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Microstructure design and mechanical properties in Mg and Mg alloys

DISSERTATION

submitted in partial satisfaction of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

in Materials Science and Engineering

by

Xin Wang

Dissertation Committee:
Professor Julie M. Schoenung, Chair
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ABSTRACT OF THE DISSERTATION

Microstructure design and mechanical properties in Mg and Mg alloys

By

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Being the lightest structural metal, Mg is a promising candidate in numerous energy-saving and environmental-friendly applications. The research interest in Mg and its alloys continues to rise in past decades, however, their commercial applications were held back by some longstanding intrinsic difficulties. Belonging to the hexagonal close packed family of metals, Mg has anisotropic slip and twinning systems, leading to strong textures invariably associated with wrought Mg and small strains-to-failure compared to those of current structural metals. Further enhancement of the performance in Mg requires mechanistic understanding of the deformation and innovative design strategies.

Microstructure is known to have tremendous influence on the mechanical and functional properties of materials. To shed light on the microstructural design for low density, high strength and formable Mg alloys, the objective of this dissertation is to advance the fundamental understanding of how microstructure affects their mechanical properties. Particular focus is on examining the influence of grain morphology (equiaxed or laminated), grain size (micro- or nano-crystalline), twin mesh features (with or without a

high density of intersecting twins) and dilute solute addition of Y in polycrystalline Mg. For this purpose, we designed the experimental strategies leveraging powder metallurgy or surface mechanical treatment approaches to achieve samples with various internal microstructures. Bulk form and in-situ mechanical testing together with multiscale microstructure characterization were carried out on the Mg samples being synthesized.

In this dissertation, we have demonstrated strong grain morphology and grain size effects on the active deformation modes in polycrystalline Mg, resulting in a reversed yield strength anisotropy and a large compressive strain >120% at room temperature, in the microlaminated and nanocrystalline Mg, respectively, that have not been observed in conventional Mg. The toughening effect of twin meshes was explored by in-situ TEM nanocompression, and was successfully achieved in a gradient twin meshed Mg polycrystal at the macroscale. Lastly, the alloying effect of Y was analyzed experimentally in regard to the slip and twinning behavior. The difference in activation barriers among the slip modes was reduced by Y addition, and the mobility of twin boundaries may be affected by the segregation of Y atoms on such boundaries.

Chapter 1 INTRODUCTION

1.1 Background and Motivation

The research and industrial interest in Mg and its alloys continues to rise due to their unique properties. Mg is the lightest structural metal ($\rho_{\text{Mg}} = \sim 1.74 \text{ g/cm}^3$) with a high specific strength (158 kNm/kg) [1, 2]. Meanwhile, Mg is the eighth most abundant element in the earth's crust. It is therefore of attractive economic and efficiency benefits to use this lightweight structural material in the automobile and aerospace industries. For Mg with its low symmetric hexagonal close packed (HCP) structure, one critical disadvantage is the relatively small strain-to-failure value at room temperature [3]. Slip and twinning are the two main deformation mechanisms in Mg [4-6]. The highly anisotropic slip systems in the HCP crystal [7] make non-basal slip on the prismatic and pyramidal planes very hard to activate [7, 8], which results in an insufficient number of independent slip systems to satisfy the von Mises criterion [9]. Deformation twins, which may occur readily in Mg depending on the stress state, offer extra deformation modes in addition to those that originate from basal slip, despite the fact that twinning is polar in nature and that the maximum twinning-induced plastic strain is recognized to be limited [8]. Furthermore, as a result of the anisotropic slip and twinning modes discussed above, strong basal texture is common in wrought Mg [10, 11] and is preserved after annealing [12], which results in severely anisotropic mechanical properties along different deformation orientations [13-16]. This plastic anisotropy complicates the processing of Mg and Mg alloys and causes their use in real applications to lag far behind that of current structural materials.

How to improve the strength of polycrystalline metals while maintaining the ductility is still a challenge with critical importance in the scientific and industrial community. Approaches reported by previous studies include: generating bimodal grain size [17], introducing pre-existing nanoscale growth or deformation twins [18], nanoparticles or precipitates [19], phase-transformation plasticity [20], and changing deformation conditions to lower temperatures or higher strain rates [21]. Though many of these strategies pointed to the importance of microstructural engineering in enhancing the mechanical properties in Mg, a systematic and profound understanding of the relationship between microstructure features, specifically the grain size, grain shape, density and characteristics of twin boundaries, etc., and the deformation mechanisms, including slip and twinning, in Mg is still lacking. Therefore, the objectives of the present study are to experimentally investigate the microstructure-dependent mechanical properties of Mg and to discern the underlying strengthening and toughening mechanisms.

The influence of grain size on the mechanical properties of Mg alloys has been the focus of considerable research efforts [22-29]. Review of the published literature shows some of the previous results demonstrated increased mechanical strength in Mg with reduced grain size [30-32], as anticipated by the Hall-Petch relationship, while many others reported a significant ductility enhancement at room temperature [29, 33, 34]. The mechanism for the drastic enhancement in strain-to-failure has been attributed to either the activation of certain deformation modes not available in coarse grains [29] or changes in texture induced by severe plastic deformation (SPD) [35]. Furthermore, synthesizing Mg with grain size below the sub-micron level is challenging by conventional SPD techniques

due to grain growth at the processing temperatures which are usually higher than the recrystallization temperatures of Mg. Tedious processing approaches, such as multi-passes temperature-step down equal channel angular extrusion (ECAE) approach [36], are developed to achieve further grain refinement.

Compared to the influence of grain size, the effects of grain morphology on the mechanical properties of Mg has not been studied as comprehensively. Grain morphology modifies the partitioning of stress and strain in the polycrystalline materials due to the local stress gradients at grain boundaries [37]. Therefore, it is interesting to examine whether elongated or disk-shaped grains can affect the selection of slip and twinning systems, and induce plastic anisotropy and mechanical strength different from those for the equiaxed grains [37]. More interestingly, whether and how the grain shape induced plastic anisotropy could help reduce the inherent plastic anisotropy in Mg caused by its HCP crystal is a subject that needs further study.

Moreover, in an effort to circumvent the paradox of strength and ductility in engineering metals, the ability of twin boundaries in strengthening without losing ductility has been reported in nanostructured face center cubic (FCC) metals [38]. The simultaneously improved strength and ductility originates from the dislocation interaction with and accumulation at twin boundaries [38]. As supported by early studies back in the 1970s [39, 40], in nanostructured FCC metals, twins could accommodate strains associated with slip bands and twin-twin intersections by activating dislocation slip inside or on the exit side of twins. This pioneering result motivates the hypothesis that twin meshes, defined as two or more intersecting arrays of twins within a grain, can be engineered to

achieve unprecedented combinations of strength and toughness in HCP metals. The deformation of HCP metals, however, is much more intriguing than that of the FCC metals, in the sense that the most common twinning plane is not a slip plane [41]. Unlike FCC metals, twinning has been widely reported in coarse-grained Mg [14], while it is rarely observed in nanostructured Mg [28]. Whether or not the premise of twin-induced strengthening and plasticity is effective in HCP metals is a scientifically and practically critical question that we investigated. Moreover, though twins are profuse in Mg, the easy propagation and growth of the common $\{10\bar{1}2\}$ twins add technical challenges to the development of a stable, high twin density and fine twin mesh structure.

1.2 Crystal structure and deformation of Mg

1.2.1 HCP crystal structure of Mg

Mg has an HCP crystal structure, as shown in Fig. 1.1, with the c/a ratio of 1.623, which is close to the ideal c/a ratio of 1.633 for the HCP lattice [41, 42]. The close-packed plane in the HCP structure is the (0001) (or basal plane), and the close-packed direction is the $\langle 11\bar{2}0 \rangle$ (or $\langle a \rangle$ direction).

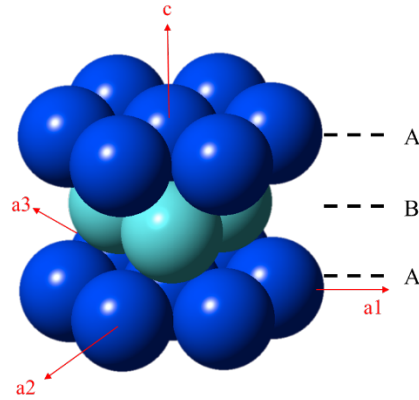


Fig. 1.1 The HCP structure of Mg with the stacking sequence of ...ABABAB... of the close packed (0001) planes.

1.2.2 Dislocation slip in Mg

Distinguished by the direction and magnitude of the Burgers vectors, there are three types of slip systems in the HCP structure, referred to as $\langle a \rangle$, $\langle c \rangle$ and $\langle c+a \rangle$ dislocations. Firstly, the full $\langle a \rangle$ -dislocations on the basal, prismatic or pyramidal planes with a Burgers vector of $\frac{1}{3}\langle 11-20 \rangle$. Secondly, the full $\langle c \rangle$ dislocations on the prismatic plane with a Burgers vector of $[0001]$. Thirdly, the $\langle c+a \rangle$ dislocations on the first or second order pyramidal planes with a Burgers vector of $\frac{1}{3}[11-23]$. The possible slip systems in Mg are summarized in Table 1.1 and illustrated schematically in Fig. 1.2 [8]. In addition to full lattice dislocations, partial dislocations $\frac{1}{3}\langle 10-10 \rangle$ on the basal plane, $\frac{1}{2}[0001]$ partial perpendicular to the basal plane, and twinning dislocations on the twinning planes are important in HCP metals, and can form via nucleation from grain boundaries or dissociation of full dislocations.

Table 1.1 Slip systems in HCP metals

Direction	Plane	Crystallographic elements	Number of independent modes
<a>	Basal	(0002)<11-20>	2
	Prismatic	(1-100)<11-20>	2
	Pyramidal	(1-101)<11-20>	4
<c>	Prismatic	{hki0}[0001]	4
<c+a>	Pyramidal	{hkil}<11-23>	5

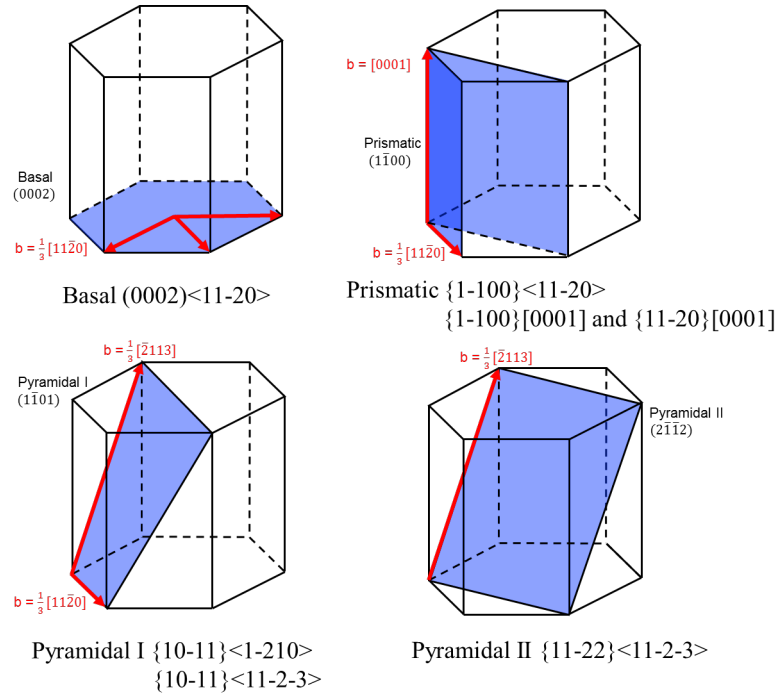


Fig. 1.2 Schematic illustrations of the slip systems in HCP metals.

The poor ductility in HCP Mg at room temperature has been recognized to be associated with its anisotropic slip systems and a lack of sufficient easy slip systems. The critical resolved shear stress (CRSS) values of different slip systems in single crystal Mg can

be seen in Table 1.2 [7, 43]. The ratio of the CRSS value for non-basal slip to that for basal slip is in the range of 40-100 in single crystal Mg and from 2.0 to 13.5 in polycrystalline Mg. The $\langle a \rangle$ -dislocations glide on the basal plane is the mode with the lowest CRSS value and the most active one at low temperatures. As can be seen from Table 1.1, basal slip provides only two independent deformation modes. The activation of $\langle a \rangle$ -dislocations on the prismatic and pyramidal planes requires much higher resolved shear stresses, and uniform activation has been only reported at elevated temperatures ($>180^\circ\text{C}$). Prismatic $\langle a \rangle$ and pyramidal $\langle a \rangle$ could offer two and four independent slip modes, respectively, in addition to the two that originate from basal slip, with which the von Mises criterion can be satisfied. However, without $\langle c \rangle$ or $\langle c+a \rangle$ dislocations, the material cannot deform arbitrarily along the c-axis [8]. Though as reported, the CRSS values for $\langle c+a \rangle$ -dislocations are as high as 40-80 MPa, it remains mysterious why they were observed to be activated in Mg [8, 44]. Considering their large Burgers vectors, dissociation of $\langle c+a \rangle$ -dislocations is expected [45, 46]. Recent studies indicated the dissociation of $\langle c+a \rangle$ -dislocations onto the basal planes which then become immobile could explain the high work hardening rate and poor ductility of Mg [47].

Table 1.2 Critical resolved shear stress (CRSS) values of different slip systems in single crystal Mg.

Slip plane	Slip direction	CRSS (MPa)
Basal	$\langle 11\text{-}20 \rangle$	0.52-0.81
Prismatic	$\langle 11\text{-}20 \rangle$	39-50
Pyramidal	$\langle 11\text{-}20 \rangle$	40
Pyramidal	$\langle 11\text{-}23 \rangle$	40-80

1.2.3 Deformation twinning in Mg

Besides dislocation slip, deformation twinning happens readily in coarse-grained Mg at room temperature. Though both of them can produce plastic strain in the lattice, there are three general differences between slip and twinning: 1) The magnitude of the shear displacement for slip is an integral number of interatomic distance nb , where b is the magnitude of Burgers vector. While the shearing magnitude for twinning is a fraction of an interatomic distance and each atomic plane shears relative to its adjacent planes. 2) Slip shear along b is equivalent to that along $-b$. While, being polar in nature, the twinning shear that occurs in one direction is not equivalent to the shear in the opposite direction. 3) Slip rotates the lattice gradually, while twinning reorients the lattice abruptly.

Multiple twinning modes have been observed in Mg, including the tension twins $\{10\text{-}12\}\langle\text{-}1011\rangle$ and $\{11\text{-}21\}\langle\text{-}1\text{-}126\rangle$ and contraction twins $\{10\text{-}11\}\langle 10\text{-}1\text{-}2\rangle$ and $\{11\text{-}22\}\langle 11\text{-}2\text{-}3\rangle$ [41]. Among all of them, the $\{10\text{-}12\}$ tension twin, which would be favored under c -axis extension, has received the most attention as it is the most profuse and the

easiest twinning mode in HCP metals [41], due to the relatively small twinning shear. In addition, this type of twinning re-orientates the c-axis of the matrix by $\sim 86^\circ$, causing remarkable changes in the texture and therefore alter subsequent deformation. Another commonly observed type of twin in Mg is the $\{10\bar{1}1\}$ contraction twin, which forms under c-axis compression. Distinct from $\{10\bar{1}2\}$ twins that can thicken to consume the entire grain, $\{10\bar{1}1\}$ twins are usually scarce and narrow in the Mg lattice [48, 49], and can nucleate a second $\{10\bar{1}2\}$ twin inside their domain [50, 51].

As discussed above, the close-packed planes for easy glide do not correspond to a twinning plane. This brings significant complications in the plastic deformation of HCP metals, and poses challenges in understanding the twin nucleation, twin-slip and twin-twin interactions. Fig. 1.3 shows stitched TEM images of a typical lens-shaped $\{10\bar{1}2\}$ twin in a deformed Mg sample. A high density of $\langle c+a \rangle$ -dislocations are observed ahead of the twin tip. Possible explanations for this are either dislocation reactions are necessarily preceding twinning nucleation and/or propagation, or the high local stress concentration at the twin tip when a twin terminates within a crystal needs to be relaxed by the nucleation of dislocations in its vicinity.

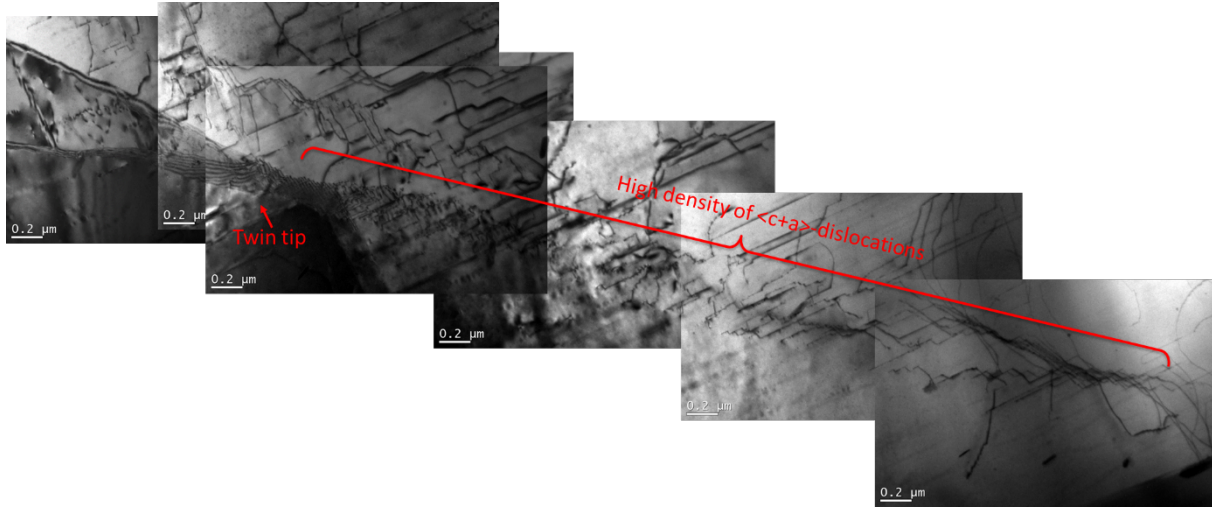


Fig. 1.3 Stitched TEM bright field images of a typical lens-shaped twin with a high density of $\langle c+a \rangle$ -dislocations in front of the twin tip. [52]

A grain size dependency of twinning behavior was noted in both FCC and HCP metals. However, they show different trends. In an FCC metal, such as copper, twinning becomes more likely when the grain size is below 100 nm, although it may disappear again once the grain size is too small, say <10 nm [53]. In HCP Mg, high frequency of deformation twins can often be observed in coarse-grained Mg [14]. However, twinning becomes rare in nanocrystalline Mg when the grain size is reduced, which is attributed to: (1) The difficulty of accommodating full dislocations in such small grains; (2) The high stress needed to nucleate partial dislocations from grain boundaries; (c) The stress required for twin nucleation increases much more rapidly compared to that for dislocation slip [53], so a twin-to-slip transition happens under a critical grain size [28]. By reducing the high stacking fault energy of pure Mg via alloying, enhanced twinning activity was reported in a nanocrystalline Mg-Ti alloy [54].

1.2.4 Mechanical properties of Mg

The easy basal slip and the $\{10\text{-}12\}$ twinning lead to highly anisotropic deformation in Mg. In Fig. 1.4 [4], when a Mg single crystal was compressed normal to the c-axis corresponding to c-axis extension, the crystal deformed mainly by twinning, during which a steady stress plateau at ~ 20 MPa was observed. After the completion of twinning, the crystal was reoriented by $\sim 86^\circ$ and the strain hardening rate increases rapidly until failure. Compared to the sample under c-axis compression, a higher ultimate strain was observed in the case of c-axis extension, which can be attributed to the resolved twinning strain.

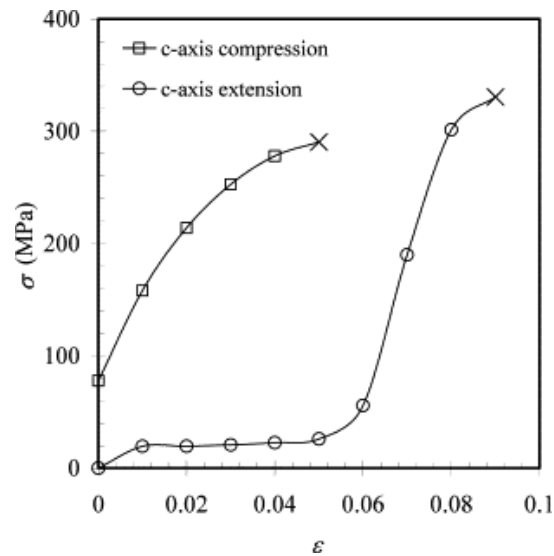


Fig. 1.4 Stress-strain curves of single crystal Mg upon channel die compression along two normal directions [4].

The intrinsically anisotropic slip and twinning modes lead to a strong basal texture in wrought polycrystalline Mg, as a result of the predominance of basal slip and $\{10\text{-}12\}$

twinning. The uniaxial compression curves for a hot-rolled AZ31 Mg alloy (with a nominal composition Mg-3.0wt%Al-1.0wt%Zn) with a basal texture is shown in Fig. 1.5 [13]. Similar to single crystal Mg, basal textured Mg exhibits a much lower yield strength upon c-axis extension compared to the yield strength upon c-axis contraction, because activating $\{10\text{-}12\}$ extension twinning at the beginning of the test is easy in the former but not favorable in the latter. The yield strength for c-axis extension is usually half to three quarters of that for c-axis contraction in polycrystalline Mg and Mg alloys with basal textures [13, 26].

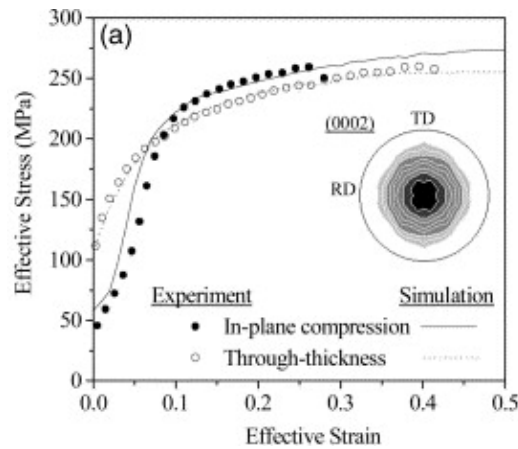


Fig. 1.5 Experimental and simulation results of uniaxial compression tests of a basal textured AZ31 rolled sheet [13].

1.3 Materials processing approaches

1.3.1 Cryomilling

Cryomilling is one type of attrition ball milling, during which powder particles are mixed and milled by milling balls in the environment of inert cryogenic liquid (commonly liquid nitrogen or liquid argon) [55]. Like other ball milling techniques, cryomilling could

generate severe plastic deformation, leading to accumulation of dislocations and effective grain refinement within the powder particles. The grain refinement during ball milling was achieved via a proposed three-stage process [55]: I. deformation localization forming high dislocation density at shear bands; II. annihilation and recombination of dislocations, forming nanometer-scale sub-grains; III. transformation of sub-grain boundary structure to high-angle grain boundaries. Recovery is also happening during ball milling. Therefore, as the milling time keeps increasing, a dynamic equilibrium state between dislocation accumulation and dislocation annihilation will be reached, corresponding to the minimum grain size that can be achieved in the powders.

Because of the cryogenic liquid medium being used, cryomilling is feasible for microstructural refinement in Mg. Liquid argon can be used to provide an inert atmosphere to prevent the rapid oxidation and contamination of Mg when exposed to air. Thanks to the cryogenic temperature that limits recovery and grain coarsening, a small grain size can be achieved in cryomilling with a shorter period of time compared to ball milling at ambient temperature [56, 57].

In addition to the capability of producing nanomaterials, another motivation to use cryomilling is to induce Mg powder particles with non-equiaxed grain morphology [55, 58]. For this purpose, Mg powder particles can be collected at the early stage of cryomilling, when powder particles have been flattened from the original spherical morphology and before these flattened particles become fragmented and cold welded into agglomerates. Innovatively using this approach, disk-shaped Mg powders with microlaminated grain morphology can be attained.

1.3.2 Spark plasma sintering (SPS)

To synthesize bulk Mg, spark plasma sintering (SPS) can be used for rapid consolidation of cryomilled Mg powder particles. SPS is a sintering process that involves the use of electric current and pressure [56, 59, 60]. The electric current passing through will directly heat the dies (usually graphite), punches (usually graphite) and powder particles (if conducting) by Joule heating. A compressive pressure is also added to aid the particle rearrangement and facilitate the sintering process.

Compared to conventional sintering, one of the main benefits of using SPS is that Joule heating provides a significantly increased heating rate, which by-passes the grain coarsening low temperature mechanisms [61]. The fast heating rate during SPS enables short sintering times leading to a limitation in grain growth. Therefore, the fine grain structures in powder particles, generated for example by cryomilling, can be retained to a large extent in the bulk samples after SPS [56, 59, 60].

1.3.3 Surface SPEX milling (SSM) treatment

SPEX milling is known as a high-energy variety of mechanical alloying and milling [62]. To mix and mill powders by SPEX milling, powder particles, together with grinding balls, can be secured in a container which will shake energetically back and forth with lateral movements at a high frequency. Due to the high frequency of shaking, the ball velocities are on the order of 5 m/s [62].

Herein, we designed an experimental strategy to impose repetitive loads in multi-directions using in an 8000M SPEX Mixer/Mill on the surfaces of Mg samples. During this process, a thin foil (~ 1 mm in thickness) of Mg is attached to one end of the vial. When the balls impact against the Mg foil, the balls will generate severe plastic deformation near the contact regions. Considering the highflying speed of the flying balls and the high frequency of the impacts, high strain and high strain rates are expected at the sample surface layer, leading to a high density of defects and refined crystallite sizes at the surface layer. Particularly, the high strain and strain rates induced by milling balls may generate twins with a high critical resolve shear stress. The strain and strain rate will decrease with an increasing depth from the sample surface, causing a gradient microstructure from the surfaces to the less deformed center of the sample.

SPEX milling processing parameters, such as the milling balls sizes and milling time, and material microstructure features, such as the initial grain size, grain morphology and texture, can be tuned to change the microstructures after milling.

1.4 Diffraction contrast analysis of dislocations in Mg using transmission electron microscopy (TEM)

Crystal defects, such as dislocations and stacking faults, may induce diffraction contrast in transmission electron micrographs. Diffraction contrast analysis was extensively used in the study herein, as it could distinguish dislocations with different Burgers vectors in Mg (i.e., $\langle c \rangle$, $\langle a \rangle$, or $\langle c+a \rangle$ dislocations) according to the $\mathbf{g} \cdot \mathbf{b} = 0$ invisibility criterion, where $\mathbf{g}$ is the diffraction vector in the reciprocal space and $\mathbf{b}$ is the

Burgers vector [42]. The visibility of different types of dislocations at several selected diffraction conditions was listed in Table 1.3. In addition to the determination of the Burgers vectors, the slip plane for each dislocation could be examined by tilting the thin foil specimen in TEM. Using this method, the active deformation modes can be identified by post-mortem TEM analysis of deformed Mg samples.

Table 1.3 Visibility of dislocations at selected diffraction vectors (**g**)

	$\langle a \rangle$ dislocations	$\langle c \rangle$ dislocations	$\langle c+a \rangle$ dislocations
g = 11-20	Visible	Invisible	Visible
g = 1-100	Visible (except b = $\frac{1}{3}[11-20]$)	Invisible	Visible (except b = $\frac{1}{3}[11-23]$)
g = 0002	Invisible	Visible	Visible

Chapter 2 Effect of grain morphology on deformation behavior of polycrystalline Mg

2.1 Abstract

To investigate the effect of grain morphology on the mechanical properties of polycrystalline Mg, two types of bulk Mg samples with equiaxed and microlaminated grain structures were fabricated by spark plasma sintering (SPS) of as-received Mg powder and cryomilled disc-shaped Mg powder particles, respectively. Based on a detailed microstructural investigation, the mechanisms by which microstructure evolves and texture development occurs were identified and are discussed. The basal fiber textures in the SPS consolidated samples allow the plastic anisotropy in such textured Mg to be investigated. Compression tests at room temperature parallel and perpendicular to the SPS compaction axis determined that, in comparison to the conventional anisotropy observed in the equiaxed sample, the anisotropy of yield strength is reversed in the microlaminated sample, with the yield strength for c-axis extension being higher than that for c-axis contraction. The reversed compressive yield strength anisotropy observed in the sample that was cryomilled is related to the low twinning activity, limited twinning growth and the anisotropy induced by the microlaminated grain structure, which offers an opportunity to reduce or even reverse the intrinsic plastic anisotropy of hexagonal close packed Mg.

2.2 Introduction

Magnesium (Mg) and its alloys are attractive lightweight structural materials for the automotive and aerospace industries, where specific strength is of significant concern [63, 64]. Unlike metals with cubic crystal structures, Mg, which has an hexagonal close packed (HCP) crystal structure, is subject to slip on multiple nonequivalent slip systems upon plastic deformation. The slip systems that have been reported for Mg are slip in the $a/3\langle 11\text{-}20 \rangle$ (or $\langle a \rangle$) directions on the basal, prismatic and pyramidal planes, and slip in the $a/3\langle \text{-}2113 \rangle$ (or $\langle c + a \rangle$) directions on the pyramidal planes [7, 65]. Unfortunately, the critical resolved shear stresses (CRSSs) vary significantly for different slip systems [7, 65]. The ratio of the CRSS value for non-basal slip to that for basal slip lies in the range of 40-100 in single crystal Mg and in the range of 2.0 to 13.5 in polycrystalline Mg [7]. The much lower CRSS value for basal slip renders slip on non-basal planes difficult to initiate. Basal slip alone, however, only provides two independent slip modes, which are insufficient for homogeneous deformation of a polycrystalline material according to the von Mises criterion [66]. Extension twins of the $\{10\text{-}12\}\langle 10\text{-}11 \rangle$ type (hereafter referred to as $\{10\text{-}12\}$ twins) are easily activated in Mg when loaded in tension along the c-axis or in compression perpendicular to the c-axis. HCP twins can provide an additional deformation mechanism despite the fact that twinning is polar in nature and that the maximum twinning-induced plastic strain is recognized to be limited [65]. As a result of the anisotropy in slip and twinning discussed above, strong deformation textures are common in wrought Mg [10, 67, 68], which lead to a plastically anisotropic stress-strain response

[13]. This plastic anisotropy complicates the processing of Mg alloys, which limits their use in many important structural applications despite the obvious density advantages.

In an effort to circumvent the limitations that originate from the plastic anisotropy that is inherent to Mg and its alloys, various approaches have been proposed. For example, texture modification, through addition of rare earth elements [69, 70], and careful selection of thermo-mechanical processing parameters [12, 71, 72], have been successfully demonstrated to reduce the plastic anisotropy and enhance the ductility of Mg. In addition to weakening the initial texture, rare earth elements can promote non-basal slip activity by significantly decreasing the critical stress required for cross-slip stress [69, 73]. The drawback of this method, however, is the high cost of rare earth elements, which limits large scale application of these alloy compositions. In addition to rare earth alloying, decreasing the grain or sample size is a promising strategy to reduce the plastic anisotropy of Mg by inhibiting twinning [28, 74] and reducing the CRSS ratio between non-basal and basal slip [75]. Dislocation density also influences the CRSS ratio in Mg [7]. With a dislocation density increased from $\sim 10^6$ to $\sim 10^{14} \text{ m}^{-2}$, the CRSS ratio between prismatic to basal slip in Mg can be reduced from 40:1 to as low as $\sim 2:1$ [7]. Interestingly, review of the published literature shows that despite numerous studies that address various microstructural factors, the influence of grain morphology on the deformation, particularly on the plastic anisotropy, of Mg has not been addressed, which provided a motivation for the current study.

To synthesize Mg with distinct non-equiaxed grain morphology, mechanical milling was used in the present work. Mechanical milling is a powder-based severe plastic

deformation material processing method that can be used to synthesize fine-grained or nanocrystalline materials in relatively large quantities [55, 76]. As such, mechanical milling techniques have been used to study a broad range of materials and have been successfully used in combination with various consolidation approaches to attain notable properties in various metals, alloys and composites [55, 76, 77]. Of interest is that, in some studies, mechanical milling has been used to fabricate disc-shaped powders, which facilitate consolidation into laminated composites with enhanced mechanical performance [78-81]. Of perhaps more interest here is a recent finding of an orientation-dependent strengthening effect in nanolaminate graphene-Al composites, where the highest compressive strength was observed when the lamellae were oriented parallel to the compression axis [81]. In view of the published literature, mechanical milling followed by subsequent sintering has been observed in a few studies to improve the mechanical properties, particularly the strength and hardness, of Mg alloys through grain refinement [56, 82]. However, none of these studies have reported on the yield anisotropy of materials processed by this method. Moreover, the microstructure of these materials has not been studied in detail and information related to texture, dislocation configurations and grain boundary characteristics is not currently available.

In the present work, we demonstrate that the plastic anisotropy for Mg can be altered through microstructural design, such as through changes in the grain morphology and dislocation structure without alloying. For this purpose, the texture and microstructure of a microlaminated Mg structure, created by spark plasma sintering (SPS) consolidation of disc-shaped powder particles obtained by cryomilling, was comparatively

studied together with a sample that was not cryomilled prior to sintering. We used scanning electron microscopy (SEM), X-ray diffraction (XRD), electron backscattered diffraction (EBSD) and transmission electron microscopy (TEM) to probe the microstructural and texture development in powder particles during cryomilling and sintered bulk samples. Uniaxial compression tests were performed on bulk samples. Notably, an uncommon compressive yield anisotropy was observed in the samples that was cryomilled, which sheds light on the possibility of reducing the plastic anisotropy in Mg through microstructural design.

2.3 Experimental procedures

The starting material used in this study was a commercially pure Mg powder (99.8% purity, 325 mesh, Alfa Aesar, Massachusetts, United States). One kg of as-received powder (hereafter referred to as AR-Mg) was attrition ball milled in liquid argon at a speed of 180 rpm with a stainless steel ball-to-powder mass ratio of 30:1. Powder samples were collected after a 1, 2, 4, 6 and 8 h milling time (hereafter referred to as 1h-Mg, 2h-Mg, 4h-Mg, 6h-Mg and 8h-Mg, respectively). To prevent excessive cold welding, ~0.5 wt% of stearic acid was added to the powders as a process control agent.

As-milled Mg powders were packed into a double-acting die arrangement, which is schematically illustrated in Fig. 2.1. SPS was applied to prepare bulk Mg samples. In all cases, Mg powders were handled in an argon-filled glove box and transferred to the SPS chamber directly to minimize oxidation reactions. SPS was carried out using a DR. SINTER SPS-825 S (Syntex Inc., Kawasaki, Japan) under vacuum to produce a cylinder-shaped bulk

sample, typically 5 mm in diameter and 5 mm in height. A 200 MPa uniaxial sintering pressure and a fast heating rate of $\sim 100^{\circ}\text{C}/\text{min}$ was achieved with this SPS apparatus and die set. The sintering parameters are summarized in

Table 2.1. The use of a fast heating rate and a low sintering temperature were intended to limit grain growth during powder consolidation. For comparison purposes, as-received (i.e., unmilled AR-Mg) powder was also sintered using identical SPS conditions.

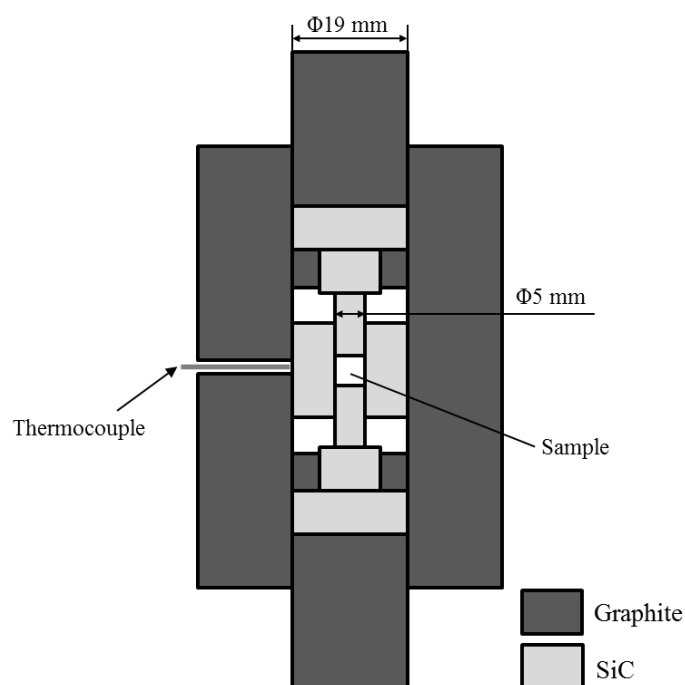


Fig. 2.1 A schematic of the double-acting die setup for SPS.

Table 2.1 The SPS parameters.

Pressure (MPa)	200
Heating rate (°C/min)	107
Holding temperature (°C)	390
Dwell time (min)	3
Pulse on/off time ratio	6:1
Starting vacuum (Pa)	<1

SEM microstructural analysis was performed on an FEI XL30 SFEG SEM. XRD measurements were carried out with a Scintag XDS2000 using Cu K α ($\lambda=0.1542$ nm) radiation at a step size of 0.02 degrees with a dwell time of 2 s per step from 20 to 80°. To prepare samples for EBSD, the SPS consolidated bulk samples were sectioned using a diamond wire-saw in a way that the viewing plane was parallel to the SPS compaction axis (CA) at the center of the cylindrical sample. The cut surface was ion-polished by a cross-section polisher (JEOL, Model SM-09010). EBSD analysis was performed utilizing an FEI Scios SEM equipped with an Oxford Instruments EBSD detector. The voltage and beam current used for EBSD data collection were 30 kV and 13 nA, respectively. The step size for EBSD data collection was 0.75 to 1 μm . EBSD post-processing was carried out using Channel 5 system from HKL Technology. TEM microstructural analysis of the as-milled Mg powders and SPS consolidated bulk samples was performed using a JEOL 2500 or PHILIPS/FEI CM 20 operating at 200 kV. To prepare TEM samples from the cryomilled powders, the powders were mixed with G-1 epoxy (Gatan) and cured at room temperature to form a disk. The powder-epoxy mixture was mechanically polished and ion-milled (dual

ion-beam Gatan PIPS). The sintered Mg samples were sectioned parallel to the SPS CA, and then thinned by the same polishing-ion-milling method.

Compression samples were electrical discharge machined into 3 mm cubes. Uniaxial compression tests were performed at room temperature using an Instron 8801 universal testing machine, parallel and perpendicular to the SPS compaction axis (CA). A displacement-controlled mode with an initial strain rate of 10^{-3} s^{-1} was employed in this study. Some of the compression tests were interrupted and a subsequent EBSD analysis was performed.

2.4 Results

2.4.1 Evolution of powder particle morphology and microstructure during cryomilling

Fig. 2.2 displays secondary electron SEM micrographs of the as-received powder particles and powder particles subjected to increasing cryomilling time of 1 to 8 h to reveal the evolution in powder morphology. The as-received Mg powder particles (Fig. 2.2 (a)) are slightly oblong in shape and mostly from 10 to 80 μm in diameter with an average particle size of $\sim 30 \mu\text{m}$. After up to 2 hours of cryomilling, (Fig. 2.2 (b) and (c)), the powder particles were flattened into disc-shaped powder particles $\sim 90 \mu\text{m}$ in diameter and $\sim 1 \mu\text{m}$ in thickness. When the milling time was further increased to 4 and to 6 hours (Fig. 2.2 (d) and (e)), non-uniform agglomerates formed as a result of impact-induced fracture of disc-shaped powder particles and random cold welding among particles. Finally, at 8 hours, when a dynamic balance between particle fracture and cold welding was attained, nearly

equiaxed faceted particles with a uniform particle size of $\sim 17\text{ }\mu\text{m}$ were obtained (Fig. 2.2 (f)).

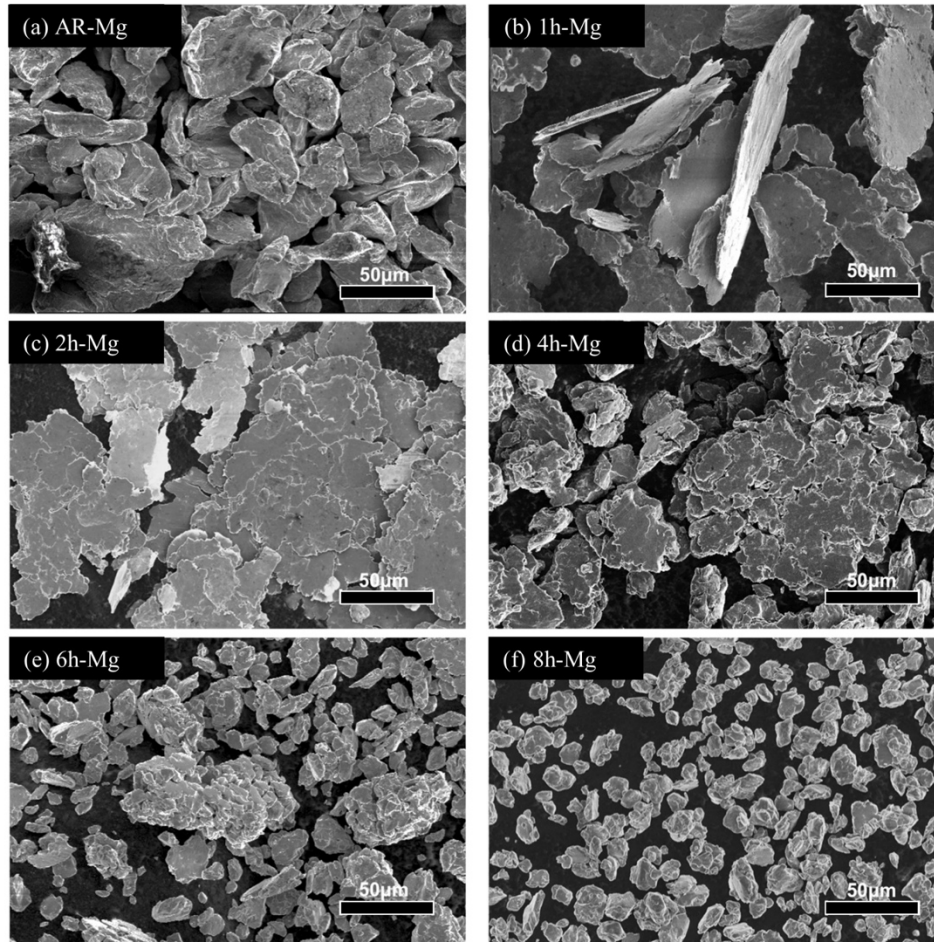


Fig. 2.2 SEM micrographs of: (a) as-received Mg powders and cryomilled powders collected after (b) 1 h, (c) 2 h, (d) 4 h, (e) 6 h and (f) 8 h milling time.

