Micromechanical response for the amorphous/amorphous nanolaminates

S.Y. Kuan\textsuperscript{a}, H.S. Chou\textsuperscript{a}, M.C. Liu\textsuperscript{a}, X.H. Du\textsuperscript{a,b}, J.C. Huang\textsuperscript{a,*}

\textsuperscript{a}Department of Materials and Optoelectronic Science, Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, Kaohsiung, Taiwan 804, ROC

\textsuperscript{b}Department of Materials Engineering, Shenyang Institute of Aeronautical Engineering, Shenyang 110034, PR China

\textbf{Article info}

\textbf{Abstract}

The uniaxial microcompression and nanoindentation responses of amorphous-ZrCuTi/amorphous-PdCuSi nanolaminates were investigated. It was found that the apparent deformation mechanism transforms from highly inhomogeneous mode in the monolithic amorphous alloys to relatively more homogeneous mode in the micropillars of nanolaminates. Similar phenomena were observed under nanoindentation. The presence of high-density sharp amorphous/amorphous interfaces in the nanolaminates, which could hinder the propagation of shear bands, is a possible reason for the observed transition in the deformation mode.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

It has been well established that room temperature deformation of metallic glasses (MGs) occurs through shear band nucleation and propagation even when the sample sizes are microscale \cite{1}. Some MGs exhibit size effect, that is the smaller the samples, the higher the critical shear stress because of the fewer cast defects compared with their counterpart with a larger size \cite{2,3}. While some other MGs such as the results of Schuster et al. \cite{4} and Dubach et al. \cite{1} show that there is no size effect. For example, the yield strength of the Zr-based BMGs does not change with pillar size even from 3 \textmu m to 0.3 \textmu m. It was recently discussed that the discrepancy in literature might be a result of various degrees of cast defects in MGs prepared by different laboratories \cite{5}. How to obtain high-performance MGs with a microscaled characteristic length is critical to their practical uses to fabricate thin film coatings and micro-electromechanical systems (MEMS) devices. Recent studies show that the brittle problem of some metallic glass thin films can be alleviated by percolating with a nanocrystalline metallic underlayer \cite{6–9}. However, such microstructures also make a mechanical isotropy.

For brittle materials, the inferior fracture properties can be modified by deliberately introducing high-density defects, i.e., the heterogeneous interfaces, which can provide effective obstacles for the propagating microcracks \cite{10,11}. Similar to crack propagation, the nucleation and propagation of shear bands are also controlled by the magnitudes of stresses at the leading edges and the reduction in system energy. Following these ideas, to design nanolaminates by tailoring the microstructure with different glassy phases seems to be a feasible choice in terms of the ductility improvement. Fortunately, it has been proved that the bulk metallic glasses composed of two glassy phases demonstrate improved deformation capability at room temperature \cite{12–15}. Thus, the purpose of the present study is to evaluate the mechanical response of the microscaled MGs with microstructure characterized by two interlaminated amorphous layers.

2. Experimental details

Amorphous–amorphous multilayer films in this study were deposited alternately on Si substrate by magnetron sputtering. One is Zr\textsubscript{55}Cu\textsubscript{31}Ti\textsubscript{14} (denoted as ZCT) amorphous layer (denoted as ZCT) and the other is Pd\textsubscript{77}Cu\textsubscript{6}Si\textsubscript{7} based amorphous layer (denoted as PCS). Monolithic ZCT or PCS thin films, as well as multilayers consisting of 5/50 nm ZCT/PCS and 50/50 nm ZCT/PCS, were prepared. For both the 5/50 and 50/50 nm multilayered samples, the first top layer touching the down-loading flat indenter is ZCT. The total film thickness was about 3 \textmu m. The nature of the deposited thin films was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Microscaled pillar samples for compression tests were fabricated.
using a Seiko SMi3050 dual focused-ion-beam (FIB) system. A series of concentric circular patterns were utilized to machine pillars to give these an optimized and minimum taper angle. Microcompression tests were conducted on the pillar samples (measuring ~1 μm in diameter and ~2 μm in height) with an MTS nanoindenter XP equipped with a flat-end Berkovich indenter (also machined by FIB) which has an equilateral triangle cross-section measuring 13.5 μm in side length [2,3,7]. The tests were performed in the loading rate control mode. Microcompression was performed at a loading rate of 1.6 × 10^{-2} mNs^{-1} to a predetermined displacement of 300 nm, which corresponds to about 15% of strain. The micromechanical testing was also carried out by using the nanoindentation technique by a conventional Berkovich indenter (without flattened by FIB).

