Improving the ductility of thin film metallic glasses via nano-twinning

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To reduce the brittle problem of thin film metallic glasses (TFMGs), the MgZrCu TFMGs, with a positive mixing heat between Mg and Zr, are fabricated via co-sputtering in an attempt to separate the pure Mg nano-rods (with or without nano-twins) from the amorphous ZrCu matrix. The nanocrystalline Mg nano-rods are expected to hinder the propagation of shear bands in TFMGs. When the Mg contents in the TFMGs vary from about 48 to 73 at%, discontinuous Mg nano-rods are dispersed in the amorphous matrix. Microcompression results obtained from the micropillars reveal that the TFMGs with Mg contents greater than 63 at% exhibit smooth and ductile behavior. The optimum Mg65 micropillar deforms by multiple shear bands. Due to the separated Mg nano-rods with nano-twins, the Mg-based TFMG composite micropillars possess rather high modulus ~80 GPa, yield stress ~1.7 GPa and lateral strain ~52%, favorable for future applications in micro-electro-mechanical systems or biomedical devices.

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1. Introduction

Metallic glasses have attracted considerable attention because of their excellent mechanical properties such as large elastic limit and high strength [1,2]. Moreover, many researchers note the potential application on the biodegradable [3] and micro-electro-mechanical systems (MEMS) [4] applications due to the lack of periodic atomic packing, indicating that there is no defect such as grain boundary, dislocation or plane defect in amorphous alloys. However, the high strength of metallic glasses is often accompanied by a virtually zero plastic strain and failed in a catastrophic manner. Plastic deformation of metallic glasses is highly localized in shear bands, which usually propagate rapidly through the sample. The brittleness problem severely limits further applications of this material.

To solve brittle problem, extensive efforts have been made to suppress the propagation of shear bands [5,6]. By using the interaction between shear bands and crystalline reinforcement phases, the shear bands can be absorbed and stopped [5,7]. Some researches show that the occurrence deformable crystalline phase is useful in improving ductility [8]. The ductility of metallic glasses can also be improved by forming multiple shear bands by the phase separation technique [6,9]. Recently, thin film metallic glasses (TFMGs) become popular and are fabricated by using sputter processes. Both monolithic and multilayered TFMGs are currently under study [4,10–12]. Crystalline/amorphous multilayers and amorphous/amorphous multilayers can be prepared to improve the ductility of TFMGs [11,12].

According to the Hall–Petch relation, the nano-scaled particles have higher strength than conventional bulk materials. In addition, many reports have demonstrated that the nano-twin structure can supply high strength and high toughness [13,14]. For example, pure Mg with nano-twins possesses much higher strength than conventional Mg [15]. Furthermore, Cu thin films with nano-twins fabricated by sputtering [16,17] and gas–solid transformation [18] also tend to form nano-twins, and the twin nucleation probability is related to twin boundary energy and deposition rate. The lower twin boundary energy and higher deposition rate would be more beneficial to form twins. The twin size decreases with increasing deposition rate [18].

In this study, we develop the nanocomposite route in improving the plasticity of TFMGs. The MgZrCu alloy thin films are fabricated by co-sputtering. The Mg addition into the ZrCu metallic glass system results in the MgZrCu TFMG. Utilizing the high diffusion mobility of Mg, we can easily fabricate nanocomposites composed of amorphous matrix and nanocrystalline reinforcement phases in various volume fractions. Furthermore, through the control of relative composition and deposition rate, Mg nano-rods with nano-twins in various amounts and sizes can be formed in the ZrCu amorphous matrix. The mechanical properties and shear banding behaviors are characterized by nanoindentation and microcompression.

