Morphological and Mechanical Stability of HCP-based Multilayer Nanofilms at Elevated Temperatures

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Abstract

The thermal stability of Mg/Ti multilayer nanofilms was investigated by examining their microstructure and nanoindentation hardness after annealing at various temperatures and time periods. The multilayers with individual layer thickness $h \geq 5$ nm exhibit excellent capability of maintaining the lamellar microstructure and high strength up to 200 °C for annealing time up to 2.0 hours. The annealed multilayer films with $h=2.5$ nm are still highly textured but characterized with discontinuous layer interfaces, in which the transition of atomic arrangement from hexagonal close-packed (HCP) to body-centered cubic (BCC) structure was observed at columnar boundaries. The degradation of uniform lamellar microstructure is related to the decrease of hardness with annealing temperature at this size scale. A diffusion based instability mechanism was proposed for this typical HCP-based nanoscale multilayer system.

Key words: Metallic multilayer; thermal stability; microstructure; nanoindentation hardness.

1. Introduction

Multilayered metallic films exhibit great potentials in engineering applications because of their impressive strength, ductility, wear and corrosion resistance. Over past decades, the deformation behavior and strengthening mechanisms of the multilayered metallic films have been widely explored [1-4]. For example, it has been found that the strength of most metallic multilayers can be remarkably improved by reducing the individual layer thickness to submicron level or even less [5]. In contrast, the thermal stability, which is an essential property to be considered in industrial environment, has not received enough attention.

Most frequently, the heating treatments on metallic multilayers were intentionally performed to trigger specific reactions between the original elements while the intermetallic or amorphous product would serve as a final constituent [6, 7]. For example, Weihs and coworkers used highly pure Cu and Zr to prepare Cu/amorphous Cu-Zr and Cu/Cu₅₁Zr₁₄ multilayers by monitoring the heating temperature of differential scanning calorimetry (DSC) [8]. However, the unexpected formation of new phases is generally deemed as an evidence of poor thermal stability because they are likely to bring about the disintegration of lamellar microstructure and degeneration of mechanical performance [9, 10]. Moreover, the inter-diffusion that is present in many miscible multilayer systems at elevated temperatures could also cause above problems and therefore impair the thermal stability [11-14]. A study from Kucharska et al. revealed serious surface discontinuities in the Cu (2 nm)/Ni (1.8 nm) multilayer specimens annealed at 220 °C. With a further increase in temperature, intensive delamination of the multilayer sample from the silicon substrate ensued [13].

For polycrystalline metallic multilayers, the grain growth within the layers always takes place as the temperature increases [15]. It has been found that the hardness of electrodeposited

Cu/Ag multilayer films drops significantly after a 150°C annealing due to the spheroidization of grains [16]. Similarly, coarsening of in-plane grain size and resultant strength loss have been observed in Ni/Ru multilayers with comparatively large periodicity (>36 nm) during annealing [17]. Misra et al., however, claimed that the multilayer spheroidization and pinch-off are more likely to occur in the annealed Cu/Nb multilayers with small individual layer thickness (h , ~ 15 nm), compared to those with $h \geq 35$ nm [18, 19]. They attributed the excellent thermal stability of films containing thicker Cu and Nb layers (up to 700 °C) to the development of zig-zag alignment of triple junctions which stabilizes the lamellar microstructure effectively. In this sense, the effect of heating on the morphological stability of metallic multilayers is much more complex than expected. Consider the change of mechanical properties described above as well as the possible alternation of magnetic, optical and electrical properties with the rising temperature [20-23], more efforts on the investigation of thermal stability in metallic multilayers are needed.

In this paper we focus on the thermal stability of hexagonal close-packed (HCP)-based metallic multilayers which have distinct deformation modes from those made up of cubic metals. To the best of our knowledge, the vast majority of such research efforts in the literature has been focused on cubic systems. The work of Lu and co-workers appears to be the first in examining the microstructure and mechanical properties of multilayer systems made of HCP metals [24]. However, no efforts can be identified in the literature on the thermal stability of nanoscale multilayer systems made of HCP metals. Therefore, in this work, a series of annealing processes will be carried out on the Mg/Ti multilayered films with various individual layer thicknesses. Annealing will be performed at various temperatures for various lengths of time. Thermal stability of the HCP multilayer specimens will be evaluated in terms of crystallography, microstructure and mechanical properties via instrumented nanoindentation.