3. Results and discussion

Fig. 1 shows the XRD diffraction patterns for the individual ZCT and PCS amorphous thin films along with the 50/50 nm ZCT/PCS multilayered film. The existence of a broad peak for the three samples showed that the microstructure is of characteristics of a glassy phase. For the 50/50 nm ZCT/PCS multilayer, XRD shows that the two superimposed broad peaks (denoted by circles A and B) and their 2θ positions correspond exactly to the individual glassy films. Cross-sectional TEM images shown as insets in Fig. 1 for the 50/50 and 50/50 nm ZCT/PCS multilayered film exhibit a well-defined layered structure with a regular-arrangement bilayer period. A single halo ring has been observed in the electron-diffraction pattern stemming from the individual PCS in the multilayered structure which is similar to the XRD measurements. The halo ring of the ZCT layer is blurred due to its minor volume fraction. All these observations affirm that the individual PCS and ZCT thin films and their multilayered structure are in an amorphous state.

In micro-indentation with Vickers tip, the intersection of semi-circle shear bands promoted by the geometrical confinement was demonstrated by Jana et al. [16] via bonded-interface technique. Intersection of shear bands and the formation of profuse secondary shear bands also occur in nanoindentation, with the failure mode being changed from catastrophic fracture to multiple shear banding [17]. In this case, multilayered structure supplies more opportunities for the intersecting of interfaces and shear band propagation, as a result of more secondary or ternary shear bands formed. This can be proved by the micro-response of multilayered samples and monolitic samples under the nanoindentation process, in which homogenous deformation mode has been observed, as shown in Fig. 2. For the monolitic PCS film, there are numerous pop-ins corresponding to the nucleation and propagation of major shear burst events. In contrast, for the 50/50 nm multilayered film, the nanoindentation response curve appears to be much smoother and the deformation appears to be much more homogenous. In the biaxial stress state, it is presumably that the interface could become the effective obstacles to the shear bands motion. Our observations are different to the study by Misra et al. [18], in which the nanocrystals could not change the deformation mode for MG matrix under nanoindentation.

The engineering microcompression stress–strain curves for the individual amorphous ZCT, PCS and ZCT/PCS multilayers are shown in Fig. 3. It is found that the monolitic ZCT, PCS film and 5/50 nm ZCT/PCS multilayers display a similar deformation mode. For all of them, the whole strain is attributed to the accumulation of individual strain bursts. Similar to many observations for amorphous micropillars [1–3], the first strain burst occurred immediately after yielding for all these samples. However, it is of interest to observe that the 50/50 nm ZCT/PCS multilayered pillar shows much higher yield stress (~2 GPa) for the occurrence of first strain burst. The inhomogeneous flow in this 50/50 nm pillar seems to be alleviated some by decreasing the amounts of strain burst, and relatively homogenous deformation can also be observed at some stages, denoted by “A” in Fig. 3.

To correlate the strain bursts with sample deformation, SEM micrographs of the compressed pillars were taken. Representative micrographs for the 50/50 and 50/50 nm pillars are displayed in Fig. 4 (a) and (c), respectively. The amount of localized shears is consistent with the number of strain burst shown in Fig. 3. Apparently, the pronounced strain bursts in the stress–strain curve are associated with the sudden sample slides resulting from localized shear. However, for the 50/50 nm ZCT/PCS multilayer pillar in Fig. 4(c),

Fig. 1. X-ray diffraction curves for PCS, ZCT glassy thin films, and their multilayered structure. The insets show the cross-sectional transmission electron microscope image and the selected area electron-diffraction pattern of the multilayered structure.

Fig. 2. Load-displacement curves under nano-indentation for the individual amorphous ZCT, PCS and ZCT/PCS multilayers.

Fig. 3. The engineering stress–strain curves under compression for the individual amorphous ZCT, PCS and ZCT/PCS multilayer micropillars.
many diffuse shear processes can be observed in the pillar top region. And the mean strain carried by each activated shear banding events decreases, indicating the propagation of shear bands is suppressed to some extent. With the increase of load, the pillar finally deforms with a catastrophic major shear process.

