Full length article

Precipitation strengthening in nanostructured AZ31B magnesium thin films characterized by nano-indentation, STEM/EDS, HRTEM, and in situ TEM tensile testing

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Thin magnesium (Mg) AZ31B (Mg-3Al-1Zn-0.4Ca-0.3Mn-0.2Si in wt%) foils were sputter deposited, aged, and mechanically tested at quasi-static strain rates. The as-deposited microstructure is a hexagonal close-packed solid solution with no second phase particles and a strong basal texture. Subsequent aging at 200 °C for up to 170 h led to nanocluster and precipitate formation that was characterized by TEM and significant hardening that was characterized by nanoindentation. Precipitates containing Al, Mn, and Mg were clustered around grain boundaries and dislocations in samples aged at 200 °C for 65 h, but were distributed uniformly in a sample aged at 400 °C for 30min. The peak hardness was greater than 2 GPa and is explained by a submicron grain size and precipitation strengthening. In situ straining TEM experiments were performed on samples aged at 200 °C for 65 h, as well as on samples aged at 400 °C for 30min, to examine the effects of nanoclusters and precipitates in obstructing dislocation motion. Dislocation glide along basal planes was identified as the main deformation mechanism in samples aged at 200 °C and 400 °C, and pinning of dislocations by precipitates was observed in the sample aged at 400 °C. Dislocations are assumed to cut through the nanoclusters in the 200 °C sample. The fracture mechanism was consistently trans-granular cracking, regardless of the thermal treatment history, and twins were not observed to nucleate or propagate within these fine-grained, highly textured samples.

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1. Introduction

Intermetallic nano-precipitates are known to improve the strength of metallic alloys. A fine distribution of precipitates can impede dislocation motion which strengthens the alloy directly [1–3]. Nano-precipitates can also pin grain boundaries during thermal processing, which impedes grain growth, limits the final grain size, and thereby inhibits plastic deformation indirectly [4–6]. Both effects can increase quasi-static yield strengths and flow stresses but their impact will vary significantly depending on the size, the chemistry, the structure, the crystallography, and the distribution of the precipitates. Precipitates can also play an important role at high strain rates and it’s necessary to understand their impact to predict dynamic and spall properties [7]. For example, recent studies of magnesium alloys have shown that nano-precipitates and micro-precipitates can act as sites and paths for void nucleation, crack initiation and subsequent crack propagation during spall failure [8].

AZ31B is one example of a metallic alloy with intermetallic precipitates, and this Mg-based alloy is being studied as a promising light weight alloy for structural applications in several industries such as automotive, aerospace, and defense. For military applications, such as armor, high strain rate behavior is very important [9–12]. Unfortunately, the presence of manganese in this alloy, even as a minor alloying element, leads to the formation of large Al-Mn intermetallic particles that degrade spall strength [8]. Further still, these particles cannot be dissolved by conventional solution heat treatments because Mn is essentially immiscible in Mg, below Mg’s melting point. To overcome this challenge and to generate foils for complementary high rate mechanical testing using laser shock and plate impact, 10 μm thick AZ31B foils were sputter deposited to obtain metastable, single-phase, polycrystalline Mg samples in which all alloying elements are in...
solution. These samples were then isothermally aged to nucleate and grow intermetallic precipitates, and the particles within the resulting foils were characterized by transmission electron microscopy (TEM). The mechanical properties of the AZ31B foils were characterized in this study using nano-indentation and in situ tension testing within a TEM.

2. Experimental

10 μm thick samples were deposited at a rate of 4.3 nm/s onto polished Al substrates using DC magnetron sputtering from an AZ31B (Mg-3Al-1Zn-0.4Ca-0.3Mn-0.2Si in wt%) target. Sputtering was performed in a vacuum chamber evacuated below 2 × 10⁻⁶ Torr and then backfilled to 1.5 mTorr with Ar (99.999% pure). Prior to the deposition of samples, the target was pre-sputtered onto a shield so as to stabilize its surface composition and thereby enable the growth of foils with the desired target composition [13]. After deposition, foils were detached by bending the substrate slightly.