2. Experimental details

A series of MgZrCu system thin films were deposited on Si substrates by co-sputtering with pure Mg (in hexagonal close-packed HCP structure) and Zr55Cu45 (in a2%) alloy targets, placed on the radio frequency (RF) and direct current (DC) cathodes, respectively. The purity of Mg and Zr55Cu45 targets are both 99.9%. Before deposition, the base pressure of the chamber was maintained less than...
6.6 × 10⁻⁵ Pa. During deposition, the working pressure is 0.4 Pa. Thus, the composition of MgZrCu alloy thin films was controlled by altering the power values of Mg and Zr55Cu45 cathodes. Even from the same ZrCu alloy target, the sputter yield of Cu and Zr is different. The deposition rate of Cu is usually much higher than that of Zr, especially at high powers. As a result, when the power of ZrCu target is lower, the Zr/Cu ratio is close to 1. The film thickness of all MgZrCu alloy thin films was maintained ~2 μm. The resulting MgZrCu films from low to high Mg contents (at%) have the compositions of Mg39Zr18Cu22, Mg43Zr16Cu21, Mg48Zr15Cu20, Mg55Zr13Cu14, Mg60Zr11Cu12, Mg65Zr10Cu10, Mg69Zr10Cu8, Mg73Zr10Cu7 and pure Mg, as determined by energy-dispersive spectroscopy with an operative voltage of 10 kV equipped in the JEOL 6330 field emission scanning electron microscopy. These samples are named as Mg39, Mg43, Mg48, Mg55, Mg60, Mg65, Mg73, Mg78, Mg84 and pure Mg, respectively.

The nature of the as-deposited MgZrCu alloy thin films was characterized by Siemens D5000 X-ray diffractometer (XRD) from 20° to 60° by using the Cu-Kα radiation. The cross-sectional transmission electron microscopy (TEM) foils of deformed micropillars were fabricated using dual-beam focused-ion-beam (FIB) system (Seiko, SM13050) with operating voltage of 30 kV and 1 pA ion beam current. The TEM foils were observed via Tecnai G20 field emission transmission electron microscopy with operating voltage of 200 kV.

The mechanical properties of the MgZrCu thin films were measured using firstly the MTS nanoindenter XP (Agilent Technologies) equipped with a standard Berkovich tip, under the loading-rate-control mode. The peak load and loading rate in all tests were set to be 5 mN and 0.1 mN s⁻¹, respectively. Then, micropillars with aspect ratio of 2 (measuring ~1 μm in diameter and ~2 μm in height) were machined by FIB and subjected to microcompression testing using the same MTS nanoindenter XP equipped with a flat-end tip [19,20], under the loading-rate-control mode at 0.02 mN s⁻¹. The peak load was set at 1.5 mN for Mg39; 1.3 mN for Mg48; 1.2 mN for Mg55, Mg60, Mg65, Mg73 and Mg84; and 0.8 mN for pure Mg, due to the fact that these pillars are intrinsically weaker with increasing Mg content.

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In this microcompression testing, the controlled parameters are loading rate and displacement. The loading rate can affect the mechanical properties of thin film metallic glasses; thus, it is fixed in this study. In addition, the set displacement of pillar is about 600 nm to avoid the tip to touch the surface of thin film. As the result, the maximum load and load time are set to be different to get the constant loading rate and displacement. Also, by numerous experiments, it is ensured that the maximum loads from 0.8 to 1.5 mN have no influence on measured mechanical properties.

3. Results and discussion

3.1. Microstructure

The mutual heat of mixing for Mg-Cu, Zr-Cu and Mg-Zr equals to −3, −23 and +6 kJ/mol, respectively [21], meaning Mg would be pushed out by Zr. With increasing Mg content, Mg atoms were eventually separated out and form nanocrystalline pure Mg particles, especially with the help of the relatively high diffusion ability of Mg atoms. According to the previous research of Kuan et al. [22], when the content of Mg reaches 48 at%, HCP Mg nano-phase start to evolve as precipitates. Mg48 and Mg55 are present as a composite structure with metallic glasses matrix and minor Mg nano rod-shaped particles. The Mg nano-rods tend to possess the (0002) basal plane parallel to the film plane, with the c-axis nearly parallel to the rod axis and the deposition direction, as evident from the XRD results shown in Fig. 1. In this study, emphasis is placed on the Mg60 and Mg65 thin films, with the optimum composite structure. As Mg content reaches 78 at%, the MgZrCu film becomes fully crystalline in HCP structure. As a result, the MgZrCu thin films can be divided into three groups. The first group for Mg39 and Mg43 possess the fully amorphous structure.