TEM longitudinal images of the deformed 5/50 and 50/50 nm ZCT/PCS multilayer pillars are shown in Fig. 4(b) and (d), respectively. For the more ductile 50/50 nm ZCT/PCS multilayer pillar, there are three different deformation behaviors. The top left corner, as shown in Fig. 4(e), presents the semi-homogeneous deformation with a high local strain of 50% to 90%. Fig. 4(f) shows the deflection-like appearance where one incoming shear band is terminated by dissipating the energy along the interface. Fig. 4(g) depicts the severe shear band deformation, the ZCT and PCS amorphous layers are both severely elongated yet still intact without breakage. The TEM layers can appear to be highly ductile in the form of thin layer.

Some researches [12–15] have shown that the existence of heterogeneous amorphous domains in composite BMGs could make the propagating of shear band more difficult, thus enhancing its global plasticity. Although the physical mechanism underlying the gain of plasticity is controversial, a well-established benefit of inhomogeneous structure is to inhibit the propagation of shear bands. It is true that, in the case of confining nanoscaled layers of metallic glass with a ductile crystalline material, the propagation of shear bands can be arrest at the interface by the significant elastic force from the nanoscaled crystalline layers [6–9]. So, if we are to gain further information on the interaction between high-density sharp interfaces and the propagation of shear bands for the amorphous/amorphous nanolaminates, we must determine the stress concentrations associated with the interfaces and the propagating shear front. In what follows, we evaluate the happening at the interface from firstly the stress aspect and then from the strain energy aspect.

The existence of stress concentration means that a propagating shear front would exert force on an interface ahead of it. The stress concentration ahead of a propagating shear front can be estimated by the assumption that it has the same form as that of a dislocation in a crystalline material [19].

$$\sigma_c = \frac{\beta G}{R}$$  \hspace{1cm} (1)

where $G$ is the shear modulus, and $\beta$ is the pre-factor related to the value of $T/T_g$. According to Johnson and Samwer [20], the value of $\beta$ at 298 K is equal to ~0.03, and decrease to ~0.02 at the temperature close to $T_g$. To the formed shear bands, it suffers the shear deformation by the top and bottom solid pieces and exhibits the liquid-like phenomenon in the shear band region. If we suppose that the shear band is different from the solid pieces, the shear strength of shear band can be established as ~0.02 G [20]. For PCS and ZCT, $\sigma_w$ would thus be around 0.96 and 0.67 GPa, respectively.

Considering the strength of the PCS/ZCT interfaces, it is suggested that the resistance to interface crossing is mainly dependent on the elastic modulus mismatches of the two amorphous layers. Due to the amorphous microstructure, the lattice mismatch is considered to be minor. Thus, the corresponding interface strength $\sigma_E$, arising from the elastic modulus ($E$) mismatch, is given by [21]:

$$\sigma_E = \frac{R \cdot (E_{PCS} - E_{ZCT})}{(E_{ZCT} + E_{PCS})} \cdot \sin \theta / 8 \pi$$  \hspace{1cm} (2)

where $R = (E_{ZCT} - E_{PCS})/(E_{ZCT} + E_{PCS})$ and $\theta = 45^\circ$ is the angle between the slip plane and the interface. The elastic modulus $E$ values of ZCT and PCS are ~90 and ~130 GPa, respectively. The interface strength of the ZCT/PCS multilayer is calculated to be ~0.31 GPa.

In comparison of the above induced stress concentration $\sigma_c$, and the interface strength $\sigma_E$, it is expected that the stress concentration ahead of a propagating shear front would be higher than the interface strength in the current multilayer pillar. Hence, a deflection phenomenon of the operating shear band on the interface of dissimilar materials would occur [22,23].

For the shearing in a micropillar, the shear band can be treated as the formation of interfaces. Similarly to crack propagation on the interface of dissimilar materials, the deflection phenomenon in some BMGs can also be explained in terms of the Dundur's

---

**Fig. 4.** SEM micrographs showing the compressed pillars to a displacement of 300 nm: (a) 5/50 nm ZCT/PCS multilayer, and (c) 50/50 nm PCS/ZCT multilayer. TEM micrographs showing the compressed (b) 5/50 ZCT/PCS, (d) 50/50 ZCT/PCS multilayer pillars to a displacement of 300 nm, the enlarged views of (e) the upper left corner, (f) the upper centered region, and (g) the severe layer deformation due to shear band propagation.
1: Penetration

2

Shear band (characteristic width 10 nm)

II: deflection

1

\[ G_d / G_p > G_{ic} / G_c \] (3)

where \( G_d \) is the strain energy release rate of a deflected crack, \( G_p \) is the strain energy release rate of a penetrated crack, \( G_{ic} \) is the fracture energy of the interface, and \( G_c \) is the mode I fracture energy of materials 1. If the inequality is reversed, then the crack will penetrate the interface and proceed into material 1. Thus, the relative tendency of a crack to be deflected by the interface or to pass through can be assessed by using this equation.