Heat treatments were performed in a tube furnace. To minimize sample oxidation, a low vacuum (less than 200 mTorr) was maintained for 20 min before backfilling the tube with high purity argon and over-pressuring it to approximately 780 Torr. The AZ31B PVD foils were aged at 200 °C for various times ranging from 5 to 170 h. 200 °C was chosen as it is close to the maximum temperature above which Al goes into solution in Mg, based on the Mg-Al phase diagram [14]; it also mimics the aging studies performed by Gonzales et al. [15]. Another set of samples were also aged at 400 °C for 30 min. All samples were cooled to room temperature inside the furnace.

Orientation mapping was performed in a Tescan MIRA-3 FEG Scanning Electron Microscope (SEM) coupled with an Electron Back Scattered Detector (EBSD) operating at 20 keV. Transmission Electron Microscope (TEM) samples were prepared by ion milling full thickness samples using a Precision Ion Polishing System (PIPS II) distributed by GATAN. TEM observations were conducted in a JEOL 2010 and a Philips CM300FEG. Scanning TEM High Angle Annular Dark Field (STEM/HAADF) pictures were taken (when not specified) with a camera length of 77 mm to maximize the Z-contrast and to reduce the electron diffraction coming from the local elastic stress. Grain sizes were calculated using both low and high angle grain boundaries (misorientation angle higher than 5°). Precipitates within TEM images were analyzed using the software ImageJ. For each analysis, the background of the picture was subtracted and a threshold was applied so that precipitates appear black and the matrix is white. Then the Analyze Particles ImageJ plugin was used to identify the total area, the average diameter, the longest dimension, the shortest dimension, and the corresponding aspect ratio for each precipitate. The distance between each precipitate, and its nearest neighbor, and the average distance between precipitates were calculated using the ImageJ plugin developed by Haeri et al. [16]. Only precipitates that are fully contained in each image were analyzed; thus, particles at the edges of each image were ignored.

To assess mechanical behavior, TEM samples were strained at quasi-static strain rates in a TEM using an in situ straining stage developed by GATAN. Nano-indentation was conducted using the iNano from Nanomechanics at an effective strain rate of 10⁻¹/₅ and a maximum force of 45 mN that led to a penetration depth close to 1500 nm. Prior to indentation, testing samples were mounted on glass slides and glued using a thin layer of epoxy. All mechanical tests were performed at room temperature. To calculate Young’s Modulus using the Oliver and Pharr method [17] we assumed a Poisson’s ratio 0.3 and a Young’s modulus and Poisson’s ratio of 1140 GPa and 0.07 for the diamond tip. Bulk samples of pure Mg and AZ31B, that were either hot-rolled or extruded for other studies [18], were also characterized using nano-indentation for comparison.

3. Results

3.1. Microstructure of the as-deposited AZ31B foils

During traditional bulk processing of AZ31B plates, that involves casting and hot rolling, elongated Mn-Al intermetallic particles form and range in width from 2 to 5 μm and in length from 50 to 100 μm, as shown in Fig. 1(a) [8,19–21]. Annealing at 500 °C for 2 h cannot dissolve these particles as shown in Fig. 1(b). In contrast, sputter deposition of AZ31B yields foils with a much finer grain size and a lack of precipitates, including Mn-Al particles, as shown in Fig. 2(a) and (b). The samples have a strong basal textured with the [0001] direction pointing perpendicular to the foil’s surface (Fig. 2(d)). The in-plane grain size varies from 100 to 600 nm, and the Inverse Pole Figure (IPF) map in Fig. 2(c) (obtained using EBSD within an SEM) shows only slight rotations around the [0001] direction for adjacent grains, thereby producing only low angle grain boundaries. The combination of a strong texture and low angle grain boundaries minimizes the driving force for grain growth and yields a microstructure that is very stable during the subsequent aging study [22,23]. However, the sharp texture prevented grain boundaries from being detected efficiently using the SEM/EBSD technique (Fig. 2). During TEM analysis, many grains are smaller than the thickness of the electron transparent area of the TEM samples, leading to an overlapping of grains that makes grain size measurement challenging. Lastly, nano-voids are present along the columnar grain boundaries but only in the top 4–5 μm of the 10 μm thick foils. Thus, all mechanical characterizations and the majority of microstructural characterizations were performed on regions near the substrate side of the foils.