The second group including Mg48, Mg55, Mg60, Mg65 and Mg73 are composites with metallic glass matrix and Mg nano-rods. Finally, Mg78, Mg84 and pure Mg are fully crystalline.

The as-deposited MgZrCu thin films (not yet deformed) were characterized by TEM. Fig. 2 presents the dark field images by using the Mg [1T00] reflections showing that the shape, for example, Mg nano-rods in Mg65 is in columnar- or rod-shape, characteristic of sputter processing, with a height of ~50 nm and a diameter of ~25 nm. The Mg rod diameter as a function of Mg content is presented in Fig. 3. The size of Mg nano-rods is larger than the typical width of shear band (~20 nm) [23]. According to the XRD and TEM results, these Mg grains are predominantly oriented with their (0002) basal planes lying on the thin film plane.

In addition, the volume fraction of Mg nano-rods is calculated by the volume fraction equation of Pauly et al. [24], the values are 6 vol%, 13 vol%, 30 vol% and 80 vol% for Mg55, Mg60, Mg65 and Mg73, respectively, also depicted in Fig. 3. The volume fraction of Mg nano-rods was calculated by the bright contrast region taken by the pure Mg [1T100] reflections in the dark-field micrograph. There are six variants in the [1T100] plane family. The dark field image
shows only one of them. The overall volume fraction is six times of the amount in the dark field image. As a result, the volume fracture of Mg nano-rods in Fig. 2 appears to be lower than the reported total volume fraction values. Some reports have shown that the volume fraction of crystalline phases can affect the ductility improvement degree in metallic glasses composites [25,26]. It appears that the metallic glass composites would be more ductile when there are a sufficient amount of Mg nano-rods.

Nano-twins are observed in Mg nano-rods with their rod diameters over 20 nm. When the nano-rods are smaller than 20 nm in diameter, such as those seen in Mg55 or Mg60, very few or no nano-twins appear. But in Mg65 or films with Mg content over 65%, nano-twins are prevailing. The twin structure in the Mg nano-rods are all of the \{001\} \langle 101 \rangle twinning mode, typical in bulk Mg [27–29], as shown in Fig. 4. It appears that there is a threshold of Mg rod size, about 20 nm in terms of the Mg rod-diameter, for the nano-twins to be embedded inside the Mg rods. When the Mg rods are too small, the accumulated dynamic energy (as as discussed below) within the precipitated Mg is too low to induce embedded nano-twins. But when the Mg nano-rods exceed 20 nm, this stress starts to induce multiple twins within the Mg rods.

Attempts have been made to explore what causes the nano-twins within the Mg nano-rods. Firstly, atomic size mismatch is frequently the cause for crystalline alloys. But for metallic glasses, the strain energy due to atomic mismatch between HCP Mg and amorphous ZrCu can be easily accommodated by the relaxation within the ZrCu glassy matrix. The atomic size mismatch should not be the main cause. Secondly, the residual stress induced by the thermal coefficient mismatch between HCP Mg and amorphous ZrCu is considered. However, the current sputtering parameters have been set intentionally to lower the sputtering heating effect, and all the sputtering conditions for Mg 39 to Mg84 are the same. It is seen that some possess no twin and some possess many. This would rule out the thermal stress as the predominant role in inducing nano-twins. Finally, it is postulated that the sputtering dynamic energy [30] is the cause. For films with lower Mg contents, the Mg atoms need to diffuse in the matrix containing basically Zr and Cu to form Mg nano-rods. The diffusion activation energy is much higher for Mg to diffuse in the ZrCu matrix; thus, the sputter dynamic energy associated with Mg atoms has

**Fig. 3.** Variation of Mg rod size (in terms of the rod diameter) and volume fraction as a function of Mg content of the sputtered thin films.