XRD patterns for the Mg powders as a function of cryomilling time (Fig. 2.3) confirmed that all powders had an HCP structure with lattice parameters matching with JCPDS #35-0821 for pure Mg. Moreover, the relative integrated intensities of XRD peaks

indicated the preferential orientations in the as-milled powder particles. The $I_{(0002)}/I_{(10-10)}$ integrated intensity ratio for the starting material is ~ 1.3 , which is similar to 1.4 for the reference pattern, indicating a random crystalline orientation in the as-received powder. As cryomilling progresses, a gradual growth in the relative intensity of (0002) peaks can be observed in 1h-Mg and 2h-Mg. After 2 hours of cryomilling, the (0002) peak showed the highest $I_{(0002)}/I_{(10-10)}$ intensity ratio of ~ 58.8 , suggesting the predominance of (0002) planes parallel to the diffracting flat-on surfaces of the lamellae. When the cryomilling time was increased to 4 hours, the (0002) peak intensity started to decline, and concomitantly losing the particle shape anisotropy, as observed in Fig. 2.2 (d). The $I_{(0002)}/I_{(10-10)}$ intensity ratio dropped back to ~ 1.4 in 8h-Mg.

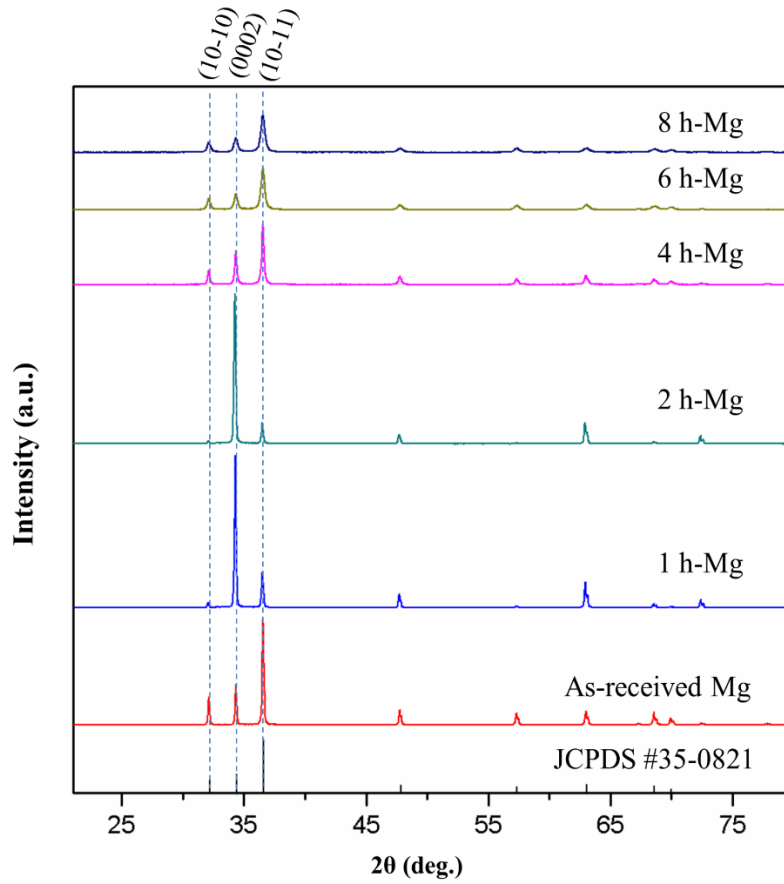


Fig. 2.3 XRD patterns of as-received and cryomilled magnesium powder particles.

The multiple whole profile (MWP) fitting program developed by Ungar et al. [83] was used to estimate the dislocation density in the cryomilled Mg powder particles. As seen in Table 2.2, the measured dislocation density first increased and reached a maximum of $\sim 9.10 \times 10^{15} \text{ m}^{-2}$ in 2h-Mg, when mostly basal planes were diffracting. The measured dislocation density then decreased when the milling time reached 4 hours, and increased again between 6h-Mg and 8h-Mg. The high dislocation densities in the cryomilled powders suggest recrystallization is largely suppressed by the cryogenic liquid argon temperature.

Furthermore, the XRD predicted dislocation densities in the cryomilled powders first increased and then decreased after 4 hours. This trend agrees with that observed for the extent of basal planes being parallel to the lamellar flat-on surfaces, suggesting a higher dislocation density on the basal planes relative to the non-basal planes.

Table 2.2 Dislocation densities of Mg powder particles after different cryomilling times.

Milling time (h)	1	2	4	6	8
Dislocation density (1/m ²)	9.54x10 ¹⁴	9.10x10 ¹⁵	9.55x10 ¹⁴	5.25x10 ¹⁴	8.69x10 ¹⁴

To further substantiate the above assessment, TEM analysis was performed on cryomilled 2h-Mg powder particles, which exhibited the highest dislocation density and the highest XRD peak intensity ratio (i.e., orientation preference). Composite bright-field TEM micrographs in Fig. 2.4 (a) show the cross section of a representative 2h-Mg lamellar particle embedded in the G1 epoxy matrix. The particle is $\sim 1.1 \mu\text{m}$ in thickness and consists of several elongated grains along the lamellar band direction, separated by nearly vertical grain boundaries. Fig. 2.4 (b) and (c) are bright field micrographs taken at the same region under the two-beam conditions with diffraction vectors $\mathbf{g} = 01\text{-}11$ and $\mathbf{g} = 0002$, respectively, near the $[2\text{-}1\text{-}10]$ Mg zone axis. According to the $\mathbf{g} \cdot \mathbf{b} = 0$ criterion, when $\mathbf{g} = 01\text{-}11$ was used, all types of dislocations ($\langle \mathbf{a} \rangle$, $\langle \mathbf{c} \rangle$ and $\langle \mathbf{c} + \mathbf{a} \rangle$) can be observed; whereas, if the $\mathbf{g} = 0002$ is used, only $\langle \mathbf{c} \rangle$ or $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations can be seen. A high density of dislocations is present in 2h-Mg when $\mathbf{g} = 01\text{-}11$, while most dislocations are not visible

when $\mathbf{g} = 0002$. Moreover, most dislocation lines in Fig. 2.4 (b) are parallel to the basal plane trace, which is nearly parallel to the lamellar band, as highlighted by the yellow dashed line. This alignment confirms that the observed dislocations are mostly basal $\langle \mathbf{a} \rangle$ dislocations. Several non-basal $\langle \mathbf{a} \rangle$ dislocations not parallel to the basal plane trace are also seen, as highlighted by the red arrows in Fig. 2.4 (b). In summary, TEM confirms that dislocations in 2h-Mg are predominantly basal $\langle \mathbf{a} \rangle$ dislocations, with a moderate density of non-basal dislocations.

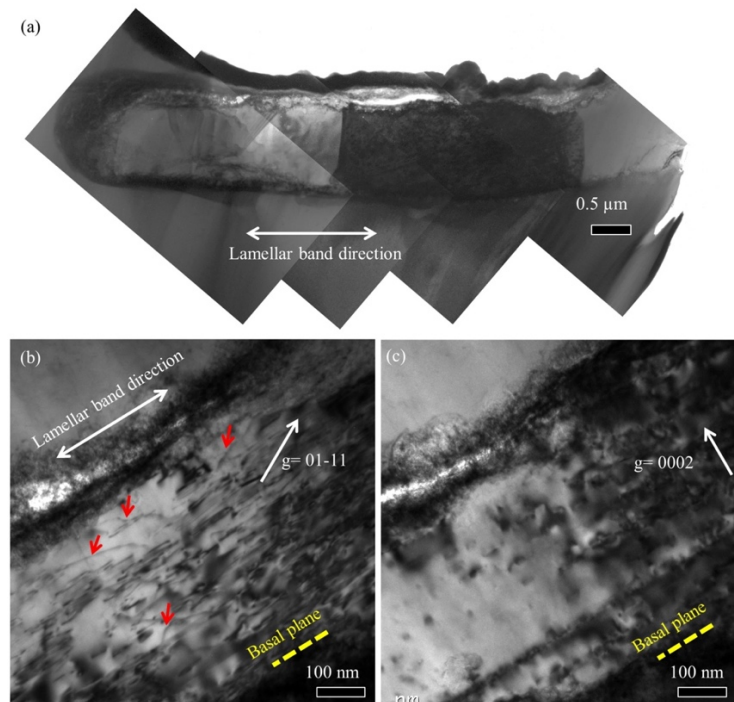


Fig. 2.4 TEM images of cryomilled 2h-Mg powder particles: (a) composite low magnification bright field image showing the structure of an as-milled lamellar particle; (b) $\mathbf{g} = 01-11$ two-beam bright field image near $[2-1-10]$ zone axis showing all types of dislocations; (c) $\mathbf{g} = 0002$ two-beam bright field image showing only $\langle \mathbf{c} \rangle$ or $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations.

2.4.2 Microstructure and texture of as-sintered Mg bulk samples

To examine the role of grain morphology during SPS processing, AR-Mg and 2h-Mg powder particles were sintered using identical pressure-assisted SPS conditions to produce bulk samples, hereafter referred to as AR-Mg-SPS and 2h-Mg-SPS, respectively. The 2h-Mg powder was selected for consolidation and subsequent characterization due to its extreme grain morphology anisotropy and high dislocation density. The 8h-Mg powder was also consolidated, but retained equiaxed nanometric grains after both cryomilling and consolidation, thus making characterization of the consolidated material beyond the scope of the current study. Findings on the 8h-Mg-SPS sample will be explored in detail in future work.

Fig. 2.5 shows the EBSD inverse pole figure (IPF) maps, color-coded with respect to the SPS CA (vertical direction in the maps), for AR-Mg-SPS and 2h-Mg-SPS, together with the corresponding grain size area fraction histograms. In the IPF maps, high angle grain boundaries (HAGBs) with misorientation angles larger than 15° are colored in black, and low angle grain boundaries (LAGBs) with misorientation angles between 2° to 15° are colored in grey. As shown in Fig. 2.5 (a), clusters of small equiaxed grains in a “necklace”-type arrangement surrounding the coarse grains can be observed from the IPF map. The grain size statistics in Fig. 2.5 (c), calculated from the EBSD map, indicate a nearly bimodal grain size distribution with grain diameter ranging from less than $1\text{ }\mu\text{m}$ to larger than $37\text{ }\mu\text{m}$. The average grain size of AR-Mg-SPS is $\sim 13.2\text{ }\mu\text{m}$. The IPF map for 2h-Mg-SPS in Fig. 2.5 (b) reveals a refined grain structure. Originating from the 2h-Mg disc-shaped powder

particles, a lamellar band structure can be viewed in this sample. Similar laminated structures are characteristic of high-strain rolled or extruded metals [84, 85], but compared to the laminated microstructure produced by rolling or extrusion, the lamellar bands in 2h-Mg-SPS are less straight and less parallel. Each band contains multiple elongated grains. Dark regions in this IPF map are areas that cannot be indexed by EBSD, due to the small grain sizes and/or high strains in these locations. A narrower grain size distribution range is found for 2h-Mg-SPS, giving an average grain size of $\sim 6.6 \mu\text{m}$. To reveal the grain sizes of laminated grains in the two perpendicular directions of interest, i.e., the directions parallel and perpendicular to the SPS CA, linear intercept grain sizes were calculated for 2h-Mg-SPS along the vertical and horizontal directions using the EBSD map in Fig. 2.5 (b). The distributions of the horizontally and vertically linear intercept grain sizes are plotted in Fig. 2.5 (e) and (f), respectively. The average intercept grain size is $\sim 2.8 \mu\text{m}$ for the vertical direction and $\sim 8.0 \mu\text{m}$ for the horizontal direction, which quantifies the average lamellar thickness and length, respectively.

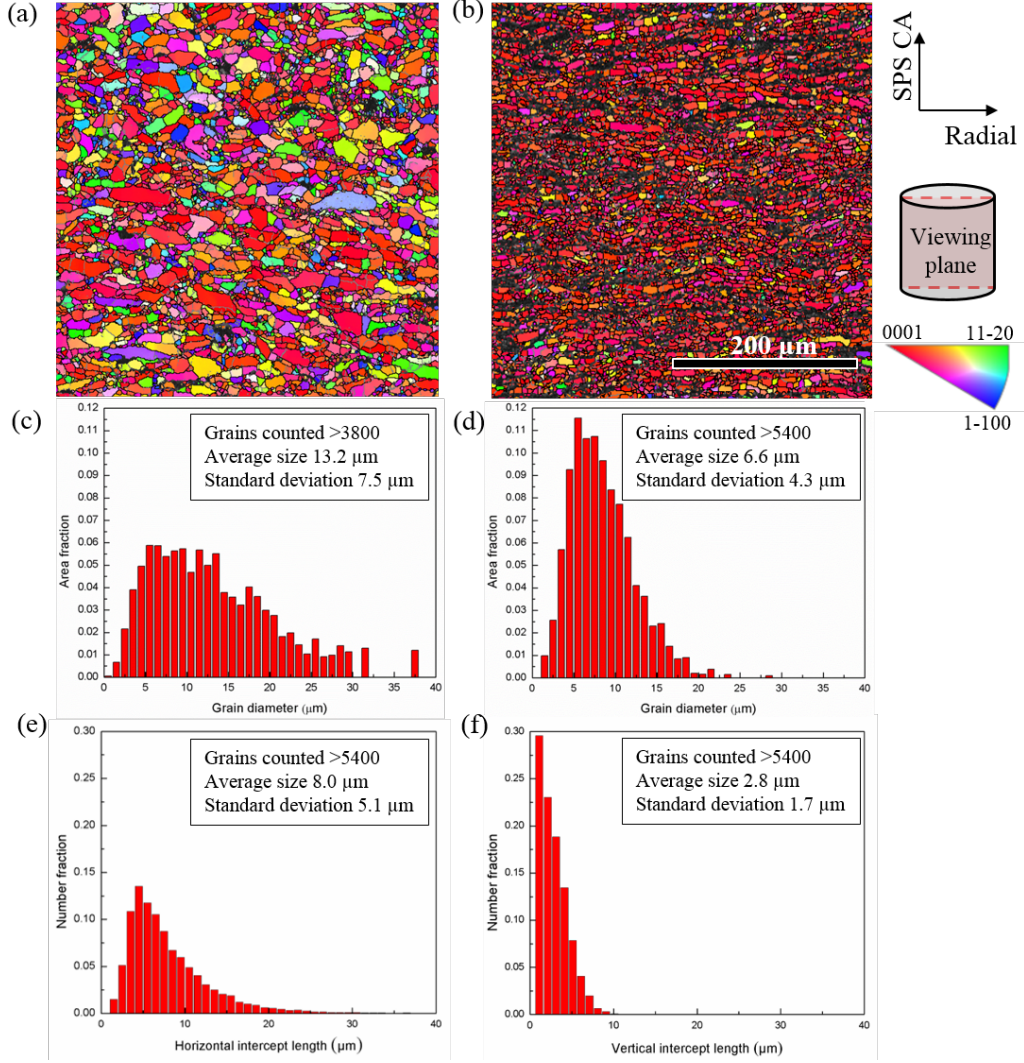


Fig. 2.5 EBSD microstructural analysis of SPS sintered Mg samples: (a) and (b) are the inverse pole figure (IPF) colored maps along the SPS compaction axis (CA) of AR-Mg-SPS and 2h-Mg-SPS, respectively. High angle grain boundaries with misorientations $> 15^\circ$ are colored in black and small angle grain boundaries with 2° to 15° misorientations are colored in grey; (c) and (d) are the grain size distributions corresponding to (a) and (b), respectively; (e) and (f) are the linear intercept grain size distributions for 2h-Mg-SPS along the horizontal and vertical directions, respectively.

Despite the differences in the processing and morphologies of the two feedstock powder particles, both as-sintered samples developed non-random crystal orientations. As visualized from the IPF maps in Fig. 2.5, most grains in the sintered samples have their c-axes close to the SPS CA, as represented by the red grain color. The (0001) and (10-10) pole figures, and the inverse pole figures from the SPS CA for AR-Mg-SPS and 2h-Mg-SPS, respectively, are displayed in Fig. 2.6 (a) and (b). From the pole figures and inverse pole figures, a basal fiber texture, i.e., with the basal poles aligned along the SPS CA, can be identified in both samples, and the intensities of the basal poles are nearly radial symmetric around the SPS CA. Peak texture intensities in units of m.u.d. (multiples of uniform density) are indicated. Compared to AR-Mg-SPS, 2h-Mg-SPS has a higher peak intensity in the basal pole figures and a narrower angular spread of basal poles from the SPS CA. Similar strong textures are often observed in pure Mg or dilute Mg alloys after conventional rolling [86-88].

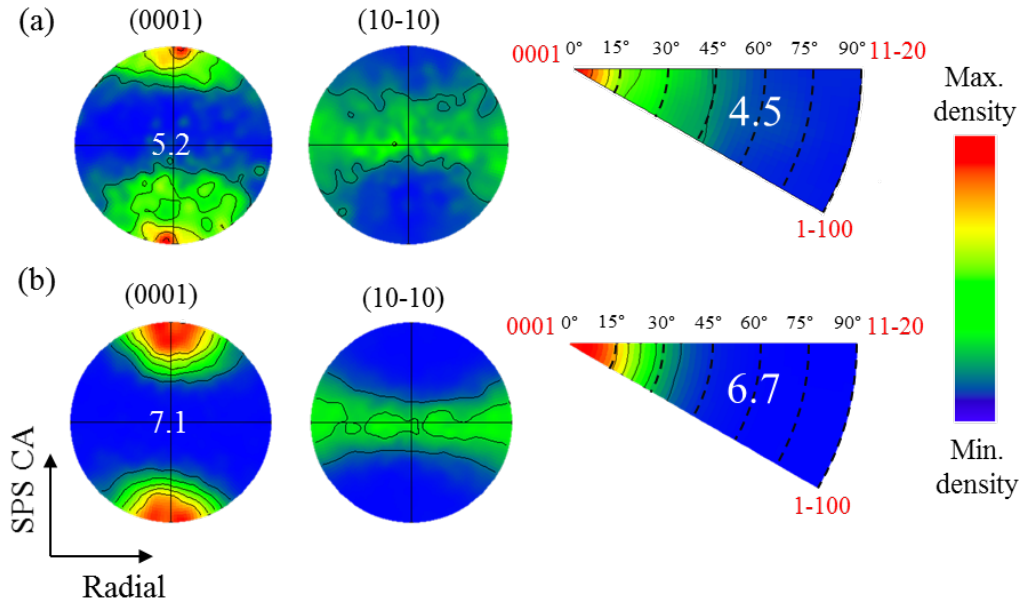


Fig. 2.6 (0001) and (10-10) pole figures and inverse pole figures along the SPS compaction axis (CA) for: (a) AR-Mg-SPS and (b) 2h-Mg-SPS.

The microstructure and dislocation structures of the 2h-Mg-SPS sample were further examined by TEM. As shown in the bright field image in Fig. 2.7 (a), the microstructure of 2h-Mg-SPS is characterized by near horizontal lamellar bands, that are perpendicular to the SPS CA. Based on sampling over ~ 100 bands, the majority of lamellar thicknesses range from 0.5 to 3 μm . A representative two-beam bright field image near the $[2-1-10]$ zone axis, with diffraction vector $\mathbf{g} = 01-1-1$, is shown in Fig. 2.7 (b). $\langle \mathbf{a} \rangle$ type dislocations parallel to the trace of the basal plane are dominant similar to that in the 2h-Mg powder. Moreover, the cross slip of $\langle \mathbf{a} \rangle$ dislocations between basal and prismatic/pyramidal planes is observed, as indicated by the red arrows. Since the stacking fault energy (SFE) on the basal planes in Mg is much lower than that on the non-basal planes [36], the cross slip observed

here is more likely cross slip from prismatic/pyramidal planes to basal planes. A dislocation wall structure is also seen in this grain, as indicated by the black dashed lines. Low angle grain boundaries in the form of dislocation cells have been reported as a result of dislocation interactions and rearrangement during recovery [48]. Fig. 2.7 (c) and (d) are two-beam dark field images of another sample region under $\mathbf{g} = 01\text{-}10$ and $\mathbf{g} = 0002$ conditions, respectively, near $[2\text{-}1\text{-}10]$ zone axis. Most $\langle \mathbf{a} \rangle$ type dislocations in Fig. 2.7 (c) are parallel to the basal plane trace, whereas some others are out of the basal plane, as highlighted with red arrows. A much lower density of $\langle \mathbf{c} \rangle$ or $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations, as compared to $\langle \mathbf{a} \rangle$ type dislocations, are present in Fig. 2.7 (d), and they tend to align with the trace of the basal plane. Therefore, the dislocations in 2h-Mg-SPS consist of a high density of basal $\langle \mathbf{a} \rangle$ dislocations and some non-basal dislocations, with some being non-basal $\langle \mathbf{a} \rangle$ dislocations, and others being $\langle \mathbf{c} \rangle$ or $\langle \mathbf{c} + \mathbf{a} \rangle$ dislocations.

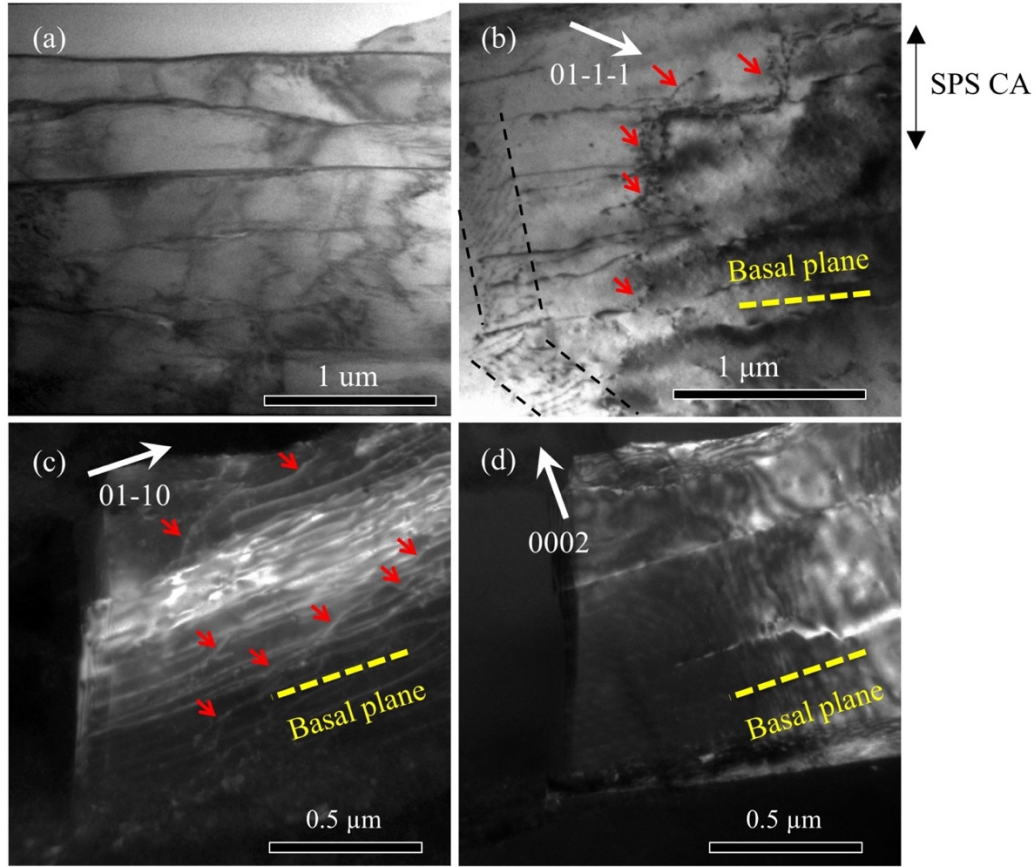


Fig. 2.7 TEM micrographs of 2h-Mg-SPS: (a) is a bright field cross-sectional TEM images showing the typical lamellar band structure; (b) is a two-beam bright field image under $\mathbf{g} = 01-1-1$ near $[2-1-10]$ zone axis; (c) and (d) are two beam dark field images at the same region under $\mathbf{g} = 01-10$ and $\mathbf{g} = 0002$, respectively, near $[2-1-10]$ zone axis.

2.4.3 Grain boundary misorientation analysis

Correlated misorientation (i.e., misorientation at grain boundaries) distributions (with a 2° lower threshold) are plotted in Fig. 2.8 (a) and (b) for AR-Mg-SPS and 2h-Mg-SPS, respectively. A strong frequency peak in the 2° to 15° low-angle grain boundaries (LAGBs) regime can be identified in both samples. In the $>15^\circ$ high-angle grain boundaries

(HAGBs) regime, the distribution exhibits a broad peak in AR-Mg-SPS, while a pronounced maxima near 30° are present in 2h-Mg-SPS. In addition, the AR-Mg-SPS exhibits a detectable frequency peak near 90° , presumably corresponding to the $\sim 86^\circ$ $\{10\text{-}12\}$ twins in Mg. However, the population of $\sim 86^\circ$ grain boundaries in 2h-Mg-SPS is almost negligible, indicating the low occurrence of twins in this sample, which is consistent with our TEM observations in Fig. 2.4. Furthermore, in the inset of Fig. 2.8, distributions of rotation axes for misorientation angle ranges of $(30\pm 3)^\circ$ and $(86\pm 3)^\circ$ in the SPS sintered samples are plotted in the form of inverse pole figures. The rotation axes for $\sim 30^\circ$ grain boundaries appear random in sample AR-Mg-SPS. In contrast, in sample 2h-Mg-SPS, the $\sim 30^\circ$ rotation axes are predominantly centered around the c-axis. The high frequency of $30^\circ/[0001]$ grain boundaries most likely corresponds to the recrystallization in HCP metals [12, 89]. In addition, the rotation axes for $\sim 86^\circ$ grain boundaries in AR-Mg-SPS are mainly clustered around the $\langle 11\text{-}20 \rangle$ direction, consistent with the $\{10\text{-}12\}$ twin boundaries with an $86^\circ/\langle 11\text{-}20 \rangle$ twin-matrix misorientation relationship. Though the frequency of 86° grain boundaries is low in 2h-Mg-SPS, clustering of 86° rotation axes around $\langle 11\text{-}20 \rangle$ suggests the possible occurrence of $\{10\text{-}12\}$ twins within some favorably oriented grains in 2h-Mg-SPS. The frequencies of the three types of characteristic grain boundaries (LAGBs, $(30\pm 3)^\circ$ grain boundaries, and $(86\pm 3)^\circ$ $\{10\text{-}12\}$ twin boundaries) in the two SPS sintered samples are compared in Fig. 2.8 (c). Though important in Mg deformation, $\{10\text{-}11\}$ contraction twins are not plotted here, since the confidence in identifying this type of twin by misorientation angle is considered low, as they are extensively reported to be thin, scarce and hard to detect [48, 90]. Moreover, $\{10\text{-}11\}$ contraction twins and $\{10\text{-}11\}$ - $\{10\text{-}12\}$

double twins are favorable sites for recrystallization [50], so they have a high propensity to be consumed by new grains. While the number frequency of LAGBs in AR-Mg-SPS is only $\sim 8.8\%$, the value in 2h-Mg-SPS is $\sim 19.5\%$. The higher fraction of LAGBs in 2h-Mg-SPS can be understood by the high density of dislocations induced by the severe plastic deformation during cryomilling, which tend to rearrange into dislocation cell structures and then convert into LAGBs [91, 92]. The fraction of $86^\circ \{10\text{-}12\}$ twin boundaries (within a $\pm 5^\circ$ misorientation tolerance) in AR-Mg-SPS is $\sim 10.6\%$, compared to $\sim 1.0\%$ in 2h-Mg-SPS. The frequency of 30° misorientation grain boundaries (within a $\pm 5^\circ$ misorientation tolerance) in 2h-Mg-SPS ($\sim 26.1\%$) is almost twice that in AR-Mg-SPS ($\sim 13.4\%$).

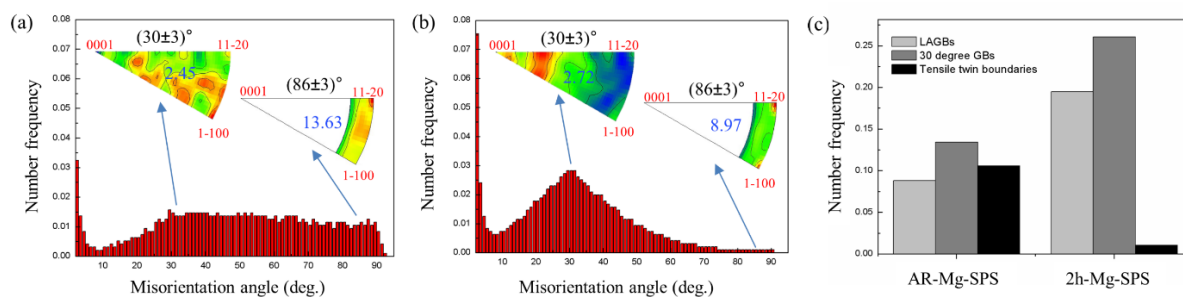


Fig. 2.8 (a) and (b) are the correlated misorientation angle distributions obtained from the EBSD data for AR-Mg-SPS and 2h-Mg-SPS, respectively. Insets are the misorientation axis distributions for two angular ranges of interest; (c) shows a comparison of the frequencies of low angle grain boundaries (LAGBs), $\sim 30^\circ$ grain boundaries and $\{10\text{-}12\}$ twin boundaries in AR-Mg-SPS and 2h-Mg-SPS.

2.4.4 Mechanical properties of and anisotropy in SPS consolidated Mg

The loading direction relative to the basal fiber texture and the laminate orientation is expected to influence the deformation behavior. In order to study the mechanical behavior along different orientations, uniaxial compression tests were performed at room temperature both parallel and perpendicular to the SPS CA, corresponding to c-axis contraction and c-axis extension, respectively, according to the texture measurements. The true stress-strain curves for AR-Mg-SPS and 2h-Mg-SPS are plotted in Fig. 2.9, and the compressive strength values are summarized in Table 2.3. For AR-Mg-SPS compressed along the SPS CA, the 0.2% yield strength and maximum strength are 130 MPa and 183 MPa, respectively. When compressed normal to the SPS CA, a concave shape for the true stress-strain curve is observed, which is typical for twinning-dominated deformation in textured Mg polycrystals; the 0.2% yield strength is 107 MPa, and the maximum strength has a value of 162 MPa. 2h-Mg-SPS exhibits higher strength than AR-Mg-SPS along both directions. When compressed parallel to the SPS CA, the 0.2% yield strength is 179 MPa, and the maximum strength is measured to be 201 MPa. When the loading direction is normal to the SPS CA, the yield strength and maximum strength are 187 MPa and 205 MPa, respectively. Compared to AR-Mg-SPS, the yield strength of 2h-Mg-SPS when compressed parallel and normal to the SPS CA increased by 38% and 75%, respectively. Moreover, 2h-Mg-SPS showed a smaller difference in yield strength values along the two directions than that corresponding to AR-Mg-SPS, despite its stronger basal texture. The possible mechanisms for this unusual behavior are discussed below.

Table 2.3 Compressive strengths of the SPS-consolidated Mg samples parallel or normal to the SPS compaction axis (CA) and the corresponding compressive yield anisotropy ($\sigma_{0.2\%}$ ratio, defined as the ratio of the yield strength for c-contraction to the yield strength for c-extension).

	Compression orientation	$\sigma_{0.2\%}$ (MPa)	$\sigma_{\max}$ (MPa)	$\sigma_{0.2\%}$ ratio (c-contraction/ c-extension)
AR-Mg-SPS	parallel to SPS CA (c-axis contraction)	130	183	1.21
	normal to SPS CA (c-axis extension)	107	162	
2h-Mg-SPS	parallel to SPS CA (c-axis contraction)	179	201	0.96
	normal to SPS CA (c-axis extension)	187	205	

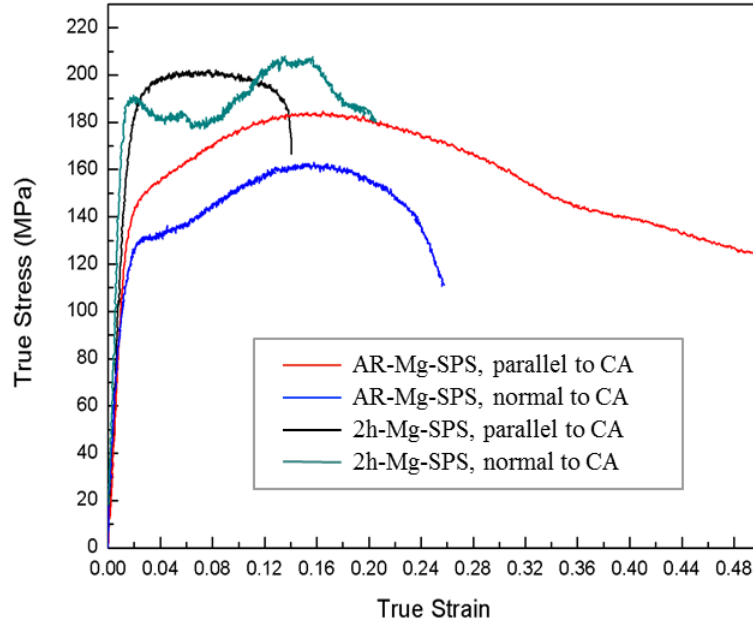


Fig. 2.9 Compressive true stress-strain curves for AR-Mg-SPS and 2h-Mg-SPS along directions parallel and normal to SPS CA.

2.5 Discussion

2.5.1 Deformation and grain refinement during milling

In the early stage of the milling process the plastic deformation that is induced by ball-powder-ball collisions effectively modifies the powder morphology from equiaxed to disc-like [55, 93, 94]. In tandem, dislocation nucleation and accumulation and the formation of sub-grain boundaries occur at the microscopic scale [32, 55, 93, 95]. In a well-established model based on metals with cubic crystal structures [55], powders undergo a three-stage process of grain refinement during milling, which include strain localization into narrow shear band zones, annihilation and rearrangement of dislocations to form

subgrains, and finally, transformation of LAGBs into HAGBs [55]. Compared to cubic crystals, the poor low-temperature ductility in Mg suggests a much higher probability of powder fracture during cryomilling, leading to a more rapid decrease in the particle size of HCP Mg. This is confirmed by the average particle size of Mg ($\sim 17 \mu\text{m}$), which is significantly smaller than the particle size of, for example, pure Cu ($\sim 34 \mu\text{m}$) or Al 5083 ($\sim 91 \mu\text{m}$) after the same 8 hours of cryomilling [82]. Moreover, the microstructural evolution in HCP metals during cryomilling is further complicated by the variety of different slip systems that are active as well as the high propensity for deformation by twinning. Therefore, the mechanisms for grain refinement, particle flattening, as well as the evolution of orientation preference during milling that occur in cubic systems may not be directly applicable to rationalize the evolution of microstructure in Mg during milling.

We provide a schematic diagram (Fig. 2.10) that illustrates a proposed mechanism to explain the evolution of the structure during cryomilling of Mg. Due to the anisotropic HCP structure with distinct CRSS values associated with different slip systems, the angle between the basal plane and the impact loading direction influences deformation behavior. To explore this relationship in the case of Mg cryomilling, we consider an equiaxed crystal without initial dislocations, with the basal planes oriented at three possible angles (denoted as θ_1 , θ_2 and θ_3 , having values between 0° to 90° as described below) relative to the impact loading axis. First, when θ_1 is approximately 45° (Fig. 2.10 (a)), a maximized Schmid factor for basal $\langle \mathbf{a} \rangle$ slip is expected for this crystal. Basal slip is therefore favorable during the deformation, which will lead to increasing changes in both grain and particle morphology, i.e., elongation perpendicular to the loading axis, as illustrated in Fig. 2.10 (b).

Consequently, although the initial impact loading direction is largely arbitrary, the following impact will have a higher chance to load perpendicular to the elongated surface. Therefore, the angle between the loading axis and the basal planes after the first scenario of impact loading will become larger than θ_1 , and will continue to increase with an accumulation in strain induced during cryomilling.

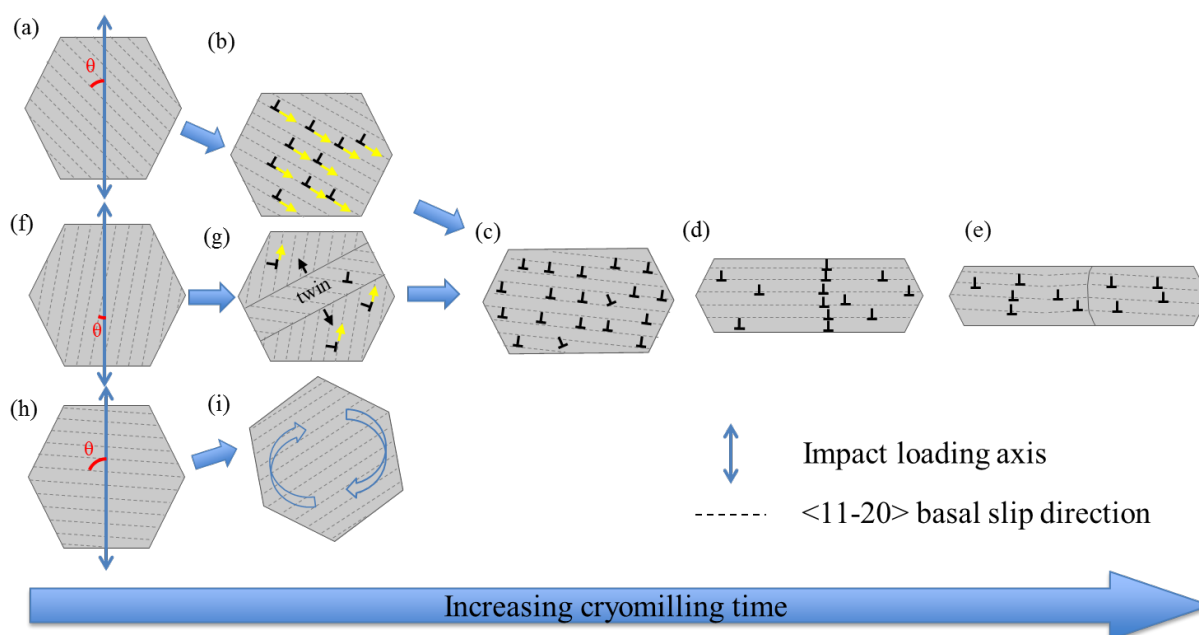


Fig. 2.10 A schematic showing the development of orientation preference and grain refinement in Mg during powder particle flattening.

Second, when θ_2 is close to 0° (Fig. 2.10 (f)), i.e., the impact loading axis is nearly perpendicular to the c-axis, $\{10\bar{1}2\}$ twins are favored. $\{10\bar{1}2\}$ twins will grow to accommodate the strain along the c-axis and will lead to a sharp reorientation of the original crystal by $\sim 86^\circ$. Consequently, the angle between the loading axis and the basal

planes after the second scenario of impact loading will be near 90° , as seen in Fig. 2.10 (g). Despite the fact that $\{10\text{-}12\}$ twinning is favored in this scenario, $\{10\text{-}12\}$ twin boundaries are not detected in 2h-Mg by TEM (Fig. 2.4). Possible explanations include: (1) the high impact loading and plastic strain introduced by the milling balls lead to the growth of the $\{10\text{-}12\}$ twins, which can easily consume the entire original matrix. Non-basal $\langle \mathbf{a} \rangle$ dislocations, as seen in Fig. 2.4 (b), can be activated over twinning to accommodate the plastic deformation; (2) although the resolved shear stress is close to zero on the basal plane according to Schmid's law, due to the relatively low CRSS, basal slip can be activated under a small misalignment when θ_2 is not exactly zero.