3.2. Hardness and microstructure of the aged PVD AZ31B foils

Using 25 indentation tests per sample, Young’s modulus and hardness were calculated and plotted versus depth for each sample, and examples of such curves are shown in Fig. 3(a) for a sample aged for 23 h at 200 °C. The standard deviation decreases with depth as expected [17], and there appears to be a small peak in hardness during the first 100 nm of penetration, which we attribute to the presence of a thin oxide layer or hardening at small depths as reported earlier [24,25]. Both hardness and modulus decrease slowly with depth, which may be due, in part, to the thin epoxy layer used to mount the substrate. For purposes of comparison, an average hardness was quantified for each sample at a penetration depth of 400 nm, and the values are plotted in Fig. 3(b) as a function of aging time at 200 °C (red data points). Error bars shown for each average are standard deviations. The hardness peaks at 2.1 GPa after 60 h of aging and then decreases slowly with time. The sample heat treated at 400 °C for 30 min exhibits a hardness of 1.9 GPa, close to the peak hardness for the samples aged at 200 °C, even though it has a larger grain size.

Nanoindentation tests were also performed on bulk samples of pure Mg and AZ31B for comparison. Pure Mg, that was hot-rolled at 160 °C and has a grain size of 50 μm, yields an average hardness of 0.68 ± 0.05 GPa and is softer than all of the alloyed samples, as expected [18], AZ31B, that was hot-rolled at 160 °C AZ31B and has an average grain size of 32 μm, yields an average hardness of 0.95 ± 0.11 GPa and is softer than the as-deposited foils (1.13 ± 0.06 GPa), which have a submicron grain size. Lastly, AZ31B, that was Equal Channel Angular Extruded (200 °C) and has an average grain size of only 2.5 μm [18], yields an average hardness of...
1.33 ± 0.05 GPa and is harder than the as-deposited foils. These bulk samples suggest grain size and precipitates both play important roles in determining hardness values.

Fig. 4 displays TEM analysis conducted on four samples aged at 200 °C for 6.5, 45, 109 and 150 h. While precipitates are not easily observed during bright field TEM imaging after only 6.5 h of aging (Fig. 4(a)), they can be seen using a STEM/HAADF technique with a camera length greater than 100 mm so as to add Z-contrast to the diffraction contrast. They are observed easily in bright field mode after 45 h of aging (Fig. 4(b)), and have nucleated mostly along pre-existing dislocations and grain boundaries. After 109 h of aging (Fig. 4(c)), some precipitates can be seen inside grains, in addition to those along dislocations and grain boundaries. A similar spatial distribution of particles is observed for the sample aged for 150 h (Fig. 4(d)).

Precipitates in the two aged samples that showed high hardness values were characterized in more detail using the STEM/HAADF pictures presented in Fig. 5(a) and (b). These correspond to samples aged at 200 °C for 65 h and at 400 °C for 30 min, respectively. As can be seen in the images and in the data in Fig. 5, the precipitates are less numerous, smaller (Fig. 5(c)), and more elongated (Fig. 5(d)) in the sample aged at 200 °C, compared to the sample aged at 400 °C. The average precipitate diameter is 8.4 ± 3.6 nm in the 200 °C, 65 h sample, while it is 12.6 ± 6.7 nm in the 400 °C, 30 min sample. The area percentage of precipitates is smaller in the sample aged at 200 °C (1.6% in Fig. 5(a)), compared to the sample aged at 400 °C (8.1% in Fig. 5(b)). In terms of spatial distributions of the precipitates, the average distance between precipitates (Fig. 5(e)) is larger for the 200 °C sample compared to the 400 °C sample, but the distance between each precipitate and its nearest neighbor (Fig. 5(f)) are similar in both samples. This disparity can be attributed to the fact that precipitates in the sample aged at 200 °C are located mainly along dislocations and grain boundaries and hence nearest neighbors are closer than if they were distributed evenly throughout the matrix.

