Nanoscaled superelastic behavior of shape memory alloy/metallic glass multilayered films

W.T. Jhou[a], C. Wang[a], S. Ii[b], C.H. Hsueh[a],*

[a] Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan, ROC
[b] Research Center of Structural Materials, National Institute for Materials Science, Tsukuba 305-0047, Japan

ABSTRACT

The mechanical properties of multilayered films with alternate layers of shape memory alloy (SMA) and metallic glass (MG) were studied. Specifically, TiNi SMA and ZrCuAlNi MG were deposited alternately on the Si substrate using magnetron sputtering. The as-deposited multilayered film was amorphous. The annealing temperature was chosen judiciously to crystalize TiNi layer while ZrCuAlNi layer remained amorphous. The superelastic behavior of SMA/MG multilayered film was characterized using nanoindentation tests. The stress required to induce martensitic transformation of TiNi layer increased as the thickness of TiNi layer decreased. Also, the multilayered SMA/MG films were found to have the better deformation recovery after indentation unloading which could be due to the synergy effects of superelasticity from SMA layers and high elastic strain limit from MG layers.

1. Introduction

TiNi-based shape memory alloys (SMAs) have many unique properties, including shape memory effect and superelasticity resulting from the reversible thermoelastic martensitic transformation [1,2], high corrosion resistance [3,4], biocompatibility and low Young's modulus [5]. These characteristics lead to its wide use in micro-electro-mechanical systems (MEMS) [6–8], the biological field [9] and actuators for smart composite structures [10–12], etc. Shape memory alloy wires have also been used to reduce thermal buckling of laminated composites [13]. When it comes to MEMS applications, the effects of the thickness and grain size of the TiNi film are an important issue. It was shown that the grain size was independent of the film thickness at micro-thickness level, while it was strongly affected by the thickness reduction at submicron or nanoscale [14,15]. For the thermal-induced martensitic transformation, the transformation temperature and the volume fraction of martensite decreased with the decreasing grain size, and the transformation behavior was completely suppressed below a critical grain size [16–18]. For the stress-induced phase transformation, a steep hardening in the stress-strain curve was observed in nanocrystalline TiNi alloy, while polycrystalline TiNi with coarse grains showed a clear plateau in the stress-strain curve [19]. Consequently, the transformation in nanocrystalline TiNi occurred at higher stresses, indicating again an over-stabilization of the parent phase [19,20]. Although the thermal- and stress-induced martensitic transformations in

nanocrystalline TiNi bulk have been well understood [21,22], the corresponding studies in nanoscaled TiNi thin film have rarely been reported.

Due to the unique amorphous structure, metallic glasses (MGs) exhibit large elastic strain limit, high strength and good wear resistance. Nevertheless, the high strength of metallic glasses is often accompanied by nearly zero plastic deformation resulting in limited applications of the materials. Currently, a large number of papers on the ductility enhancement of MGs have been reported. For example, the ductility of metallic glasses could be improved by introducing the crystalline or amorphous second phase into the metallic glass matrix [23,24]. The amorphous MG layers could be combined with ductile metal layers to form multilayered structure to enhance the plasticity of MG [25–27]. By precipitating shape memory alloy particles in MG matrix, good ductility and work-hardening were obtained for the MG composite [28,29]. Also, MG layers have been laminated with carbon fiber reinforced epoxy for aircraft applications [30]. However, utilizing the high elastic strain limit of MGs to enhance the deformation recovery of SMAs after the reverse martensitic transformation during unloading has not been studied yet.

The purposes of the present study are to (i) examine the thermoelastic martensitic transformation behavior in nanoscaled TiNi thin films and (ii) utilize the high elastic strain limit of MGs to enhance the deformation recovery of SMAs after the reverse martensitic transformation upon unloading. To achieve this, multilayered films with

---

* Corresponding author.
  E-mail address: hsuehc@ntu.edu.tw (C.H. Hsueh).

alternate layers of TiNi SMA and ZrCuAlNi MG were deposited on the Si substrate using magnetron sputtering. By controlling the annealing temperature, fully amorphous as-deposited multilayered films could be transferred to alternate layers of crystalline TiNi SMA and amorphous ZrCuAlNi MG. The thickness effects on the stress-induced martensitic transformation behavior of SMA/MG multilayered films were investigated using nanoindentation tests. To characterize the superelastic recovery effect and stress-induced martensitic transformation behavior during nanoindentation, the remnant depth ratio (RDR) extracted from the load-displacement curve was used [31].

2. Material and methods

2.1. Shape memory alloy/metallic glass multilayered films

$Ti_{52}Ni_{48}/Zr_{43}Cu_{30}Al_{10}Ni_{17}$ multilayered thin films were deposited alternately on Si substrate using magnetron sputtering. The radio frequency (RF) powers for the $Ti_{56}Ni_{44}$ (in at.%) and ZrCuAlNi alloy targets were fixed as 200 W and 100 W, respectively. To achieve a uniform film composition for each layer, the sample holder was rotated at 100 rpm during sputtering. The total number of the TiNi and ZrCuAlNi layers in multilayer was 10 with 5 layers each and the total film thickness was approximately 2 μm. Unless noted otherwise, the top layer was TiNi and the bottom layer was ZrCuAlNi. Two different types of multilayered films were processed (see Table 1). For Film I, the thicknesses of individual TiNi and ZrCuAlNi layers were 240 and 170 nm, respectively. For Film II, the thicknesses of individual TiNi and ZrCuAlNi layers were 360 and 60 nm, respectively. To examine the film thickness effects, monolithic TiNi thin film with a thickness of 2 μm was also deposited on Si substrate. The as-deposited films were amorphous. To take the advantages of superelasticity (SE) from SMA and high elastic strain limit from MG, control of annealing is required to crystalize TiNi layers while keeping ZrCuAlNi layers amorphous. In the present study, the multilayered films were annealed at three different temperatures, 300 °C, 350 °C and 400 °C, for 1 h and their structures were examined after annealing, and the monolithic TiNi film was annealed at 400 °C as the control specimen in nanoindentation tests.