Third, when compressed nearly perpendicular to the basal planes (Fig. 2.10 (h)), i.e., θ_3 is about 90° , contraction twins and $\langle \mathbf{c} \rangle$ or $\langle \mathbf{c} + \mathbf{a} \rangle$ slips should be favored. However, due to the cryogenic environment, contraction twins and dislocation slip with $\langle \mathbf{c} \rangle$ or $\langle \mathbf{c} + \mathbf{a} \rangle$ can only be activated under conditions that involve high stresses and/or strain rates, if material fracture does not occur prior to the activation of these modes. Therefore, this direction is considered as a hard direction on which inadequate strain can occur. Consequently, the particle will retain its initially equiaxed morphology, so the following impact direction relative to the crystal orientation could be arbitrary (Fig. 2.10 (i)) and possibly on soft directions, as in the first two scenarios. Particle fracture is also expected to occur readily under this loading condition. Similarly, some basal slip is expected when the Schmid factor for basal slip is not exactly zero.

As discussed in the first two scenarios, although a gradual lattice rotation by basal slip in the first scenario and an abrupt lattice reorientation induced by $\{10\text{-}12\}$ twinning in

the second scenario, the c-axis of the crystal becomes closer to the impact loading axis during powder flattening, as shown in Fig. 2.10 (c). This is consistent with the crystal orientation preference observed in 2h-Mg from the XRD results (Fig. 2.3). TEM results in Fig. 2.4 confirmed the relationship between powder flattening and the concomitant increase in density of basal $\langle a \rangle$ dislocations during 2h of cryomilling. The high-density of basal dislocations then rearrange into subgrain boundaries perpendicular to the flattened lamellar surface (Fig. 2.10 (d)), and subgrain boundaries will continuously evolve into low or high angle grain boundaries leading to refinement of the microstructure (Fig. 2.10 (e)).

2.5.2 Microstructural evolution during SPS consolidation

Despite the limited exposure time at elevated temperature during SPS, the microstructure of the AR-Mg-SPS reveals small equiaxed grains formed along the serrated coarse grain boundaries with a “necklace-like” grain structure (Fig. 2.5 (a)), which suggests the occurrence of dynamic recrystallization during SPS [36]. The presence of $30^\circ/[0001]$ grain boundaries (Fig. 2.8 (a)) is another feature that has been reported as an indicator of dynamic recrystallization in many thermo-mechanically processed Mg alloys [12, 89]. Although the rotation axes for $\sim 30^\circ$ misorientation appears random for AR-Mg-SPS (Fig. 2.8 (a)), and shown again in Fig. 2.11 (a) for comparison), when the rotation axes distribution for $\sim 30^\circ$ misorientation is plotted with only small recrystallized grains (a $7\ \mu\text{m}$ cutoff grain size is used), the IPF displays an obvious intensity peak around the c-axis, as displayed in Fig. 2.11 (b). A $7\ \mu\text{m}$ grain size threshold is selected due to the first peak position in the grain size histogram (Fig. 2.5 (c)). Therefore, owing to the small

recrystallization fraction present in the AR-Mg-SPS, the frequency of $30^\circ/[0001]$ grain boundaries is low, and the overall misorientation distribution of the complete set of grains is observed to be random. In contrast, the notably higher frequency of $30^\circ/[0001]$ grain boundaries for 2h-Mg-SPS suggests a higher fraction of recrystallized microstructure. In the SPS sintered Mg samples, the occurrence of dynamic recrystallization is feasible considering the 390°C sintering temperature, which exceeds the recrystallization temperature of Mg ($T_{RX} \approx 0.4T_m \approx 100^\circ\text{C}$). The 200 MPa uniaxial pressure applied to the Mg powder provides the major driving force for dynamic recrystallization in AR-Mg-SPS. In 2h-Mg-SPS, however, the stored lattice energy due to a high dislocation density created during cryomilling can provide a higher driving force for recovery and recrystallization, resulting in a higher recrystallization fraction. Considering the low stacking fault energy (SFE) ($\sim 36 \text{ mJ}/\text{m}^2$) on the basal planes and high SFEs on the non-basal planes ($\sim 265 \text{ mJ}/\text{m}^2$ and $\sim 344 \text{ mJ}/\text{m}^2$ for prismatic and pyramidal planes, respectively) [36], dislocations on the non-basal planes have a tendency to cross-slip onto the basal planes during dynamic recovery [36]. This is consistent with the TEM observation of cross-slipping dislocations in 2h-Mg-SPS (Fig. 2.7 (c)).

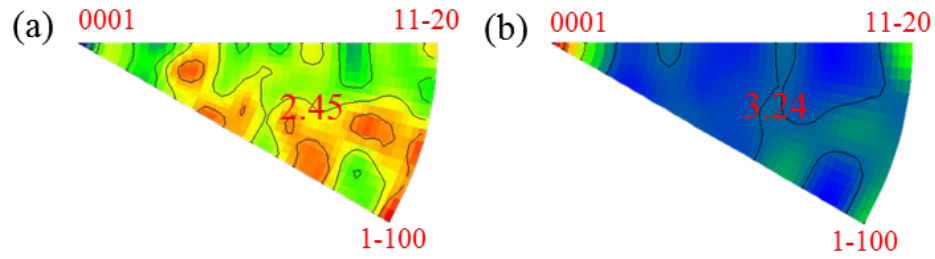


Fig. 2.11 Comparison of rotation axes distributions for grain boundaries with $(30\pm3)^\circ$ misorientation angles for AR-Mg-SPS when: (a) all grains are included and (b) only recrystallized grains (grains with diameters smaller than $7\text{ }\mu\text{m}$) are included.

Regarding texture evolution, both AR-Mg-SPS and 2h-Mg-SPS did not show any deformation or recrystallization texture unique to SPS. Recrystallization is not effective in randomizing the texture, as noted in previous studies [96]. A basal fiber texture typical for wrought Mg and Mg alloys was observed in the SPS-consolidated samples. The basal texture being formed in AR-Mg-SPS without experiencing cryomilling can be attributed to the thermo-mechanical SPS process. The sharper texture in 2h-Mg-SPS is a mixed result of the preferred crystal orientations in the disc-shaped cryomilled powder and the SPS thermo-mechanical effect.

2.5.3 Mechanisms for the reversed compressive yield strength anisotropy in 2h-Mg-SPS

Generally, basal textured Mg exhibits a much lower yield strength upon c-axis extension compared to the yield strength upon c-axis contraction, because activating $\{10\text{-}12\}$ extension twinning is easy in the former but not favorable in the latter [14, 67, 97]. The

yield strength for c-axis extension is usually one half to three quarters of that for c-axis contraction in polycrystalline Mg and Mg alloys with basal textures [13, 26, 98]. Compressive yield strengths for the two SPS consolidated Mg samples, together with compressive data from the literature for textured commercially pure Mg [99] and dilute AZ31 Mg alloys [97, 100, 101] with equiaxed grain structure, are summarized in Fig. 2.12 as a function of average grain size. With decreasing grain size, the yield strength increases, as anticipated on the basis of the Hall-Petch relationship. However, for all the samples with equiaxed grain structure, the reduced grain size is not effective in reducing the compressive yield strength anisotropy. In contrast, both of the SPS sintered Mg samples display less anisotropic yield strength values, when compressed at room temperature. This can be partially explained by the weak texture in Mg processed via powder metallurgy. However, the difference in yield strength values for c-axis contraction and c-axis extension was further reduced in 2h-Mg-SPS relative to AR-Mg-SPS, despite the stronger intensity of basal texture in 2h-Mg-SPS. In the present study, we report for the first time a reversed yield strength anisotropy, i.e., the yield strength under c-axis extension being higher than that under c-axis contraction, in commercially pure Mg. Reversed yield strength tension/compression asymmetry has been previously observed in Mg-rare earth alloys and has been attributed to the interaction between dislocations and precipitates and solutes during deformation [102, 103]. However, yield strength asymmetry and/or anisotropy in pure (including commercially pure) Mg and dilute Mg alloys without rare earth additions has not been previously observed. To study the deformation mechanisms leading to this unusual mechanical behavior, post-mortem EBSD analysis was performed on a 2h-Mg-SPS

sample compressed normal to the SPS CA, or c-axis extension mode, to $\sim 4\%$ true strain, at which point the test was interrupted. The EBSD IPF map after interrupted compression is shown in Fig. 2.13 (a). The grains were color-coded with respect to the compression axis, which is the vertical direction in the image. Grain boundary misorientation analysis in Fig. 2.13 (b) shows that the percent of grain boundaries satisfying $86^\circ \pm 5^\circ$ misorientation angles is $\sim 2.5\%$, compared to $\sim 1.0\%$ before the compression test. The rotation axes of $\sim 86^\circ$ grain boundaries are mostly around $\langle 11\text{-}20 \rangle$, correlating to $\{10\text{-}12\}$ twins. These grain boundaries were colored in white in Fig. 2.13 (a). The frequency of $\{10\text{-}12\}$ twinning is considerably lower in 2h-Mg-SPS even though the loading direction is favorable for twinning. As discussed previously that the yield strength anisotropy of Mg is mainly due to the $\{10\text{-}12\}$ twinning, the smaller differential in compressive yield strengths observed in 2h-Mg-SPS can be explained by the low occurrence of $\{10\text{-}12\}$ twinning.

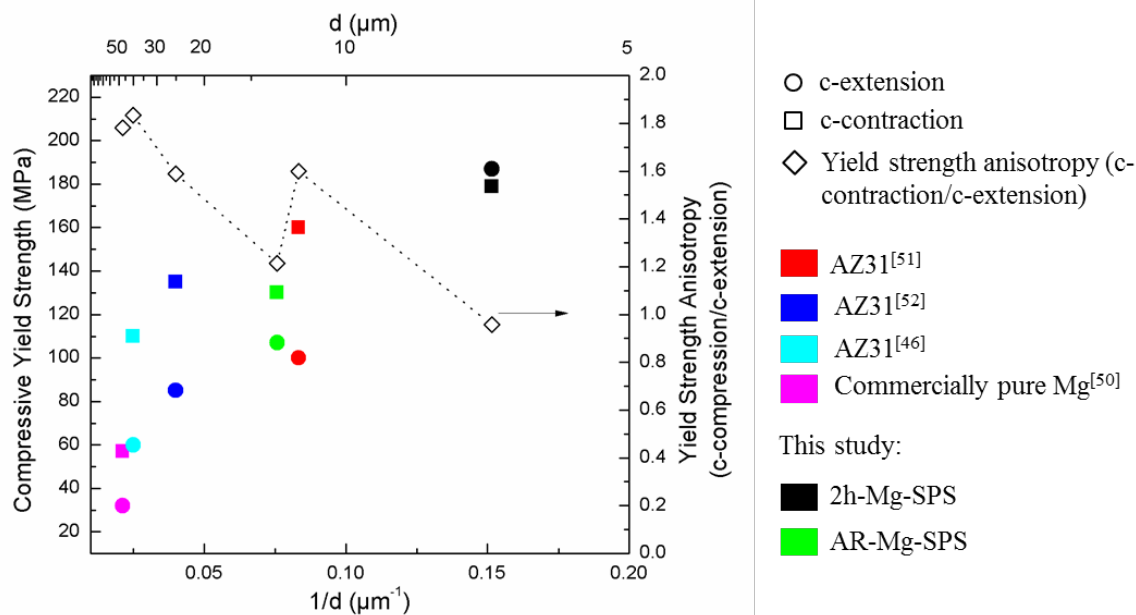


Fig. 2.12 Compressive yield strengths under c-axis compression and c-axis extension, and the yield strength anisotropy (c-contraction/c-extension) for Mg and dilute Mg alloys with different grain sizes.

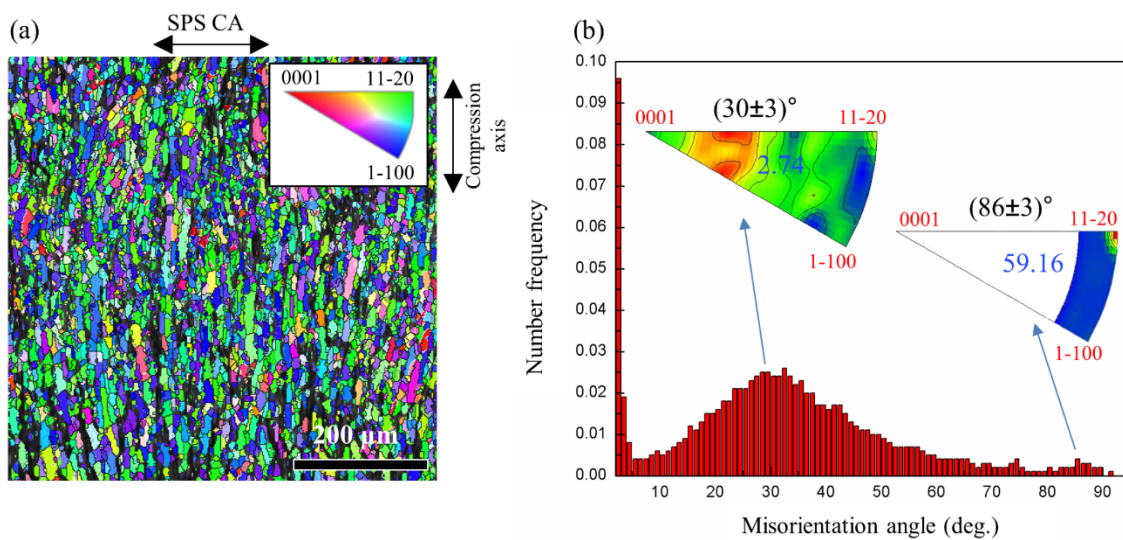


Fig. 2.13 Post-mortem EBSD microstructural analysis of 2h-Mg-SPS compressed to ~4% true strain normal to SPS CA: (a) shows the IPF colored map, and (b) is the corresponding

correlated misorientation angle distribution. Insets in (b) are the misorientation axis distributions for two angular ranges of interest.

The influence of grain size is likely related to the scarcity of twins in fine to ultrafine grained Mg. As extrapolated from the model derived by Barnett et al. for Mg alloys [26], the critical grain size for transition from twinning-dominated to slip-dominated deformation is less than 2 μm at ambient temperature and quasi-static strain rate. The average equivalent spherical grain size in 2h-Mg-SPS is $\sim 6.6 \mu\text{m}$, which should fall in the twinning dominated regime. For example, in a hot rolled AZ31 with an average grain size of 8.1 μm , though the grain size is comparable to the average equivalent spherical grain size of 2h-Mg-SPS, the yield strength for c-axis contraction is almost twice that for c-axis extension [104], indicating that the reduced grain size may not be the dominant mechanism for the reversed compressive yield strength anisotropy observed in 2h-Mg-SPS. However, it should be pointed out that in the non-equiaxed microstructure of 2h-Mg-SPS, the average linear intercept grain size along the lamellar thickness direction is only $\sim 2.8 \mu\text{m}$, which is close in value to the critical grain size for the suppression of twins. Further effort is still needed to explore the effects of different grain size parameters on the suppression of twin nucleation in polycrystalline Mg with non-equiaxed microstructures. In addition to twin nucleation, grain morphology may also influence the growth of twins. It is expected that the propagation and thickening of twins will be more difficult in 2h-Mg-SPS compared to equivalent behavior observed in equiaxed grain structures with similar equivalent spherical grain sizes, because of the smaller dimensions along the lamellar thickness

direction. For this reason, the grain morphology evidently affects the stress required for twin growth, which could contribute to the reversed yield anisotropy observed in the microlaminated 2h-Mg-SPS.

As illustrated schematically in Fig. 2.14, Mg crystals show an intrinsically anisotropic mechanical behavior. An equiaxed grain structure, which usually induces isotropic properties in cubic materials with random textures, results in anisotropic compressive yield strength in textured Mg and profuse {10-12} twins can be activated at preferred stress orientations. In contrast, a laminated microstructure in cubic materials often leads to anisotropic properties for different loading orientations with respect to the lamellar planes, e.g., stronger when strained parallel to the lamellar plane [81]. However, it is proposed that the grain morphology induced deformation anisotropy observed in the present study offers an opportunity to reduce or even reverse the intrinsic compressive yield strength anisotropy of basal textured Mg. In addition, compared to an equiaxed structure with similar grain size, a laminated microstructure provides fewer sites for local stress concentration at grain boundaries that may facilitate twin nucleation, as seen in Fig. 2.14. Therefore, we attribute the reversed compressive yield strength anisotropy and low frequency of twins observed in 2h-Mg-SPS to its microlaminated grain structure.

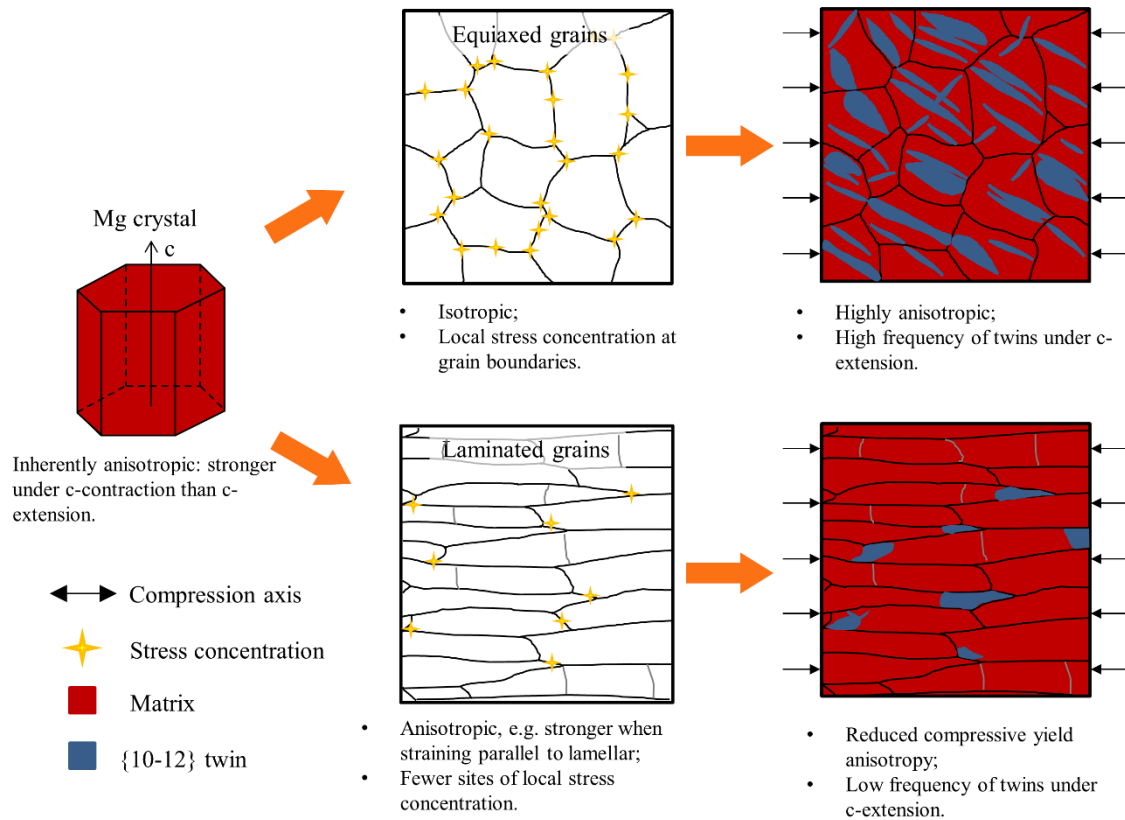


Fig. 2.14 Schematic showing the effects of equiaxial and laminated grain structure on the yield strength anisotropy of Mg.

Another plausible explanation for the inhibition of twinning in 2h-Mg-SPS is the high density of basal dislocations. As discussed in the previous sections, basal slip is dominant during cryomilling, and recovery on the basal plane with low stacking fault energy is difficult in Mg while non-basal dislocations tend to cross-slip onto basal planes during recovery. As a result, a high density of basal dislocations in both 2h-Mg and 2h-Mg-SPS was observed by TEM (Fig. 2.4 (b) and Fig. 2.7 (c)), which can considerably harden basal slip

and decrease the CRSS ratio for non-basal to basal slip. Therefore, due to the more isotropic slip systems, the contribution of twinning in deformation could be reduced.

2.6 Summary

Mg with a microlaminated grained structure was produced by cryomilling followed by consolidation using spark plasma sintering. Rigorous microstructural characterization was performed to explain the observed mechanical behavior. The following conclusions can be drawn from these analyses:

1. Particle-flattening occurred in the first two hours of cryomilling. A high density of basal dislocations was introduced into the powder particles (2h-Mg), together with a moderate amount of non-basal dislocations. The predominance of basal slip led to the formation of a preferred crystal orientation with the c-axis nearly perpendicular to the surface of the disc-shaped particles.

2. EBSD analyses indicate that after SPS consolidation, a basal fiber texture developed in samples starting with either the as-received powders (AR-Mg-SPS) or those after two hours of cryomilling (2h-Mg-SPS). The stronger texture in 2h-Mg-SPS is attributed to the preferential orientations developed in the disc-shaped particles and the thermo-mechanical effect of SPS. Dynamic recovery and recrystallization also occurred and promoted dislocation cross-slipping.

3. 2h-Mg-SPS achieves higher compression yield strengths than AR-Mg-SPS under both c-axis contraction and c-axis extension. Though AR-Mg-SPS exhibits a compressive yield anisotropy linked with its basal texture, a reversed compressive yield anisotropy was

observed in 2h-Mg-SPS, with a low occurrence of twinning activity during compression normal to the basal pole.

4. The low twinning activity, limited growth of twins and the anisotropy induced by the laminated grain structure are important contributors to the reversed yield anisotropy in 2h-Mg-SPS.

Chapter 3 Effect of nanocrystalline grain size on the room temperature plasticity and deformation mechanisms in Mg

3.1 Abstract

Bulk nanocrystalline (NC) Mg processed by cryomilling of commercially pure Mg (99.8%) powder particles followed by spark plasma sintering demonstrates a large compressive strain (>120%) at room temperature and strain rates up to 10^{-2} s^{-1} . Compressive tests at strain rates ranging from 10^{-4} to 10^{-1} s^{-1} reveal a strain rate sensitivity of ~ 0.17 . Microstructural investigation reveals obvious grain coarsening accompanied with the ultra-large plastic deformation, which, along with the analysis of the deformation kinetics and texture, suggests that the excellent compressive plasticity in NC Mg originates from grain boundary mediated deformation mechanisms and basal slip dominated dislocation gliding.

3.2 Introduction

Mg and Mg alloys have received extensive research interest, because of the significant economic and efficiency benefits of using this lightweight structural material in the automotive and aerospace industries [105, 106]. However, Mg is intrinsically brittle at room temperature, a behavior that originates from the insufficient number of available deformation modes in the hexagonal close-packed (HCP) structure [66]. Elevated temperature can help activate more deformation modes, including slip on the pyramidal planes [28, 107, 108], and is often required for mechanical processing of Mg structural

components [109]. This substantially increases the manufacturing cost and limits their application in many fields.

Among previous attempts to achieve formability enhancements in metals, the superplasticity that has been observed in some fine-grained and nanocrystalline (NC) metals is particularly motivating [110, 111]. Results from these studies suggest that superplasticity readily occurs at high homologous temperatures ($T > 0.5 T_m$, T_m is the melting temperature), when grain boundary sliding and motion becomes dominant [29, 112]. Some approaches have been effectively employed to promote grain boundary mediated superplasticity at lower temperatures and higher strain rates, including (a) using novel processing techniques to fabricate materials with low content of contaminations and full density [111], (b) alloying to reduce the melting temperature at eutectic compositions [113], (c) refining the crystallite size [29, 114-117], and (d) segregation at grain boundaries to enhance the grain boundary diffusivity [118].

One challenge for obtaining a large plastic strain in Mg at room temperature, corresponding to a homologous temperature of $\sim 0.32 T_m$, is the difficulty to achieve a small grain size in pure Mg or dilute Mg alloys. Top-down severe plastic deformation (SPD) techniques, e.g., equal channel angular pressing and high-pressure torsion, are not effective in reducing the grain size of Mg due to the high processing temperatures required. Meanwhile, few analyses have yet been performed to fabricate bulk NC Mg by bottom-up powder metallurgy techniques with the use of mechanically milled Mg powders [119]. Moreover, the mechanisms controlling the plastic deformation of NC Mg at room

temperature are still poorly understood, as compared to cubic-structured or coarse-grained counterparts.

In light of the above discussion, the present study was devised to address whether it is possible to synthesize bulk NC Mg with an ensuing microstructure that will facilitate superplastic behavior. To address this question, we implemented the following approach. Bulk NC Mg was synthesized using cryomilling of Mg powders followed by spark plasma sintering. Compressive tests were carried out at room temperature and at different strain rates, and an analysis of the strain rate sensitivity was performed to evaluate the rate controlling mechanisms for plastic deformation. The deformation modes in the sample were systematically investigated by microstructural and texture characterization.

3.3 Experimental procedures

To synthesize Mg with NC grain sizes, commercially pure Mg powder particles (99.8%, 325 mesh, Alfa-Aesar) were cryomilled using a modified Szegvari-type attritor for 8 hours in flowing liquid argon. Stainless steel balls, 6.4 mm in diameter, were used as the attrition media, with a ball-to-powder weight ratio of approximately 30:1. Cryomilled Mg powder was loaded into a 20 mm inner diameter graphite die and consolidated into bulk samples by spark plasma sintering (SPS-825S DR. SINTER, SPS Syntex Inc., Japan). Powders were sintered under vacuum at a sintering temperature of 390 °C and a holding time of 3

min. A 90 MPa uniaxial compression pressure was applied (see Supplementary Fig. 3.1).

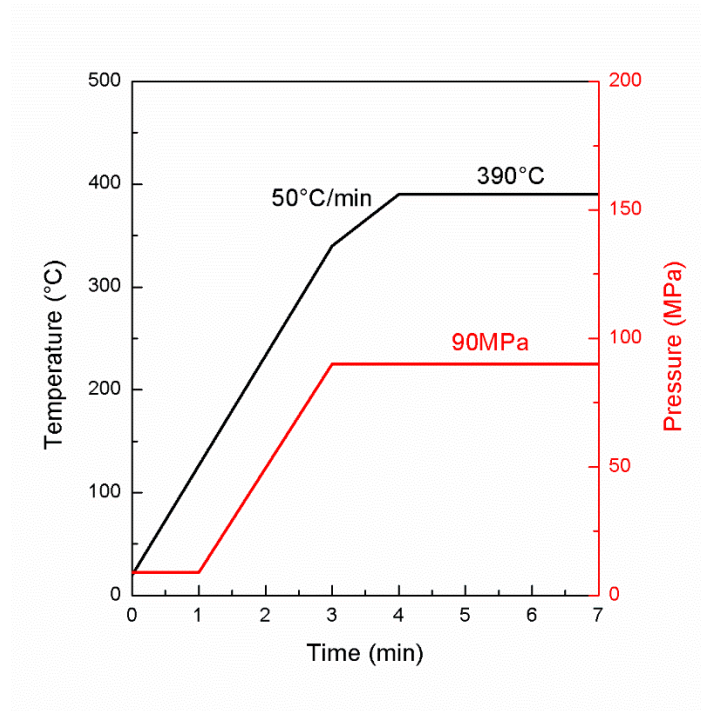


Fig. 3.1 Temperature and compaction pressure profiles during SPS sintering

Compression cuboids with dimensions of 4 x 4 x 6 mm were machined using electrical discharge machining such that the compression direction was parallel to the SPS compaction axis. Compression tests were performed at room temperature using a servohydraulic testing machine operating under displacement control mode. To study the strain rate sensitivity, the bulk Mg samples were compressed at various strain rates of 10^{-4} , 10^{-3} , 10^{-2} and 10^{-1} s^{-1} . Compression tests performed at or below 10^{-2} s^{-1} were manually stopped when true strain reached $\sim 120\%$ because the samples did not fracture during compression.

Microstructure and elemental composition of the cryomilled powder particles and the bulk Mg were characterized by X-ray diffraction (XRD, Smartlab, Rigaku, Cu K α radiation), a scanning electron microscope (SEM, XL 30, FEI) equipped with an energy dispersive spectroscopy detector (EDS, Oxford Instruments), and transmission electron microscopy (TEM, CM20, FEI/Philips and JEM-2100, JEOL). TEM specimens were prepared by mechanical grinding and ion milling. The operation of slip systems was determined by diffraction contrast analysis at multiple diffraction conditions in a Mg sample compressed to 30% strain (hereafter designated as 30%Mg). In-plane XRD pole figures were measured for the as-consolidated Mg samples as well as samples after compression to different strain levels. The sample surfaces being diffracted were perpendicular to the compression axis.

3.4 Results and discussion

3.4.1 Microstructure of the cryomilled powder particles and bulk nanocrystalline Mg

A representative SEM secondary-electron micrograph in Figure 1 (a) illustrates that the cryomilled powders consist of faceted and close-to-equiaxed particles, with an average particle size of $\sim 11.5\ \mu\text{m}$. The corresponding particle size distribution is plotted in Fig. 3.2 (b). A detailed discussion on the evolution of powder morphology during 8 hours of cryomilling can be found in [120]. The bright field and dark field TEM micrographs of the cryomilled powder particles in Fig. 3.2 (c) and (d) show the formation of NC grains (the average grain size is approximately 50 nm) with irregular shape. The inset in Fig. 3.2 (c) is the selected area electron diffraction (SAED) rings corresponding to polycrystalline HCP Mg.

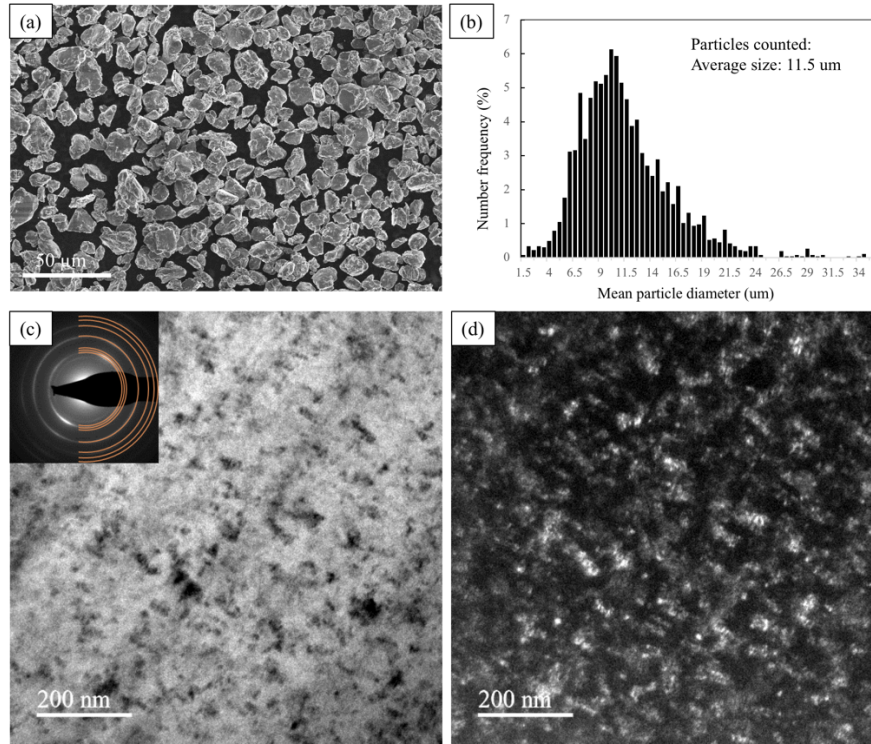


Fig. 3.2 Microstructural characterization of cryomilled Mg powder particles: (a) representative SEM image; (b) histogram of the mean particle diameter distribution; (c) and (d) TEM bright and dark field images.

After SPS, the relative density of the bulk Mg samples measured by the Archimedes method was $\sim 99.6\%$. SEM EDS analysis (see Fig. 3.3) reveals the content of O (~ 3.5 wt%) in the bulk Mg. TEM images in Fig. 3.4 (a) and (b) show a NC structure with a nearly equiaxed grain morphology. A statistical distribution of grain diameters (Fig. 3.4 (c)) was measured from the TEM images, showing a narrow grain size distribution in which $\sim 85\%$ of the grains are smaller than 100 nm and $\sim 3.2\%$ of the grains have diameters larger than 200 nm, with the average grain size being ~ 70 nm.

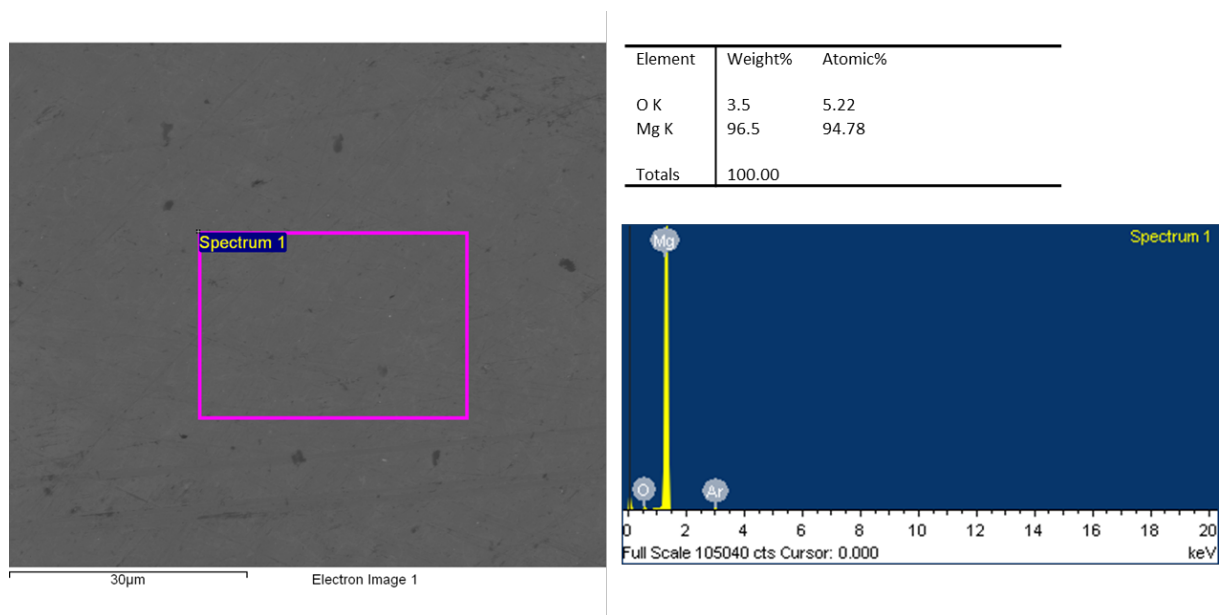


Fig. 3.3 SEM energy dispersive spectroscopy (EDS) spectrum and the summary of chemical composition in the SPS consolidated bulk Mg.

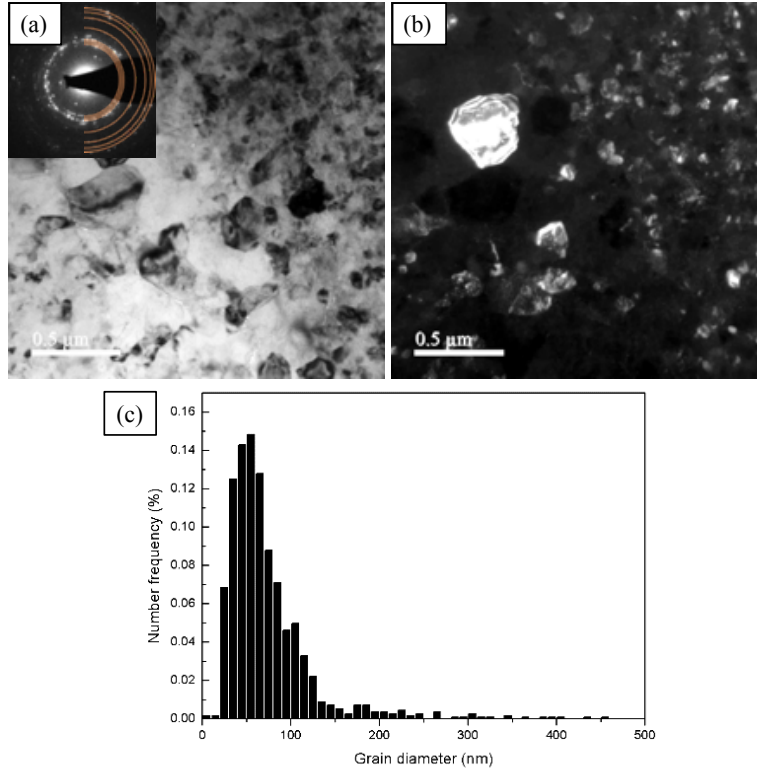


Fig. 3.4 Microstructural characterization of the bulk NC Mg sample: (a) and (b) TEM bright and dark field images; (c) histogram of the grain size distribution measured from the TEM images.

Quantitative XRD analysis (see Fig. 3.5) using the Williamson-Hall Method [121] yielded average grain sizes for the cryomilled powder and the bulk Mg of 46 ± 4 nm and 61 ± 2 nm, respectively, and microstrain values of $(2.17 \pm 0.17) \times 10^{-3}$ and $(3.82 \pm 0.35) \times 10^{-4}$, respectively. Grain coarsening is limited during sintering as SPS allows higher heating rates and shorter holding time compared to conventional hot pressing. A high microstrain (often induced by dislocations, faults and other defects) is typically observed in cryomilled powders, as a result of high-energy ball milling and the suppressed dynamic recovery at

cryogenic temperature [55, 122]. The microstrain decreases after sintering due to recovery and recrystallization at the relatively high sintering temperature ($\sim 0.72 T_m$).

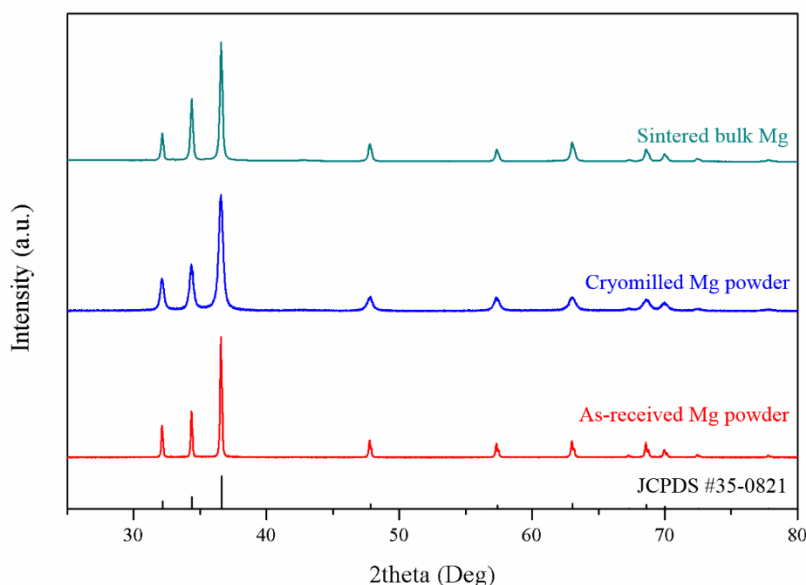


Fig. 3.5 XRD patterns for the as-received Mg, cryomilled Mg powder particles, and bulk Mg samples.

3.4.2 Room temperature compression at various strain rates

The results of the uniaxial compressive tests at strain rates of 10^{-4} to 10^{-1} s^{-1} are shown in Fig. 3.6(a). The yield stress increases from $\sim 80 \text{ MPa}$ at a strain rate of 10^{-4} s^{-1} to $\sim 260 \text{ MPa}$ at a strain rate of 10^{-1} s^{-1} . Compared to coarse-grained wrought Mg, which usually exhibits a strain below $\sim 30\%$ during room temperature compression [13, 99, 123], the bulk Mg in this study showed an exceptionally high compressive strain-to-failure, larger than 120% at strain rates at or below 10^{-2} s^{-1} . Even at a high strain rate of 10^{-1} s^{-1} , the

samples did not fracture after a ~60% compressive strain. The samples exhibit strain softening after yielding at low plastic strain, which is typical in NC materials with limited activation of intragranular dislocation slip [124, 125].

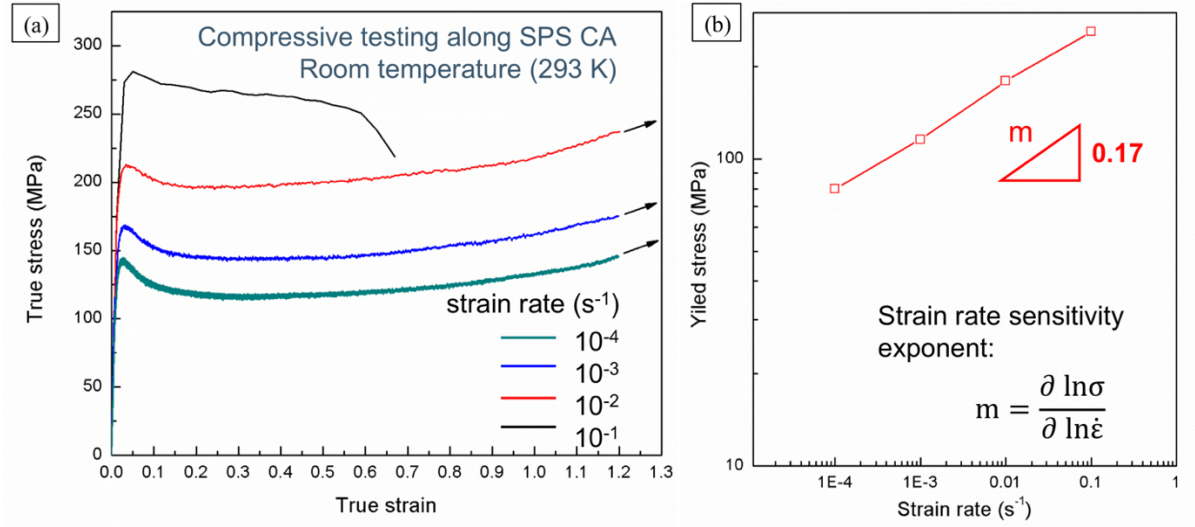


Fig. 3.6 (a) True stress-strain curves for bulk Mg samples under compression at room temperature and various strain rates; (b) double-log plot of yield stress versus strain rate.