Using a STEM/HAADF technique and higher magnifications, local elemental segregation can be seen in the samples aged at 200 °C. Fig. 6(b) shows many nano-clusters smaller than 4 nm (black arrow) in the sample aged for 65 h, that are absent in the sample aged for 0 h (Fig. 6(a)). We differentiate nano-clusters from precipitates here by the fact that the clusters are much smaller and cannot be observed at high resolution due to a lack of clear interfaces with the matrix. The diameters of these clusters are reported in Fig. 6(c). The smallest clusters are assumed to have diameters above 1 nm, as ones smaller than that could not be clearly identified and were considered to be a background artefact. The average distance between the 10 nearest clusters is 33 ± 11 nm, and the distance between each cluster and its nearest neighbor is 16 ± 9 nm (Fig. 6(d)). In contrast, in the sample aged at 400 °C, nanoclusters are absent, but a second set of larger-scale precipitates can be seen when imaging at lower magnification (Fig. 6(e)). These precipitates range in diameter from 45 to 250 nm (Fig. 6(g)) and are randomly distributed. Also, they are present along the grain boundaries, which is not the case for the smaller precipitates. Moreover, they lead to a lack of smaller precipitates around them, as can be seen in Fig. 6(f).
STEM/EDS was performed to identify the composition of precipitates in the samples aged at 200 °C for 65 h and 400 °C for 30 min. Results are similar for the two samples, and an exemplary image is shown in Fig. 7 for the sample aged at 400 °C. EDS mapping (Fig. 7(b)) of the area presented in Fig. 7(a) shows Al and Mn are segregated to the precipitates, independent of their sizes. Zn is distributed fairly homogeneously. Six local measurements were performed in the matrix (Fig. 7(c)) and in the precipitates (Fig. 7(d)) and they confirm that Mn is only present in the precipitates. They also show a large increase of Al content to minimum values ranging from 2 to 5 wt% in the precipitates. (The measured values are considered very low estimates given the precipitates do not extend...
through the full thickness of the TEM samples and EDS analysis averages across the full specimen thickness). Chemical segregation could not be identified in the nanoclusters due to the 4 nm step size used in the analysis.

Approximately ten precipitates with diameters between 5 and 45 nm were studied at high resolution in the TEM for samples aged at 200 °C, 65 h and 400 °C, 30 min. Those in the sample annealed at 200 °C were primarily at the grain boundaries while those in the sample annealed at 400 °C were within the grain interiors. Semi-coherent particle/matrix interfaces were observed, as shown in Fig. 7(e), with stacking faults at the interfaces, surrounded by two dislocations (Fig. 7(f)). A few a type dislocations can be observed in the matrix surrounding these precipitates as well (Fig. 7(g)).

The increase in grain size in the sample aged at 400 °C for

Fig. 4. Bright Field (BF) and STEM/HAADF pictures taken at different magnifications in 4 samples aged at 200 °C for a) 6.5 h, b) 45 h, c) 109 h, and d) 150 h.

Fig. 5. Precipitate geometries and distributions in samples aged at 200 °C for 65 h and at 400 °C for 30 min. a) and b) STEM/HAADF pictures taken in the sample aged at 200 °C and 400 °C, respectively. c) Precipitates diameters. b) Precipitates aspect ratio. c) Average distance between precipitates. d) Distance between each precipitate and its nearest neighbor. All numbers in brackets are averages.