**Fig. 4.** High-resolution TEM image showing the nano-twin embedded in the Mg nano-rods in the Mg65 thin film. The insert is a schematic drawing of the multiple nano-twins in one Mg rod.

**Fig. 5.** Variation of (a) elastic modulus and (b) hardness measured from nano-indentation of the MgZrCu thin film as a function of Mg content. (c) Load–displacement curves of the MgZrCu alloy thin films.
been mostly consumed by diffusion. In addition, such a much lower energy or stress inside the Mg nano-rods would not induce embedded nano-twins. On the other hand, in films with much higher Mg contents, Mg diffusion becomes much easier. Thereby, the precipitated Mg nano-rods are still experienced sufficient dynamic energy. Slip in Mg is still difficult in nano-rods measuring a few tens of nanometers. It follows that nano-twins become the dominant products to accommodate the residual dynamic energy. It is seen that the twin volume fraction is also increasing with increasing Mg content, or increasing Mg rod volume fraction, as shown in Fig. 3.

3.2. Mechanical measurements

The elastic modulus (E) and hardness (H) of the MgZrCu films, measured by nanoindentation, are shown in Table 1. It is obvious that the modulus decreases from ~90 to ~70 GPa and hardness from ~5.5 to ~1.5 GPa, with increasing Mg content. Fig. 5(a) and (b) shows the nanoindentation load–displacement curves. It can be seen that when the Mg content increases from 43 to 65 at%, the pop-in events are gradually reduced and the load–displacement curve becomes gradually smoother. It is implied that the pop-in events decrease as the Mg nano-rods and nano-twins are developed. It can be explained that the propagation of major shear bands is blocked by Mg nano-rods (with nano-twins) under nanoindentation loading, and multiple shear banding takes over, making the overall deformation more homogeneous. Finally, when the film structure changes from composite to fully crystalline, a smooth load–displacement curve is seen, without any pop-in event that might be induced by shear banding.

Microcompression testing is performed to investigate the uniaxial compression mechanical properties. For thin film metallic glasses, the stress–strain curves would exhibit the characteristic strain bursts. The first apparent strain burst is usually defined as the yield stress. Fig. 6 shows the variation trend of the yield stresses with increasing Mg content. The yield stress first decreases with increasing Mg content from Mg39 to Mg48 due to increasing Mg atoms in the amorphous structure. Upon reaching Mg55 with appreciable Mg nano-rods and nano-twins, the yield stress starts to increase again. The hardness readings of the MgZrCu thin films shown in Fig. 5(b) are seen to decrease continuously with increasing Mg content. However, the yield stress data shown in Fig. 6 do not show the similar trend. Mg55, Mg60 and Mg65 can still maintain a high compressive yield stress ~1.7 GPa, not much different from Mg39. It implies that the occurrence of Mg nano-rods with (0002) texture perpendicular to the deposition orientation, and the micro-pillar long axis as well as the compressive loading axis, can enhance compressive strength. The Mg nano-rods with nano-twins are inherent with high strength and can impose resistance against the propagation of shear bands, as discussed below. Furthermore, when the slip plane (0002) is perpendicular to compressive load, it would be hard to deform. It needs a higher stress to drive the propagation of shear bands. As the result, the strength is enhanced. For Mg73, Mg78 and Mg84, due to the same reasons that the c-axis of the Mg phase is parallel to the micropillar axis and the loading direction, the applied uniaxial compression load is hard to activate the basal dislocation slip in the beginning. With the additional strengthening effect by the nano-twins, the yield stresses of Mg73, Mg78 and Mg84 do not decrease with increasing Mg content [22], all varying near 1.6 GPa. This effect will not apply for these three samples under triaxial nanoindentation loading, as shown in Fig. 5(b) that the nano-hardness continuously decreases with increasing Mg content.