To elucidate the origin of the high compressive strain in the bulk Mg at room temperature, the strain rate sensitivity and activation volume were calculated. The strain rate sensitivity exponent, m , can be calculated from the yield stress - strain rate relationship,

$$m = \frac{\partial \ln \sigma}{\partial \ln \dot{\epsilon}} \quad (1)$$

where σ is the yield stress and $\dot{\epsilon}$ is the strain rate. The 0.2% offset yield stresses obtained in room temperature compression are plotted as a function of the strain rates in a

double-logarithmic graph in Fig. 3.6 (b). From the slope of the curve in Fig. 3.6 (b), an m value of ~ 0.17 was calculated. The activation volume V^* can then be calculated using,

$$V^* = \frac{\sqrt{3}kT}{\sigma_m} \quad (2)$$

where k is the Boltzmann constant ($k = 1.38 \times 10^{-23}$ J/K) and T is absolute temperature ($T = 300$ K). The activation volume was calculated to be $\sim 10.7 b^3$, where b is the value of the Burgers vector for basal slip in Mg. For coarse-grained Mg deformed at room temperature, the activation volume is much higher ($\sim 400 b^3$) [23]. The difference arises because in traditional Mg comprised of much larger grain sizes, the primary deformation mechanisms are obstacle formation by the storage of forest dislocations within the grains and dislocation-grain boundary and dislocation-twin boundary interactions. When grain boundary sliding dominates, the activation volumes decrease substantially. For instance, in ultrafine grained Mg deformed at high temperatures, the activation volume of $\sim 1 b^3$ has been reported [23]. In the present, bulk nanocrystalline Mg deformed at room temperature, dislocation mechanisms continue to contribute to the overall compressive strain. Therefore, the activation volume calculated here for the bulk nanocrystalline Mg sample indicates an enhanced activity of grain boundary mediated mechanisms.

3.4.3 Texture and microstructure evolution in bulk nanocrystalline Mg after compression

To further probe the deformation mechanisms in the bulk Mg sample during compression, the texture evolution was examined after deformation at a moderate strain rate of 10^{-3} s^{-1} . Fig. 3.7 (a) shows the (0001) pole figures measured on the Mg sample in the

as-sintered state and after 2%, 9% and 30% room-temperature compressive strain. The samples all exhibit a basal texture with the basal pole parallel to the SPS compaction axis, which is also the compression direction. The peak texture intensity in the unit of multiple of uniform distribution (m.u.d.) is indicated in each pole figure. Although the main character of basal texture remained the same during deformation, the peak intensity of the basal texture slightly increases with an increasing strain from 8.3 m.u.d. in the as-sintered sample to 9.7 m.u.d. after deformation to ~30% strain. This suggests that, besides grain boundary sliding, basal slip is activated within the Mg grains during room temperature compression and leads to an enhanced basal texture.

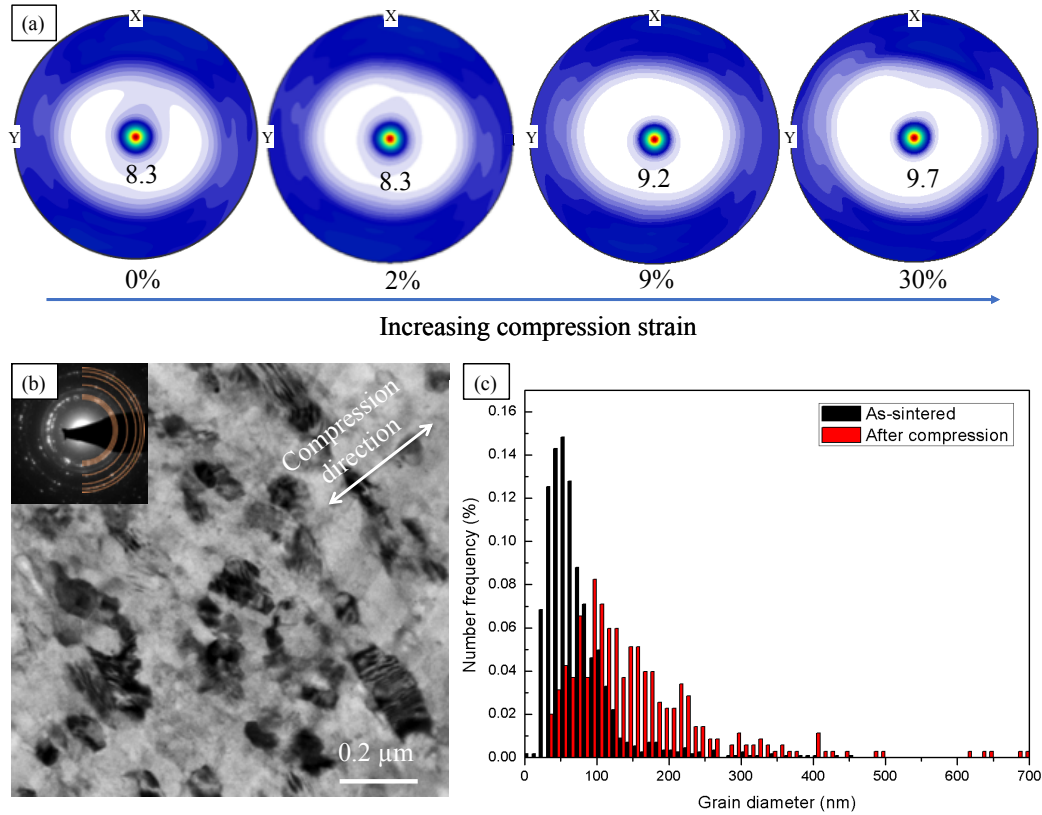


Fig. 3.7 (a) Pole figures showing the texture evolution during compression of the bulk NC Mg sample at increasing strain levels. The inset number is the peak intensity for each pole figure in the unit of multiples of uniform distribution (m.u.d.); (b) TEM image showing the microstructure of the bulk NC Mg sample after $\sim 30\%$ compressive strain; (c) A comparison of the grain size distributions for the Mg sample before and after $\sim 30\%$ strain compression.

30%Mg was further studied using TEM to reveal the microstructural evolution upon deformation. A TEM bright-field image of 30%Mg is shown in Fig. 3.7 (b). The compression direction is indicated in the micrograph by a white arrow. The grains in the deformed microstructure appear elongated in the direction perpendicular to the compression

direction. The grain size statistics for 30%Mg, measured from the TEM micrographs, are plotted in Fig. 3.7 (c), together with those for the as-sintered Mg sample. It is clear that grain coarsening occurred during compression at room temperature. The average grain size increased from ~ 70 nm for the as-sintered sample to ~ 110 nm for 30%Mg, which is in agreement with previous investigations that have reported superplasticity and strain-induced grain growth occurring concurrently as a result of an enhanced grain boundary sliding activity [126].

In 30%Mg, although dislocations were less frequently found in grains smaller than 100 nm in diameter, dislocations were clearly observed in relatively large ultrafine grains. Different diffraction conditions were used to discern the types of dislocations, i.e., $\langle a \rangle$, $\langle c \rangle$ and $\langle c+a \rangle$ types, in a representative ultrafine Mg grain with a grain size of ~ 550 nm. According to the $g \cdot b \neq 0$ visibility criterion, when $g = 01\text{-}10$ was used, most $\langle a \rangle$ and $\langle c+a \rangle$ dislocations can be observed; whereas, if $g = 0002$ is used, most $\langle a \rangle$ dislocations become invisible. Fig. 3.8 (a) and (b) show the two-beam bright field and dark field micrographs, respectively, taken with diffraction vector $g = 01\text{-}10$. Further, most of the dislocations have lines of contrast along the basal plane trace, while some of them lie out of the basal planes. Dislocations parallel to the basal plane trace are marked by red arrows in the figure, and dislocations out of the basal planes are marked by green. Fig. 3.8 (c) and (d) show the bright-field and dark-field micrographs, respectively, taken at the $g = 0002$ two-beam condition for the same sample region. The majority of dislocations lose contrast when $g = 0002$. The visible dislocations are highlighted in the figures with blue arrows. Combining the facts that a high density of dislocation lines was observed when $g = 01\text{-}10$, while only

few dislocations were visible when $g = 0002$, it follows that most of the dislocations present in the ultrafine grains are $\langle a \rangle$ dislocations on the basal planes. Moreover, few twins were detected in 30%Mg (as seen in Fig. 3.9).

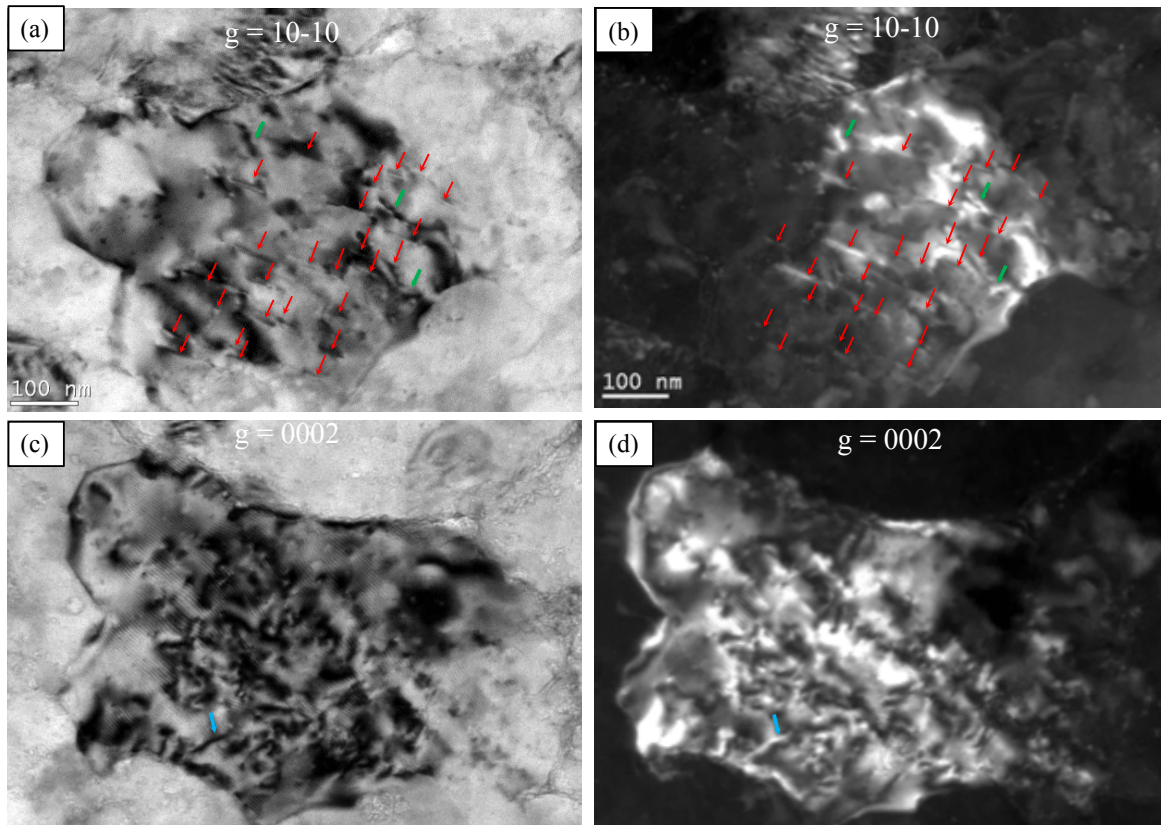


Fig. 3.8 (a) and (b) Bright and dark field images for Mg sample after compression when the diffraction vector $g = 10\bar{1}0$; (c) and (d) bright and dark field images of the same region with the diffraction vector $g = 0002$.

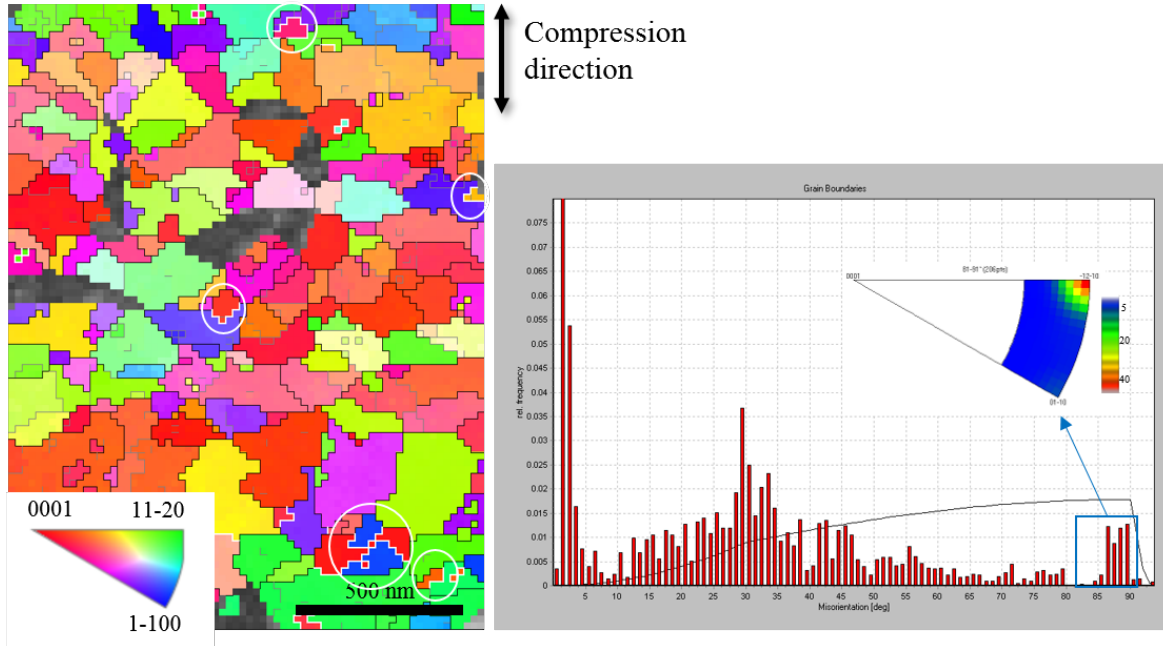


Fig. 3.9 Transmission Kikuchi diffraction (TKD) map of 30%Mg and the corresponding histogram of the grain boundary misorientation distribution (the insert is the inverse pole figure showing the distribution of rotation axes for grain boundaries with misorientation in the range of $86 \pm 5^\circ$). A few $\{10\text{-}12\}$ twins were observed in 30%Mg, which are marked by white circles.

In a coarse-grained pure Mg with basal texture, when compressed parallel to its basal pole, the strain along the c-axis needs to be accommodated by slip with non-basal Burgers vectors [65]. Under this deformation condition, Mg samples usually exhibit strong work hardening, accompanied by a low strain-to-failure at temperatures below 200°C [47]. This phenomenon has recently been correlated to the anomalous basal dissociation behavior of the $\langle c+a \rangle$ dislocations [47]. In contrast, in the NC Mg sample with a basal texture, in the current study, TEM diffraction analysis suggests the scarcity of $\langle c+a \rangle$

dislocations and twins after c-axis compression. Although a fair number of basal dislocations have been observed in the deformed microstructure in Fig. 3.9 (a, b), basal slip alone cannot accommodate the high compressive strain being observed. In addition, an overall strain softening after yielding was observed in the NC Mg sample, indicating the suppression of $\langle c+a \rangle$ dislocation slip and the activation of grain boundary mediated mechanisms as alternative deformation modes, possibly involving grain boundary sliding, rotation and diffusion creep [127, 128].

3.5 Summary

In summary, a bulk NC Mg was fabricated by cryomilling and SPS in the present study. An ultra-large $\sim 120\%$ strain was observed during compression at room temperature with a strain rate up to 10^{-2} s^{-1} . The results show that grain boundary refinement induced an increased strain rate sensitivity with $m = \sim 0.17$. Enhanced grain boundary mediated activity together with basal slip are the contributing mechanisms for the large compressive strain being observed at room temperature.

Chapter 4 Toughening Magnesium Using Twin Meshes

4.1 Abstract

In the present study, an experimental strategy was developed using a SPEX mixer/mill to induce high frequency, multi-directional deformation strain in the surface of a coarse-grained, hot-rolled, commercially pure Mg. The microstructural features and texture of the layer close to the treated surface were characterized by optical microscopy, electron backscattered diffraction and transmission electron microscopy. Twin meshes, defined as two or more intersecting arrays of twins within a grain, were activated in most grains. and the initially strong rolling texture of the starting material was effectively randomized. Our results reveal that the development of twin meshes and grain refinement during surface SPEX milling (SSM) treatment occur by: (a) formation of $\{10\text{-}12\}$ extension twins; (b) intersection of twins with different variants; (c) formation of dislocation walls and $\{10\text{-}11\}$ contraction twins; (d) division of twin lamellae into polygonal blocks and evolution of dislocation walls into subgrain boundaries and then high angle grain boundaries. Uniaxial tensile test results indicate that the samples after SSM treatment have higher ultimate tensile strengths and two fold increases in ductility as compared to those of the untreated samples. Furthermore, SEM in-situ micropillar compression testing was performed at various distances from the treated surface to provide fundamental insight into the mechanisms that govern the relationship between twin mesh structures and mechanical response.

4.2 Introduction

Hexagonal close packed (HCP) metals usually exhibit poor ductility in comparison to that of cubic structured metals due to their low symmetry crystal structure [14, 42, 106]. Anisotropic slip and twinning systems are characteristic of HCP metals. In Mg, basal slip is the most readily activated deformation mode, while activating slip modes out of the basal plane are more difficult [7, 43]. The critical resolved shear stress (CRSS) value reported for basal slip is less than 1 MPa, while that for prismatic slip is approximately 40-50 MPa in pure Mg [7]. Deformation twinning, frequently observed in the $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$ system, also plays a role to accommodate non-basal strain to a certain extent [14, 41]. Much effort has recently been devoted to concurrently enhancing the strength and ductility of Mg, due to the desire to use this lightweight engineering structural metal in more applications in automotive and aerospace industries.

In an effort to circumvent the paradox of strength and ductility in engineering metals, the contributions of twin boundaries (TBs) to strengthening without losing ductility has been reported in nanostructured face center cubic (FCC) metals [38, 53, 129]. The simultaneously improved strength and ductility originate from the dislocation accumulation at and interaction with TBs [38, 53, 129]. TBs can obstruct the motion of dislocations and twins, like regular grain boundaries, though less effectively, for material strengthening. Moreover, dislocations in FCC metals can glide along and transverse across TBs via dislocation-TB interaction, which is beneficial to material deformation. As supported by early studies back in the 1970s [39, 40], in nanostructured FCC metals, twins can accommodate stress concentrations associated with slip bands and twin-twin

intersections by activating dislocation slip inside or on the exit side of twins. The twin-slip and twin-twin interactions of HCP metals, however, are much more complicated than those in the FCC metals, since there are many more distinct modes of twins, with vastly differing characteristics [41]. Moreover, unlike in FCC metals, deformation twinning has been widely reported in coarse-grained pure Mg and some Mg alloys at room temperature [14], and not often observed in nanostructured Mg and Mg alloys [28]. Twins and twin intersections are often associated with twin chains and stress concentrations and could be responsible for instabilities or loss of ductility. However in one recent study using an Mg-4%Li alloy, fine networks of intersecting twins and double twins, or twin meshes, developed in the grains during deformation, and it was reported that the twin-mesh configuration did not lead to premature failure or weakening, compared to the same alloy with finer grains and not twins. The objective of this study was to ascertain whether it is possible to promote twin-mesh-induced strengthening and plasticity in HCP metals.

Deformation twins generated by monotonic straining and their effect on the subsequent deformation response have been explored in Mg alloys. For instance, {10-12} twins induced by pre-compression have demonstrated a positive effect on the material properties during recompression in hot-rolled Mg [130]. However, the twins created by uniaxial pre-compression are coarse and mostly single variant within a grain, and, probably due to this, the increase in compressive strength and ductility after pre-strain was limited [130]. Although twins were profuse in Mg, the easy propagation and growth of the common {10-12} twins add technical challenges to the development of a stable, high twin density, and fine twin structure. Approaches being reported to effectively harden twin growth in Mg

include segregation of alloying elements at twin boundaries [131], formation of lamellar-shaped precipitates and, most cost-effectively, by twin-twin intersections [132]. As such, it is hypothesized that if multiple types and/or variants of twins can be generated at the grain level, a fine twin-mesh structure will form and promote an enhanced strength-ductility combination in Mg.

SPEX milling is conventionally used for pulverizing and mixing powders. In the present study, however, we use this process to generate repetitive and multi-directional impacts onto a sample surface to create twin meshes within grains of polycrystalline pure Mg. Different SPEX milling parameters (ball size and impact velocity) were employed to investigate their influence on the microstructure developed. Using a suite of microscopy techniques, ranging from optical microscopy to EBSD and to TEM, the microstructures created as a function of depth from the surface SPEX milling (SSM) treated Mg were closely examined. We show that this method can create twin meshes comprised of different types and variants of twins. Most significantly, we demonstrate that the material containing twin meshes not only strengthens the material but also increases its ductility two-fold compared to coarse-grained Mg.

4.3 Experimental methods

The starting material in this study is an as-rolled commercially pure Mg sheet (99.9%, Goodfellow Corporation, Oakdale, PA) 6 mm in thickness. Table 4.1 lists the chemical composition of the starting material as specified by the supplier. The as-received

Mg sheet was annealed in a tube furnace at 200°C for 2 hours to minimize dislocations and twins prior to the surface treatment.

Table 4.1 Chemical composition of the as-received commercially pure Mg sheet.

Al	Cu	Fe	Mn	Ni	Si	Zn	Mg
0.007	0.002	0.028	0.017	<0.001	0.005	<0.002	Balance

4.3.1 Surface SPEX milling (SSM) treatment

SSM treatment was carried out in air at room temperature using a SPEX 8000M Mixer/Mill equipped with a cylindrical stainless steel grinding vial. Mg foil samples ~ 12 x 6 x 1 mm were sectioned using electrical discharge machining (EDM) with two different orientations, 1) perpendicular and 2) parallel to the normal direction (ND) of the rolled Mg sheet, as shown in Fig. 4.1. These two samples were designated as perpendicular-type and parallel-type samples, respectively. They were polished with SiC grinding paper down to grade 1200 and then attached to the end plate of the grinding vial using a carbon adhesive tape. Spherical steel balls with clean and smooth surfaces were loaded in the vial as milling media. To understand the effects of different SSM conditions, nine samples were treated with various sample orientations, steel ball sizes, and milling times. Table 4.2 presents the designations for these samples. Both sides of the foils were milled for 2 min with an operating clamp speed of 1080 cycles/min. The impact velocity in the SSM process is approximately 2 m/s. To achieve a more uniform distribution of ball impacts on the sample

surface, the SSM treatment was interrupted every 30 s, in order to rotate the grinding vial by 90°.

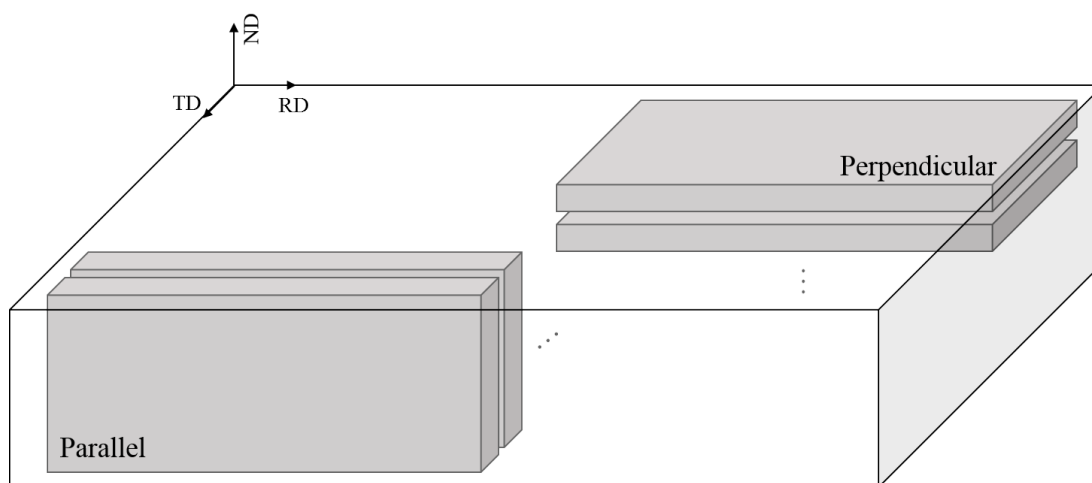


Fig. 4.1 Orientations of the Mg foil samples for SSM treatment. RD, TD and ND stand for rolling direction, transverse direction and normal direction, respectively.

Table 4.2 SSM treatment parameters.

Specimen number	Operating clamp speed (Hz)	Diameter of steel balls (mm)	Orientation of the treated surface relative to the normal direction	Treatment time on each side (min)
M1	17.67	0.1	Parallel	2
M2		0.3	Parallel	2
M3		0.9	Parallel	2
M4		2.0	Parallel	1
M5			Perpendicular	1
M6			Parallel	2
M7			Perpendicular	2
M8		6.4	Parallel	5
M9		12.7	Parallel	0.5

4.3.2 Microstructural characterization

The SSM treated samples were sectioned along the cross-sectional (CS) plane and mechanically polished and etched with a 20% HCl ethanol solution. This treatment prepared these etched CS surfaces for imaging using an optical microscope (OM, Axio A.1, Carl Zeiss, Germany). To further prepare these samples for electron backscattered diffraction (EBSD) microstructural analysis, the CS sample surfaces were ion-polished by a cross-section polisher (Model SM-09010, JEOL). EBSD analysis was performed in a scanning electron microscope (SEM, FEI Quanta 3D) equipped with an HKL EBSD detector. The voltage and beam current used for EBSD data collection were 30 kV and 12 nA, respectively. The step size for EBSD data collection was 1 μm . EBSD post-processing was carried out using Channel 5 system from HKL Technology. Site-specific transmission

electron microscopy (TEM) samples at different depths beneath the treated surface were prepared by standard focused ion beam (FIB) lift-out method on a polished CS sample surface. A low ion beam current of 10 pA was used for final surface cleaning to minimize the damage layer induced by FIB. The TEM microstructural analysis was performed using a JEOL 2100F operated at 200 kV.

4.3.3 Mechanical testing

The effect of the SSM treatment on the mechanical properties of Mg was studied by uniaxial tensile tests and SEM in-situ compression of cylindrical micropillars. To perform tensile tests, dog-bone shaped samples with dimensions shown in Fig. 4.2 were cut from the SSM treated Mg foils using EDM. For comparison, tensile samples with the same geometry were also sectioned from as-annealed Mg without SSM treatment. Tensile tests were conducted using an Instron E3000 testing system at room temperature with a constant nominal strain rate of 10^{-3} s^{-1} . The deformation strain was measured by a non-contacting video extensometer. For all surface treatment orientations, the tensile stress direction lie parallel to the rolling direction (RD). The tests were carried out to failure and in every case, fracture occurred within the gauge section.

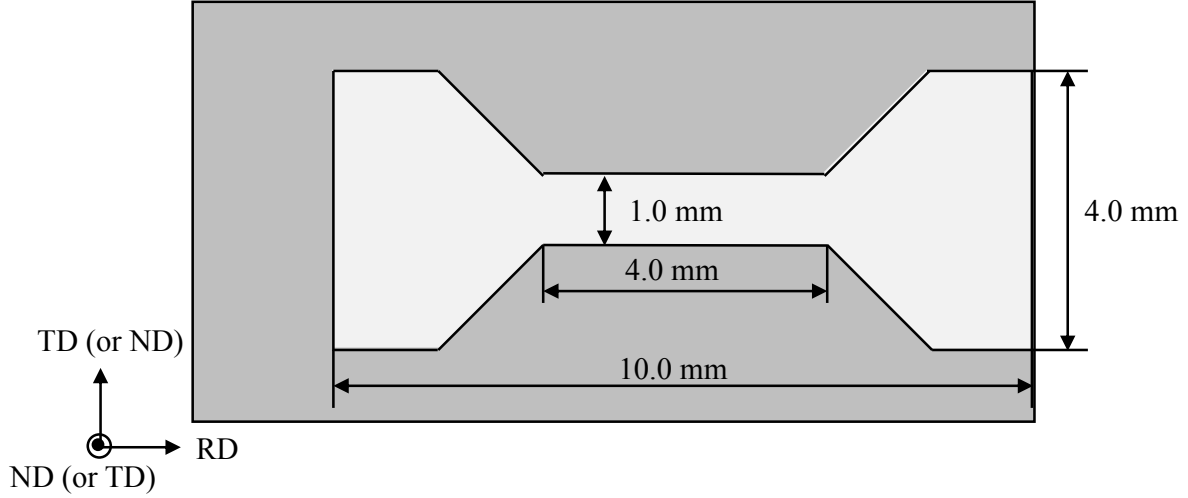


Fig. 4.2 Specifications of the dimensions of the dog-bone shaped tensile coupons. RD, TD and ND in the figure stand for rolling direction, transverse direction and normal direction, respectively.

In-situ compression was carried out using a PI 85 Picoindenter system (Bruker/Hysitron Inc.) equipped with a flat-top conical diamond probe 20 μm in diameter inside an FEI Quanta 3D SEM. Mg micropillars with diameters $\sim 5 \mu\text{m}$ and a height-to-diameter aspect ratio of $\sim 3:1$ were machined by FIB over the sample cross sectional area at different distances (~ 80 , ~ 180 , ~ 280 and $\sim 370 \mu\text{m}$) away from one SSM treated surface. Similar for all FIB sample preparation processes, a low ion beam current of tens of pA was used as a final step to clean the pillar surfaces in order to minimize the FIB damage. After the final cleaning procedure, the taper angle for all the micropillars was less than 2° . SEM in-situ compression was performed under displacement-controlled testing mode with an indentation rate of 15 nm/s (i.e., a nominal strain rate of 10^{-3} s^{-1}) and a maximum indentation depth of 3 μm .

4.4 Results

4.4.1 Microstructure of the SSM treated Mg samples

The impacts from the ball at the surface is expected to cause a gradient in strain rate and accumulated strain from being high at the surface and diminishing with depth. OM is used to analyze the resulting gradient in microstructure. In Fig. 4.3, we present representative CS microstructures from the SSM treated sample, sample M6 in this case, as observed by OM. The micrographs illustrate the formation of a gradient structure from the surface to the center of the foil. Profuse twin lamellae formed and a higher density exists closer to the SSM treated surfaces. Moreover, grain refinement was observed in the regions next to the SSM treated surfaces with the very top layers showing grain sizes below the resolution of OM.

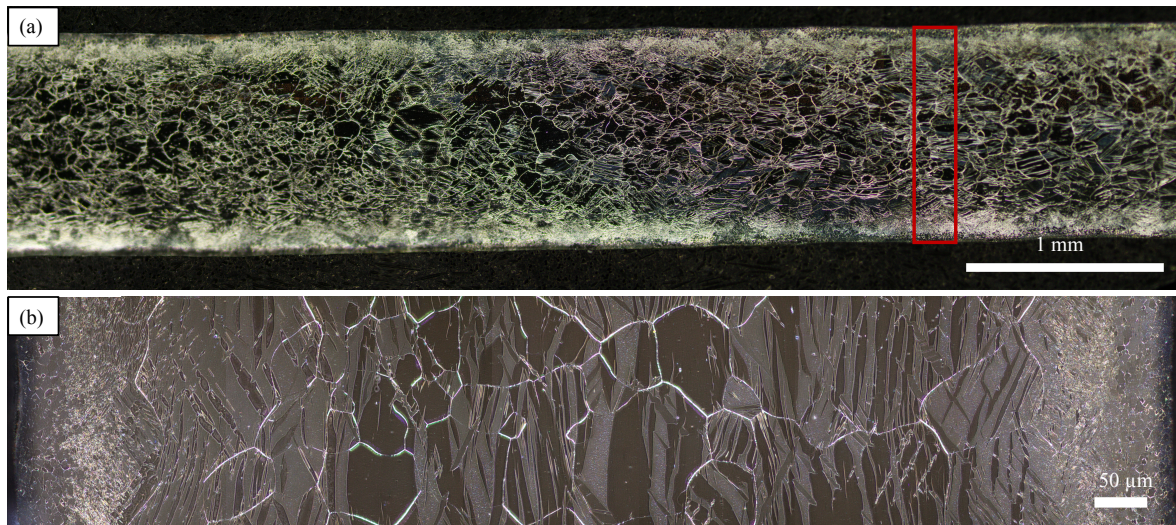


Fig. 4.3 (a) Optical micrographs of the cross sections of SSM treated M6. (b) is the magnified image of the area in (a) marked by the red rectangle.

From the OM analysis, we have identified three distinct microstructural regions in the SSM treated Mg samples based on proximity from the treated surface: I. a nanocrystalline or ultrafine grained layer; II. a refined structure region, in which the sizes of grains are smaller than that in the as-received samples; III. a deformed coarse grain region, with grain sizes on the order of the initial grain size, containing profuse deformation twin lamellae.

The microstructures of the as-annealed and SSM treated samples were further investigated using EBSD. The EBSD inverse pole figure (IPF) colored map for the as-annealed Mg sample is shown in Fig. 4.4 (a). In these figures, the grains are color-coded relative to the horizontal direction, which is the surface normal direction of the SSM treated samples. Before SSM treatment, the microstructure consists of nearly equiaxed grains, with an average grain size of $\sim 80\text{ }\mu\text{m}$, which are almost free of deformation twins. Hot rolling produced a strong basal texture characterized by the single peak observed in the basal pole figure. $\langle c \rangle$ -axes, indicating that the c-axis of a majority of the grains were aligned about the normal direction (ND). The peak texture intensity in the units of multiples of uniform density (m.u.d.) is indicated in each pole figure.

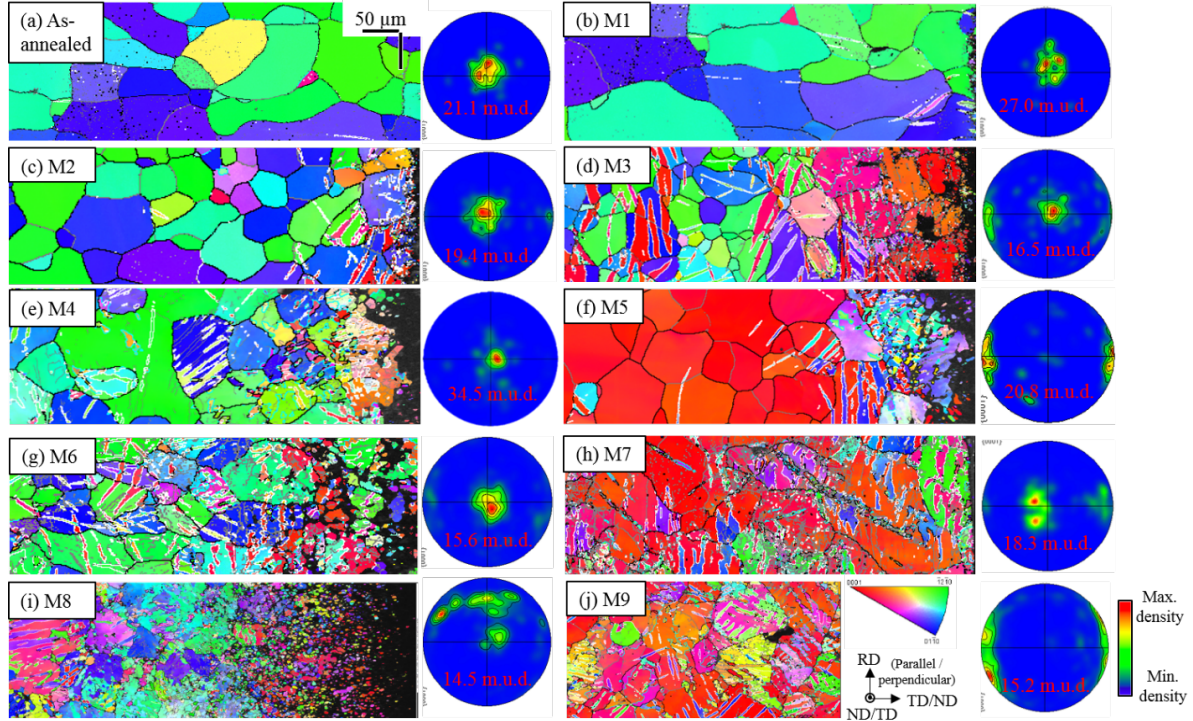


Fig. 4.4 EBSD mapping on the cross-sectional surface of the SSM treated Mg foils: (a) As-annealed sample, (b) M1, (c) M2, (d) M3, (e) M4, (f) M5, (g) M6, (h) M7, (i) M8, (j) M9.

The SSM-induced microstructures (Fig. 4.4 (b - j)) vary with the treatment parameters. The SSM treated surface is on the right side of each map. When small balls (0.1 mm in diameter) were used, lamellar-shaped deformation twins were not extensive after SSM treatment. With an increase in the size of steel balls or treatment time, a deformed layer, containing profuse lamella-shaped deformation twins, formed close to the treated surface and grew thicker (Fig. 4.4 (b - j)). The frequency of intersecting twin-twin junctions in the grain interior also increased as the density of the deformation twins increased. Together with an increment in twin density, the occurrence of low angle grain boundaries, as indicated by the grey lines in the EBSD maps, also increased. Also, micron to submicron-

sized fine grains formed close to the SSM treated surface, as shown in Fig. 4.4 (d - f), provided that the ball size and time are sufficiently large and long, respectively. The top layer regions could not be indexed and appears dark in the EBSD maps, a likely result of the high residual strain and small grain sizes. Yet it is clear that the fraction of fine grains increases with the increase in steel ball size and treatment time. As the bulk deformation behavior of Mg largely depends on the crystallographic texture, sample orientation is also expected to impact the SSM treated microstructures. Two perpendicular-type samples, M5 and M7, were examined in this study. In comparison to the lamellar shaped twins in parallel-type samples, twins in the perpendicular-type samples seen in Fig. 4.4 (e) and (g) are more irregular in shape. In addition, more contraction twin boundaries, which are colored in light blue, were found in perpendicular-type samples.

The strong basal texture in the initial material was randomized after SSM treatment. Multiple peaks appear in the basal pole figures of the SSM treated samples, as seen in the insets of Fig. 4.4 (c-j), indicating the $\langle c \rangle$ -axes were tilted away from the normal direction of the Mg foil. These peaks can be associated with the formation of deformation twins. For example, $\{10\bar{1}2\}$ extension twins in Mg will reorient the matrix by $\sim 86^\circ$ about the $\langle 11\bar{2}0 \rangle$ axis, and the $\{10\bar{1}1\}$ contraction twins will cause a $\sim 56^\circ$ grain reorientation about $\langle 11\bar{2}0 \rangle$. The nature of deformation twins in the SSM treated sample was investigated in more detail using EBSD. Correlated misorientation angle (i.e., misorientation angles calculated from neighboring grain or twin pairs) distributions for as-annealed Mg and SSM treated Mg are shown in Fig. 4.5. In the distribution of misorientation angles for the as-annealed sample, there is a distinct intensity peak at $\sim 30^\circ$, which is often observed in Mg and Mg

alloys after thermomechanical processing at elevated temperatures. The fraction of misorientation angles around 86° is low in the as-annealed sample, indicating that the as-annealed Mg was nearly free of twins. In contrast, in SSM treated samples, $\{10-12\}$ extension twins and $\{10-11\}$ contraction twins were activated, corresponding to the intensity peaks observed at $\sim 86^\circ$ and $\sim 56^\circ$, respectively, in the grain boundary misorientation distribution profile in Fig. 4.5 (b-j). Distribution of rotation axes for misorientation angle ranges of $(84-88)^\circ$ and $(54-58)^\circ$ in sample M6 are also plotted in the insets of Fig. 4.5 (g). The $\sim 86^\circ$ and $\sim 56^\circ$ rotation axes are predominantly centered around the $\langle 11-20 \rangle$ axes, consistent with the twin-matrix misorientation relationship for $\{10-12\}$ and $\{10-11\}$ twins, respectively.