30 min, compared to samples aged at 200 °C, is highlighted by the SEM/EBSD image in Fig. 8(a). This EBSD map has the same magnification as the EBSD map for the sample aged at 200 °C (Fig. 2(c)) and shows an in-plane grain size that is approximately 2–3 times larger. For the sample heated at 400 °C, grains are well defined and the basal texture appears to have shifted from the sample normal (Fig. 8(b)). However, this shift of the c-axis, compared with the 200 °C annealed samples (Fig. 2(d)), is attributed to a misalignment of the foils in the SEM during the mapping and not to a change in crystallographic texture of the samples aged at 400 °C.

### 3.3. In situ TEM mechanical testing

**In situ** TEM tensile tests were conducted using two sputter deposited AZ31B samples. The first one was aged at 200 °C for 65 h, to generate mechanical properties similar to those for samples showing the hardness peak value. The second sample was aged at 400 °C for 30 min, which contained more and larger precipitates within the grain interiors, no nanoclusters, and a similar hardness. In both samples, the main deformation mechanism activated within the field of view, during **in situ** TEM straining, was glide of type dislocations in basal planes. Dislocations appear to nucleate at grain boundaries and triple junctions, with the latter being more common.

In the 200 °C sample with fewer and smaller precipitates within the grain interiors, but many nanoclusters, we see evidence of dislocations gliding quickly across the grains with limited bowing as illustrated in Fig. 9(a); they are likely cutting through the nanoclusters. One can see changes in contrast within the main grain over the 1.2 s of imaging, suggesting a rapid increase in dislocation density. In contrast, for the 400 °C sample (Fig. 9(b)), dislocation motion is slower and with no rapid increase in contrast, the dislocation density appears to be relatively constant. Using arrows, Fig. 9(b) identifies dislocation motion through a sequence of images. Within the first 0.16 s, one dislocation is emitted at a corner of the grain boundary (bottom of the grain not shown in the images), glides on the basal plane, and then is pinned by precipitates located on the slip plane. The red arrows in the TEM pictures at 0 s and 0.16 s (Fig. 9(b)) identify the same location and highlight the dislocation in question. Then, a segment of this dislocation jumps from one pinned position to another between 0.16 and 13.76 s. This situation is represented by a schematic drawing in Fig. 9(e), allowing us to measure the angle (47°) the dislocation makes when bowing between two precipitates. The crystallographic orientation of the grain studied in the samples 200 °C and 400 °C during these **in situ** TEM straining experiments are reported in Fig. 9(c) and (d) and the loading direction is given in Fig. 9(f).

While the hardness testing and the vast majority of TEM characterizations were performed on the lower half of the foils, nearest the substrate side, one **in situ** observation was made in the upper half of the foils where nanovoids were present (Fig. 10(a)). This leads to our only observation of dislocation glide on a prismatic plane, but it occurred within a slip band that appeared in front of a propagating crack. Fig. 10(b)–(g) depict a sequence of 6 TEM pictures taken during this event and was imaged in a sample aged at 200 °C for 65 h. One can see a slip band forming on the (1 1 0 0) plane in the <1 0 0> direction between Fig. 10(b) and (e), followed by a thinning of the TEM foil prior to cracking (Fig. 10(f) and (g)). The slip band and the crack in Fig. 10 propagated from one nanovoid to another one, after crossing a grain boundary, suggesting the voids act to concentration stress and deformation. We believe slip and fracture are aided by the presence of nano-voids that appear at columnar grain boundaries during the late stages of sputter deposition. Thus, sputter conditions will be adjusted to avoid nano-void formation when producing samples for laser shock and plate impact experiments.

### 4. Discussion

As shown in Fig. 2, the rapid quench rates inherent to magnetron sputtering enabled deposition of a fully solutionized AZ31B
Precipitates and nanoclusters are absent from the as-deposited magnesium alloy and alloying elements such as Al, Mn, and Zn are contained within the crystal lattice as point defects. Most importantly, this processing method eliminates the large Mn-Al precipitates that are present within bulk AZ31B samples (Fig. 1) and cannot be removed from the bulk samples through solution treatments. The as-deposited solid solution and the ability to grow a fine dispersion of precipitates without larger Mn-Al particles suggests that sputter deposition is a promising method for fabricating thin foil specimens for laser shock and plate impact experiments. This argument, of course, assumes that process parameters can be adjusted to avoid the formation of nano-voids along the
columnar grain boundaries.

