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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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ABSTRACT

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 age 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.

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

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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 20min 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 Philipps 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}/s 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