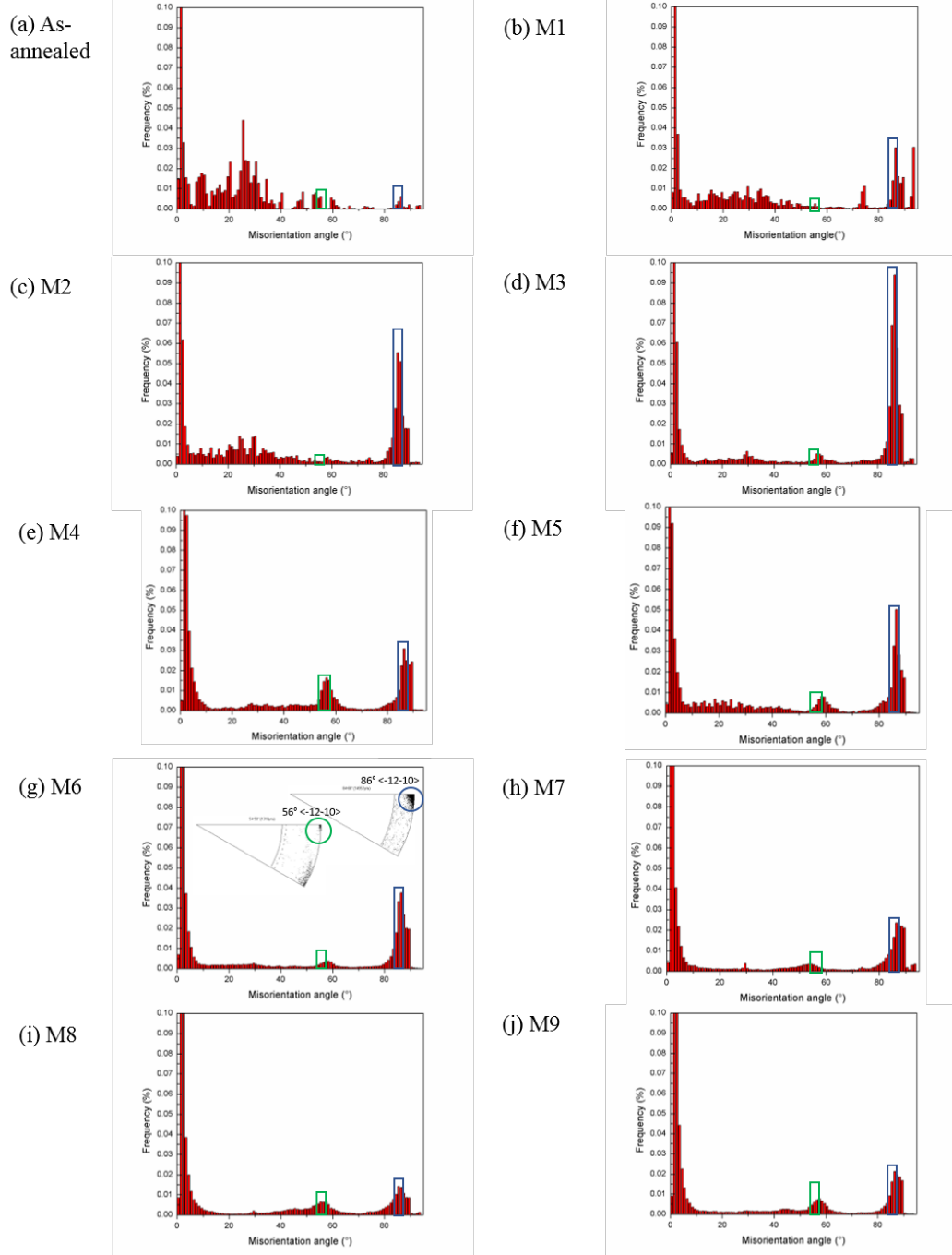


Fig. 4.5 Correlated misorientation profile of: (a) as-annealed Mg, (b) M1, (c) M2, (d) M3, (e) M4, (f) M5, (g) M6, (h) M7, (i) M8, (j) M9.

The percentage of $\sim 86^\circ$ grain boundaries increases from sample M1 to sample M2 to sample M3, as the diameter of milling balls increases from 0.1 mm to 0.9 mm. These results indicate that, with the same SSM treatment time of 2 min, when larger, and therefore heavier, steel balls were used as milling media, a higher density of {10-12} extension twins was generated. The fraction of {10-11} contraction twins remains low in samples M1, M2 and M3. Evidently the strain and strain rates in these samples are not sufficient to activate contraction twins in the deformed layer. When the milling ball size or the SSM treatment time further increases, the percentage of {10-12} extension twins starts to decrease, while the percentage of low angle grain boundaries with misorientations less than 15° increases. Moreover, the fraction of {10-11} contraction twins relative to that of {10-12} extension twins is much higher when larger milling ball and longer milling time were used (samples M8 and M9).

4.4.2 TEM observations at various distances beneath the SSM treated sample surface

Further effort has been devoted to reveal the twin mesh development and grain refinement process during SSM treatment. Due to the gradient variation in strain and strain rate along the sample thickness, the microstructural evolution under different levels of strain and strain rates can be examined by TEM at different depths beneath the SSM treated surface. Specimens at depths of ~ 200 , 100, and 50 μm from the surface for sample M6 were prepared for TEM investigation.

In the deformed layer ~ 200 μm below the SSM treated sample surface, TEM reveals profusely twinned grains containing twin lamellae with thicknesses varying from hundreds

of nanometers to several microns (Fig. 4.6 (a-c)). The bright and dark field TEM images in Fig. 4.6 (a, b) show parallel twins within a grain. Twin lamellae of the same twin variant may grow rapidly and combine with each other to form a coarser twin. Some intersecting twins were also observed at this depth, as seen in Fig. 4.6 (c). In addition, a high density of dislocations can be observed in both the matrix regions and within the twin lamellae (Fig. 4.6 (a-c)), including dislocation pile-up near the grain boundaries (Fig. 4.6 (d)).

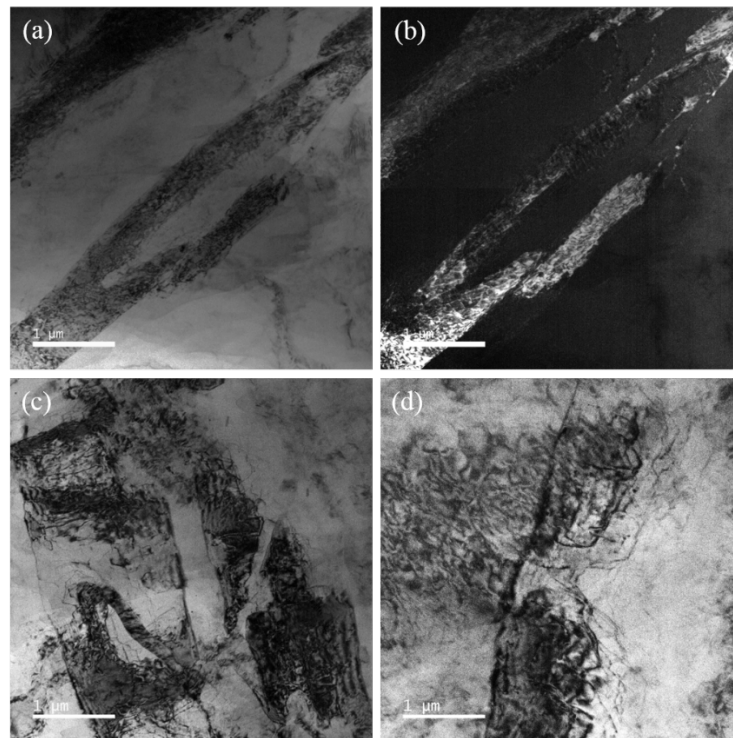


Fig. 4.6 (a) A bright-field and (b) a dark-field TEM image of twin lamellae; (c) A bright field image of intersecting twin lamellae and high density of dislocations; (d) Dislocation pile up adjacent to a grain boundary.

Compared to the $\sim 200 \mu\text{m}$ layer, more grains with intersecting twins were observed in the layer ~ 100 beneath the treated surface. The TEM bright field image in Fig. 4.7 (a)

shows a representative intersecting twin lamellae structure. A transmission Kikuchi diffraction (TKD) map taken at the same sample region, shown in Fig. 4.7 (b), illustrates that the twin boundaries developed in the SSM treated sample are not straight, which suggests that these twin boundaries contain copious incoherent segments and defects as a result of local stresses induced by ball impacts. As shown in Fig. 4.7 (b), the mapped area contains two different $\{10\text{-}12\}$ extension twin variants, T5 and T6, both of which have $\sim 86^\circ$ misorientation relationship with the matrix but with different $\langle 11\text{-}20 \rangle$ zone axis. The crystallographic orientations for the twin lamellae and matrix are indicated by the superimposed HCP unit cells in the TKD map. Low angle grain boundaries visible in the TKD map correspond to dislocation walls seen in the inset of Fig. 4.7 (c) with higher magnification. The selected area electron diffraction (SAED) pattern (inset in Fig. 4.7 (c)), acquired from the area in the red circle when T6 twin boundary is close to “edge on”, further confirms that T6 is a $\{10\text{-}12\}$ extension twin. Furthermore, the bright field image at the twin-twin junction in Fig. 4.7 (d) reveals that the contrast in the twin-twin intersecting region within T6 is different from that for the rest of T6, indicating a small misorientation angle between them.

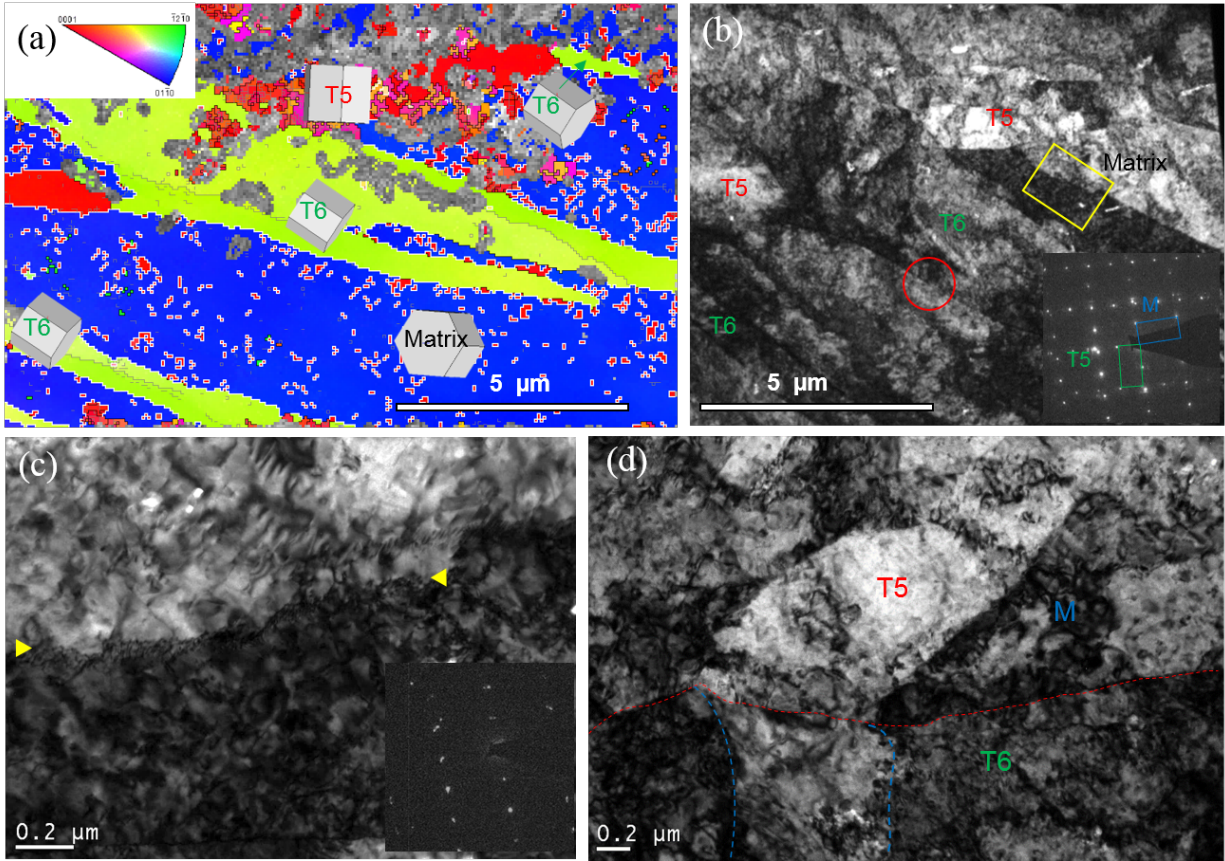


Fig. 4.7 (a) Transmission Kikuchi diffraction map of a twin-twin joint region. T5 and T6 denote the two different twin variants. The HCP unit cells indicate the crystallographic orientations for the twin lamellae and matrix; (b) TEM bright field image of the same region in (a). Inset is the selected area electron diffraction pattern acquired from the twin boundary area marked by the red circle. (c) A higher magnification image of the dislocation wall structure visible in the yellow box in (b) and the corresponding diffraction pattern. The yellow arrows mark the position of the dislocation wall; (d) A higher magnification image at the twin-twin boundary.

TEM examination of the layer $\sim 50 \mu\text{m}$ below the SSM treated surface of sample M6 reveals the occurrence of obvious microstructural refinement. The bright and dark field

images in Fig. 4.8 (a, b) show the formation of submicron spaced lamellae bands, as marked by the yellow arrows. A high density of dislocations is observed on and near the lamellae boundaries. The twin lamellae observed at depths of ~ 200 and ~ 100 μm are not observed at this depth. Instead the microstructure is comprised of micron to submicron polygonal grains. As seen in Fig. 4.8 (c, d), the refined polygonal grains are irregular in shape, having grain sizes in the range of 500-1500 nm. Some fragmented twin lamellae are also visible in this region. These fragments may be remnants of twins that were subsequently subdivided by the formation of subgrains during the SPEX processing. Evidence of accumulated strain in this region appears as variations in the contrast within the twin lamellae and Mg matrix due to lattice deformation. The lattice deformation suggests that subdivision of matrix grains and twin lamellae into polygonal blocks joined by subgrains leads to further grain refinement. In some regions, the deformed microstructure is characterized by more uniformly distributed ultrafine grains, as shown in Fig. 4.9. From the TEM bright and dark field images, it can be determined that the uniformly distributed ultrafine grains have an average grain size of ~ 500 nm.

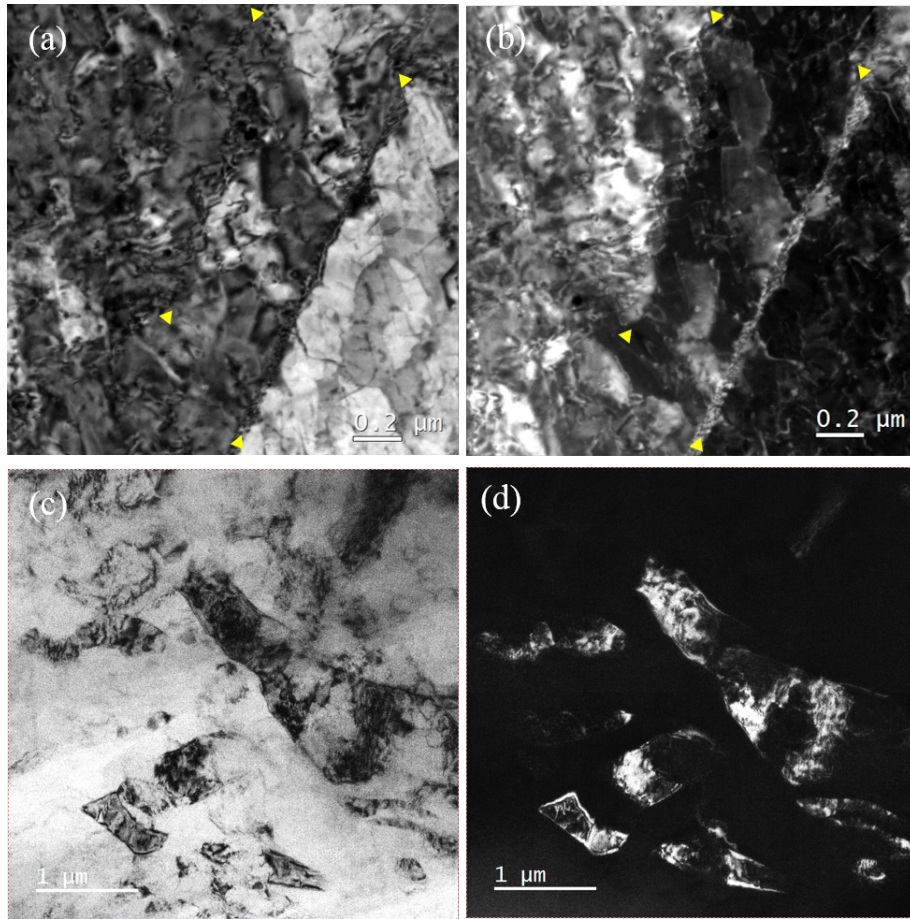


Fig. 4.8 (a) Bright and (b) dark field images showing lamellae bands with dislocations along and close to the lamellae boundaries. The yellow arrows mark the positions of the lamellae boundaries. (c) Bright and (d) dark field images of polygonal micron to submicron sized grains.

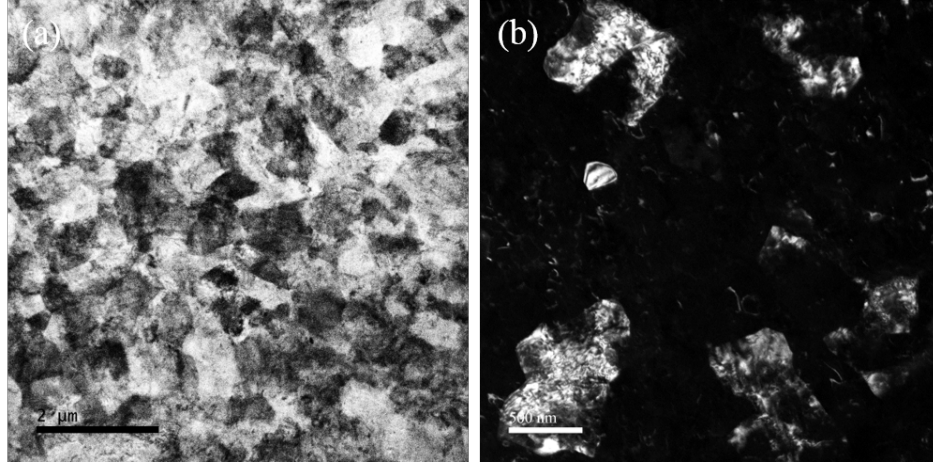


Fig. 4.9 (a) Bright and (b) dark field images showing ultrafine grained microstructure.

4.4.3 Mechanical properties

a. Tensile tests

Uniaxial tensile tests were carried out at a strain rate of 10^{-3} s^{-1} at room temperature. The tensile direction was parallel to the rolling direction of the Mg sheet, which triggers non-basal slip in rolled Mg with a strong basal texture. In addition to an untreated rolled Mg sample, selected SSM treated samples, M6 and M7, with the same geometry, were also tested to examine the effect of the SSM treatment on mechanical properties. The stress-strain curves are shown in Fig. 4.10 and the corresponding tensile property data are summarized in Table 4.3. The ultimate tensile strength (UTS) mildly increases from 207 MPa (as-annealed) to 223 MPa (sample M6) and 230 MPa (sample M7) after SSM treatment, while the tensile ductility increases by more than a factor of two. The as-annealed Mg sample shows a rapidly decreasing strain hardening rate and failed at a

limited true strain of 2.9%. In comparison, the strain hardening rates in samples M6 and M7 decrease less rapidly after yielding. These results are in agreement with the more uniform elongation in the two samples than in the as-annealed one. The 0.2% offset yield strength $\sigma_{0.2\%}$ decreases by 34% and 4% for samples M6 and M7, respectively, after surface treatment, which can be related to the weakening of the initial rolling texture.

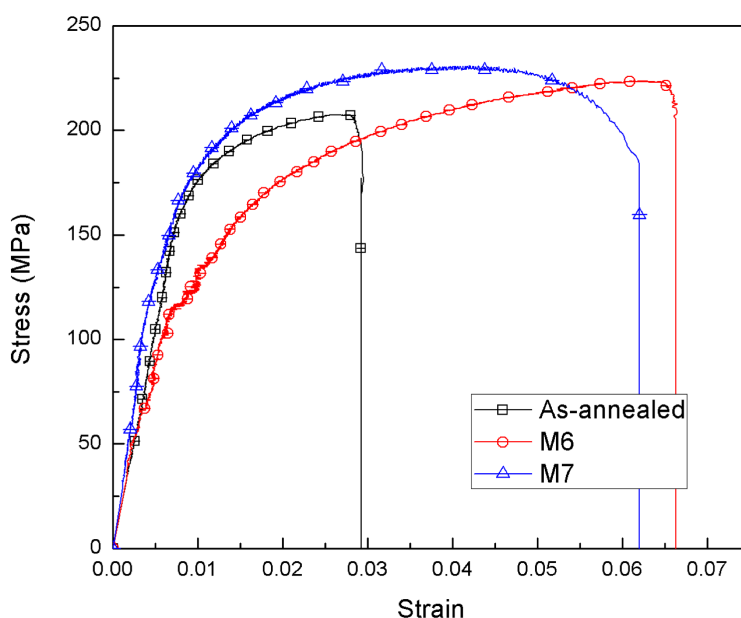


Fig. 4.10 Tensile mechanical behavior of the SSM treated Mg.

Table 4.3 Mechanical behavior of Mg with and without SSM treatment.

Sample	$\sigma_{0.2\%}$ (MPa)	UTS (MPa)	Strain at fracture (%)	Elongation (%)
As-annealed	178	207	2.9%	2.0%
M6	118	223	6.7%	5.5%
M7	171	230	6.2%	5.6%

b. In-situ compression in the SEM

Our tensile tests of Mg foils containing SSM treated layers demonstrated an enhanced tensile ductility and UTS, but owing to the SSM treatment induced gradient structure, the mechanisms contributing to these increments need further investigation. In-situ compression of micropillars fabricated at different distances from the SSM treated surface provides a way to examine the variation in mechanical behavior along the thickness from the treated surface. A series of micropillars (with a diameter of $\sim 5\ \mu\text{m}$ and an aspect ratio within the range of 3-4) were fabricated along the CS surface of sample M7 at: (A) $\sim 80\ \mu\text{m}$, (B) $\sim 180\ \mu\text{m}$, (C) $\sim 280\ \mu\text{m}$ and (D) $\sim 370\ \mu\text{m}$ from the SSM treated surface. The compression direction was parallel to the rolling direction of M7. During compression, videos were recorded with the scanning electron microscope.

True stress-strain curves obtained by compression of the four series of micropillars are shown in Fig. 4.11. For all four samples, sigmoidal shaped stress-strain curves were obtained, which is characteristic of deformation dominated by the formation of extension twins. The yield strength $\sigma_{0.2\%}$ for pillar A is the highest ($\sim 70\ \text{MPa}$) relative to pillars B ($\sim 60\ \text{MPa}$), C ($\sim 60\ \text{MPa}$) and D ($\sim 50\ \text{MPa}$). Pillar A also has the highest compressive flow stress ($\sim 325\ \text{MPa}$) with flow stress decreasing for pillars increasing in distance from the surface B ($\sim 308\ \text{MPa}$), C ($\sim 242\ \text{MPa}$) and D ($\sim 295\ \text{MPa}$).

In addition to having the highest yield and flow stress, pillar A also exhibited the highest range of stable plastic flow. The stress-strain curve for pillar A (Fig. 4.11 (a)) is characterized by multiple non-catastrophic intermitted stress drops during the high strain

hardening regime. These stress drops are non-catastrophic as the stress does not decrease to close to zero before it starts to strengthen again. For samples further away from the SSM treated surface, predominant stress drops were observed in Fig. 4.11 (b, c) within the low strain hardening plateau regime at lower stress and strain values, corresponding to catastrophic shear events as seen in the corresponding in-situ recorded videos.

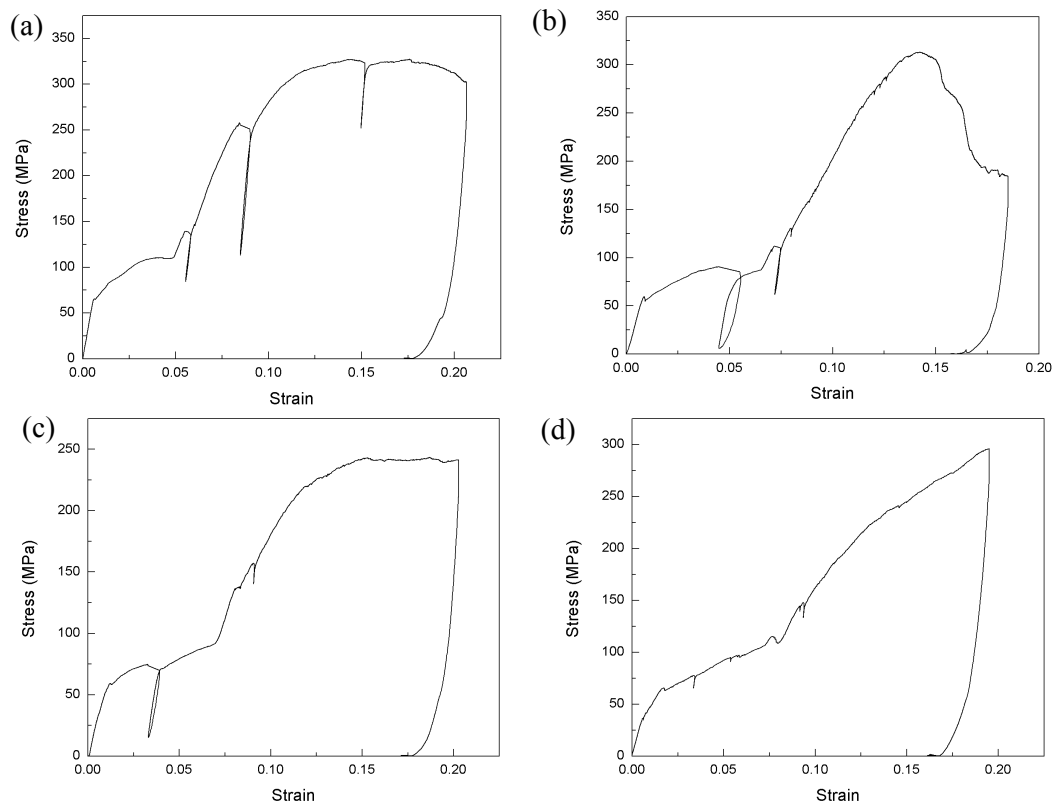


Fig. 4.11 True stress-strain curves obtained from compression of micropillars fabricated at: (a) 80 μm , (b) 180 μm , (c) 280 μm and (d) 370 μm from the SSM treated surface.

SEM images for the micropillars after in-situ compression are presented in Fig. 4.12. Pillars C and D failed by gliding of the top part relative to the bottom part of the pillars along a parallel set of planes. Pillar B shows a similar deformed pillar shape with pillars C and D, but the gliding steps seen on the sample surface are along two intersecting planes. Pillar A, however, shows a distinct deformed pillar shape compared to pillars B to D. Multiple gliding steps in different orientations are visible on the surface of pillar A, but none of the steps cut through the whole pillar.

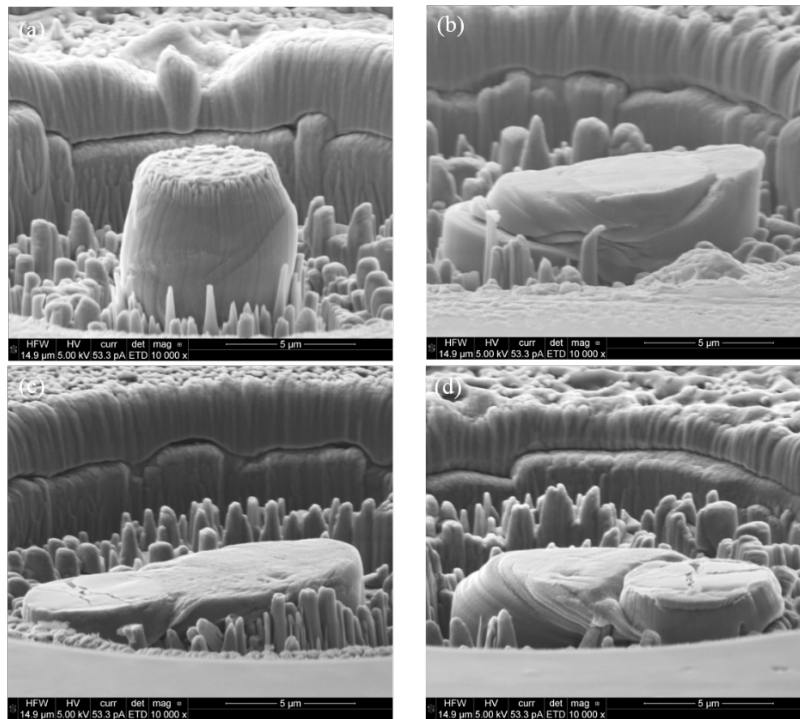


Fig. 4.12 SEM images of ~20% strain deformed micropillars at: (a) 80 μm, (b) 180 μm, (c) 280 μm and (d) 370 μm from the SSM treated surface.

4.5 Discussion

4.5.1 Microstructural evolution during SSM treatment

The highly anisotropic slip systems in HCP Mg make non-basal slip on the prismatic and pyramidal planes very difficult to activate [8, 133], which results in an insufficient number of independent slip systems to satisfy the von Mises criterion [134]. Therefore, besides dislocation slip, deformation twinning plays an important role in the deformation of Mg at room temperature. Multiple twinning modes have been observed in Mg, including extension twins $\{10\text{-}12\}\langle\text{-}1011\rangle$ and $\{11\text{-}21\}\langle\text{-}1\text{-}126\rangle$ and contraction twins $\{10\text{-}11\}\langle10\text{-}1\text{-}2\rangle$ and $\{11\text{-}22\}\langle11\text{-}2\text{-}3\rangle$ [40]. Among all of them, the $\{10\text{-}12\}$ extension twin, which would be favored under $\langle c \rangle$ -axis extension, has received the most attention as it is the easiest twinning mode in Mg [41], due to the relatively small twinning shear. Another commonly observed type of twin in Mg is the $\{10\text{-}11\}$ contraction twin, which would form under c -axis compression. Distinct from $\{10\text{-}12\}$ twins that can thicken to consume the entire grain, $\{10\text{-}11\}$ twins are usually scarce and narrow in the Mg lattice [48, 90], and can nucleate a second $\{10\text{-}12\}$ twin inside their domain [50, 51].

Our microstructural investigation revealed dislocations and $\{10\text{-}12\}$ extension twins in the region close to the center of the Mg foil, which experienced low strains and strain rates, indicating these deformation modes were activated in the very early stage of SSM treatment. Compared to uniaxial deformation modes, the multi-directional and repetitive surface impacts can increase the possibility to form more than one twin variants in the Mg grains. Propagation and growth of intersecting $\{10\text{-}12\}$ twin variants will lead to the development of twin meshes. As the strain increases, for example when larger milling balls

or longer treatment times were used, the relatively harder to form $\{10\text{-}11\}$ contraction twins were observed by EBSD analysis. A $\{10\text{-}11\}$ contraction twin may intersect with $\{10\text{-}12\}$ extension twins and/or other $\{10\text{-}11\}$ twins. A gradient twin mesh structure formed as a result of $\{10\text{-}11\}$ contraction twin- $\{10\text{-}12\}$ tensile twin formation as the strain increased. The twin meshes not only reduce the length scale of the rolled Mg microstructure, but also randomize its strong basal texture.

During further straining of the twin mesh structures, the dislocation density increases dramatically as dislocations can pile up at twin boundaries and twin-twin intersections. As the strain increases, dislocation walls formed by planar rearrangement of dislocations were observed by TEM, which corresponds to low angle grain boundaries observed by EBSD. The formation of these dislocation walls and their development into low angle grain boundaries may reduce the energy of the severely strained microstructure. These low angle subgrain boundaries will then develop into blocks surrounded by high angle grain boundaries and cause the formation of micron to submicron polygonal grains being observed. Finally, the formation of a uniformly distributed ultrafine grained structure was developed close to the SSM treated surface, when the accumulated strain was sufficient.

4.5.2 Influence of twin mesh structure on the deformation behavior

Tensile tests of Mg foils containing the SSM treated surface layers demonstrated an increase in tensile ductility and UTS when compared to the untreated as-annealed material. From the tensile stress-strain curves, a longer uniform elongation region was observed in samples M6 and M7, characterized by more slowly decreased strain hardening rates

compared to the as-annealed Mg. The relatively stable strain hardening rate and high UTS possibly originate from the slip-twin and twin-twin interactions in the microstructure containing twin meshes.

There is growing evidence in the literature [39, 135] that, similar to the FCC and BCC metals, twin-twin interactions in HCP metals resembles twin-slip interactions in the sense that they can facilitate or impede thickening of participating twins. Slip-twin interactions lead to strengthening in HCP metals by three well accepted mechanisms: 1) texture hardening due to lattice reorientation by twins, 2) the Basinski hardening mechanism due to transmutations of dislocations from glissile to sessile [136, 137], and 3) the obstacle effect of twin boundaries on dislocation slip [138].

In addition, the mild decrease in yield strength is possibly caused by the SSM-treatment induced weakening in basal texture. During tension in the rolling direction, most grains in the as-annealed rolled Mg foil are in the “hard-to-deform” orientations, and non-basal slip with high CRSS values need to be activated to accommodate the strain. Deformation twins can reorient the crystals to “softer” orientations and the gradient twin mesh structure as a whole shows a slightly lower yield strength. Another explanation for the decrease in tensile yield strength is the migration and detwinning of twin meshes. Further stabilization of the twin mesh structures may help increase the tensile yield strength of the SSM treated samples.

4.6 Summary

In this work, we aimed to create and investigate the effect of twin meshes on the tensile and compression response of polycrystalline pure Mg. A surface mechanical attrition strategy was used to impose repetitive, multi-directional loads on the sample surface using a SPEX Mixer/Mill to achieve a gradient microstructure consisting of variation from a ultrafine grained to twin meshed structure, in a hot-rolled commercially pure Mg sample. The main conclusions from the microstructural characterization and mechanical testing are:

1. With increasing strain and strain rate, microstructure evolution occurs in Mg by formation and interaction of deformation twins, dislocation slip and development of dislocation walls, and grain refinement by division of multiply-crossed twin lamellae into fine to ultrafine polygonal subgrains.
2. The SPEX milling was effective in creating twin meshes. Two or more twin types and variants were activated in most grains in the twinned coarse grain region.
3. The twin meshes being produced effectively randomized the initially strong texture of the starting material.
4. The tensile test results demonstrated that the samples after SSM treatment show a two-fold increase in tensile ductility and ultimate strength over the as-annealed hot-rolled Mg.
5. SEM in-situ compression testing has been performed to probe the mechanistic explanations for the improved mechanical properties.

Chapter 5 Alloying effects of Y on the deformation behavior of Mg

5.1 Abstract

Alloying has long been recognized as a critical method to enhance the mechanical performance of metals, however its effects on slip and twinning in hexagonal close packed materials are less clear. In this chapter, a detailed multiscale experimental investigation is performed to investigate the effects of Y addition on the mechanical properties and deformation mechanisms in Mg. For this purpose, four Mg-Y binary solid solutions, with 0.2, 0.6, 1 and 3 wt.% nominal concentrations of Y and similar grain sizes of 20 - 30 μm were processed by casting followed by rolling and annealing. Uniaxial tension and compression tests were performed at room temperature and liquid nitrogen temperature. X-ray diffraction (XRD) pole figure measurement was used to measure the textures in as-annealed and deformed alloys. Mg-Y alloys demonstrate weakened rolling textures, significantly increased low temperature ductility and a higher activation of non-basal slip when compared to pure Mg. To further examine the microstructure of the non-basal dislocations activated in Mg-Y, post-mortem transmission electron microscopy (TEM) investigation was carried out, which reveals a more uniform distribution of non-basal dislocations and a higher fraction of non-basal dislocations on the pyramidal I and pyramidal II planes. Additionally, the distribution of Y atoms in the deformed Mg-Y alloys was revealed by high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM). Feasible mechanisms for the interaction between solute atoms and twin boundaries are proposed.

5.2 Introduction

For centuries, alloys have received important research attention due to their wide industrial applications, particularly in areas where the pure metal is difficult to use. Solid solution alloying is well known as an important metallurgical strategy to strengthen pure metals, as well as introducing novel functional properties. Solute-dislocation interaction, i.e., the hindering effect on dislocation motion caused by the solute misfit strain, can increase the critical resolved shear stress (CRSS) for slip. Besides the interaction with dislocations, in metals that deform by deformation twinning, the pinning effect of segregating solutes on the twin boundaries leads to further strengthening [131].

In an effort to enhance the mechanical performance of hexagonal close packed metals, recent research interest in solid solution alloying can be partly attributed to the progress in fundamental understanding of how alloying elements impact the energetic barriers to activate different slip and twinning systems [139-141]. As was discussed in the previous chapters, pure Mg suffers from severe plastic anisotropy due to its hexagonal close packed (HCP) structure, and that leads to limited room-temperature ductility. The difficulty for activation of non-basal $\langle c+a \rangle$ slip, which can be quantified by the CRSS values, is almost 100 times higher than that for basal slip. For generalized deformation to occur in polycrystalline Mg, the “hard” non-basal slip systems need to be activated to satisfy the von Mises criterion’s five independent slip systems. Upon alloying, the effect of solute-dislocation interactions on various slip systems can influence the relative difficulty of the non-basal slip modes to the basal $\langle a \rangle$ slip. As such, solid solution alloying may play a vital

role in determining the activity of slip modes, and modifying the textures, strength and ductility of HCP metals.

The alloying effects of rare earth (RE) elements (e.g., Y, Ce, Gd), have been extensively studied recently both experimentally [3, 13, 142] and theoretically [140-143], as they are effective in yielding excellent ductility in Mg, even with very low concentrations below 1 wt.%. Many of the previous studies have attributed the observed behavior to the weakening of the basal texture and easier activation of non-basal slip [3, 13, 142]. In addition to the impact on the activation of slip systems, recent studies show that alloying can also affect the dislocation dynamics [47, 139]. Density functional theory (DFT) calculations reveal that certain solid solution elements, such as rare earth elements (Y, Ce, Gd, Er) can notably enhance the cross-slip rates of $\langle c+a \rangle$ dislocations by reducing the energy barrier for pyramidal II to pyramidal I cross-slip via solute-stacking fault (SF) interactions [139].

Moreover, alloying with some RE elements also has significant impacts on twinning in Mg, as suggested by first principle calculations of the twin boundary stacking fault energies [144]. However, without a fundamental understanding of the twin nucleation mechanisms and the slip-twin nucleation relations, it is hard to determine the critical energetic parameters for twinning in the simulation studies. An in-situ TEM study was also performed in a Mg-Ce alloy to experimentally measure the critical resolved shear stress (CRSS) for various deformation modes [145]. Ce addition causes an obvious reduction in the CRSS value for twinning. However, the mechanism for this alloying effect on twinning is

unclear. All the aforementioned critical questions regarding the alloying effects in Mg motivated the present study on Mg-Y and our future research endeavors.

5.3 Experimental

5.3.1 Alloy preparation

Mg with four different contents of Y, 0.2, 0.6, 1 and 3 w.t.%, designated as Mg-0.2Y, Mg-0.6Y, Mg-1Y and Mg-3Y, respectively, were prepared by our collaborators at Helmholtz-Zentrum Geesthacht. Gravity-cast alloys were hot rolled and annealed to achieve similar grain sizes (except Mg-0.2Y with a slightly larger grain size). The heat treatment parameters being used can be seen in Table 5.1. After heat treatment, equiaxed and twin-free structures were achieved for all Mg-Y alloys. The average grain sizes for the annealed alloys measured from the optical microscopic images are listed in Table 5.1.

Table 5.1 Thermo-mechanical treatments of Mg-Y alloys.

Alloy	Heat treatment	Average grain size (μm)
Mg-0.2Y	400°C, 10min	40
Mg-0.6Y	400°C, 10min	21
Mg-1Y	400°C, 10min	22
Mg-3Y	450 °C, 10min	25

5.3.2 Mechanical testing

Uniaxial tensile tests along the rolling direction (RD) were performed at room temperature using an Instron 8801 universal testing machine at an initial strain rate of 10^{-3} s^{-1} . Dog-bone shaped tensile coupons with a gauge length of $\sim 15 \text{ mm}$ and a cross section

area of $\sim 4 \times 1.5$ mm were machined using electrical discharge machining. Compression tests along either the rolling direction (RD) or the extrusion direction (ED) were performed on cuboidal samples with a dimension of $\sim 3 \times 3 \times 5$ mm. At least two samples were tested for each condition. In addition to tension and compression at room temperature, cryogenic temperature compression was carried out in liquid nitrogen.

5.3.3 Texture and microstructure characterization

Texture of the annealed and deformed Mg-Y alloys was measured by X-ray diffraction (XRD) pole-figures using Rigaku Smartlab diffractometer operating at in-plane mode. Three pole figures were obtained for each sample from $\{10\cdot10\}$, (0002) and $\{10\cdot11\}$ peaks. Standard theta-2theta XRD scanning was performed on each alloy prior to pole figure analysis to determine the positions of the corresponding Bragg peaks.

Specimens for transmission electron microscopy (TEM) observation were prepared by mechanical grinding followed by ion milling. FEI/Philips CM20, JEOL 2100 and JEOL 2800 microscopes (operating at 200 kV) were employed for TEM imaging. To discern the types of dislocations present in the Mg alloys by diffraction contrast imaging, different two-beam conditions were selected and the “ $g\cdot b=0$ ” invisibility criterion were employed. To probe the distribution of Y with atomic resolution, high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) was used, using an aberration corrected JOEL ARM300F operating at 300 kV. For higher Z contrast, a short camera length of 12 cm was used for HAADF STEM imaging.

5.4 Results

5.4.1 Texture and deformation behavior of Mg-Y alloys at room temperature and cryogenic temperature

Microstructure of the as-rolled (AR) and annealed alloys was characterized by optical microscopy (Fig. 5.1). Our focus is to correlate the mechanical properties with the deformed microstructures in different Mg-Y alloys in order to answer the critical question of how Y alloying affects the slip (especially $\langle c+a \rangle$ slip) and twinning behavior.