As expected, the sputter deposited foils have much finer grains than the bulk samples and they range in size from 100 to 600 nm. This smaller grain size is thought to be the main factor as to why the as-deposited AZ31B foils are harder (1.13 ± 0.06 GPa) than the bulk, hot-rolled pure Mg (0.68 ± 0.05 GPa) and AZ31B (0.95 ± 0.11 GPa).
samples (Fig. 3). These bulk samples have much larger average grain sizes of 50 μm and 32 μm, respectively. Only the extruded AZ31B bulk sample (1.33 ± 0.05 GPa) proved harder than the as-deposited foils, due to its combination of a relatively small grain size (2.5 μm) and precipitate hardening. However, once the sputtered foils are aged at 200 °C for just a few hours, their hardness rises significantly. The foils reach a peak in hardness of 2.1 GPa, after 65 h at 200 °C, and then begin to soften, gradually, with extended aging times. This classical aging behavior is attributed to the formation of nanoclusters and precipitates that eventually coarsen into larger particles with a greater average spacing between the particles. With no measurable variation in grain size or crystallographic texture during aging at 200 °C, the variations in hardness seen in Fig. 3 for the sputtered foils are attributed solely to the effects of alloying and precipitation strengthening.

As shown in Fig. 7, a clear segregation of aluminum and manganese can be observed in the STEM/EDS map and the local EDS measurements. The precipitates that form are rich in Mn and Al compared to the matrix and have slightly less Mg. Because the EDS measurements have limited accuracy and are influenced by the matrix both above and below any particle being analyzed, exact particle chemistries cannot be identified. However, the acquired data suggests that, contrary to literature reports for similar alloys containing aluminum and manganese, such as AZ91 [3,26–29], AZ61 [29,30], and AZ31 [31,32], the precipitates observed here are not Mg17Al12 but Mg-Al-Mn rich intermetallic instead. For the precipitates ranging in diameters from 5 to 20 nm, their interfaces with the matrix are semicoherent, with the lattice mismatch parallel to the interface being accommodated by an arrangement of stacking faults (Fig. 7(f)) and a few a type dislocations (Fig. 7(g)). The interface between the nanoclusters and the matrix was not identified.

While the chemistry and interfacial structure of these precipitates are similar for both the 200 °C and 400 °C annealing conditions, the location of the precipitates are different. Aging at 200 °C provides a higher thermodynamic driving force for nucleation than aging at 400 °C, due to the larger undercooling, but there is less thermal energy available to assist the diffusion that is required for nucleation of intermetallic particles [33]. Thus, precipitates form primarily at crystalline defect sites where diffusion is faster, such as grain boundaries and dislocations [33,34–36]. The stress field of dislocations [37] can also lower the activation energy for the nucleation of coherent precipitates and may be assisting nucleation. The resulting heterogeneous distribution of precipitates in samples aged at 200 °C can be seen in Fig. 4(b). Only at longer annealing times do precipitates appear within the grain interiors as shown in Fig. 4(c) and (d). In contrast, precipitates appear across the grain interiors after annealing for only 30 min at 400 °C. The defect assisted diffusion that assists precipitate growth at 200 °C is thought to lead to less symmetric precipitates as well. The aspect ratio of the precipitates formed after 65 h at 200 °C is 0.6 while it is only 0.8 for the precipitates formed at 400 °C in 30min.

Comparing the 200 °C, 65 h sample to the 400 °C sample also contains a second set of larger precipitates that measure 45–250 nm in diameter (Fig. 6(g)). These participate are randomly distributed within the grains but are distinct in that they appear to scavenge alloying elements from the surrounding area as smaller precipitates immediately around them are absent (Fig. 6(f)).