2. Experimental procedure

The Mg/Ti multilayered thin films with equal layer thickness of Mg and Ti (from 2.5 to 100 nm) were deposited onto Si (100) substrates at room temperature via magnetron sputtering technique, as described elsewhere [24]. The total thickness of each film was kept as 1.0 μm by varying the number of layers. Afterwards, as-deposited Mg/Ti specimens were subjected to annealing treatments at 50, 100, 150 and 200 $^{\circ}\text{C}$, respectively. Since the constituents in Mg/Ti multilayer system are reactive with oxygen and prone to get oxidized at elevated temperatures, we wrapped the specimens in Al foils before placing them into the **Barnstead-Thermolyne Model FA 1500 furnace** flowed with **high-purity** Argon gas. **The annealing time was varied from 0.5 to 2.0 hours and the heating rate was controlled at 12K/min. After the annealing treatment, the specimens were furnace-cooled to room temperature.** The following X-ray diffraction results demonstrate the effectiveness of such a treatment in preventing the oxidation of Mg/Ti multilayers.

Bruker AXS D8 Discover X-ray diffractometer with $\text{Cu-K}\alpha$ radiation was used to examine the phases and crystallography of the annealed Mg/Ti films. Their cross-sectional microstructures were inspected by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) on the JEOL 2100 microscope operated at 200kV. All the TEM samples in this study were cut, milled and finished by Focused Ion Beam (FIB) technique on an FEI Nova 600i dual beam FIB system (US Army Research Laboratory).

The mechanical properties of the annealed specimens were mainly characterized by hardness, which was measured on an Agilent NanoIndenter G200 equipped with a Berkovich diamond tip. We adopted the continuous stiffness method (CSM) proposed by Oliver and Pharr [25] in the nanoindentation tests. Considering the substrate effects [26], the maximum indenter

penetration depth was set as 120 nm (~10-15% of the total thickness for each film). At least ten indentation points were made on each annealed film.

3. Results

Fig. 1 shows the X-ray diffraction (XRD) patterns of Mg/Ti multilayer nanofilms annealed at 200 °C for 2 h. In consistency with the experimental results of as-deposited Mg/Ti multilayers, both Mg and Ti nanolaminates are preferentially orientated along *c*-axis. However, annealing led to a slight shift of the major reflections, Mg (0002), Ti ($10\bar{1}0$) and Ti (0002), to larger angle 2θ , as reflected by the difference in XRD pattern of the annealed multilayer and the as-deposited one (the dotted line in Fig. 1) at $h=100$ nm. It is suggested that the shrinkage of lattice parameter in Mg and Ti during annealing is associated with their different thermal expansion parameters from that of silicon substrate as well as relaxation of the lattice strain in the as-deposited films. We recorded the angle shift for each specimen and calculated the strain as small as ~0.3%. Therefore, with respect to the high strength of Mg/Ti metallic multilayers [24], the stress introduced during annealing is quite small and could be negligible.

As illustrated by the satellite peaks situating symmetrically around the major reflections in Fig. 1, Mg/Ti multilayers retained the lamellar microstructure even upon annealing at 200 °C. In addition, there is no characteristic peak of magnesia or titania (e.g. MgO (200) at ~44° and TiO₂ (004) at ~37°) detected from the XRD spectra, indicating that the constituents of annealed films are still Mg and Ti. It should be mentioned that the highest annealing temperature of 473K has exceeded half of the melting point of pure Mg (473 K vs 923 K). Such a high annealing temperature should be able to induce substantial atomic diffusion in Mg layers.

To further evaluate the morphological stability of Mg/Ti multilayers at elevated temperatures, the microstructure of annealed films was investigated via TEM. Fig. 2a is a typical bright-field micrograph illustrating the cross-sectional microstructure of $h=20$ nm Mg/Ti multilayers after annealing at 200 °C for 2 hrs, in which the interfaces are clearly still continuous. In other words, the individual Mg and Ti layers are intact, without any pinch-off or breakdown. At this layer thickness level, epitaxial growth pattern OR.1 (Mg $\{0002\}$ // Ti $\{0002\}$) and non-epitaxial growth pattern OR.2 (Mg $\{0002\}$ // Ti $\{01\bar{1}0\}$) were found to coexist in the as-deposited films [24]. Similarly, both of them have been identified in these annealed specimens. Fig. 2b is the selected-area diffraction pattern (SADP) corresponding to Fig. 2a, showing the existence of OR.2.

Unlike the uniform lamellar structure in Fig. 2a for $h=20$ nm, the cross-sectional area of the annealed $h=2.5$ nm Mg/Ti multilayers is characterized with discontinuous interfaces separated by columnar boundaries, as shown in Fig. 3a. The average columnar width is approximately 80 nm. Columnar growth is very common in vapor-deposited films and is largely determined by the sputtering parameters. It has been reported in Ag/Cu [27], Ni/Ru [17], Cu/Nb [18], Cu/V [28], Fe/Ti [29] and other metallic multilayer nanofilms. In each column, Mg and Ti hold the epitaxial growth pattern, with a typical SADP shown in Fig. 3b. Our crystallographic investigation also demonstrates that the mis-orientation between adjacent columns is extremely small.