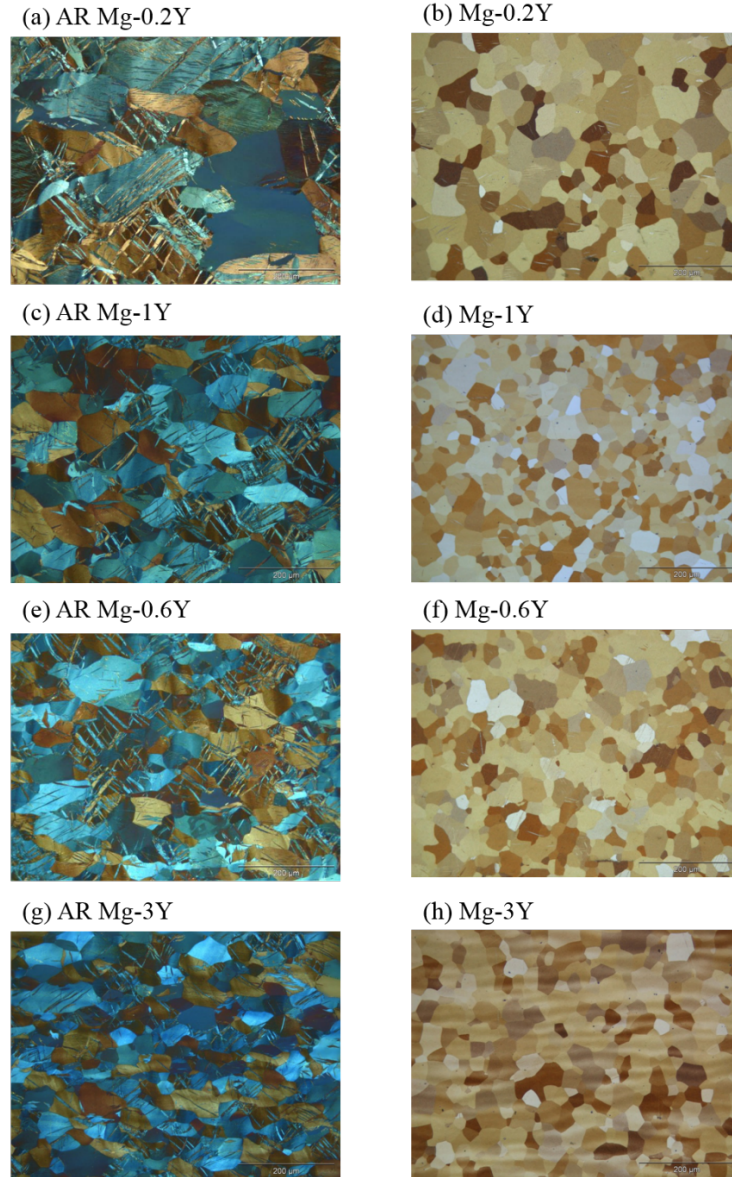


Fig. 5.1 Optical micrographs of: (a) as-received (AR) and (b) annealed Mg-0.2Y, (c) AR and (d) annealed Mg-0.6Y, (e) AR and (f) annealed Mg-1Y, and (g) AR and (f) annealed Mg-3Y. It is noted that the grain sizes are similar among Mg-0.6Y, Mg-1Y, and Mg-3Y, whereas Mg-0.2Y exhibits larger grain size due to the limited grain-refining effect of the low Y content.

X-ray diffraction (XRD) patterns for Mg-Y alloys are shown in Fig. 5.2. XRD was measured on the rolling direction (RD) x transverse direction (TD) surface of the Mg-Y plates (i.e., the surface is perpendicular to the plate normal direction (ND)). The primary phase in all Mg-Y alloys being investigated is the HCP Mg phase, together with weak peaks visible for second phase precipitates. Moreover, the relative peak intensity of the (0002) planes decreased with an increasing content of Y. This can be explained by a weakened rolling texture caused by Y addition.

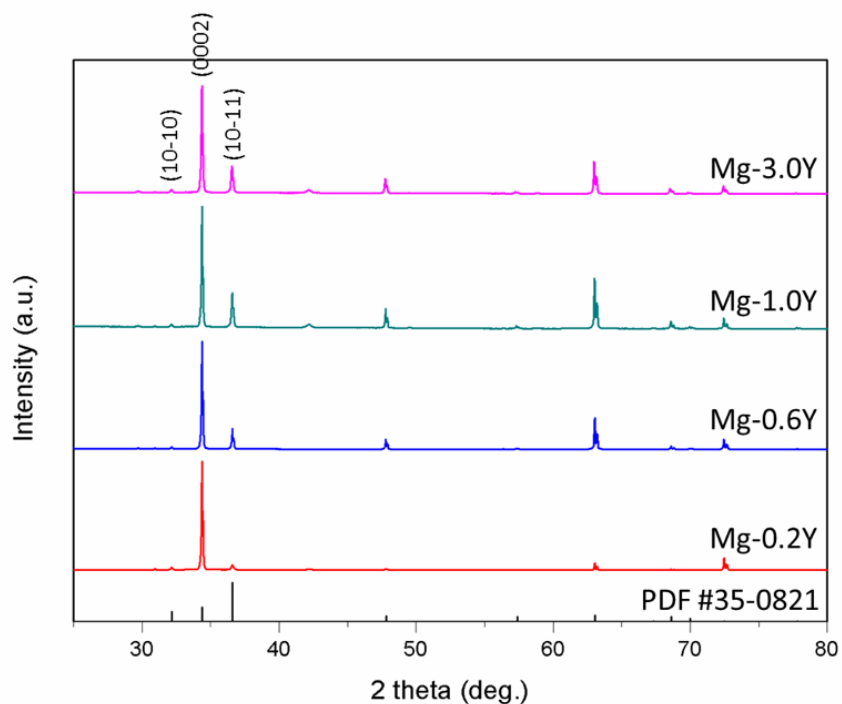


Fig. 5.2 XRD patterns of the Mg-Y alloys. The diffracted sample surface is perpendicular to the plate normal direction (ND).

To analyze the texture weakening effect of Y in Mg, we measured the texture of as-annealed Mg-Y alloys. XRD pole figures (Fig. 5.3) under the as-annealed condition shows a typical basal fiber texture in all Mg-Y samples, which orients the basal planes perpendicular to the normal direction (ND). For Mg-Y with the most dilute solute composition, 0.2 wt.%, the strong basal texture is similar to that of pure Mg. With an increasing content of Y from 0.2 wt.% to 3.0 wt.%, the peak intensity in (0002) pole figure decreased dramatically from ~21 to ~5.3 multiple of uniform distribution (m.u.d.). The stronger texture weakening effect with an increasing rare earth element addition has been reported in the literature [13]. Many of these studies have attributed this observation to an enhanced activity of $\langle c+a \rangle$ slip with rare earth element alloying [13]. Despite the drop in the texture intensity, the basal pole tends to spread along the RD direction in the low Y content samples (Mg-0.2Y and Mg-0.6Y), while it tends to spread towards the TD when the content of Y is high (Mg-1Y and Mg-3Y). The change in the shape of the basal pole figures indicates Y alloying may have altered the activities of different slip modes, including the basal slip, prismatic slip and pyramidal slip, during hot rolling.

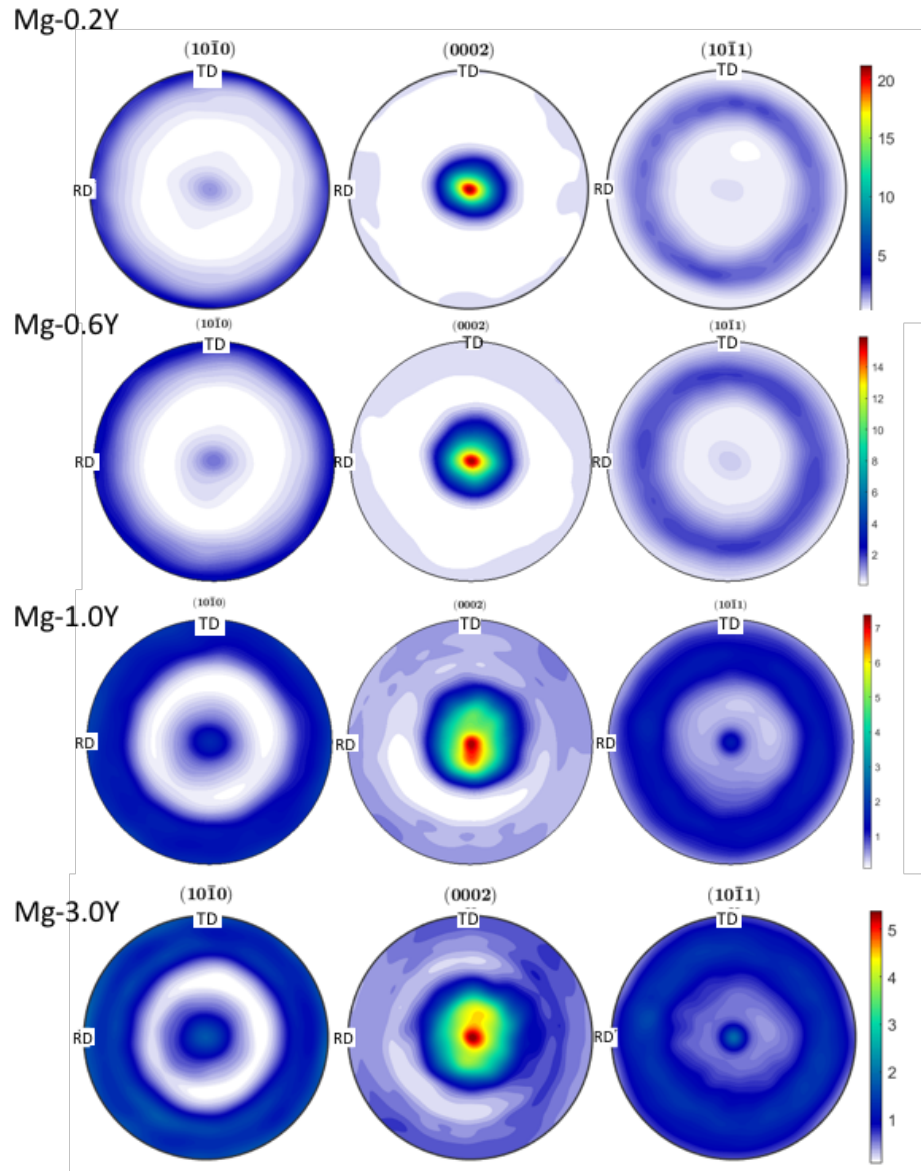


Fig. 5.3 $\{10\bar{1}0\}$, (0002) and $\{10\bar{1}1\}$ pole figures showing the initial texture of the Mg-Y alloys measured using XRD.

Room temperature compression tests along the RD and ND, and tension tests in the RD, were performed to study the strength, ductility, and yield strength anisotropy of Mg-Y alloys. The compressive data in Fig. 5.4 demonstrates that, with an increased level of Y, the

yield strengths along both RD and ND directions increased moderately. When compressed along RD, a clear twinning sigmoidal signature during strain hardening is expected due to the rolling texture with c-axes favorably oriented for activating $\{10\text{-}12\}$ tensile twinning. The compressive yield strength for RD compression (CYS-RD) increased from 46 MPa in Mg-0.2Y to 78 MPa in Mg-3Y. When compressed along ND, twinning was not favored, and pyramidal $\langle c+a \rangle$ slip contribute to the compressive strain, therefore the twinning signature is not observed. The compressive yield strength along ND (CYS-ND) increases from ~ 83 MPa to ~ 105 MPa as the content of Y increases from 0.2 wt.% to 0.6 wt.%, and it saturates when the Y content further increases. The compressive yield anisotropy, defined as the ratio of CYS-ND to CYS-RD, for Mg-0.2Y, Mg-0.6Y, Mg-1.0Y and Mg-3.0Y are 1.8, 1.6, 1.4 and 1.3, respectively. Moreover, the compressive strain-to-failure was significantly enhanced with Y addition. During ND compression, the Mg-Y alloys showed an obvious transition from the first stage of rapid strain hardening to the second stage with much lower hardening or strain softening, and it is interesting to note that this transition point occurred at about 11% strain for all Mg-Y alloys. The rapid decrease in strain hardening rate has been reported to be related to the large activation of secondary deformation mechanisms that can accommodate significantly larger strains prior to failure. Therefore, an enhanced activity of secondary deformation modes, presumably the pyramidal $\langle c+a \rangle$ dislocations, could explain the larger compressive strain during the second (low strain hardening rate) stage in the Mg alloys with high Y content.

The yield asymmetry, defined as the ratio of yield strength for RD tension to RD compression was calculated and presented in Fig. 5.5. The yield strength asymmetry

decreases with an increase in Y content. The decreased intensity of basal texture is one reason for decreased yield asymmetry along the RD. Some other plausible explanations, such as an enhanced non-basal dislocation slip activity and reduced deformation twinning activity due to Y alloying, may also contribute to the reduced yield asymmetry in Mg-Y compared to that observed in pure Mg. Visco-Plastic Self-Consistent (VPSC) polycrystal plasticity modeling [146, 147] was used to predict the activation of various slip systems in the Mg-Y alloys. The modeling results are discussed later in the discussion section.

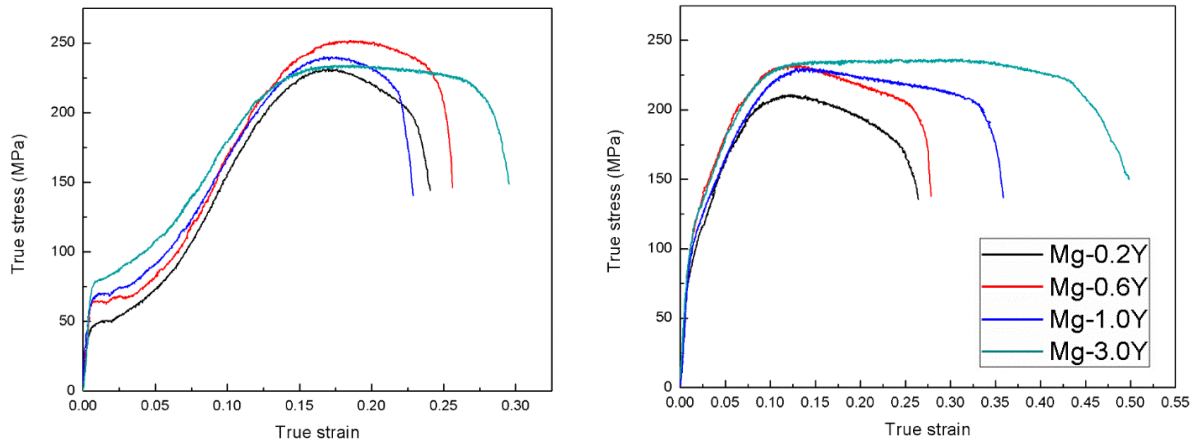


Fig. 5.4 Room temperature compressive true stress-strain curves for Mg-Y along (a) the rolling direction (RD) and (b) the normal direction (ND).

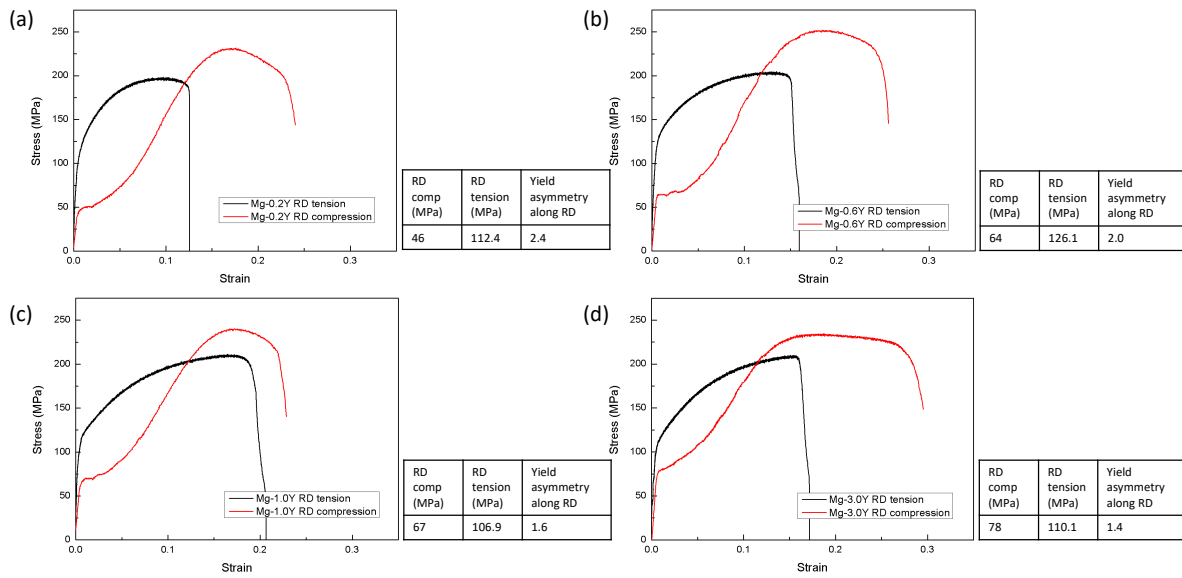


Fig. 5.5 Stress-strain curves for tension and compression along RD: (a) Mg-0.2Y, (b) Mg-0.6Y, (c) Mg-1.0Y, (d) Mg-3.0Y.

Fig. 5.6 shows the representative SEM images of the fracture surfaces of Mg-0.6Y, Mg-1.0Y and Mg-3.0Y after ND compression tests. The fracture surfaces are characterized by cleavage facets, dimple patterns and steps. The frequency of brittle cleavage planes decreases and the ductile dimples increases as the Y content increases. This indicates that with an increasing Y addition, the fracture in Mg-Y alloys changed from a semi-brittle mode to a more ductile fracture mode. The differences in the dimple size can be explained by factors such as the intensity of basal textures, and the types and sizes of inclusions.

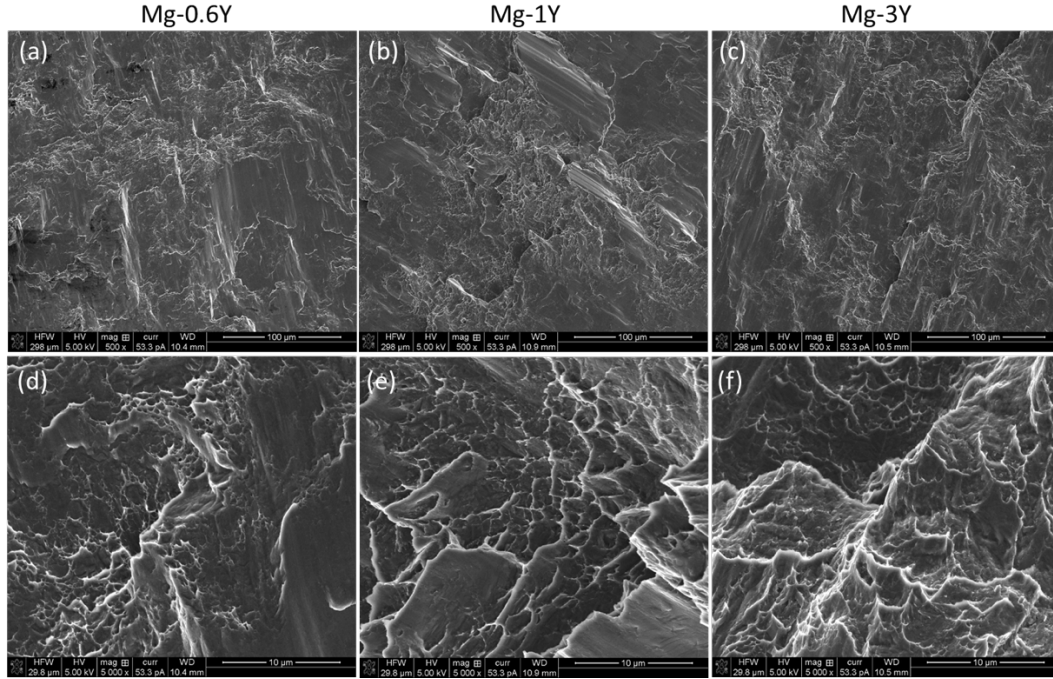


Fig. 5.6 SEM fracture surfaces of (a, d) Mg-0.6Y, (b, e) Mg-1.0Y and (c, f) Mg-3.0Y after compression to failure along ND.

To investigate the deformation behavior of Mg-Y at cryogenic temperatures, Mg-1Y and Mg-3Y were compressed along ND and RD at liquid nitrogen temperature ($\sim 77\text{K}$). The stress-strain curves for the cryogenic tests along ND and RD are shown in Fig. 5.7. The strengths at failure are 410 MPa (RD) and 375 MPa (ND) for Mg-1Y, and 430 MPa (RD) and 425 (ND) for Mg-3Y. The compressive strain at such low temperature is $\sim 16\%$ (RD) and $\sim 12\%$ (ND) for Mg-1Y and $\sim 15\%$ (RD and ND) for Mg-3Y. The compressive yield strength anisotropy increased, from 1.4 to 2.0 for Mg-1.0Y and from 1.3 to 1.8 for Mg-3.0Y, when the temperature drops from room temperature to liquid nitrogen temperature. This can be partly explained by the fact that, compared to dislocation slip, the critical resolve shear stress for twinning is less sensitive to the deformation temperature [148]. Therefore, at low

temperature, CYS-ND, corresponding to the yield stress for non-basal slip, is much higher than that at room temperature, while CYS-RD, corresponding to $\{10\text{-}12\}$ deformation twinning remains insensitive to temperature.

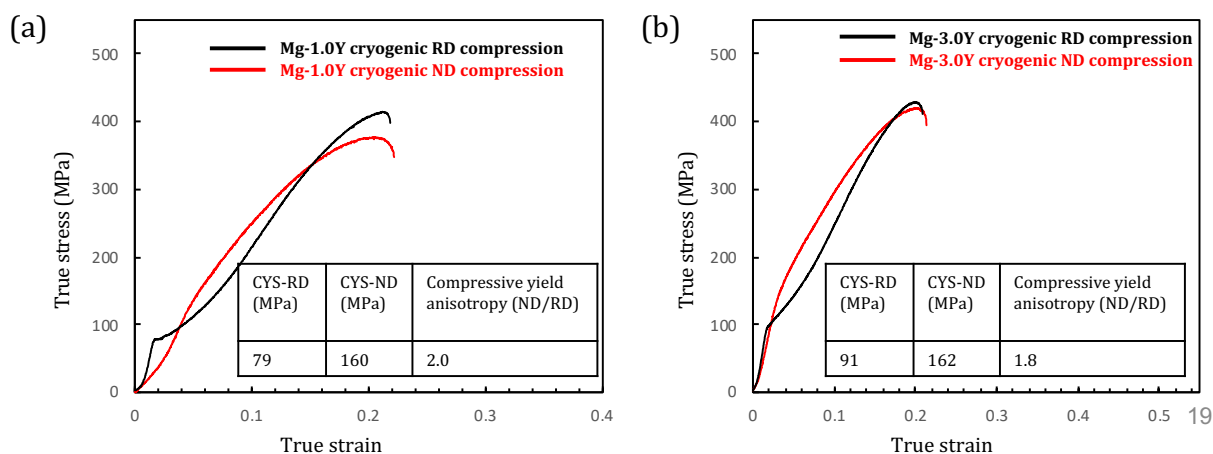


Fig. 5.7 Cryogenic temperature compressive true stress-strain curves for (a) Mg-1.0Y and (b) Mg-3.0Y along RD and ND.

5.4.2 TEM study of slip and twins in the deformed microstructure in Mg-Y alloys

In an effort to probe the deformation mechanisms of Mg alloys with Y addition, dislocations and twins in deformed Mg-Y microstructures were analyzed by TEM. Fig. 5.8 (a) and (b) show the TEM micrographs of the dislocation structures in pure Mg and Mg-1Y, respectively, after $\sim 2\%$ ND compression at liquid N_2 temperature to activate non-basal dislocations. All micrographs were taken near $\langle 11\text{-}20 \rangle$ zone axis using $g = 0002$ diffraction vector, enabling the observation of only $\langle c \rangle$ containing dislocations. Pure Mg exhibited a low density of non-basal dislocations, the majority of which are either at grain boundaries

or adjacent to deformation twins, while Mg-1Y showed a high density of non-basal dislocations uniformly distributed in the grain interior (Fig. 5.8 (b)). This demonstrates that, in comparison to pure Mg, Y can significantly enhance the $\langle c+a \rangle$ activity in alloys.

In addition, the configuration of non-basal dislocations in Mg-Y alloys is also distinct from that in pure Mg (Fig. 5.8 (a)). One main feature of the non-basal dislocations in deformed pure Mg is that they typically have long, straight segments parallel to the basal plane traces. The dissociation of $\langle c+a \rangle$ dislocations on the basal planes has been predicted to be energetically favorable in Mg using molecular dynamic simulation methods [47, 139]. Once the dislocation lines dissociate onto the basal planes, they become immobile obstacles for dislocation motion, which is responsible for the high strain hardening rate and poor ductility in Mg. In contrast, the dislocations with $\langle c \rangle$ component in Mg-1Y, although they also have some segments parallel to the basal plane, they are mostly wavy in shape without straight and long segments. After in-situ heat treatment at 400°C (Fig. 5.8 (c)), dislocation dissociation onto the basal plane was observed and straight long dislocation segments parallel to the basal plane formed.

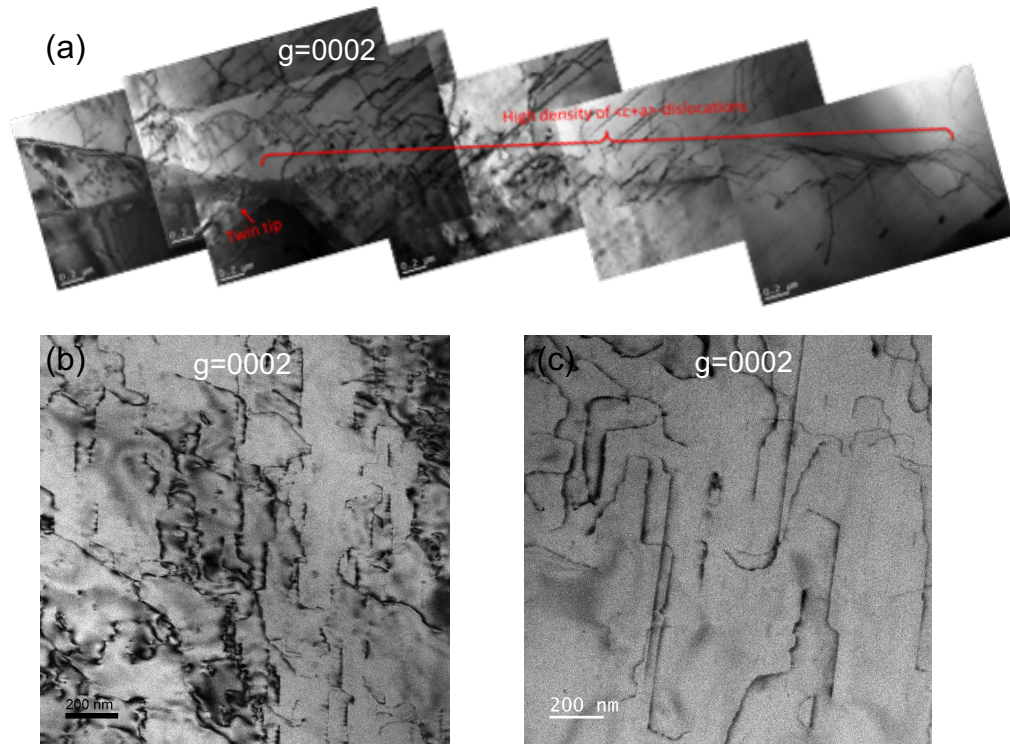


Fig. 5.8 TEM micrographs of the dislocation structure in (a) pure Mg and (b) Mg-1Y, after $\sim 2\%$ ND compression at liquid N_2 temperature. (c) is the dislocation structure in (b) after in-situ heating at 400°C .

To further discern the microstructure of $\langle c+a \rangle$ dislocations in Mg-Y, a Mg-3Y sample compressed along ND at room temperature was studied. TEM two-beam analysis was performed at different zone axes and diffraction vectors. As shown in Fig. 5.9, $\langle c+a \rangle$ dislocations were observed on either pyramidal I and pyramidal II planes. Most of the $\langle c+a \rangle$ dislocations show a stair-like configuration, alternating between pyramidal and

basal planes. Therefore, our results demonstrate that $\langle c+a \rangle$ dislocations in Mg-Y still tend to dissociate onto the basal planes, similar to those in pure Mg.

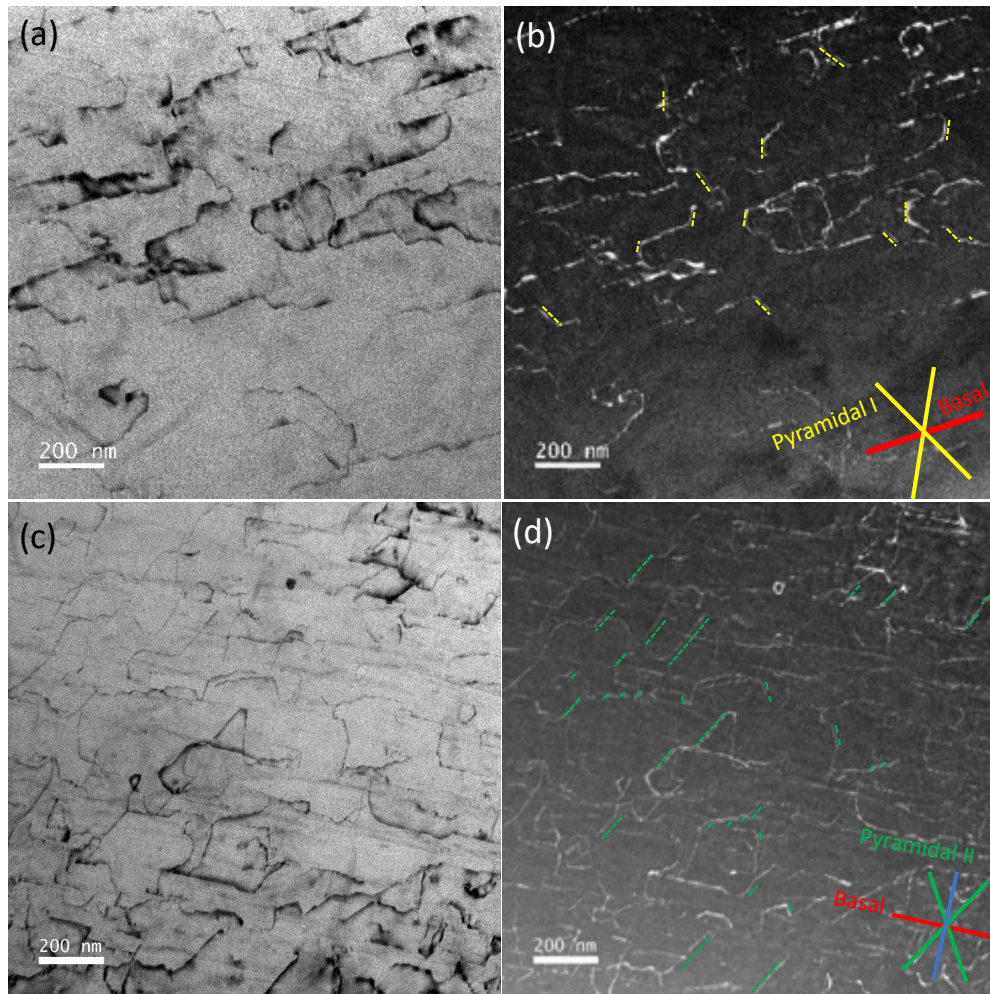


Fig. 5.9 TEM diffraction contrast analysis showing the structure of $\langle c+a \rangle$ dislocations in Mg-3Y after $\sim 2\%$ ND compression at room temperature: (a) Two beam bright field and (b) dark field images taken close to a $\{11-20\}$ zone axis with a diffraction vector $g = 0002$; (c) Two beam bright field and (d) dark field images taken close to a $\{10-10\}$ zone axis with a diffraction vector $g = 0002$

In addition to the higher activation of $\langle c+a \rangle$ dislocation slip, profuse $\{10\text{-}12\}$ tensile twins were activated in Mg-1Y after RD compression to a strain of 2%. Fig. 5.10 shows the high resolution TEM micrographs near a $\{10\text{-}12\}$ twin. The small shear $\{10\text{-}12\}$ twin boundaries (TBs) have both coherent TBs and basal/prismatic (B/P) and prismatic/basal (P/B) facets. It is observed that here is a higher density of B/P and P/B facets close to the twin tip comparing to the twin side, which is corresponding to the higher mobility of the twin tip. The twin tip comprises a pair of relatively long B/P (24 and 23 atomic layers in the matrix and twin, respectively), and P/B (36 and 37 atomic layers in the matrix and twin, respectively).

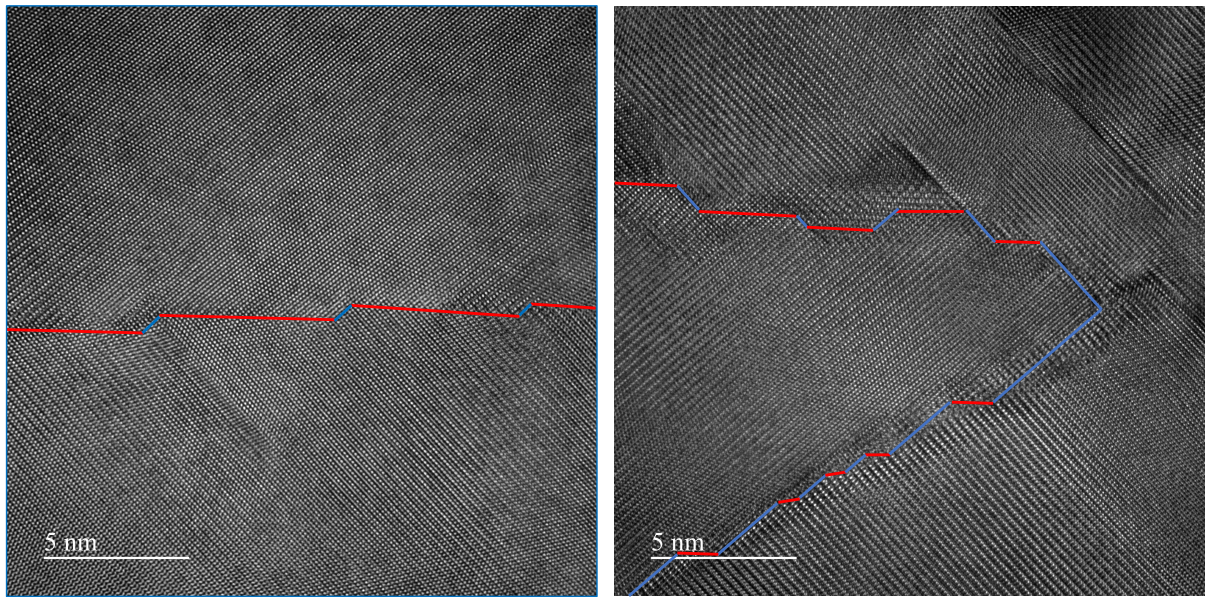


Fig. 5.10 Atomic resolution TEM micrographs of a $\{10\text{-}12\}$ deformation twin in a $\sim 2\%$ strain RD compressed Mg-1Y sample: (a) high resolution TEM (HRTEM) image at the twin

side; (d) HRTEM image at the twin tip. Edge-on coherent twin boundaries are colored in red, and B/P and P/B interfaces are colored in blue.

5.4.3 Distribution of Y solute elements in Mg-Y studied by HAADF-STEM

Fig. 5.11 shows a low-magnification HAADF-STEM and bright field STEM image of a typical {10-12} deformation twin in Mg-1Y after 2% compression along RD. The width of the twin is approximately 200 nm. Furthermore, the TBs exhibit brighter contrast in this HAADF-STEM image in Fig. 5.11 (a), indicating some solute segregation of Y at TBs as the image intensity in a HAADF image is approximately proportional to the square of the atomic number.

The higher magnification HAADF-STEM image in Fig. 5.12 shows selected regions from the TB in Fig. 5.11. It is observed that the coherent twin planes are separated by multiple P/B steps. The brighter dots in this HAADF-STEM image correspond to Y-rich columns. It is noted that even in the as-deformed Mg-1Y without subsequent annealing, the distribution of Y atoms is inhomogeneous close to deformation twins. Some bright Y-rich columns exist as clusters or single dots close to the TB. A closer inspection of the images reveal that the Y-rich columns are all in the matrix region, adjacent to the P/B facets on the TBs (boundaries colored in blue). Furthermore, the Y-rich columns are not necessarily on the P/B interface, instead they can be one or two layers away. How the Y and other selected solutes interact with the TBs and affect migration is beyond the scope of the research being presented here, but will be pursued in future activities. With such understandings, we may

be able to tailor the mobility of certain twin segment types and control the twin mesh microstructure.

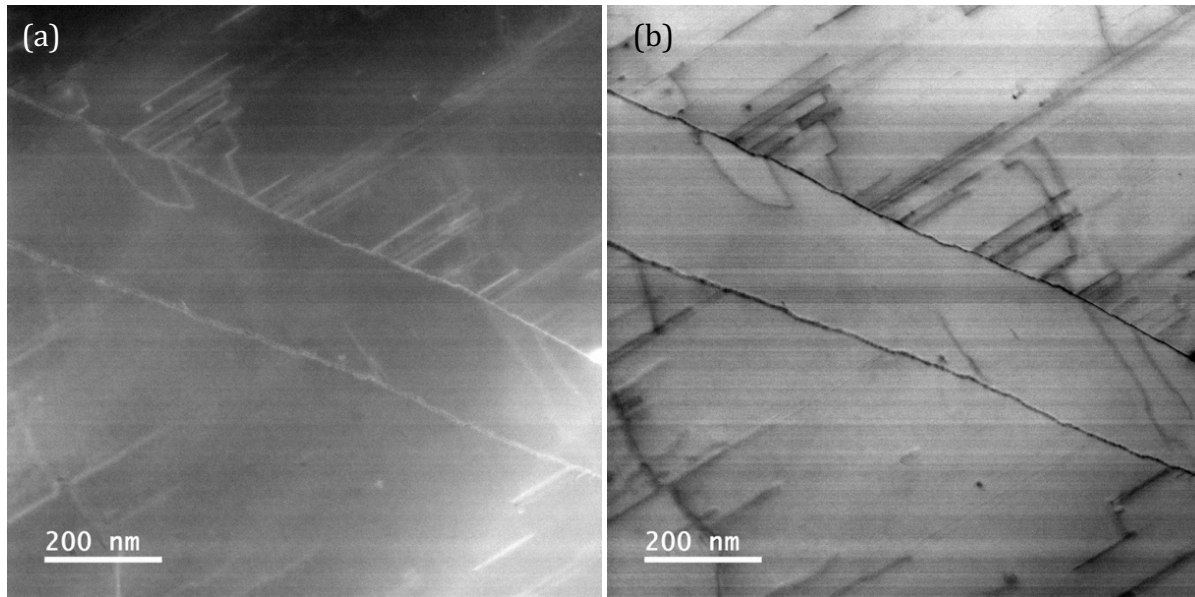


Fig. 5.11 (a) Low-magnification HAADF-STEM image and (b) the corresponding bright field STEM image showing a $\{10\text{-}12\}$ twin in Mg-1Y after $\sim 2\%$ RD compression. Electron beam is parallel to a $\langle 11\text{-}20 \rangle$ zone axis

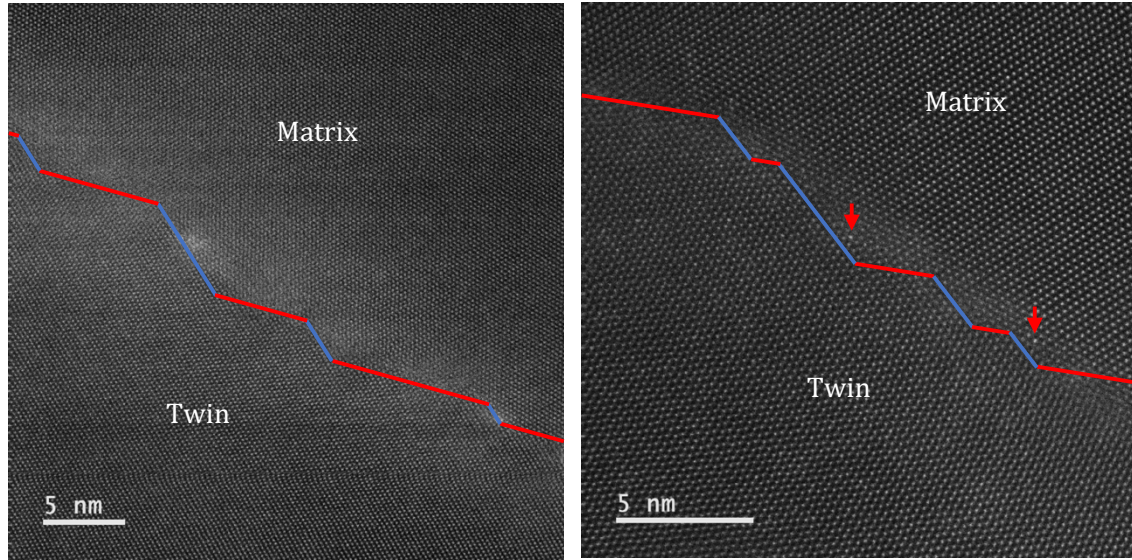


Fig. 5.12 (a) and (b) are atomic-scale HAADF-STEM image showing the distribution of Y-rich columns in two regions along the $\{10-12\}$ twin boundary shown in Fig. 5.11.

