Mechanical response of amorphous ZrCuTi/PdCuSi nanolaminates under nanoindentation

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Abstract

In this paper, the relationship between mechanical response and shear band evolution for ZrCuTi (ZCT)/PdCuSi (PCS) nanolaminates under nanoindentation is discussed. Comparing to the monolithic amorphous ZCT and PCS films, the ZCT/PCS nanolaminates exhibit enhanced hardness and a more homogenous deformation mode. Cross-sectional transmission electron microscopy observations show that the shear-band patterns beneath the indent in ZCT/PCS nanolaminates are irregular and convoluted, and appear to be a mixture of the semi-circular shear bands and radial shear bands.

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1. Introduction

Monolithic metallic glasses are regarded as the good model materials for observing the elastic/plastic mechanical response by micro/nanoindentations owing to their isotropic and no work-hardening behavior during uniaxial testing [1]. For this kind of materials, due to the absence of strain hardening, incomplete shear bands (such as the semi-circular and radial shear bands, as depicted schematically in Fig. 1) beneath the nanoindent are usually observed [2–8]. The indenter tip is encased in an elastic hemispherical core of material which assumed to be a hydrostatic pressure [3]. The center of the hemispherical core is located at the indenter tip. There exists a plastic hemispherical zone surrounding the hydrostatic zone and the semi-circular shear bands are propagated along plastic zone. Furthermore, Chen and Lin [9] found that radial shear bands, which have corresponding circular centers at the intersections of sample surface and semi-circular shear bands, are nuclear and propagate along maximum shear stress plane. Which shear banding patterns to the dominant mode of shear banding would depend on the inherent mechanical nature of the tested materials. For highly ductile Pd based metallic glasses, similar to ductile metals, the semi-circular shear banding pattern is more expected [2–4]. On the other hand, the less-ductile Zr or Fe based metallic glasses, similar to brittle silicate glasses, are more prone to form radial bands dominant pattern [5–8].

How the shear bands evolve for the composite multilayered metallic glasses remains as an interesting topic. Recently, we discovered that the amorphous ZrCuTi/amorphous PdSiCu composite structure demonstrates relatively more homogeneous mode [10]. However, fundamental understanding of the micro-mechanical reasons for such a behavior is inadequate. Fortunately, nanoindentation is a viable method to be used in such a case. By this way, the relationship between mechanical response and laminated structure in a two-dimensional region can be mapped, thus providing a window to understand how shear bands develop [11–13]. Hence, in the present study, by using nanoindentation, the mechanical response and the associated shear band patterns under indents of amorphous ZrCuTi/PdSiCu multilayered films are investigated.

2. Experiment details

Amorphous–amorphous multilayer films in this study were deposited alternately on Si substrate by magnetron sputtering. One is the Zr53Cu31Ti14 amorphous layer (denoted as ZCT) and the other is the Pd77Cu8Si5 based amorphous layer (denoted as PCS). Monolithic ZCT or PCS thin films, as well as the ZCT 50 nm/PCS 50 nm multilayers, were prepared. For the 50/50 nm multilayered samples, the first top layer touching the down-loading flat indenter is ZCT. The total film thickness was about 2.5 μm. The nature of the deposited thin films was characterized by X-ray diffraction (XRD). The results of XRD have been reported previously [10]. The existence of a broad halo for the three samples implies that the sputtered thin films are characteristics of glassy phases. For the 50/50 ZCT/PCS multilayer, XRD shows that the superimposed broad halo and the peak 2θ position lies in between those of the monolithic ZCT and PCS amorphous films. The micro-mechanical testing was carried out by using the nanoindentation technique with a conventional Berkovich indenter. The hardness and modulus of thin film were first measured with a preset displacement of 200 nm and at a loading rate of 0.25 mN s⁻¹. The indentation
surface marks were systematically examined by scanning electron microscopy (SEM) in film specimens indented to 200, 500, and 1000 nm at a loading rate of 0.25 mN s\(^{-1}\). The systematical cross-sectional transmission electron microscopy (TEM) characterization was conducted on the same indented samples. The cross-sectional TEM foils were fabricated using a Seiko SMI3050 dual focused-ion-beam (FIB) system.

3. Results and discussion

The load-displacement curves as well as the surface morphology of the tested materials after indentation to 1000 nm are shown in Fig. 2. It is found that compared to the monolithic ZCT or PCS amorphous films in Fig. 2a and b, the first pop-in event of the ZCT/PCS multilayered films appears at a higher displacement. As shown in Fig. 2c, the first pop-in event is seen to occur at the displacement of 720 nm. To make sure of this phenomenon, SEM examinations were also done on the ZCT/PCS films indented to 200 and 500 nm, as shown in Fig. 2d for the indentation to 500 nm. It is confirmed that the underneath shear bands in the 50/50 ZCT/PCS multilayered film did not penetrate out of the multilayer surface and the indentation load-displacement curve is quite smooth up to 500 nm indentation depth.