2.2. Characterizations

The structure of the top layer of the multilayered film was determined by grazing incident diffraction (GID). A low grazing angle of X-ray incidence was set at 0.7°, and the detector was scanned in the 2θ range from 20° to 80° at 4°/min. On the other hand, the structure of the entire multilayered films was analyzed by X-ray diffraction (XRD) with 2θ ranging from 20° to 65° at 4°/min. All the XRD measurements were conducted at room temperature. The multilayered films for TEM observation were prepared using focus ion beam (FIB). The microstructure and element distributions of the multilayered film were observed by transmission electron microscopy (TEM, FEI Tecnai G2 F20) with an energy dispersive X-ray spectroscopy (EDX) and a scanning transmission electron microscopy (STEM) with a high angle annular dark field (HAADF) detector. The nanoindentation test was performed using Hysitron TI 950 TriboIndenter with a conical probe of 5 μm tip radius.

Table 1
Processing of multilayered films (5 layers each), Films I and II, and monolithic TiNi film.

	Layers	Sputtering RF Power (W)	Sputtering Time (min)	1 h Annealing Temperature (°C)	Thickness (nm)
Film I	TiNi/ ZrCuAlNi	200/100	20/20	300, 350, 400	240/170
Film II	TiNi/ ZrCuAlNi	200/100	30/10	300, 350, 400	360/60
TiNi	TiNi	200	150	400	2000

The loading function was fixed at a constant strain rate of 0.2 s^{-1} without holding time.

3. Results and discussion

3.1. GID and XRD

The GID results of the as-deposited and annealed Film I are shown in Fig. 1(a). For as-deposited and 300 °C annealed films, there was only a broad hump around 2θ = 42.5°, which suggested an amorphous structure. For annealing at 350 °C, the intensities of the broad hump decreased and the peak of austenite (B2) appeared at 2θ = 42.5° which indicated partial crystallization of the TiNi layer. With the increase of annealing temperature, the peaks of austenite (B2) became sharper. For annealing at 400 °C, there were three obvious peaks at 2θ = 42.5°, 61.5° and 77.8°, which corresponded, respectively, to (110), (200) and (211) reflections of parent phase (B2) structure of TiNi, implying complete crystallization of the TiNi layer. The GID results of the as-deposited and annealed Film I are shown in Fig. 1(b) for ZrCuAlNi being the top layer. When the annealing temperature was 400 °C and below, there was only a broad hump around 2θ = 39° indicating the amorphous structure of ZrCuAlNi layer. The XRD profiles of the as-deposited and annealed Film I are shown in Fig. 1(c). The as-deposited and 300 °C annealed films showed a broad hump, which suggested both TiNi and ZrCuAlNi layers were amorphous. When the annealing temperature was 350 °C, the TiNi layers started to crystallize. The dotted-frame region in Fig. 1(c) is enlarged and shown in Fig. 1(d), which displayed the superposition of a diffraction peak at 2θ = 42.5° for B2 phase of crystallized TiNi on a broad hump around 2θ = 39° for amorphous ZrCuAlNi.

Similar to Fig. 1 for Film I, the corresponding results for Film II are shown in Fig. 2. Compared to full crystallization of TiNi in Film I at 400 °C annealing temperature, full crystallization of TiNi in Film II occurred at 350 °C. The difference in the crystallization temperature of TiNi layer between Films I and II was attributed to the thickness effect. It has been reported that the crystallization temperature of amorphous layer increased with decreasing film thickness, and crystallization could not occur below a certain critical thickness [32]. To ensure full crystallization of TiNi layers while keeping ZrCuAlNi layers amorphous, 400 °C was hence chosen as the annealing temperature in the present study. A question was raised as to the crystallization temperature of our sputtered TiNi films seemed relatively low compared with others because it was reported to be above 450 °C elsewhere [33]. However, the crystallization temperature of above 327 °C was also reported for sputtered TiNi films with 48.0–51.3 at.% of Ti [34] which was in agreement with our present results. The discrepancy in crystallization temperature obtained by different groups is presently unknown. However, it is worth noting that the crystallization temperature of sputtered TiNi films could be reduced by ~30 °C when small amount of Ni was replaced with Cu [35] and diffusion of Cu and Al from the MG layer to TiNi layer in our multilayered films (will be shown in Fig. 4) could potentially lower the crystallization temperature of TiNi layer.

3.2. Transmission electron microscopy analysis

The TEM bright field image of the cross-section of Film I annealed at 400 °C for 1 h is shown in Fig. 3(a). The contrast in TiNi layers revealed the polycrystalline structure. While the grain growth normal to the layer was limited by the thickness of TiNi layer, the grain could grow laterally and the width was about 300–400 nm. In the meanwhile, the contrast in the ZrCuAlNi layers is featureless due to their amorphous structure. Using the selected area diffraction, the diffraction pattern of area A in Fig. 3(a) is shown in Fig. 3(b) and it reveals the austenite (B2) phase. The selected area diffraction pattern of area B in Fig. 3(a) is shown in Fig. 3(c), and it contains a diffused halo ring from the amorphous ZrCuAlNi and some small diffraction spots, which could