Noteworthy is a feature present at the bottom of Fig. 3a, where there is breakdown of constituent layers at columnar boundaries, which has been rarely seen in the $h=2.5$ nm Mg/Ti multilayers in the as-deposited condition. The HRTEM image in Fig. 4a provides us a close-up view of the interrupted layers. It is evident that a great deal of lattice distortion occurs in the

vicinity of layer breakdowns. However, the layer termination or grain spheroidization that is always found to accompany the heat treatments of immiscible multilayers has not been observed here. A representative area containing rearranged atoms (the yellow square in Fig. 4a) was selected and then enlarged in Fig. 4b. Apparently, the atomic configuration is different from the normal HCP lattice. The planar spacing d_1 and d_2 sketched out in Fig. 4b were measured as ~ 0.25 and 0.30 nm, respectively. Fig. 4c is the Fast Fourier Transformation (FFT) image of Fig. 4b, which is also distinct from that in Fig. 3b. In this regard, metastable phases are believed to evolve in the $h=2.5$ nm Mg/Ti multilayers during annealing. Although the intermixing between constituents is not expected in Mg/Ti multilayers, it is still difficult to discriminate Ti and Mg atoms located at the column boundaries since they have almost identical FFT images. Examination of the regions right above the yellow square in Fig. 4a reveals that d_2 shrinks to ~ 0.28 nm. Thus the region enclosed by the yellow square is more likely to be migrated Mg atoms. With concerns about the appearance of such an atomic rearrangement and its influence on the mechanical behavior of Mg/Ti multilayer nanofilms, we will present a detailed discussion later.

The evolution of hardness as a function of annealing temperature for the Mg/Ti multilayer nanofilms is plotted in Fig. 5. Given the annealing time up to 2 hours, no significant change of hardness is noted in the multilayers with $h \geq 5$ nm. However, the hardness of $h=2.5$ nm Mg/Ti multilayers exhibits a descending trend as the annealing temperature increases, eventually reaching the minimum of ~ 3.30 GPa at 200°C . According to the Tabor's law, the flow strength corresponding to the minimum hardness is roughly 1.22 GPa, which is still very impressive in the community of metallic multilayers. Additionally, the effect of annealing time on the hardness of Mg/Ti multilayers is illustrated in Fig. 6. Similar to annealing temperature, the annealing time has limited impacts on the strength of Mg/Ti multilayers when $h \geq 5$ nm. Holding at 200°C for 2

hrs brings about a remarkable drop in hardness of the $h=2.5$ nm Mg/Ti films. This dependence of strength on the annealing time implies the occurrence of diffusion-related processes in Mg/Ti multilayers at elevated temperatures.

4. Discussion

In what follows, we will attempt to provide some in-depth discussion with respect to the experimental results presented in the previous section. Our focus will be primarily on the microstructural stability and evolution of mechanical properties of the Mg/Ti multilayer films when subjected to thermal annealing.

4.1. Microstructural stability

The experimental results presented above indicate the excellent microstructural and mechanical property stability of Mg/Ti multilayer nanofilms with $h \geq 5$ nm upon annealing at up to 200 °C. Thermally induced changes on the lamellar microstructure and mechanical properties were mainly manifested in the annealed films with $h=2.5$ nm. Hence, the following discussions are primarily based on the microstructural evolution of Mg/Ti multilayers at this length scale.

With regards to the lamellar microstructure, there are several instability mechanisms derived from the studies of eutectic and eutectoid composites (i.e. Ti/Al alloys), including direct cylinderization, edge spheroidization, boundary splitting, termination migration and so on [30-32]. Our microstructural investigation on the annealed Mg/Ti multilayers reveals the absence of granular morphology, suggesting the deterioration of lamellar structure at $h=2.5$ nm largely results from the boundary thermal grooving. However, considering the fact that the boundaries could hardly be discerned in Mg and Ti individual layers except at column walls (Fig. 3a and Fig. 4a), the classic model, which describes the groove development at intersections of grain boundaries and phase interfaces, cannot be directly used to the Mg/Ti multilayers. Here we

propose a modified thermal grooving model to interpret the morphological instability of Mg/Ti multilayers.

