluss auf das Materialverhalten hat, selbst wenn beide unterschiedliche RE-Elemente vollständig gelöst enthalten sind. Es wurde
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It has been found that the segregation behavior is not only determined by the solubility, but also to a large extent by further factors such as cluster formation/order phenomena and phase formation energies. It is assumed here that the higher tendency of Gd for cluster formation/ordering increases segregation at grain boundaries, thus also increasing the influence on the texture development during the heat treatment.
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