Given the peak in hardness during aging experiment is thought to mark the transition from dislocations cutting precipitates to dislocations bowing between precipitates, we can estimate the contribution to hardening in the 200C, 65 h sample using the average spacing of the nanoclusters or particles (33 nm) on the Orowan bowing equation. To estimate the shear stress needed to bow a dislocation between two precipitates, we consider the force applied to the precipitates by a single dislocation using the following equations:

\[ F = 2l \cos(\theta) \]  
\[ F = \tau b L \]

where \( F \) is the force, \( l \) the line tension of the dislocation, and \( \theta \) is the angle the dislocation line makes when bowing between the precipitates. The force on the bowing dislocation can be given by

\[ \Gamma = \frac{1}{2} G b^2 \]

By combining equations (1)–(3), the shear stress, \( \tau \), required to bow the dislocation between the precipitates can be expressed as:

![Image](https://placehold.it/300x200)

**Fig. 11.** Evolution of the shear stress required to push a dislocation past two precipitates as a function of the distance (L) between the precipitates. The curve is based on Equation (4). Error bars correspond to a ± 20° variation of the angle, \( \theta = 47° \), made by the dislocation around precipitates.
\[ \tau = \frac{Gb}{L} \cos \theta \]  

(4)

\( \tau \) is plotted in Fig. 11 as a function of precipitate spacing assuming a shear modulus \( G \) of 16.5 GPa, \( b \) equals 0.32 nm, and \( \theta \) is 47°, based on the measurement made using Fig. 9(e). The error bars are produced by letting the angle vary as \( \theta = 47° \pm 20° \) in Equation (4). For the sample aged for 65 h at 200 °C, an average nanocluster spacing of 33 nm yields an increment in the required shear strength of approximately 115 MPa (Fig. 11). This is equivalent to an increase of 230 MPa in the required normal stress using the Tresca criterion [38], and an approximate increase of 764 MPa in hardness following the calculation used in Ref. [39]. This increment accounts for much of the 970 MPa increase in hardness seen in Fig. 3, on going from the as-deposited state with a hardness of 1.13 GPa to the peak aged hardness of 2.1 GPa. In a similar manner, the 47 nm average spacing of the small particles in the sample aged for 30 min at 400 °C would account for 531 MPa of the 770 MPa increase in hardness for this sample, compared to the as-deposited state. The smaller particle strengthening and the larger grain size explains why the 400 °C, 30min sample exhibits a lower hardness than the 200 °C, 65 h sample.

During the in situ straining experiments, the c-axis is perpendicular to the loading axis for most of grains within the sputtered foils (Fig. 2). Since tension applied perpendicular to the c-axis is equivalent to compression being applied along the c-axis, one might expect to nucleate contraction twins during the in situ loading [40–43]. However, contraction twins are rarely observed at quasi-static strain rates because of the high Critical Resolved Shear Stress (CRSS) [6,11] and the very small grain sizes in the sputtered deposited samples that will inhibit twin formation significantly [44]. In agreement with these arguments, twinning was not observed during the in situ straining experiments, only dislocation glide and fracture.

When the samples aged at 200 °C were deformed in situ, the density of dislocations gliding in the basal plane grows quickly as one can see in Fig. 9(a). A grain is filled by dislocations in less than a second during the straining of a sample aged at 200 °C for 65 h. While dislocations are bowing between nanoclusters, as assumed above, or cutting through nanoclusters, they are gliding too quickly for their motion to be observed during the in situ straining. In contrast, when the sample aged at 400 °C for 30min was strained, we observed dislocations being emitted at a grain boundary and then being pinned by precipitates, as shown in Fig. 9(b). Between time 0.16s and 13.76s, a dislocation segment (highlighted by red arrows) moved from one pinned position to another one. After jumping between these two positions, the dislocation segment remained stationary as the local stress was insufficient to overcome the next row of precipitates. To accommodate additional macroscopic deformation, other dislocations were emitted from the same nucleation site.