Fig. 7a schematically illustrates the microstructure of an as-deposited Mg/Ti multilayer nanofilm. It is well known that the morphology of thin films is considerably sensitive to the deposition conditions such as deposition pressure and substrate temperature. Therefore, in spite of the prevalent continuity of Mg and Ti layers throughout the film, the appearance of tiny morphological perturbations (e.g. interfacial waviness) in Mg/Ti multilayers is practically inevitable, which can be possibly attributed to the competition between instabilities arising from discrete atomic deposition and stabilizing influence of surface diffusion [33]. Due to the curved interface geometry where chemical potential gradient lies, the diffusive mass transportation associated with increasing temperature will intensify the grooving as shown in Fig. 7b. The tendency to relieve the stress caused by **thermal strain and misfit strain** might be another driving force for the deep grooves in the annealed Mg/Ti multilayers. The schematic diagrams in Fig. 7a and Fig. 7b basically elucidate the presence of thermal grooves in the preferentially grown multilayer nanofilms where grain boundaries are scarce.

Rather than the conspicuous layer recession in annealed Cu/Nb multilayers [19], the atomic diffusion gives rise to a transition zone (enclosed by the red dotted lines in Fig. 7c) on the cross-sectional microstructure, in which Mg and Ti have a different atomic configuration from the HCP structure. As a matter of fact, both Mg and Ti have a strong propensity to phase transformation, particularly at high temperature, high pressure or other favorable conditions. For example, pure Ti experiences a natural transition from α phase (HCP structure) to β phase (BCC structure) at approximately 1115 K. Alloying with beta stabilizers, i.e. Mo, Ta, Fe and Co, is able to lower the transition temperature. Increasing strain was also observed to promote the α -to- β

phase transition in a Ti alloy even at ambient temperature [34]. Nevertheless, the phase transition of Mg is more dependent on the pressure than on the temperature. The calculation results based on first-principles theory from Jona and Marcus revealed a martensitic transition of Mg from HCP structure to BCC structure at hydrostatic pressure larger than 500kbar [35]. Moreover, the metastable BCC Mg were experimentally observed in the magnetron sputtered Mg/Nb multilayers with individual layer thickness of 5 nm, while subsequent density functional theory calculations demonstrated that the stabilization of BCC Mg deposited on BCC Nb substrate is analogous to the stabilization of BCC Mg under high pressures because of the mechanical constraints imposed on Mg [36, 37].

Although our observation shows that Mg lattice in the transition zone is no longer exclusively HCP structure, it is not a perfect BCC or FCC lattice either. The FFT image in Fig. 4c is analogous to the diffraction pattern of BCC crystals with [111] zone axis but still shows small discrepancies from it, which essentially originates from the difference between d_1 and d_2 in Fig. 4b. Therefore, the Mg at the columnar boundaries could be a metastable phase that possesses a transitional lattice structure from HCP to BCC. This speculation is also applicable for Ti. Since the transition zones only make up a small volume of the annealed Mg/Ti nanofilms, the reflections of these metastable phases are too weak to be identified from the XRD patterns.

As mentioned previously, the degradation of lamellar structure was detected in the annealed Mg/Ti films with $h=2.5$ nm, but is absent from other specimens. We believe this is indicative of the influence of individual layer thickness h on the morphological stability in Mg/Ti multilayer system. Such a size-dependent phenomenon could be explained from different perspectives. Firstly, the interfaces of Mg/Ti multilayers with smaller h is energetically less stable due to the high density of Mg/Ti interfaces. The interfacial strain originating from the

mismatch in elastic modulus and lattice parameter between constituents cannot be fully relaxed during quick alternating layer deposition. With more layers stacked together, the accumulative stress, which might be beneficial to the strength, makes the interface vulnerable to thermal exposure and in turn impairs the microstructural integrity upon annealing. Secondly, there might exist more structural imperfections at interfaces of the multilayers with smaller h . An early study about the columnar growth of multilayers from Czigány and Radnóczy has pointed out that during low temperature depositions the interface wavelength of waviness (equals column width) is nearly proportional to the individual layer thickness at nanoscale h [38]. These surface irregularities potentially act as initial sites of atomic rearrangements as described above. Thirdly, boundary splitting is easier to take place at smaller h because the diffusion distance is shortened. A critical d/h ratio (d denotes the grain size) correlated to the grain-boundary energy of layer constituents was even proposed by Josell et al., below which the layer pinch-off is restricted [39]. Unfortunately, owing to the ambiguous grain boundaries in Mg/Ti multilayers, it is almost impossible to determine the average value of d . Thereby, we did not attempt to quantitatively derive this critical ratio for Mg/Ti multilayer system in this study.