The mechanical responses of the monolithic ZCT film, monolithic PCS film, and 50/50 ZCT/PCS multilayered film are characterized by the values of Young’s modulus, nanohardness and plasticity (or the ease of shear banding activity, cf. the argument below) under nanoindentation in the present study. The values are listed in Table 1. Here, it is interesting to note that, compared to the monolithic ZCT and PCS films, the ZCT/PCS multilayered films demonstrate a higher value of nanohardness, which should be a result of the restraint against shear banding nucleation and propagation in the multilayered films.

Nanoindentation provides a viable way to measure the magnitude of deformation. Usually, the plastic criterion \(R_W\) is defined as the ratio
The generally more ductile Pd based PCS metallic glass has the highest this parameter is calculated to be 0.837, 0.862 and 0.822, respectively.

The mechanical properties of the tested materials measured by nanoindentation.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Modulus $E$ (GPa)</th>
<th>Nanohardness $H$ (GPa)</th>
<th>$E/H$</th>
<th>$R_W$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZCT</td>
<td>90</td>
<td>5.3</td>
<td>17.0</td>
<td>0.837</td>
</tr>
<tr>
<td>PCS</td>
<td>130</td>
<td>5.8</td>
<td>22.4</td>
<td>0.862</td>
</tr>
<tr>
<td>ZCT/PCS</td>
<td>110</td>
<td>6.5</td>
<td>16.9</td>
<td>0.822</td>
</tr>
</tbody>
</table>

For monolithic ZCT, monolithic PCS, and laminated ZCT/PCS films, this parameter is calculated to be 0.837, 0.862 and 0.822, respectively. The generally more ductile Pd based PCS metallic glass has the highest $R_W$, followed by Zr based ZCT. It can be noticed that, though the extent is very slight, the multilayered ZCT/PCS structure seems to reduce the deformation ability [14,15]:

$$R_W = \frac{W_{\text{plastic}}}{W_{\text{total}}} = \frac{h_t}{h_{\text{max}}}$$  \hspace{1cm} (1)

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Now, we can do some analyses on these mechanical responses. The Young’s modulus of the ZCT/PCS multilayered films can be modeled by the rule-of-mixtures. Nevertheless, the triaxial stress state under nanoindentation makes the situation not exactly under iso-strain or iso-stress condition. The modulus should be in between those predicted by these two ideal conditions, namely

$$E_{\text{ZCT/PCS}(\text{iso-strain})} = E_{\text{ZCT}}V_{\text{ZCT}} + E_{\text{PCS}}V_{\text{PCS}},$$  \hspace{1cm} (2)

$$1/E_{\text{ZCT/PCS}(\text{iso-stress})} = V_{\text{ZCT}}/E_{\text{ZCT}} + V_{\text{PCS}}/E_{\text{PCS}}.$$  \hspace{1cm} (3)

Taking the data in Table 1 for $E_{\text{ZCT}}$ (90 GPa), $E_{\text{ZCT}}$ (130 GPa) and $V_{\text{ZCT}}$ (0.5), $V_{\text{ZCT}}$ (0.5) from the equal layer thickness, Eqs. (2) and (3) give $E_{\text{ZCT/PCS}} = 110$ and 106 GPa, respectively, which are essentially the same as the experimental value.

Similarly, the nanohardness of ZCT/PCS multilayered films can also be estimated by the iso-strain and iso-stress rule-of-mixtures. The calculated $H_{\text{ZCT/PCS}}$ hardness values are 5.55 and 5.54 GPa, respectively. However, the measured hardness value is 6.5 GPa, suggesting significant enhancement in nanohardness is observed in the ZCT/PCS multilayered films. Because the plastic deformation of metallic glassy materials at room temperature originates mainly from the shear banding behavior, the magnitude of the hardness could be used to evaluate the activity of shear bands. The higher nanohardness value suggests the greater difficulty for shear bands to move. In the present study, the amorphous ZCT/PCS multilayered films demonstrate higher hardness ($H$) as well as lower plasticity ($E/H$ and $R_W$ in Table 1), suggesting the movement of shear bands constrained. Such a case, a direct TEM observation on the development of shear bands under the indenter can provide more evidence to illustrate the issue.