Considering again the texture of these sputter deposited AZ31B samples, the loading axis during in situ straining should be parallel to most of the basal planes, thus leading to a very low Schmid factor for basal glide. If the alignment was truly parallel, prismatic glide should be the favored slip system [43,45,46]. However, very little prismatic glide was seen and no pyramidal slip observed, contrary to observations of deformation in Mg-2.7A-0.4Zn ternary single crystals compressed along the c-axis [47]. Two reasons are suggested. First, all basal planes may not be perfectly parallel to the loading direction, and sufficient shear stresses may be present on the basal planes to overcome the very low critical resolved shear stresses (CRSS) for basal slip [48,49]. Second, the thickness of the TEM thin foil might have hidden the prismatic activity. The prismatic planes are essentially perpendicular to the TEM specimen during straining so the distance traveled by a dislocation on a prismatic plane is very short, before it exits the TEM specimen. Prismatic glide was only observed in slip bands (Fig. 10) that were acting as crack propagation paths and locally were thinning the TEM foil. In these cases, stress concentrations may have raised the local shear stress above the CRSS for prismatic slip, which is reported to be 20 to 100 times higher than the CRSS for basal slip [50].

The friction mechanism observed in multiple sputter deposited AZ31B samples aged at 200 °C can be defined as dislocation-driven, trans-granular cracking along prismatic planes. Fracture was preceded in all samples by the formation of prismatic slip bands. The deformation depicted in Fig. 10, though, is unique among the multiple in situ experiments studied here in that it also involved nano-voids. The presence of these nano-voids is attributed to the fact that this sample was thinned from the top half of a 10 µm thick foil aged at 200 °C for 65 h. All other in situ samples were thinned from the lower half of aged samples. The sequence of 6 images in Fig. 10(b)–(g) show slip bands forming on the f(T 0 0) plane in the <TT 2 0> direction and propagated from one nano-void to another one, even through grain boundaries. This sequential motion suggests that the nano-voids which appear along the columnar grain boundaries act to concentration stress and deformation. When producing samples for laser shock and plate impact experiments, argon gas pressure and deposition rates will be lowered to avoid nano-void formation. More generally, we note that the trans-granular cracking observed in these TEM specimens is different than the intergranular fracture observed when large-grained Mg alloys [51–53] and other nano-crystalline metals [54] are deformed at low rates. This suggests that fracture behavior is likely a function of strain rate, grain size, structure, and composition, as observed in other alloy systems [54,55].

5. Conclusion

AZ31B magnesium alloy samples were successfully vapor deposited into a fully solutionized state using a single sputter target. Large Mn-Al particles and all possible intermetallic precipitates were absent in the 10 µm thick, as-deposited foils. When these basal-textured foils were aged at 200 °C for 65 h, nanoclusters and small precipitates appeared and hardness increased by almost 2x to 2.1 GPa. However, the nano-scale grain size and strong basal texture remained constant. The nanoclusters had an average spacing of 33 nm while the precipitates were found to be Mg-Al-Mn rich, semi-coherent with the surrounding matrix, and most prevalent at grain boundaries and dislocations. When as-deposited samples were aged at 400 °C for 30min, small and large precipitates appeared with a similar chemistry and coherency. The average spacing of the small precipitates was 47 nm, and they were distributed uniformly throughout the grains. This difference in distribution — heterogeneous versus homogeneous — is attributed to low atomic diffusion at 200 °C, except along grain boundaries and dislocations, and much higher bulk diffusion at 400 °C. The larger spacing between the precipitates in the 400 °C sample, and its larger grain size, explain its slightly smaller increase in hardness. In situ TEM straining of aged samples showed that the major deformation mechanism was basal slip. Basal dislocations were clearly seen to be pinned by the small precipitates in samples aged at 400 °C for 30min. The fracture mechanism in all TEM foils was trans-granular cracking and followed slip band formation along prismatic planes.

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