4.2. Mechanical stability

To a large extent, the mechanical stability of metallic multilayers is controlled by their morphological stability. In the literature, grain growth and layer coarsening are two major factors that impact adversely on the mechanical properties at elevated temperatures. For example, Misra et al. found that the decrease of hardness (~ 0.3 GPa) in $h=75$ nm Cu/Nb multilayers during a short-time anneal at 700 °C was primarily caused by the apparent in-plane grain growth from ~ 75 nm to ~ 200 nm. As for the $h=15$ nm Cu/Nb multilayers, a dramatic drop of hardness by a factor of two was noticed when the annealing temperature approached 600 °C, at which

spheroidization of the lamellar microstructure began [19]. The detrimental impacts of layer spheroidization on the mechanical integrity were also reported in Ni/Ru (at 600 °C) [17] and Cu/Ag multilayers (at 149 °C) [16].

For our $h \geq 5$ nm Mg/Ti multilayer nanofilms following thermal annealing, the nearly unchanged hardness as shown in Fig. 5 and Fig. 6 is fundamentally connected with their impressive resistance to the deterioration of lamellar microstructure. The decrease of hardness in annealed Mg/Ti multilayer specimens with the smallest h ($h=2.5$ nm) should account for the thermally induced transition zones since neither grain growth nor layer coarsening has been observed. It is suggested that, the appearance of transition zones with rearranged atoms disrupted the continuous interfaces and thus weakened their impeding effects toward the Orowan-type dislocation sliding as well as the subsequent dislocation transmission. On this basis, a further decrease of strength is predicted if the annealing temperature or annealing time increases.

5. Summary and Concluding Remarks

A variety of thermal anneals were performed on the magnetron sputtered Mg/Ti multilayer nanofilms to evaluate their thermal and mechanical stability. These HCP-based multilayers possess impressive capability of maintaining the lamellar microstructure as well as high-level hardness up to 200 °C when the individual layer thickness h is no less than 5 nm. In the annealed Mg/Ti multilayers with $h=2.5$ nm, transition zones characterized with atomic arrangement from HCP to BCC lattice appear at the columnar boundaries. Owing to the interruption of continuous interfaces, the hardness of Mg/Ti multilayers at this length scale of h exhibits a descending trend with the annealing temperature and reaches the minimum of 3.3 GPa after annealing at 200 °C for 2 hrs.

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Figure Captions:

Fig. 1. XRD patterns of Mg/Ti multilayer nanofilms annealed at 200 °C for 2 hours. They are very similar to the XRD results of the as-deposited multilayer films, except for a small angle shift of major reflections [24]. For detailed comparison, the XRD pattern of as-deposited Mg/Ti multilayer with $h=100$ nm is illustrated by the dotted line.

Fig. 2. (a) The bright-field TEM micrograph illustrating the cross-sectional microstructure of $h=20$ nm Mg/Ti multilayers upon annealing at 200 °C for 2 hrs, with the corresponding selected area diffraction pattern (SADP) displayed in (b). Both the TEM image and the SADP indicate negligible change in the microstructure of the annealed specimen. The same orientation relationship between Ti and Mg phases is detected as in the as-deposited specimen [24].

Fig. 3. (a) The bright-field TEM micrograph illustrating the cross-sectional microstructure of $h=2.5$ nm Mg/Ti multilayered nanofilm annealed at 200 °C for 2 hrs. Mg layers are in bright while Ti layers are in dark. (b) A typical SADP within the column illustrating the epitaxial growth between Mg and Ti. Compared to the as-deposited specimen [24], the significant change associated with thermal annealing is the emergence of the columnar structure.

Fig. 4. (a) An HRTEM image illustrating the breakdown of individual layers at column boundaries in the annealed Mg/Ti multilayers with $h=2.5$ nm. (b) The enlarged HRTEM image shows the detailed atomic rearrangement, with the corresponding FFT image in (c). At the column boundaries, body-centered cubic regions can be detected. See text for detailed discussion.

Fig. 5. The hardness of Mg/Ti metallic multilayers annealed at various annealing temperatures for 2 hrs. It is observed that except for the $h=2.5$ nm specimen, all other specimens exhibit outstanding thermal and mechanical stability. This is particularly surprising as the highest annealing temperature is more than half the melting point of Mg.

Fig. 6. The hardness of Mg/Ti metallic multilayers annealed at 200°C for various annealing time periods. Again, except for the $h=2.5$ nm specimen, most specimens possess extraordinary thermal and mechanical stability upon annealing at this temperature, which is more than half the melting point of Mg.

Fig. 7. Schematic diagrams of the morphological instability in Mg/Ti multilayers. This analysis applies to very small h values.

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