Fig. 7 shows the deformed Mg39, Mg65, Mg84 and pure Mg micropillars. For the monolithic metallic glassy Mg39 micropillar in Fig. 7(a), the deformation characteristics are still dominated by shear band propagation, but the metallic glass composite Mg65 in Fig. 7(b) shows much more ductile behavior with multiple shear banding. For micropillars with complete HCP crystalline phase, such as Mg 84 and pure Mg, the deformation is gradually governed by the deformation instability of nanocrystalline Mg.
To further assess the film ductility, the lateral strain of the micropillars is measured from the upper quarter of deformed pillar. The lateral strain is calculated from the region below the pillar tip for about 100 nm. Fig. 8 shows that the lateral strain of the MgZrCu micropillars increases from ~25% for the monolithic amorphous Mg39 to ~52% for the composite Mg65 with many Mg nano-rods containing nano-twins, and finally to ~100% for Mg84 and 150% for pure Mg, which are already fully crystalline metal. The 52% lateral strain is considered to sufficiently ductile for MEMS application. This means that a thin film metallic glass with ~30 vol% precipitated crystalline second phase with sufficient strength, such as HCP Mg nano-rods with multiple nano-twins, would appreciably improve the TFMG ductility.

Zong et al. [31,32] and Donohue et al. [31,32] have shown that nanocrystals can suppress or restrict the propagation of shear bands. In addition, Jang et al. [14] reported that nano-twins can result in higher strength. In addition, Yu et al. [15] found that the Mg with {1011} <10T2> nano-twins possesses high strength and high toughness under compressive and bending testing. The typical compressive normal strength for pure Mg in nano-scale is only about 200 MPa, while it would be about 800 MPa when the Mg contains multiple nano-twins [33–35]. Under bending testing, the occurrence of nano-twins can deflect the crack. Similar to crack propagation, the propagation of shear bands can also follow the phenomenon related to the Dundur’s parameter [12,36,37]. The much higher strength of Mg with nano-twins (~800 MPa) is thought to be capable to impose effective resistance against the shear band propagation and help in initiating multiple shear bands. As a result, the deformation of Mg65, with abundant HCP Mg nano-rods (30% in volume fraction) containing multiple nano-twins, appears to be sufficiently ductile (with 52% lateral strain), with no sacrifice of strength (maintaining 1.7 GPa).

4. Conclusions

The microstructure and mechanical properties of the sputtered MgZrCu thin films and their FIB-machined micropillars are examined as a function of Mg content from 39 to 100 at%. The Mg48, Mg55, Mg60, Mg65 and Mg73 are all composites. As Mg content is 78 at%, the MgZrCu thin film becomes fully HCP crystalline. In the optimum Mg65 specimen, the separated Mg appears to be rod-shaped, measuring ~50 nm in height and ~25 nm in diameter. The c-axes of such Mg nano-rods are basically parallel to the sputtering deposition direction, as well as the rod long axis and compressive loading direction.

Nano-twins are induced in Mg nano-rods greater than 20 nm in diameter. Such nano-twins significantly strengthen the Mg nano-rods to ~800 MPa and can impose sufficient resistance against the propagating shear bands, promoting multiple shear-banding in the micropillars. This leads to both the strengthening and toughening in the optimum Mg65 specimen, which contains abundant HCP Mg nano-rods (30% in volume fraction) with multiple nano-twins, and exhibits sufficiently ductile behavior (with 52% lateral strain) and promising high strength (maintaining 1.7 GPa). The evolution of nano-twins in TFMs can result in metallic glass composites exhibiting satisfactory strength and ductility, favorable for future applications in MEMS or biomedical devices.

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