Fig. 3 shows the cross-sectional TEM images of the shear banding pattern for the ZCT/PCS multilayered films indented to 500 and 1000 nm displacements. Many investigations have well established that the shear banding patterns generated underneath the nanoindents of monolithic amorphous materials are smooth, regular and either semicircular or radial in shape dependent on the nature of materials [2–8]. In the current multilayered ZCT/PCS thin films, however, the shear bands are obviously irregular and convoluted in shape. Fig. 3a is a low-magnification TEM cross-sectional image showing that the semi-circular and radial shear bands both occur in the ZCT/PCS multilayered films under nanoindentation loading. The irregular convoluted shear bands appear to be a result of strong reaction of different kinds of shear bands. In Fig. 3b, a strong interaction between semi-circular shear band and radial shear band can be observed and at the intercrossed sites; the irregular and convoluted shear bands form owing to the distorted stress fields. The interaction of shear bands (in three dimensions) reduces their sharpness, restrains their rapid development and increases the difficulty for shear bands movement resulting in the increase of hardness. For this, a similar explanation has been given in the research by Das et al. [16]. With the increase of load displacement, some individual shear bands become “broken” owing to the strong interaction of plastic work ($W_{\text{plastic}}$) and the total work ($W_{\text{total}}$) in nanoindentation process [14]. In the present study, the ratio of the residual depth of penetration upon complete unloading, $h_t$, to the maximum penetration depth prior to unloading, $h_{\text{max}}$, is indicative of the extent of plastic deformation [14,15]:

$$R_W = \frac{W_{\text{plastic}}}{W_{\text{total}}} = \frac{h_t}{h_{\text{max}}}$$  \hspace{1cm} (1)

![Fig. 3](image-url) (a) Full view of shear bands patterns beneath nanoindent indented to 1000 nm. The enlarged views of the shear bands indented to (b) 500 nm and (c) 1000 nm.
among the shear bands and multiple convoluted shear bands pattern forms, as shown in Fig. 3c. The resultant multiple shear banding patterns in the ZCT/PCS multilayered films can be used to explain the absence of apparent pop-in events at the early deformation stage, as observed by various experiments [11,17–19].

First, we make an analysis on the observed shear banding pattern for the ZCT/PCS multilayered films. It is known that metallic glassy materials undergo no work-hardening during uniaxial testing, so their behavior under nanoindentation would be expected to agree with the predictions of either cutting mechanisms [20] or the expanding cavity model [21]. For the highly ductile amorphous PCS, with the E/H more than 20, its continuum response under uniaxial stress is similar to ductile metal, i.e., an elastic–perfectly plastic uniaxial compressive response [22]. Several studies have shown that for ductile metals, the plastic flow underneath the indenter is dominated by the compression mechanism underneath the indent [23,24]. This kind of deformation behavior can be well described by the expanding cavity model wherein a hemispherical radial mode of deformation is formed [25]. Hence, the formation of concentric semi-circular shear bands is the dominant deformation mechanism for the PCS materials under nanoindentation, as observed in this study and before [2–4]. For the less-ductile metallic glasses, with lower E/H (less than 20), similar to inherently brittle silicate glasses [26], the cutting mechanism proposed by Lockett is possible [27]. In such cases, dominant radial bands appear, as shown in some Zr and Fe based metallic glasses [5–8].

In the present study, due to the significant difference in mechanical nature of monolithic ZCT and PCS, the ZCT/PCS multilayered thin films are not isotropic, and this will affect the shear banding development. In one hand, in the plastic region, two kinds of dominant shear bands will be produced simultaneously underneath indenters, i.e., the semi-circular shear bands and radial shear bands. During the deformation process, both of them will interact when they encounter. At the cross point, a distorted stress field forms, thus producing back stress to prevent the smooth development of shear bands, making the deformation focus on a limited region. As a result, no fully-developed shear band can be observed; thus no apparent shear step has been resulted in, meaning that the deformation is realized in a more homogeneous mode.

One the other hand, the ZCT/PCS interfaces are relatively weak in shear and easily sheared by the stress field of the shear bands by the stress field approaching the interface, causing shear band spreading within the interface plane. This also provides a high barrier for shear band transmission. The barrier effects for shearing along the weak interfaces can be evaluated by the interface strength. The lower the interface strength is, the stronger the barrier effect for shear band transmission would be [28].

The corresponding interface strength $\sigma_{fi}$, arising from the elastic modulus (E) mismatch, is given by Ref. [29]:

$$\sigma_{fi} = R \cdot E_{PCS} \cdot \sin{\theta} / 8 \pi,$$

where $R = (E_{ZCT} - E_{PCS}) / (E_{ZCT} + E_{PCS})$ and $\theta$ is the angle between the shear bands and the interface. Under indenter, with the increase of distance from the surface, the $\theta$ becomes smaller and smaller, and hence, the interface strength becomes lower and lower. Therefore, with the increase of distance from the surface, the deflection of shear bands along the interface becomes easier, as shown in Fig. 3c.

4. Conclusions

Due to the above two factors (strong interaction of the semi-circular and radial shear bands and the weak interface strength) for the ZCT/PCS multilayered thin films, the shear bands’ evolution is significantly complicated owing to the heterogeneous microstructure. As a result, multiple shear bands form: Thus no pop-in events can be observed at the early deformation stage. The present study shows that ZCT/PCS multilayered composite structure at nanoscales is of interest and deserves further extensive study. The promising mechanical response offers the potential for using the ZrCuTi/PdCuSi multilayered materials as advanced coatings of bulk materials.

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References