Although most of Y atoms are randomly distributed as solute atoms in the Mg matrix, as seen in Fig. 5.13 (a), and they are close to a regular grain boundary, obvious clustering of Y-rich columns is seen in Fig. 5.13 (b). Since an important twinning nucleation mechanism is from grain boundaries, the amount of solute segregation at the grain boundary and their atomic, site-dependent distribution may strongly affect the nucleation of twins and will continue to be the focus of our future work.

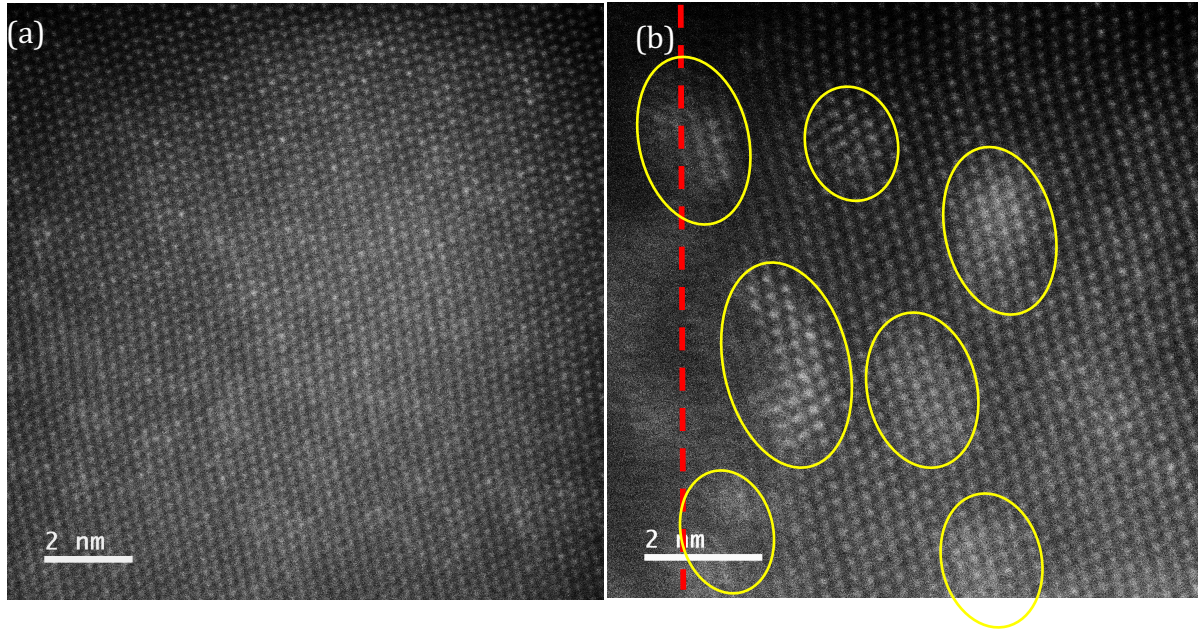


Fig. 5.13 (a) Atomic resolution HAADF-STEM images in Mg-3Y (a) in the Mg matrix and (b) close to a regular grain boundary (marked by the red dashed line).

5.5 Discussion

5.5.1 Influence of Y on the activation of different slip and twinning modes

VPSC modeling has been performed by our collaborator at UCSB to provide insight into the activity of different slip and twinning systems in Mg-Y alloys. The VPSC-predicted CRSS values needed to activate different slip systems are listed in .

Table 5.2. It is seen that with an increased concentration of Y, the CRSS values for all slip systems (basal, prismatic and pyramidal slips) and tensile twinning increased. The CRSS value for basal slip is estimated to be 10 MPa in Mg-0.2Y, which is almost double the value in Mg-1Y. Meanwhile, the CRSS values for pyramidal slip are 80 MPa and 95 MPa in

Mg-0.2Y and Mg-1Y, respectively. The enhanced CRSS values for all slip and twinning systems can be a reasonable explanation for the enhanced yield strength in Mg-Y compared to that in pure Mg when deformed along both RD and ND.

The CRSS anisotropy of non-basal to basal slip was also calculated in .

Table 5.2. A reduced CRSS anisotropy was observed with an increase in Y concentration. A more isotropic CRSS among various slip systems may lead to the easier activation of non-basal dislocations. This is consistent with the post-mortem TEM observation of ND compressed Mg-1Y, which shows a uniform distribution of $\langle c+a \rangle$ dislocations. and the improved compression and tension ductility.

Table 5.2 VPSC simulated CRSS values for various slip systems considered in Mg-Y [149]

	Slip system	CRSS	$CRSS_{(pyr)}/CRSS_{(basal)}$	$CRSS_{(prism)}/CRSS_{(basal)}$
Mg-0.2Y	Basal	10	8	3
	Prismatic	30		
	Pyramidal	80		
	{10-12} twin	14		
Mg-0.6Y	Basal	17	6.5	2.3
	Prismatic	39		
	Pyramidal	110		
	{10-12} twin	16.5		
Mg-1Y	Basal	18	5.3	2.3
	Prismatic	42		
	Pyramidal	95		
	{10-12} twin	19.5		

5.5.2 The effect of Y on twin boundary migration

As indicated by our HAADF STEM analysis, in as-deformed Mg-Y alloys, Y atoms tend to segregate at grain boundaries and at deformation TBs. By taking a closer look at the incoherent TBs in Mg-Y, we notice that Y atoms are observed more frequently on or adjacent to the B/P or P/B interfaces rather than the coherent TBs.

The heterogeneous distribution of Y along TBs in the as-deformed Mg-Y alloys has motivated us to investigate the interaction between solute atoms and the moving TBs. This interaction can be critical as it will affect the kinetics of TB migration, and therefore influence the twin mesh structure and mechanical properties of Mg alloys. However, few

studies have focused on this type of interaction in the literature. Nie et. al. studied Mg alloys including Mg-Gd and Mg-Zn, and they found that solute atoms can form periodic segregation at coherent twin boundaries after annealing, which will provide a pinning effect on twin boundaries [131]. However, no details about the pinning mechanisms were discussed in their study. Moreover, the interaction of solute atoms with a moving TB may differ from that with a static TB.

The following Y-TB interaction mechanisms are proposed:

1. TBs may get pinned by Y atoms until they break away from the solutes at a sufficiently high stress level;
2. Y atoms may provide a dragging force on twinning dislocations in Mg;
3. Y atoms may diffuse along the twin boundaries and B/P and P/B interfaces;

To provide more insight into the effects of solute atoms on twin boundary motion, in-situ mechanical testing in TEM and molecular dynamic simulations will be conducted in the future study.

5.6 Summary

Microstructure and mechanical properties of four Mg-Y alloys with different Y concentrations were studied to probe the alloying effect of Y on the deformation mechanisms of Mg.

Our results reveal the following findings:

1. Y addition at dilute concentrations (0.2, 0.6, 1, 3 w.t.%) has effectively randomized the rolling texture and increased the strength and ductility of Mg in

all tested conditions (uniaxial tension or compression at room temperature or cryogenic temperature);

2. VPSC simulations indicate that with an increased concentration of Y, the CRSS values for all slip and twinning systems increased, while the CRSS anisotropy among non-basal and basal slip systems decreased.
3. In Mg-Y alloys, $\langle c+a \rangle$ dislocations distributed more uniformly with higher activity comparing to that in pure Mg. $\langle c+a \rangle$ dislocations segments lie on pyramidal I and pyramidal II planes with frequent plane changes to basal planes;
4. In the as-deformed Mg-Y alloys, Y atoms segregate at grain boundaries as clusters and at BP/PB interfaces along incoherent twin boundaries;
5. The solute atom-twin boundary interaction may affect the propagation and growth of deformation twins and thus the formation and stability of twin meshes in Mg.

Chapter 6 Design and application of some in-situ electron microscopy characterization methods

6.1 Abstract

In-situ electron microscopy techniques are a fast-growing field of study motivated by the downsizing of modern electronic devices and scientific challenges to elucidate the properties of materials at the nanoscale and the mechanisms of many dynamic processes, such as mechanical deformation. In this chapter, some in-situ electron microscopy methods, combining electron microscopy (including scanning electron microscopy and transmission electron microscopy and scanning transmission electron microscopy) for real-time imaging and external stress stimuli applied by special instruments, that were developed and used in our group are introduced. The experimental set-ups, sample preparation methods using focused ion beam (FIB), and possible application examples of these methods are discussed. The in-situ electron microscopy methods presented in this chapter, each having its own capabilities, can be applied to a wide range of materials to shed light on the fundamental mechanisms by which the material deformations at the nanoscale and to provide critical evidence for related theoretical simulations.

6.2 Introduction

The applications of electron microscopy have significantly accelerated materials research and development by facilitating our understanding of the materials microstructures. Most of the early electron microscopic investigations on structural materials are ex-situ, i.e., performed prior to the deformation and/or post mortem, which

provide only stationary characterization of the dynamic deformation processes without time resolution. More recently, in-situ techniques inside scanning electron microscopy (SEM) or transmission electron microscopy (TEM) have drawn remarkable scientific attention and has become one of the most vigorous field of research. Such techniques offer the capability to directly record the evolution of sample shape, size, crystallography and defects during mechanical testing.

Tremendous efforts have been devoted to developing various instruments/techniques for a broad range of applications from materials science to biochemistry. Although many qualitative in-situ observations have been used to resolve longstanding questions on deformation behavior [150], quantitative in-situ mechanical testing techniques are an important branch that can assist our understanding of the structure-property relationships in materials. Dedicated sample holders are often required for quantitative in-situ mechanical tests, which usually incorporates the utilization of an indenter as the external stress stimulus. A transducer and piezoelectric actuator system is often used to precisely control the movement of indenter while measuring the force and displacement during deformation. The advanced design of in-situ holders has now developed to support mechanical testing as a function of heating, cooling, electrical and magnetic biasing.

Sample preparation is an important part of in-situ testing. Standard tensile and compressive samples are dog-bone and cylindrical shape, respectively, with a specific range of length to width/diameter aspect ratios. For TEM investigations, the specimens also need to be electron transparent, so the sample thickness is typically less than 300 nm.

Thanks to the recent development of focused ion beam (FIB) milling technique, small scale specimens for tension, compression or bending tests can be fabricated in a relatively easy and time-efficient manner. Moreover, FIB allows the selection of the exact region of interests for in-situ measurement. However, some fabrication defects, such as Ga⁺ ion implantation damage, sample taper and surface roughness, which originate from the FIB machining, may complicate the analysis of in-situ results. Some methods that can minimize such FIB induced artifacts are also discussed in this chapter.

6.3 Quantitative in-situ micropillar compression in SEM

Quantitative mechanical tests in combination with SEM is a powerful approach to obtain insights in the material plasticity. Compared to in-situ studies in TEM, SEM provides lower spatial resolution and less defect diagnosis capabilities. However, the large SEM chambers allow a higher degree of flexibility for more complicated experimental design and larger samples to be investigated. The latter is specifically important if the specimens need to contain a statistically sufficient number of grains of a polycrystal to represent the bulk form tests and to avoid possible size effects usually reported in small sample tests down to the nanometer scale.

Uniaxial deformation properties of small scale samples can be studied via micropillar compression testing inside SEM. A Hysitron/Bruker PI85 SEM PicoIndenter (as shown in Fig. 6.1 (a)) was used for this purpose in our study. Samples prepared by FIB should be attached to the sample stage. Compression of the micropillars was performed by a diamond flat punch (as shown in the top part in Fig. 6.1 (b)), typically with a 1 to 20 μm

circular diameter top, under load or displacement control by the transducer. The PI85 indentation system allows fully quantitative measurement of the load-displacement curve during loading and unloading. During compression, SEM video imaging, which illustrates the microstructural evolution, can be recorded simultaneously using the software. Therefore, each frame in the in-situ video will correspond precisely to a point in the load-displacement curve. This direct correlation of the microstructure characterization and stress-strain measurement enables the deformation events that occur during the compression process to be discerned and better understood.

In addition, with the PI85 PicoIndentation system, in-situ mechanical tests can be carried out at elevated temperatures up to 400°C to explore the deformation mechanism as a function of temperature. In-situ SEM experiments can also be performed with electrical bias to understand how the mechanical and electrical properties are coupled.

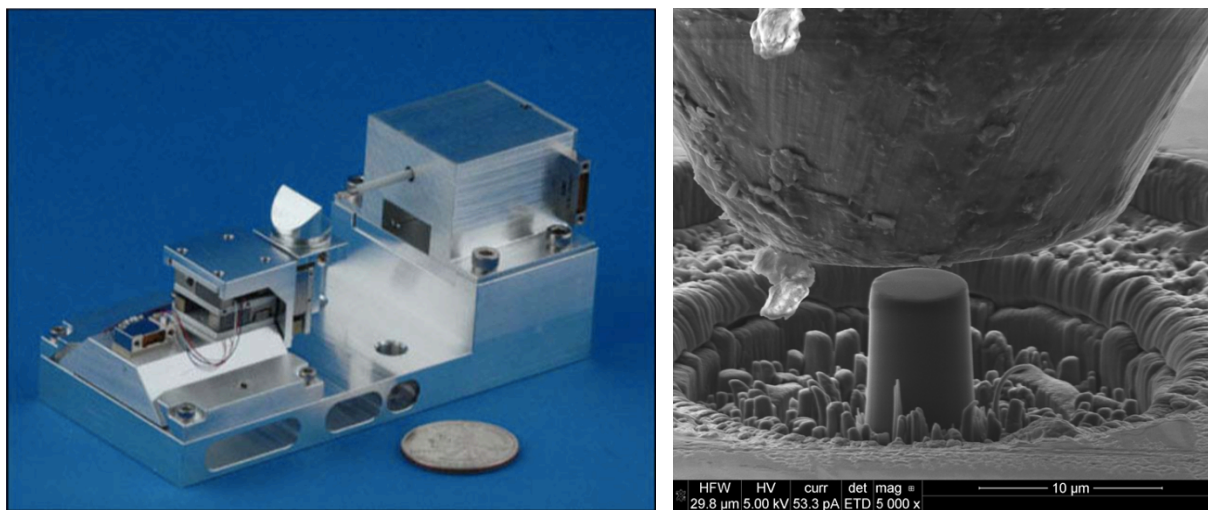


Fig. 6.1 (a) PI85 SEM PicoIndenter stage control unit. (b) SEM image of the indentation probe and a compression pillar.

6.3.1 Micropillar fabrication

As was mentioned earlier, sample fabrication is an important aspect of in-situ mechanical tests. Although the development of FIB techniques has greatly reduced the cost of time and effort on the fabrication of micropillars from bulk materials, there are still many challenges for sample preparation that can affect the reliability of the data obtained from in-situ mechanical tests. The first and foremost challenge for sample fabrication is the lack of standards for small sample tests, which is however beyond the scope of the current study. But it is important to point out that, compared to mechanical tests at the macroscopic scale, small sample tests are similarly or even more sensitive to the size, aspect ratio, and surface roughness of the samples. Therefore, better-established technical standards for in-situ mechanical testing is indispensable in the near future for this fast-growing field of study.

The second sample preparation challenge is the almost inevitable surface ion implantation artifacts induced by the high energy Ga ions used for FIB milling. To tackle this issue, low enough ion beam accelerating voltage (e.g., 5 kV) and current (e.g., several pA) are needed in the final steps to reduce the thickness of damage layers at the sample surface before the final pillar dimension is achieved.

The third sample preparation challenge is to fabricate taper-free micropillars. Pillars fabricated by FIB milling in a fixed direction perpendicular to the sample surface often exhibit a tapered shape, with the diameter on top of the pillar being smaller than that on the bottom of the pillar. A FIB lathe milling sequence has been developed by Uchic et. al.

[151] to fabricate micropillars with a uniform cross-sectional area. Instead of milling the pillar with the beam perpendicular to the bulk sample surface, the lathe milling method involves continuous movement and rotation of the sample so that the FIB column is close to the tangent direction of the pillar side surface. To enable a semi-automatic lathe milling process, a circular fiducial mark can be made on the top surface of the pillar and image-recognition software can be used to align the center of the pillar with the FIB cuts. More details on this method can be found in [151].

6.4 In-situ nanopillar compression in TEM

Experiments combining real-time TEM characterization with nanoindentation is a powerful approach to directly monitor the material's microstructure throughout the deformation. With specially designed mechanical testing TEM holders, quantitative nanomechanical testing in TEM has contributed to an unprecedented understanding of the relationship among mechanical behavior, mechanical properties and the inner and external material structure. A Hysitron/Bruker PI95 TEM PicoIndenter (as shown in in Fig. 6.2 (a)) was used in the present study. Similar to the PI85 SEM PicoIndenter, PI95 in-situ holders deform the samples by precisely controlling the positioning of the tip (as shown in the bottom left in Fig. 6.2 (b)) under load or displacement control mode by the transducer.

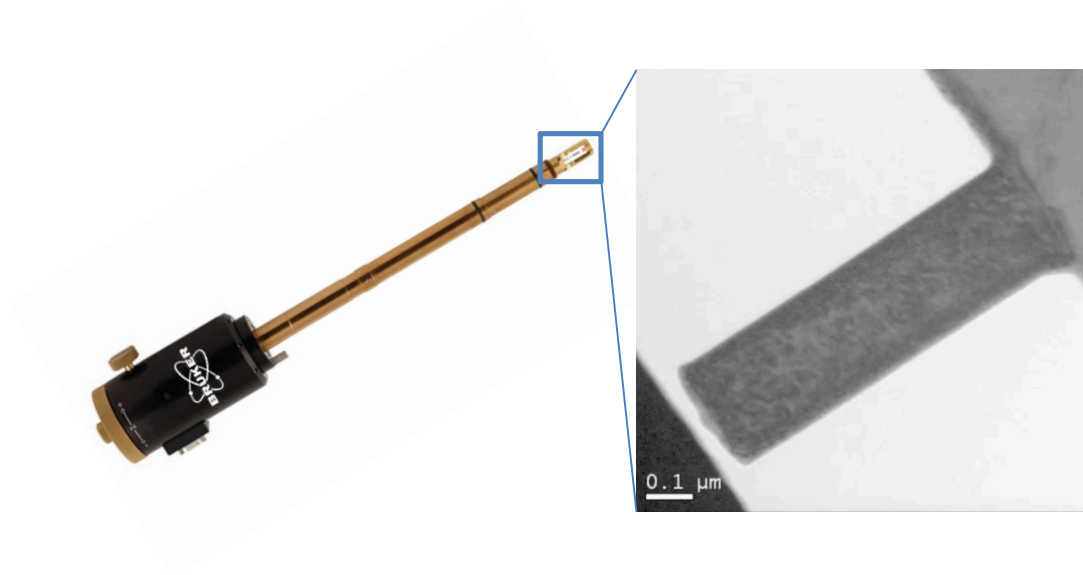


Fig. 6.2 (a) PI95 TEM PicoIndenter. (b) TEM bright field image of the indentation probe (bottom left) and a nanopillar.

With continuous advances in TEM technologies, in-situ TEM characterization at the sub-nanometer or even atomic scale spatial resolution and milli-electronvolt energy resolution is now possible. However, challenges remain in in-situ mechanical testing at the atomic level, largely due to the mechanical resonance of the indentation tip during motion in high vacuum. Moreover, in combination with advanced high-speed cameras for fast data acquisition, in-situ TEM experiments can be carried out with a high time-resolution to capture some ultrafast dynamic processes in materials, such as twin nucleation. Future endeavors may enable detection techniques with improved sensitivity for fast imaging.

6.4.1 Nanopillar fabrication

To fabricate nanopillars for in-situ TEM experiments, a half disk (3 mm in diameter) sample $\sim 50\text{ }\mu\text{m}$ in thickness was prepared followed by mechanical polishing. Chemical etching was performed to remove the damage layers on the surfaces caused by polishing. Then H-bar type foils (typically $20\text{ }\mu\text{m}$ in length, $10\text{ }\mu\text{m}$ in height and $\sim 2\text{ }\mu\text{m}$ in thickness) can be prepared by FIB thinning. A lower voltage and current should be used for the final milling steps to minimize FIB induced damage at the sample surfaces. Flat-top rectangular or circular pillars can then be made with a thickness or diameter of less than 300 nm and an aspect ratio within the range of 2:1 to 4:1. A low beam current should be used in the final steps to minimize Ga^+ implantation and surface amorphization.

6.4.2 Applications: In-situ TEM investigation of twin nucleation and propagation in geometrically designed nanopillars

The geometric effects of the pillars on the twinning nucleation and propagation were studied by in-situ TEM compression. In the present study, bullet-shaped pillars with different tip size (Fig. 6.3) were designed to reveal the twinning mechanisms in HCP metals. The bullet-shaped pillar with tip size of 400 nm (Fig. 6.3 (b)) was designed to observe how twins interact with each other. The bullet-shaped pillar with tip size of 250 nm (Fig. 6.3 (c)) was designed to observe how twin boundaries and twin tips propagate during the in-situ TEM compression. The bullet-shaped pillar with tip size of $<50\text{ nm}$ (Fig. 6.3 (d)) was designed to observe how twins nucleate during the in-situ TEM compression. The design is

based on the idea that the smaller pillar tip is, the larger stress concentration will be in the tip, and thus smaller deformation strain is needed for twin nucleation.

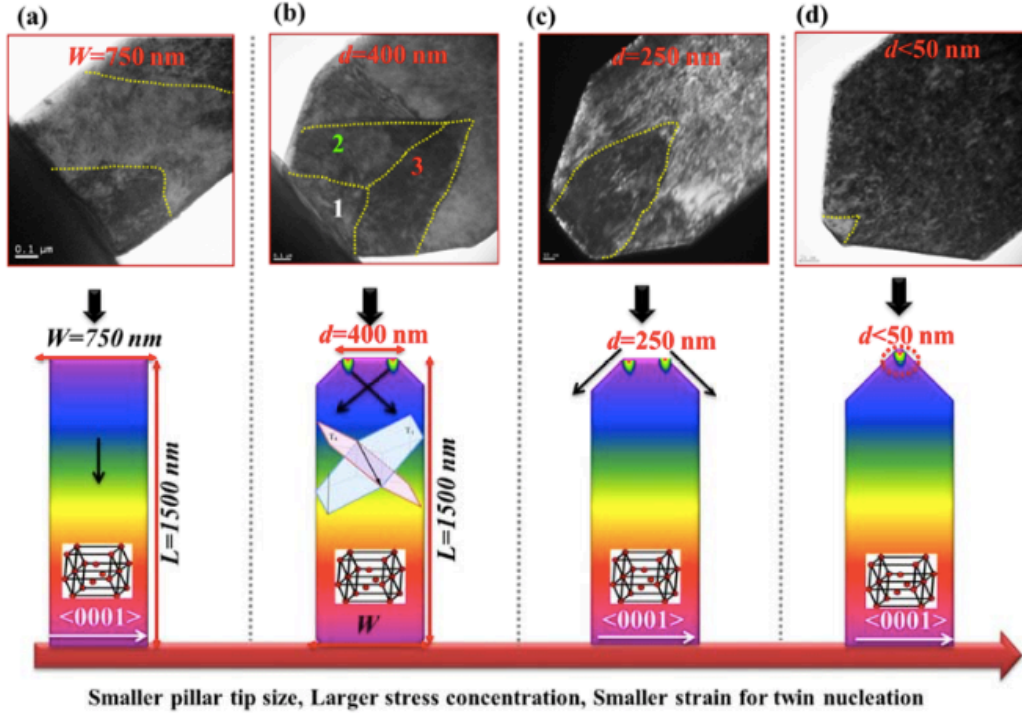


Fig. 6.3 Geometric effects of the pillars on the twinning nucleation: (a) regular rectangular with width of 750 nm; bullet-shaped pillar with tip size of (b) 400 nm for capturing twin-twin interaction; (c) 250 nm for capturing twin tip propagation; (d) <50 nm for capturing twin nucleation.

In order to know why we need to design the pillar geometric to reveal the twin nucleation, we also performed the in-situ TEM compression on a regular rectangular-shaped pillar. As seen in Fig. 6.4, in regular pillar, a gigantic twin suddenly nucleated from the corner of the pillar tip and propagated ultra-fast, causing a large strain burst (Fig. 6.4 (f)) and the twin boundary is 45 degree to the compression direction (c-axis). Thus,

twinning happens too fast in the regular pillars for us to capture the details of twin nucleation.

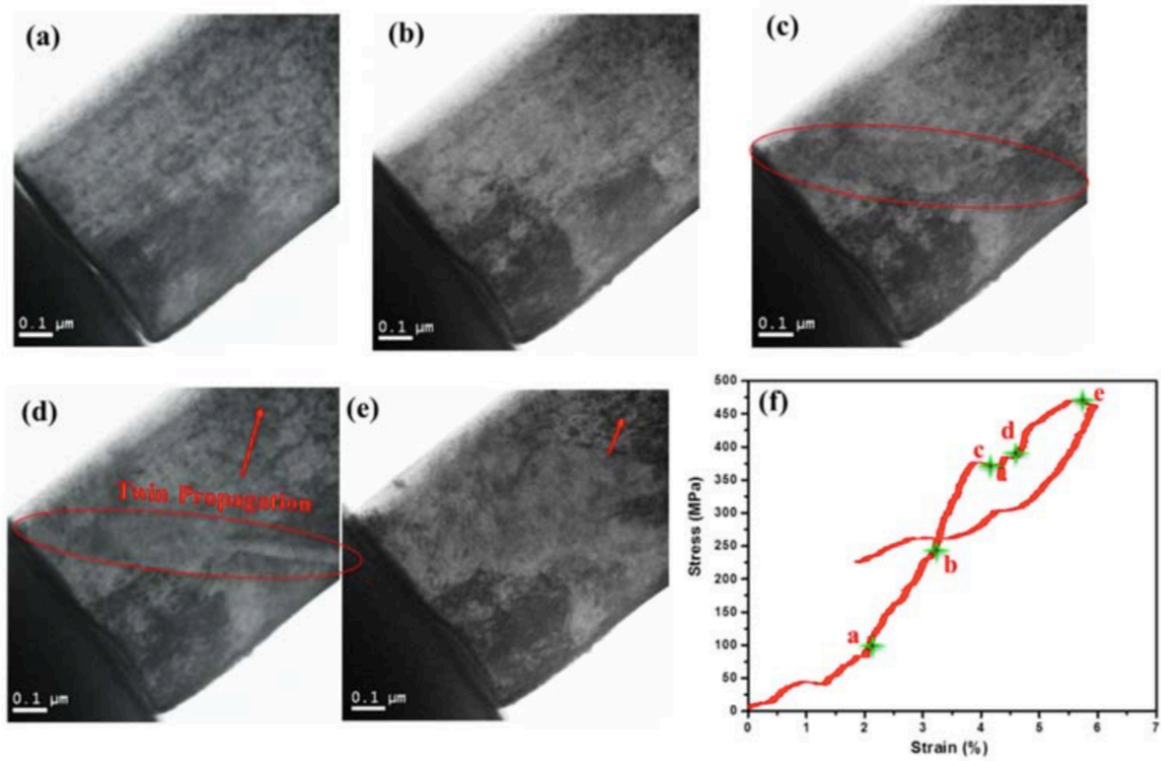


Fig. 6.4 (a-e) TEM snap-shots and (f) corresponding in-situ compression curve to show twinning events in the regular pillar during in-situ TEM compression. Points in the curve are related to the TEM snap-shots of (a-e).

In the bullet-shaped pillar with the 400 nm tip (Fig. 6.5), we captured the twin-twin interactions during in-situ TEM compression. First, Twin 1 nucleated at the pillar tip as seen in Fig. 6.5 (a); Then, two co-zone twins nucleated at the boundaries of Twin 1 and propagated continuously during further compression. The TEM characterization on this pillar after in-situ compression confirms that the formed Twins 2 and 3 are $\{10\text{-}12\}$ co-

zone twins (Fig. 6.6) and they shared a twin boundary with a small lattice misorientation of only several degrees (Fig. 6.6 (d)). Note that the required strain for nucleating twin (Fig. 6.5 (f)) in this kind of pillar is much smaller than that of the regular pillars (Fig. 6.4(f)).

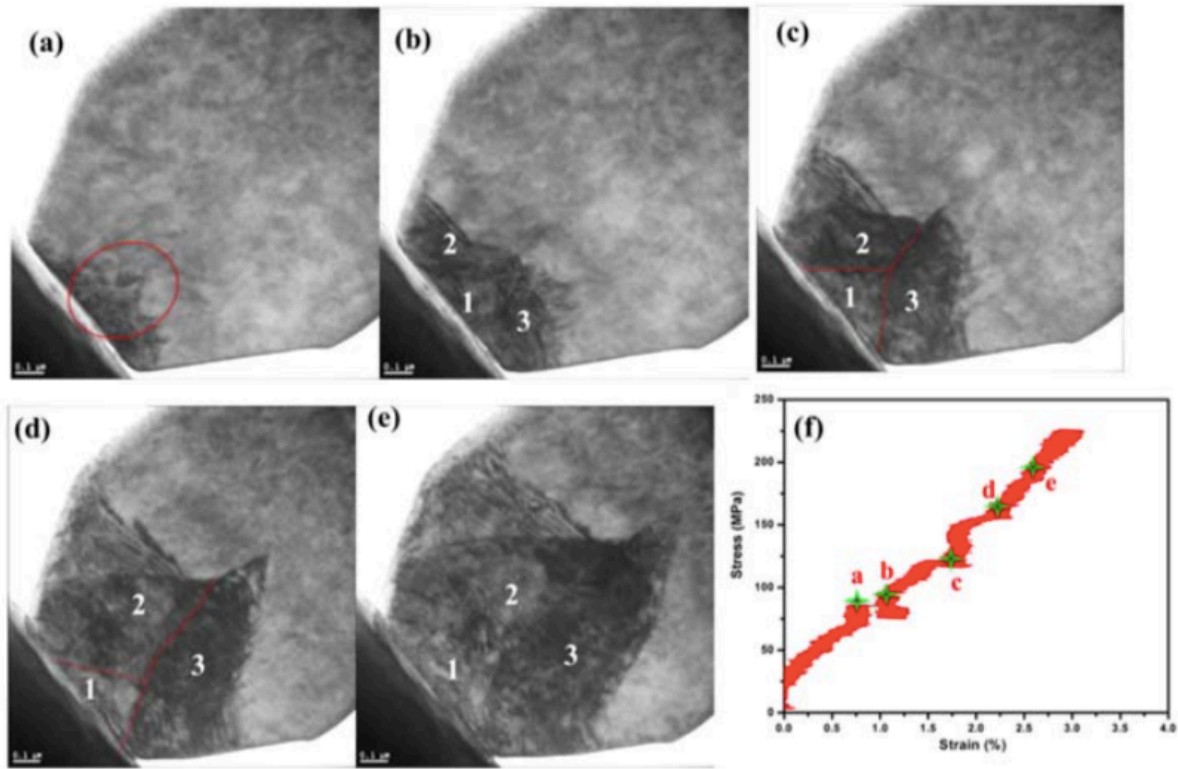


Fig. 6.5 (a-e) TEM snap-shots and (f) corresponding compression curve to show twin-twin interaction in the bullet-shaped pillar with tip size of 400 nm during in-situ TEM compression. Points in the curve are related to the TEM snap-shots of (a-e). Number 1, 2, 3 correspond to different twins.

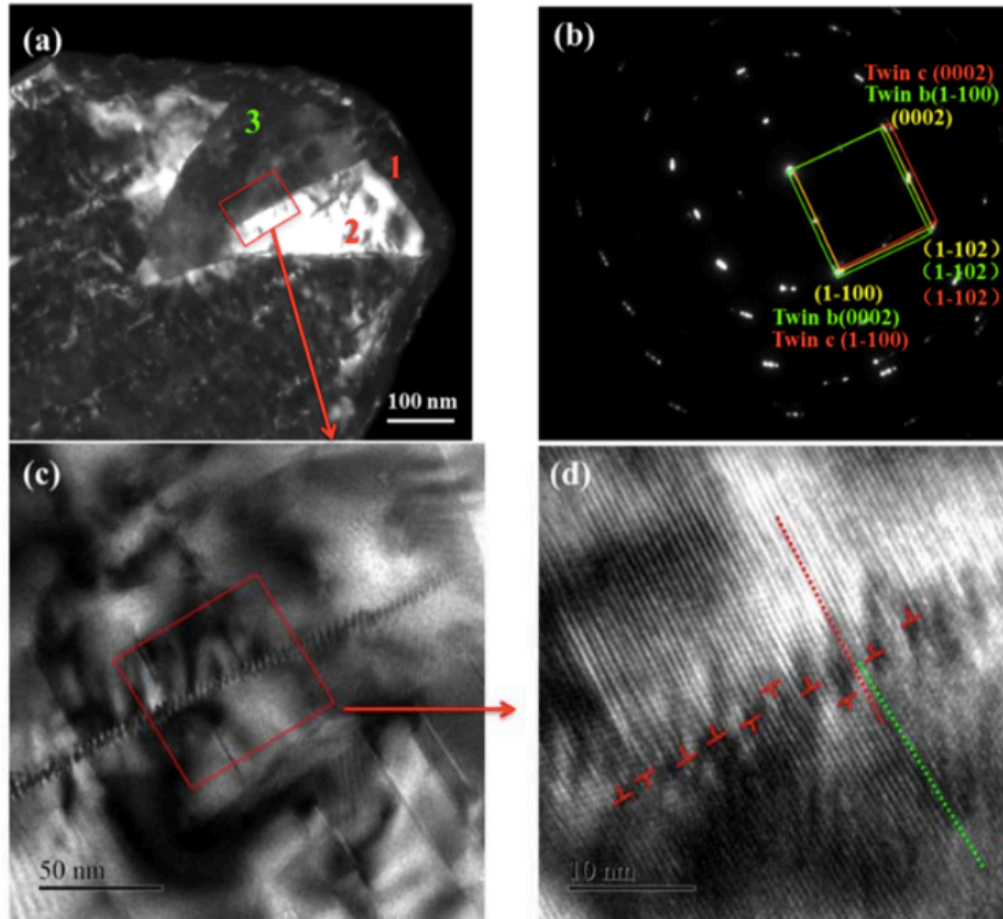


Fig. 6.6 (a) Dark field TEM image; (b) selected area diffraction pattern corresponding to the TEM image (a) to confirm that the Twins 2 and 3 are co-zone twins; (c) and (d) HRTEM to show co-zone twin- twin boundaries in the bullet-shaped pillar with tip size of 400 nm after in-situ TEM compression.

In the bullet-shaped pillar with the 250 nm tip, dislocation slip was observed first before the twin nucleation. After that, a twin nucleated at the pillar tip and then the basal dislocation slip was highly activated around the twin boundary as the twin propagated into the pillar (Fig. 6.7). During the interaction between basal dislocation slip and twin boundary propagation, the twin boundary was gradually turned to be parallel to the basal

plane of the matrix (Fig. 6.7). From the TEM characterization after compression (Fig. 6.8 and Fig. 6.9), clearly, a high density of stacking faults and $\langle c+a \rangle$ dislocations were found at the twin tip after the in-situ compression test. Also, dislocations were found to accommodate the lattice strain at the connection of the straight twin boundary and the curved twin boundary (Fig. 6.8 (b-c)).

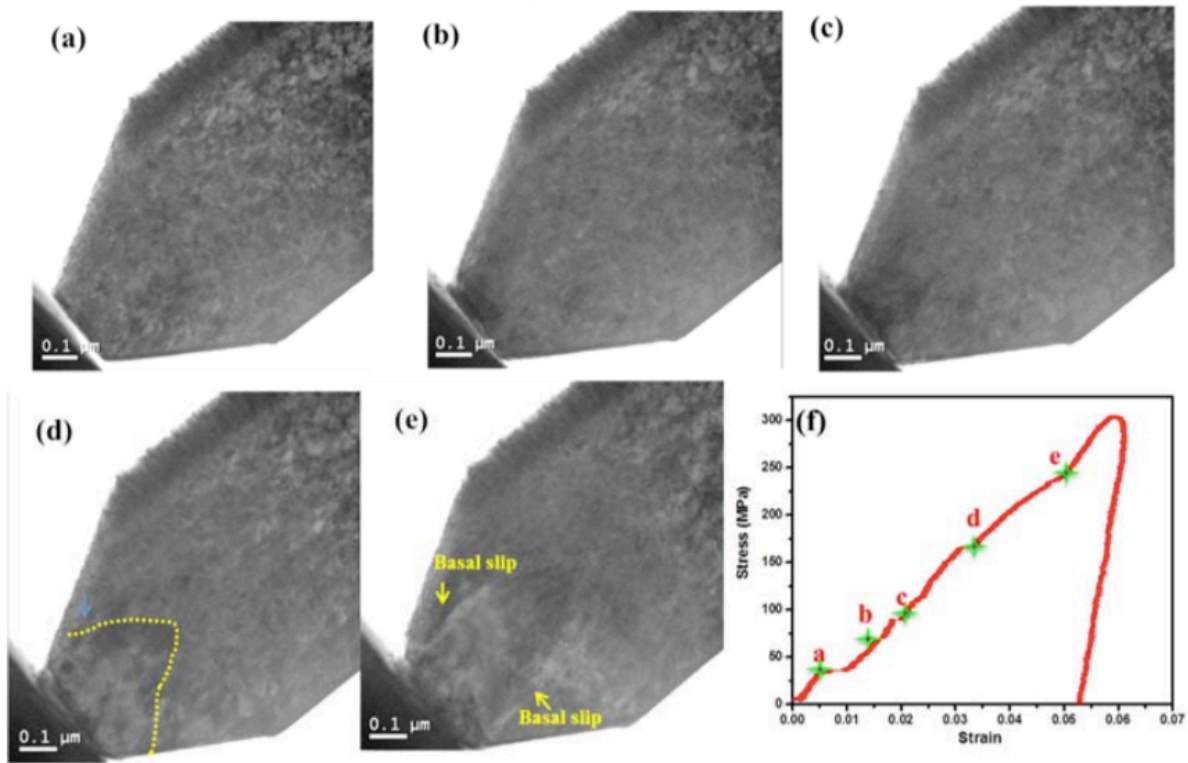


Fig. 6.7 (a-e) TEM snap-shots and (f) corresponding compression curve to show twin tip/boundary propagation in the bullet-shaped pillar with tip size of 250 nm during in-situ TEM compression. Points in the curve are related to the TEM snap-shots of (a-e).

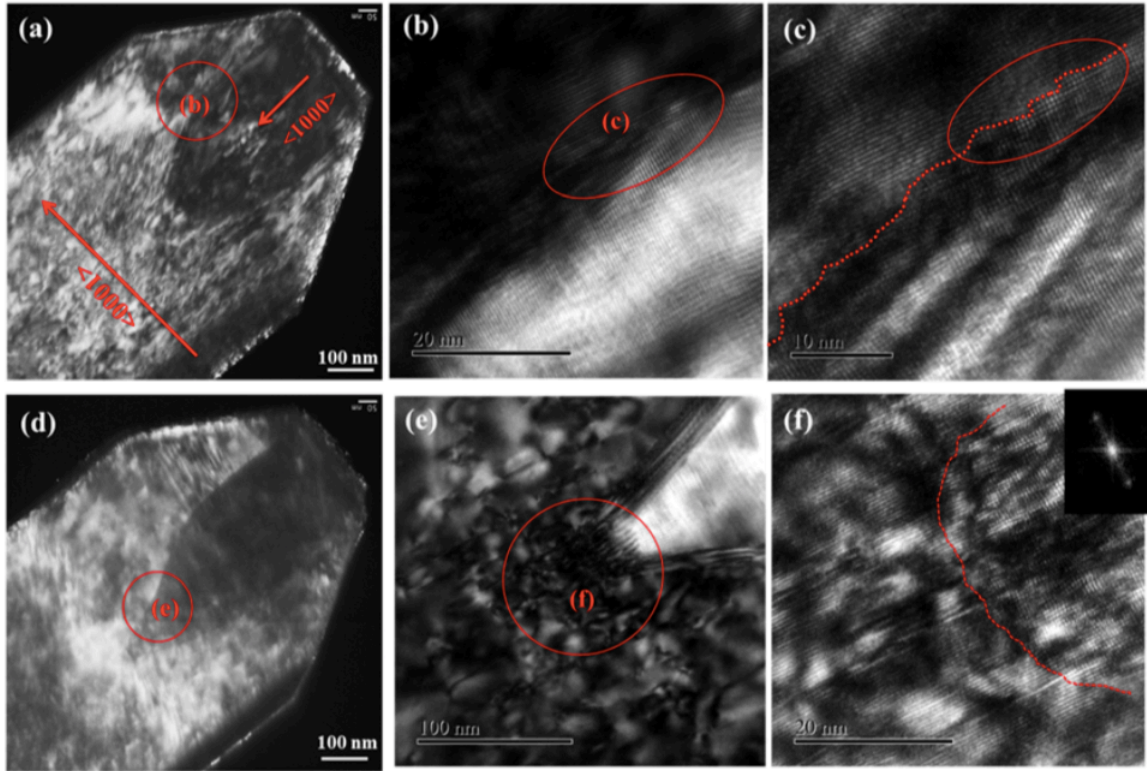


Fig. 6.8 (a) Dark field TEM and (b-c) HRTEM show the connection between straight boundary and curved boundary. (d) Dark field TEM and (e-f) HRTEM to show stacking fault around the twin tip in the bullet-shaped pillar with tip size of 250 nm after in-situ TEM compression.