The effect of the mismatch in materials properties on \( G_d / G_p \) in Eq. (3) depends on the first non-dimensional parameter, the elastic mismatch parameter \( \alpha \) (similar to \( k \) but with the consideration of the Poisson ratio \( v \)) defined as [26]:

\[ \alpha = \frac{(E_1 - E_2)}{(E_1 + E_2)} \] (4)

where \( E = E/(1 - v^2) \) is the plane strain tensile modulus. For the ZCT/PCS interface with \( \alpha \approx 0.12, G_d / G_p \) can be estimated to be \( 0.8 \) [27]. Thus, in order to be effective in impeding the initial propagation of shear bands cracks, \( G_d / G_c \) should be smaller than 0.8, or the interface toughness \( G_{ic} \) should be less than 80% of the toughness of the PCS or ZCT \( G_c \) in Eq. (3). When both materials are resistant to plastic deformation, the toughness of a sharp interface, \( G_{ic} \), between two dissimilar materials can be very low, typically on the order of 1–5 J/m² [28]. With the low value of \( G_{ic} \) in the current amorphous/amorphous multilayered film, the ratio of \( G_d / G_c \) is very likely to be less than 0.8, indicating that the ZCT/PCS interlayer could have the capability to deflect the propagating shear bands. Similar result has been observed by the study of Sharma et al. [12] for deformed Zr-based/La-based glassy multilayered structure. Based on the above evaluation from both the stress and strain energy aspects, the deflection of the propagating shear band is highly likely to occur at the amorphous layer interface. In this study, the deflection of propagating shear bands indeed occurs in the 50/50 nm PCS/ZCT pillars. However, another important factor is the thickness of the nanolaminates. According to the result of Madani et al. [27] when the ratio of the shear band thickness to the individual layer thickness is smaller than 0.5, the above deflection effect would become weak. The critical shear band thickness estimated by Zhang and Greer [29] via transmission electron microscopy is 10–20 nm. In terms of the 5/50 nm ZCT/PCS nanolaminates, the thin ZCT layers of only 5 nm might not provide deflection capability.

Similar toughening of the multilayered micropillars has also been observed in our parallel studies on the ZrCu/Zr [7, 30, 31], ZrCuCu [32], and ZrCuTi/Ta [33] systems. The elastic modulus \( E \) values of ZrCu, Zr, Cu, ZrCuTi, Ta, and PdCuSi are \( \approx 100, \approx 125, \approx 135, \approx 110, \approx 220, \) and \( \approx 130 \) GPa, respectively. The calculated \( R \) factor \( \frac{1}{E_1 + E_2} \) values for the ZrCu/Zr, ZrCu/Cu, ZrCuTi/Ta, and the current ZCT/PCS systems are 0.11, 0.15, 0.33, and 0.08, respectively. From our microcompression results from these multilayered micropillars, the average strain levels achieved in the top portion of the above four deformed pillars are \( \approx 55\%, \approx 40\%, \approx 20\%, \) and \( \approx 30\% \). Since the above multilayer systems have different layer thicknesses, different metal crystal structure (HCP, FCC, or BCC), it is not yet decisive to judge whether there is direct correspondence between the modulus mismatch and pillar plasticity. Research along this line is worthy of further study.

4. Conclusions

The present study demonstrates that the brittle problem of amorphous metallic glass thin films can be alleviated by inter-laminating another metallic glass layer with a different modulus. It was found that the apparent deformation mechanism transforms from highly inhomogeneous mode in the monolithic amorphous alloys to relatively more homogeneous mode in the micropillars of nanolaminates. Similar phenomena were observed under nanoindentation. The presence of high-density sharp amorphous/amorphous interfaces in the nanolaminates, which could hinder the propagation of shear bands, is a possible reason for the observed transition in the deformation mode. The effect of interlayer to the deformation mode significantly depends on the elastic modulus mismatch and loading types. Our results present a feasible way for making shear banding more stable, leading to the toughening of brittle metallic glassy thin films and potentially broadening their applications.

Acknowledgements

The authors gratefully acknowledge the sponsorship from National Science Council of Taiwan, ROC, under the project No. NSC 98-2221-E-110-035-MY3.

References