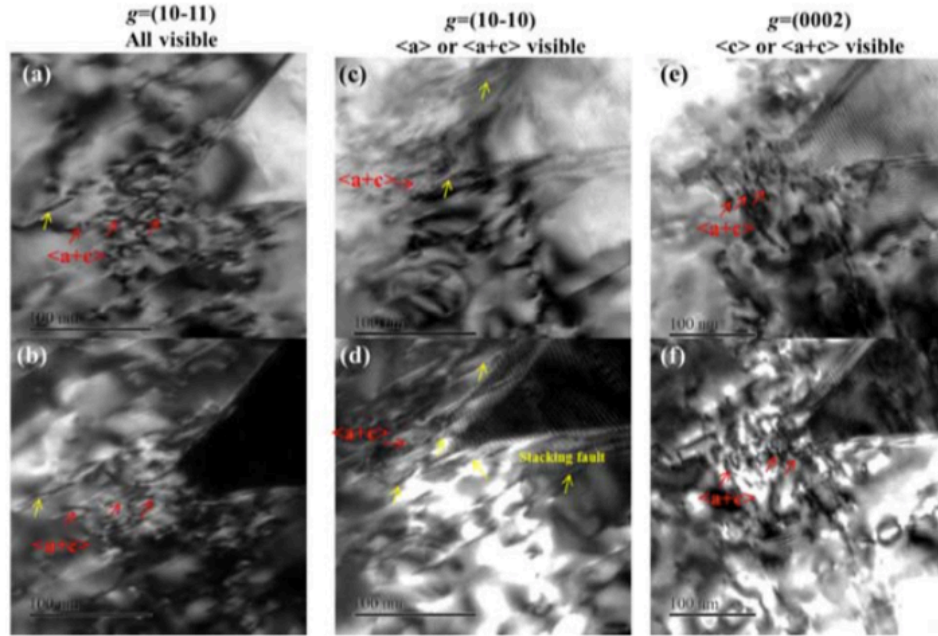


Fig. 6.9 (a-b) TEM images at two beam condition $g=(10-11)$; (c-d) TEM images at two beam condition $g=(10-10)$; (e-f) TEM images at two beam condition $g=(0002)$ to show stacking faults and dislocations around the twin tip in the bullet-shaped pillar with tip size of 250 nm after in-situ TEM compression.

In the bullet-shaped pillar with the <50 nm tip, a twin nucleus with size of 10 nm was formed (Fig. 6.11). The size of the nucleated twin in this pillar is much smaller than those in the other pillars. Note that the twin nucleus shows an ingot-like shape (Fig. 6.11), instead of triangle shape. This indicates the captured twin nucleus is at the very beginning of nucleation stage. Fig. 6.10 shows the snap-shots of the twin nucleation during in-situ TEM compression. Based on the experimental results, the nucleation of twins is also schematically shown in Fig. 6.12. First, $\langle c+a \rangle$ dislocations were emitted from two corners, then accumulated and interacted with each other at the region near the pillar tip (Fig. 6.10

(c)); then, after the local dislocation density reaches a certain value, a twinning loop nucleated and propagated (Fig. 6.10 (d-e)); finally, twin loop was turned into an ingot-like twin embryo with the further compression (Fig. 6.11 and Fig. 6.10 (f)). This ingot-like twin embryo will eventually grow to become a twin with triangle shape as schematically shown in Fig. 6.12 (f).

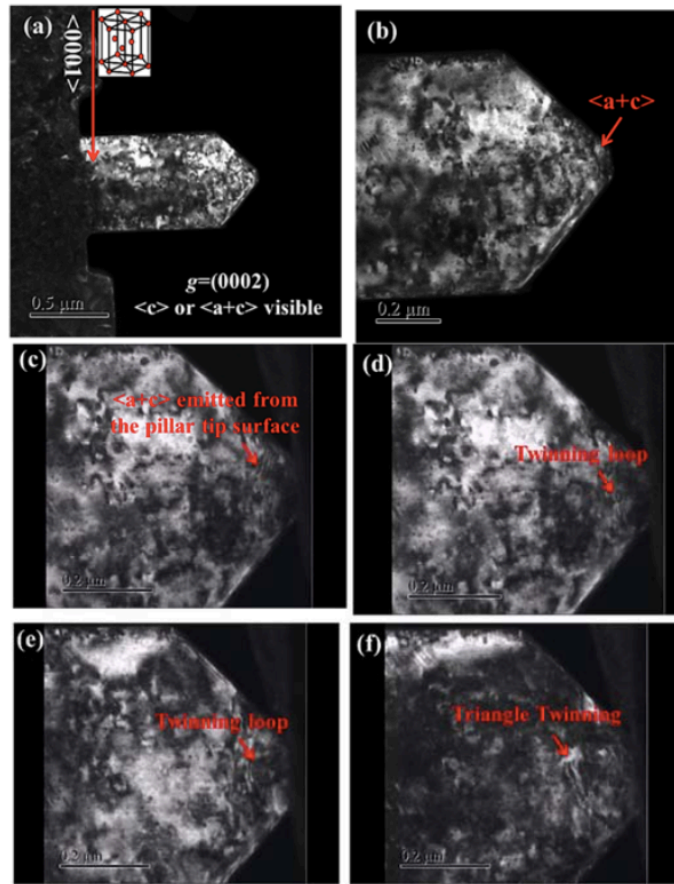


Fig. 6.10 (a-b) Two beam dark field TEM images of the bullet pillar with tip size <50 nm; (c-f) Two beam dark field TEM snap-shots to show twin nucleation in the bullet-shaped pillar with tip size of < 50 nm during in-situ TEM compression.

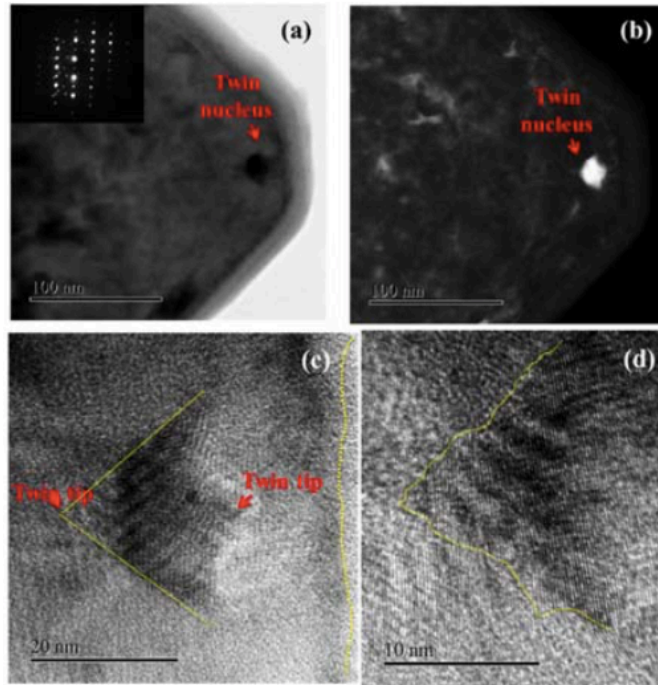


Fig. 6.11 (a) Bright field (b) dark field TEM and (c-d) HRTEM to show the ingot-like structure of the twin nucleus in the bullet-shaped pillar with tip size of < 50 nm after in-situ TEM compression. The inset of (a) is a corresponding diffraction pattern.

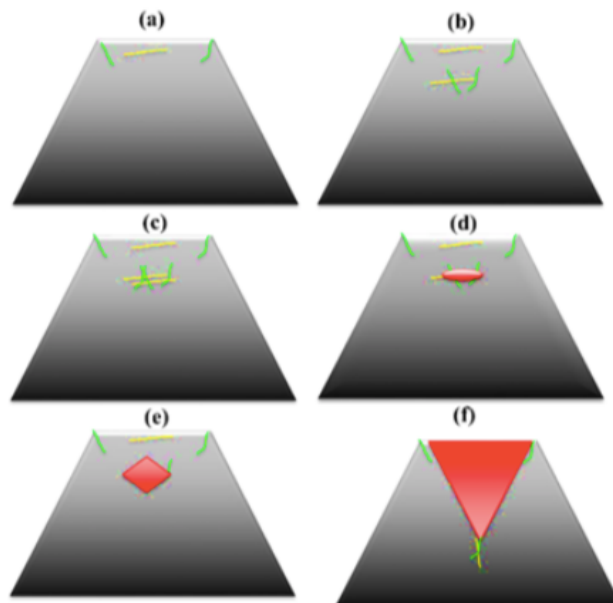


Fig. 6.12 Schematic to show the twin nucleation in the bullet like pillar: (a-b) emission of $\langle c+a \rangle$ dislocations from two corners; (c) dislocation accumulation and interaction at the region near pillar tip; (d) nucleation of a twin loop; (e) growth of the twin loop into a ingot-like twin nucleus; (f) growth of the ingot-like twin nucleus into a triangle twin.

In summary, the twin nucleation in Mg was well revealed by the combination of in-situ TEM compression and geometrical design of the pillars. The $\langle c+a \rangle$ dislocations were involved in the nucleation of twin loops and basal dislocation slip confined the twin boundary propagation. Also, the structure of the very beginning twin embryo in the bullet-shaped pillar was found to be ingot-like.

6.5 In-situ STEM thin film poking

Despite the advances in spatial, energy and time resolutions and the capability to add various stimuli for in-situ nanoindentation in TEM, its remaining drawbacks include the extremely constrained space limited by the TEM pole piece gap, and the requirement for the indentation direction to be perpendicular to the electron beam, i.e. parallel to the TEM specimen. Developing novel in-situ techniques to overcome such challenges without losing to much of the resolutions is necessary.

In-situ STEM poking is a unique method developed in our group as an extension of the in-situ SEM mechanical tests. Like in TEM, this technique requires thin and electron transparent specimens to be used. A STEM detector located beneath the specimen is used for imaging. A nanoscale Omniprobe is used to perpendicularly compress the thin film

sample in the direction parallel to the electron beam. The experimental set-up was schematically shown in Fig. 6.13. The advantage of using STEM over conventional SEM is the improvement in spatial resolution and the capability for crystalline defect analysis. But it needs to be pointed out that, unlike the quantitative in-situ compression assessment in SEM and TEM described above, this STEM approach is phenomenological with our current design.

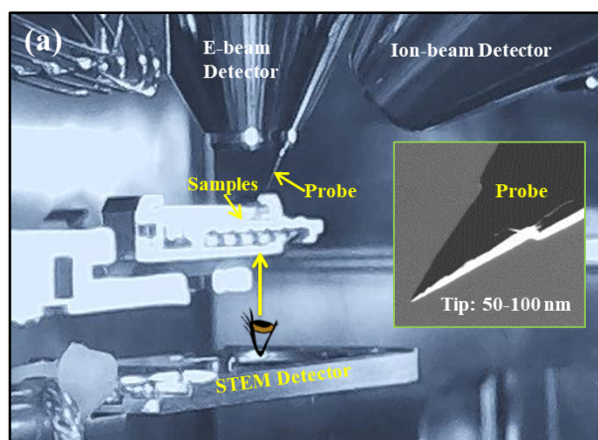


Fig. 6.13 An image showing the apparatus for in-situ STEM local stressing in a SEM/FIB chamber, the inset shows the nanoscale probe.

The special in-situ STEM thin film poking experiment was designed to capture the ultrafast twinning events and target the very initial structure of the twin nucleus. Compared to conventional in-situ SEM and TEM techniques, this method has some advantages: First, the in-plane STEM view, was selected to allow for the possibility of revealing twinning variants, which might not be visible under conventional SEM and certain TEM viewing conditions. Bright-field, dark-field, a mixture of bright-field and dark-

field, and high angular dark-field STEM views can be utilized to capture the twinning events simultaneously. The combined instrumentation and different in-plane STEM views allow the twin embryos to be distinguished from the stress band contrasts introduced by the nanoscale probe. Second, a very sharp needle was used to apply the local stress. This experimental set-up allowed for the application of only a very small stress concentrated area around the probe tip, designed to trigger the nucleation of deformation twins in a constrained area which enables easy in-situ observation. In contrast, during uniaxial deformation, the nucleation sites of deformation twins are statistically random, which make the observation of the initial stage such events very difficult.

6.5.1 Fabrication of single crystal thin film/H-bar specimen

Performing STEM observation in a SEM requires the specimen to be electron transparent at an accelerating voltage of 30kV. A slice sample (~500 μm thick) was first sectioned from a bulk single crystal using a wire saw with minimal speed and load. Then the slice sample was mechanically polished and then chemically etched in order to remove the damage layer at the surfaces. A cross-sectional ion polisher was utilized to cut a straight edge on the specimen. Then H-bar type foils (typically 20 μm in length, 10 μm in width and <150 nm in thickness) can be prepared by sample thinning using FIB. The fabrication procedure of H-bars is identical to the thinning steps for TEM sample preparation. A lower voltage and current should be used for the final milling steps to minimize FIB induced damage at the sample surfaces.

6.5.2 Applications: Twin nucleation and crack propagation from a notch tip

Notch tips are well recognized as “stress concentrators” in a stressed solid with dislocations piled up in their vicinity, which can serve as potential homogeneous or heterogeneous nucleation sites for deformation twins. Despite the intensive studies on the onset of twinning, twin nucleation at a dynamic notch tip is less studied, in hcp metals in particular. An in-situ STEM approach was used in this study to investigate deformation mechanisms in the vicinity of a notch tip. Single crystal Mg thin lamellae with basal plane V-notches were prepared by FIB. During the test, a probe ~600 nm in diameter at the tip was used to apply loads to induce stress concentration near notch-tips. The dynamic processes of twin nucleation and crack propagation at the notch tip were monitored under real time by the STEM detector inside a high-resolution SEM (FEI Scios DualBeam) operating at 30 kV. An image of the experimental setup is shown in Fig. 6.14 (a). The probe stressing direction is parallel to the viewing direction, i.e. perpendicular to the thin specimen surface. As the probe was moving downwards, the specimen was fracture tested under Mode III (anti-plane shearing) loading. Fig. 6.14 (b) is a schematic illustrating this testing mode. The simulated equivalent plastic distribution in the specimen at full loading condition is shown in Fig. 6.14 (c). A STEM image showing the specially designed specimen during an in-situ fracture test is shown in Fig. 6.14 (d).

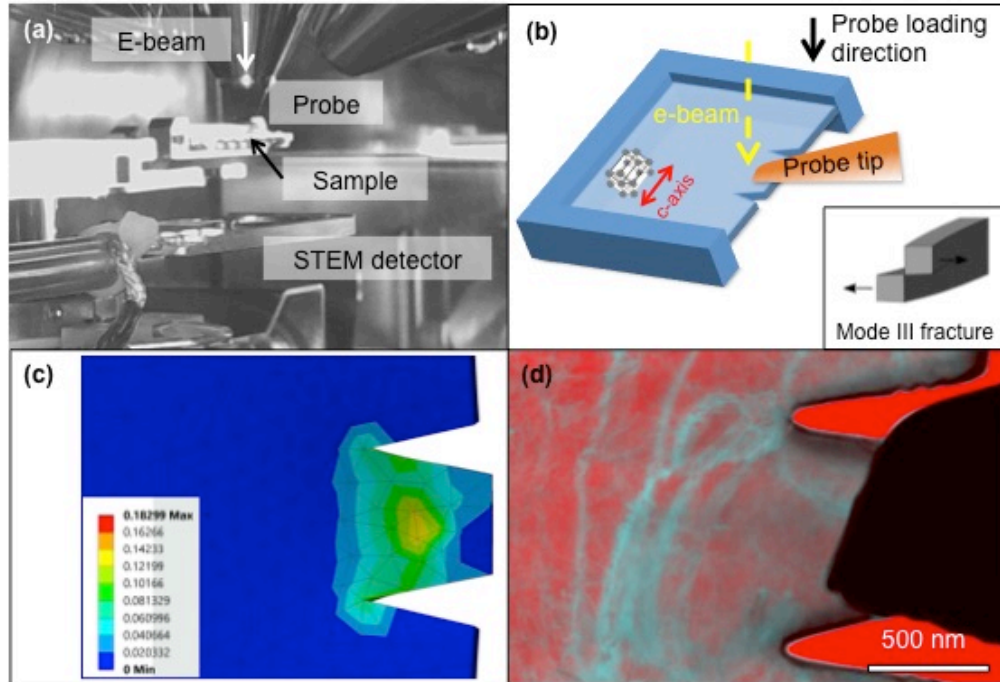


Fig. 6.14 (a) An image showing the apparatus for in-situ STEM testing in a SEM chamber; (b) A schematic illustration of the sample and the anti-plane shearing loading direction; (c) ANSYS simulated equivalent plastic strain distribution in the specimen when the probe moved downward by 500 nm; (d) STEM image of a specimen being tested. Contrast bands indicating the localized stress concentration near the notch tip.

By employing the in-situ STEM stressing method described above, nucleation of twins at basal plane notch tips in a twin-free single crystal Mg was successfully captured during a mode III fracture test. A series of in-situ STEM images in Fig. 6.15 reveal the dynamic process during notch tip deformation. At the early stage of deformation, Fig. 6.15 (a) - (c), contrast bands caused by localized strain concentrated near the notch tip. A twin nucleated at the notch tip was observed in Fig. 6.15(d). Twin nucleation altered the local strain distribution near the notch tip, as suggested by the movement of contrast bands

from the notch tip towards the twin tip. Continuous stressing caused the notch tip twin to grow in both the length and width directions. Finally, the notch tip propagated from the FIB fabricated notch tip, as marked by red circles in Fig. 6.15 (f) - (i).

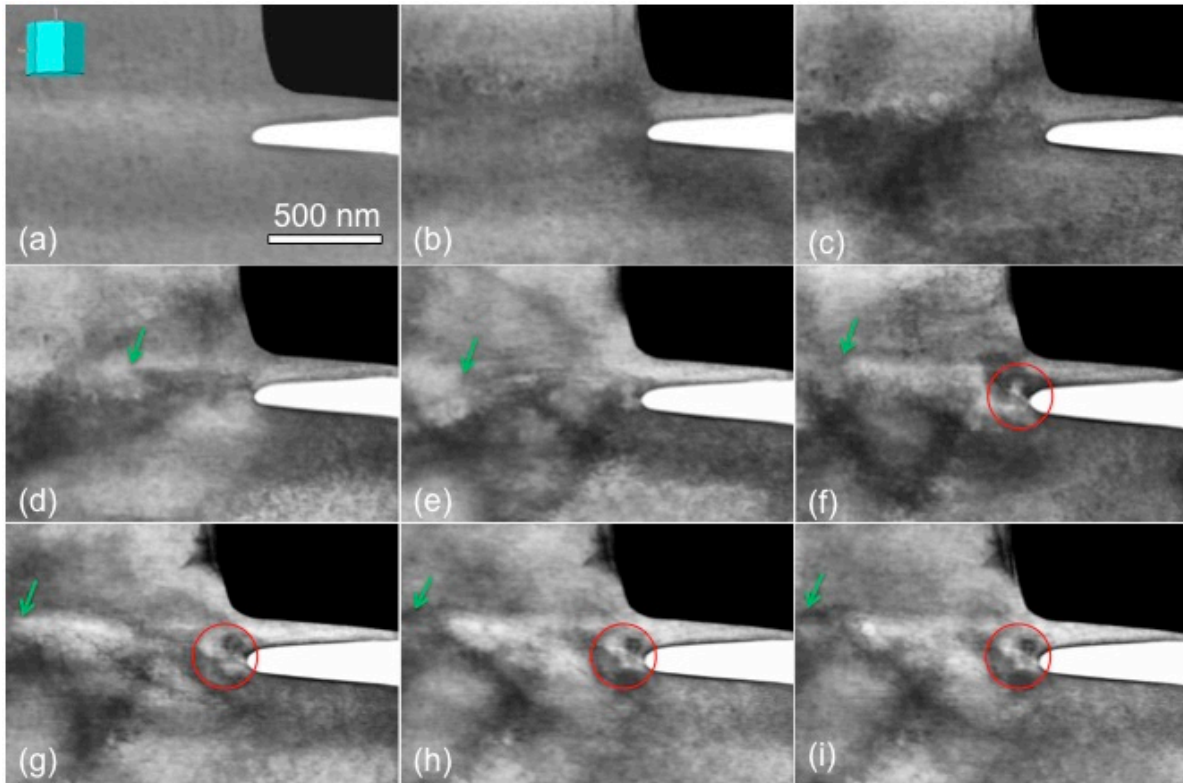


Fig. 6.15 (a)-(i) In-situ STEM images recorded during an in-situ fracture test with increasing strain. The twin nucleated at the notch tip is pointed out by green arrows and notch tip propagation steps are marked by red circles.

EBSD analysis of the fracture tested single crystal Mg revealed the twins being formed at the notch tips are $\{10\bar{1}2\}$ tensile twins with $\sim 86^\circ$ twin-matrix misorientation. EBSD band contrast figures and the corresponding IPF (inverse pole figure) colored maps

are shown in Fig. 6.16. IPF maps reveal that different $\{10\text{-}12\}$ twin variants formed near basal plane notch tips. Besides, matrix on two sides of the twins show subtle difference in grain orientations, as seen from the IPF maps in Fig. 6.16, suggesting local strains in the vicinity of twins.

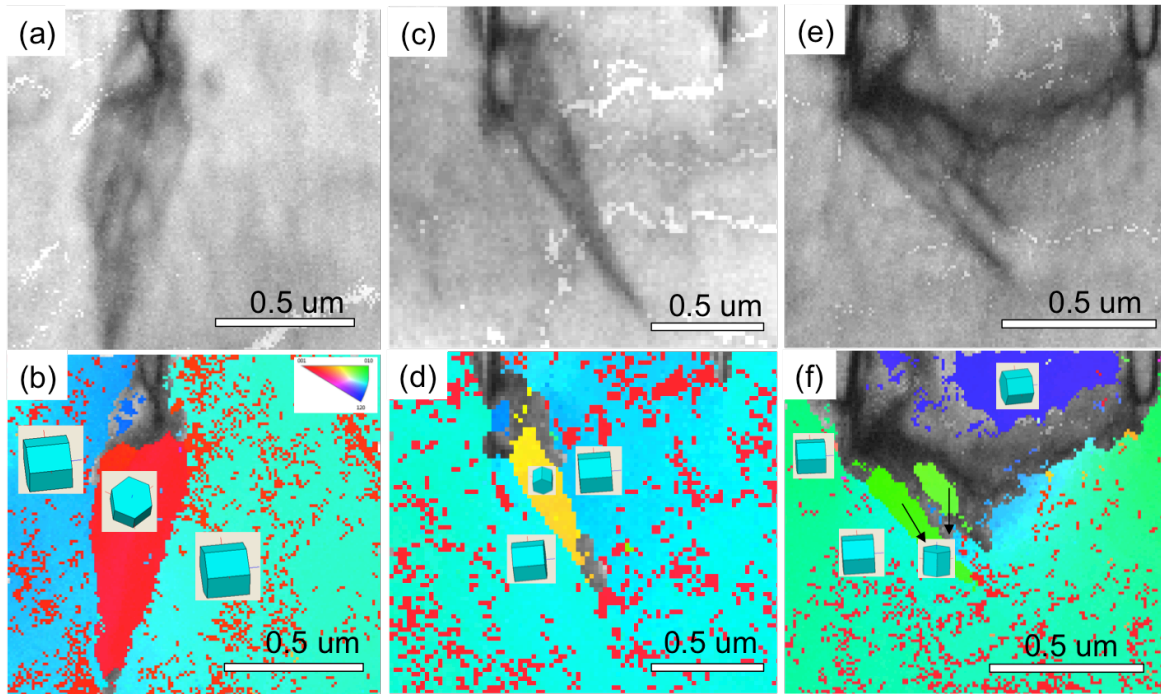


Fig. 6.16 (a) (c) (d) EBSD band contrast figures, and (b) (d) (e) the corresponding IPF colored maps (constructed on the plane normal direction) of in-situ fracture tested single crystal Mg specimens show characteristics of the twins formed at notch tips.

To understand the microstructure of the notch tip twin and its surrounding matrix, a specimen was tested and stopped soon after twin nucleation event was recorded in-situ. Post mortem TEM results are shown in Fig. 6.17 and Fig. 6.18. A bright field image taken on $[2\text{-}1\text{-}10]$ zone axis and the corresponding diffraction pattern (from the region marked by a

white dashed circle) revealed the nucleation of a $\{10\bar{1}2\}$ tensile twin ~ 20 nm in width and ~ 200 nm in length. Two beam conditions with $g=01\bar{1}1$ and $g=0002$ of the same sample region were shown in Fig. 6.17 (c) and (d), respectively. According to the $g \cdot b = 0$ distinction criteria, dislocations with all types are visible when the $g=01\bar{1}1$ diffraction vector is used, while only $\langle c \rangle$ or $\langle c+a \rangle$ type dislocations can be seen when $g=0002$ diffraction vector is chosen. By comparing the bright field images taken with different diffraction vectors, line contrasts parallel to the traces of basal planes can be observed in Fig. 6.17 (c), while no line contrasts are present in Fig. 6.17 (d). Therefore, deformation of the matrix near the notch tip generated mostly $\langle a \rangle$ -type dislocations on its basal planes. No obvious $\langle c \rangle$ or $\langle c+a \rangle$ type dislocations are observed near the notch tip after twin nucleation, which is understandable considering the high critical resolved shear stress (CRSS) of non-basal dislocations in Mg at ambient temperatures.

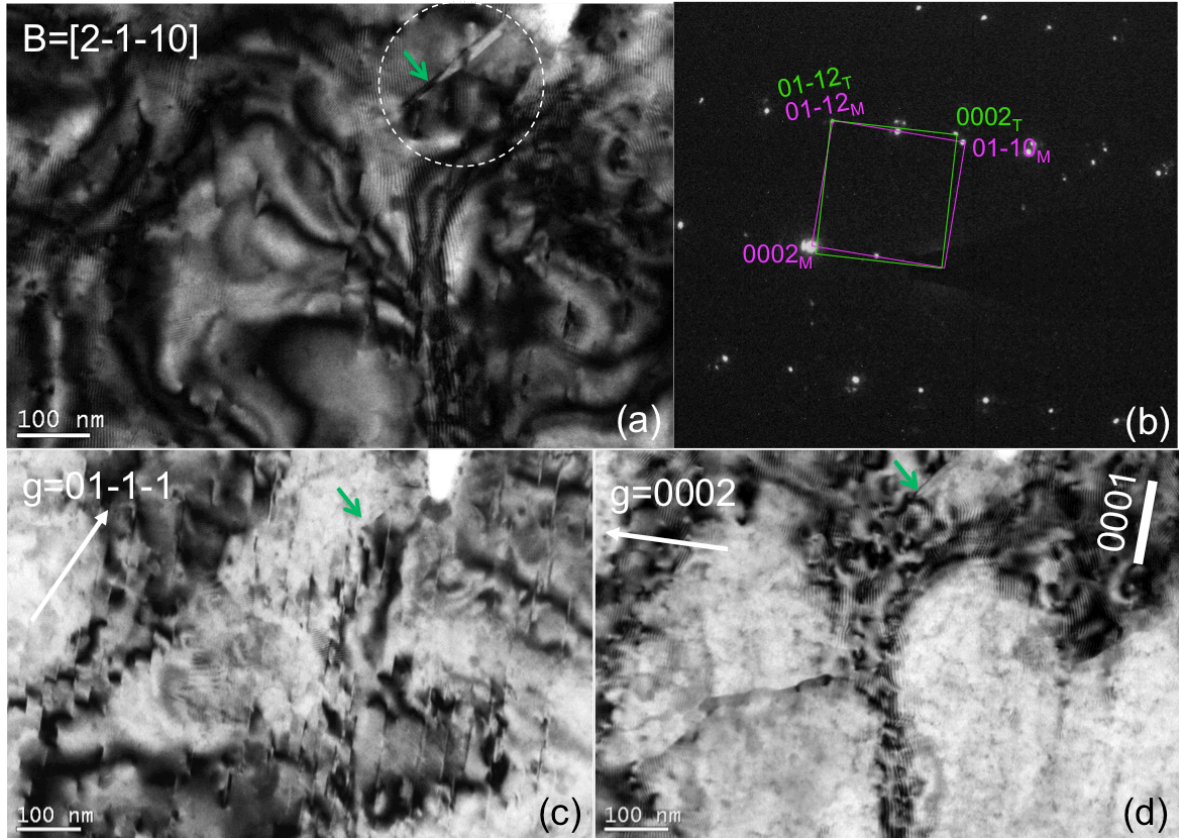


Fig. 6.17 Post mortem TEM characterization of a fracture tested specimen near the notch tip. (a) Bright field image on $B=\{2-1-10\}$ zone axis; (b) selected area diffraction pattern taken from the region enclosed by a white dashed circle in (a); (c) and (d) are two beam bright field images with diffraction vectors $g=01-1-1$ and $g=0002$, respectively.

The twin tip and notch tip were further characterized using high resolution TEM. Defects are readily visible in these regions. Fig. 6.18 (a) shows the matrix in front of a twin tip. High density of stacking faults on the basal planes present near the twin tip, while a much lower density of stacking faults was detected away from the twin. Whether these stacking faults involved in the nucleation of notch tip twins, or general twin nucleation mechanism, needs further investigations. Fig. 6.18(b) shows the microstructure at a notch

tip. The FIB fabricated crack is at the bottom left in the image. The twin boundary near the notch tip is outlined by a red dashed line.

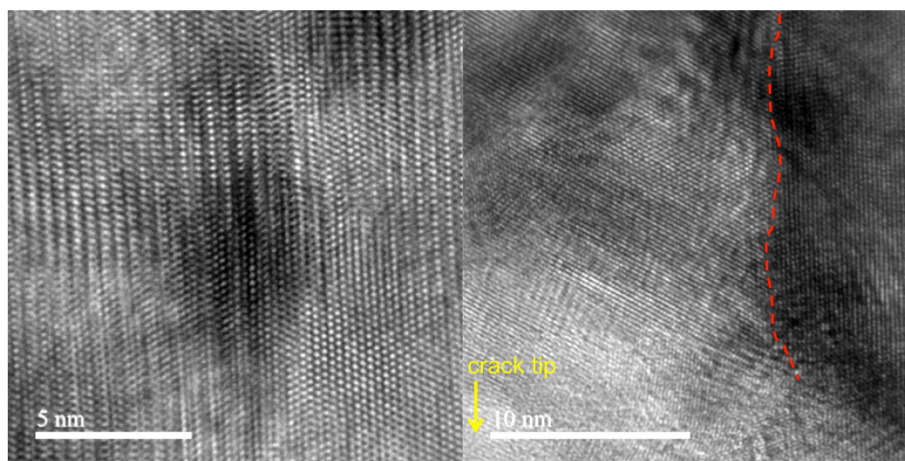


Fig. 6.18 High-resolution TEM images of the (a) twin tip and (b) notch tip regions. Red dashed line marked the twin boundary at the notch tip.

A fracture test was also performed with a twin boundary present near a notch tip to probe the influence of twin boundaries on the notch tip behavior. Twin boundary migration and nucleation of a secondary twin inside the pre-existing twin at the notch tips were observed. Fig. 6.19 shows the STEM images recorded during an in-situ fracture test near a straight $\{10\text{-}12\}$ twin boundary. With increasing strain, the initially straight twin boundary (marked by white dashed lines) migrated towards the matrix and became curved (red dashed lines). Post mortem EBSD analysis also revealed the bulging of the twin boundary. A low-angle subgrain boundary was also formed in the area contacting the probe, due to the large local strain during the process. The nucleation of a secondary twin at the notch tip inside a $\{10\text{-}12\}$ twin (where the notch tip is closely parallel to the prismatic plane of the

twin) was observed in another fracture test. Post mortem EBSD band contrast and IPF colored map are shown in Fig. 6.20 demonstrated the secondary twin is in the same crystal orientation with the matrix.

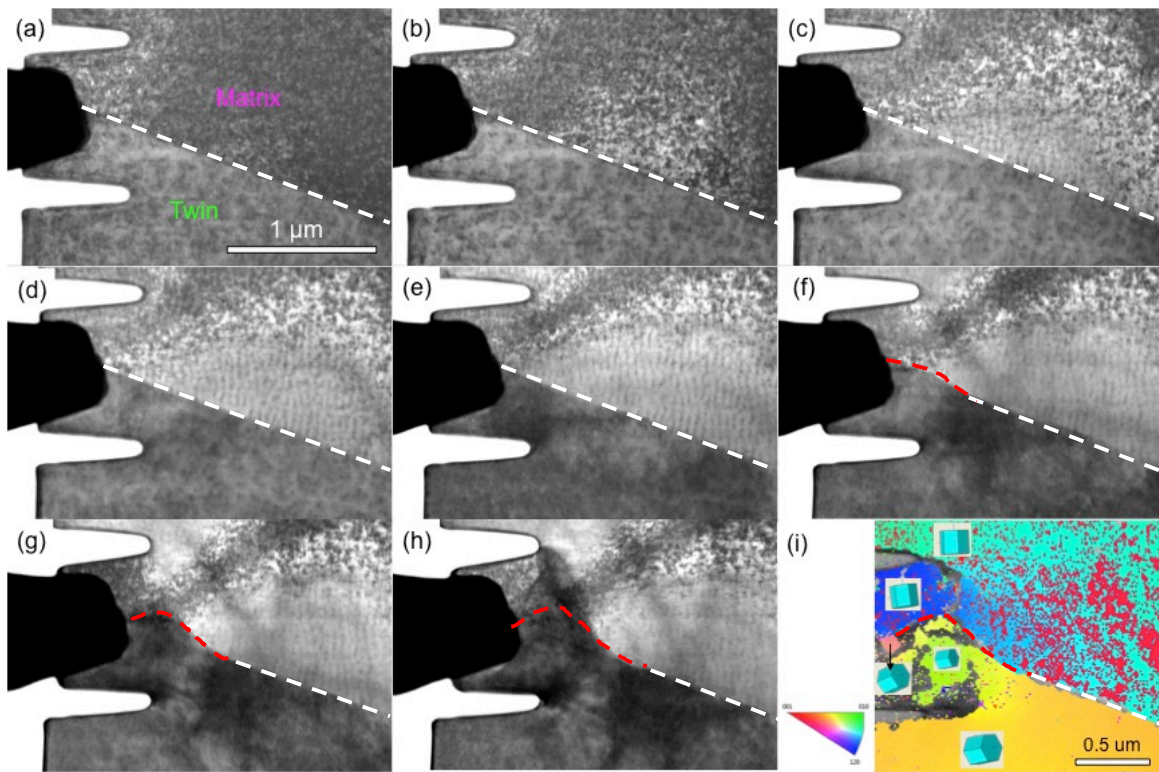


Fig. 6.19 Process during a fracture test with a initially straight twin boundary near the notches. (a) - (h) STEM images recorded during in-situ loading; (i) Post mortem EBSD characterization after the fracture test.

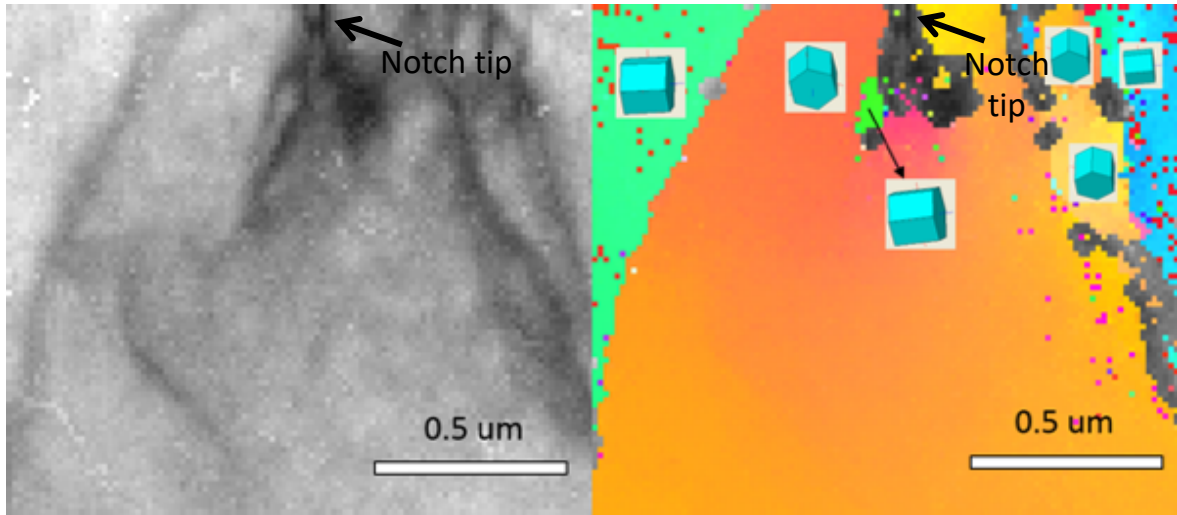


Fig. 6.20 EBSD analysis of a notch tip fracture tested specimen with a notch tip inside the twin. (a) The band contrast figure; (b) the corresponding EBSD IPF colored map. Only the tip of notch is shown in these images, as pointed to by a black arrow.

6.6 Summary

In this chapter, some quantitative and qualitative in-situ electron microscopy methods used or developed in our group were discussed. Some of our preliminary in-situ testing results have been briefly introduced as examples to demonstrate the application of these techniques to solve materials related problems. The in-situ deformation techniques, sometimes in combination with conventional ex-situ characterization, are essential tools to shed light on the correlation between the mechanical properties and dynamic microstructural changes. Challenges remain in, for example, in-situ characterization of the microstructure and elemental distribution at the atomic level under mechanical stimuli and ultrafast imaging with high signal-to-noise ratio. In addition to the development of the in-

situ electron microscopy technique itself, improved data storage and processing capability is necessary once fast in-situ data acquisition become routine.

Chapter 7 Future work

Microstructures have significant effects on the deformation mechanisms and mechanical behavior of Mg. In this research, we have demonstrated that grain morphology, grain size, twin meshes and solid solution alloying can all be tuned to influence the mechanical responses Mg. Among these microstructural parameters, the strengthening and toughening effects of twin meshes observed in pure Mg motivates our future activities to pursue optimized twin meshes in Mg alloys.

Our on-going first principle calculations (by Zhifeng Huang and Yang Hu in Prof. Rupert's group) in more than 20 binary solid solutions will be used to help select solute atoms and their concentrations that are favorable for the formation of fine spaced twin meshes. On the experimental side, we will take advantage of the state-of-the-art TEM and STEM facility to probe the alloying effects of selected alloying elements. Particular focus will be paid to understand the segregation of solute atoms at interfaces or other defects, and the roles played by these segregating alloying elements on the nucleation, propagation and growth of different types twins.

To design twin meshes for optimal strength and toughness, future work will be conducted to understand the strengthening and toughening mechanisms induced by particular twin mesh features. There is growing evidence in the literature [39, 135] that, similar to the FCC and BCC metals, twin-twin interactions in HCP metals resemble twin-slip interactions in the sense that they can facilitate or impede thickening of participating twins. Slip-twin interactions lead to strengthening in HCP metals by three well accepted mechanisms: 1) texture hardening due to lattice reorientation by twins, 2) the Basinski

hardening mechanism due to transmutations of dislocations from glissile to sessile [136, 152], and 3) the obstacle effect of twin boundaries on dislocation slip [138].

Moreover, in view of the reported studies, there is a debate regarding whether or not certain twin-twin intersections will lead to fracture. Mahajan [153] shows in a BCC structured Mo alloy the strains of crossing twins were accommodated by slip and twinning without forming micro-cracks. It was also reported in FCC metals that the twin crossing is completed by secondary twinning inside the crossed twin [40]. Compared to studies in cubic structured metals, there is far less evidence reported on the twin-twin interactions in HCP metals. More recently, Yu et al. [135] reported an experimental and theoretical study on twin-twin interactions in Mg. They classified twin-twin intersections into two categories: two twins sharing the same $\langle 11\text{-}20 \rangle$ zone axis, and two twins having different $\langle 11\text{-}20 \rangle$ zone axes. They conclude that, in both cases, “apparent crossing”, defined as twins impinging independently on each side of the crossed twin with the formation of twin-twin boundaries containing boundary dislocations, occurs instead of twin transmission. They also indicated that under cyclic loading, twin-twin interactions caused the formation of quilted-looking, apparent crossing, and double twins or secondary twins in the Mg structure, which can be correlated with material hardening. Moreover, recent work by Lentz et al. [51] showed that, although double twins have often been correlated with crack nucleation in pure Mg, a lack of easy $\langle c+a \rangle$ dislocation slip is the intrinsic reason for this observation. By introducing 4 wt% Li in Mg, significant strengthening can be achieved by stable $\{10\text{-}11\}$ - $\{10\text{-}12\}$ double twinning without sacrificing formability.

Therefore, as a next step in the twin mesh study, in-situ electron microscopy deformation method can be used to probe the microstructural evolution of materials with particular forms of twin-twin intersections upon deformation and seek evidence on whether or not crack will nucleate. Different forms of twin meshes can be isolated from a twin meshed polycrystal in combination with the EBSD technique. Meanwhile, with this study we may be able to give answers to which types of twin meshes give rise to the best combinations of strength and toughness.

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