Mechanical property evaluations of an amorphous metallic/ceramic multilayer and its role in improving fatigue properties of 316L stainless steel

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ABSTRACT

We have used nanoindentation to investigate mechanical properties of 200-nm-thick amorphous multilayer consisting of alternating layers of Zr-based thin film metallic glass (TFMG) and holmium scandium oxide (HSO). Nanoindentation results show that TFMG/HSO multilayer exhibits the high hardness and Young's modulus. Owing to its high hardness, smooth surface, and good adhesion properties, TFMG/HSO multilayer is then employed as a protective coating to improve the four-point bending fatigue properties of 316L stainless steel. With coating, the fatigue life is increased from $2.4 \times 10^5$ to $4.9 \times 10^6$ cycles, at the stress of 700 MPa. A crack retardation mechanism has been proposed to explain the role of TFMG/HSO multilayer in improving fatigue properties of 316L stainless steel substrate.

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1. Introduction

Thin film metallic glasses (TFMGs) have been gaining considerable attention in the past decade [1–3]. Compared to conventional crystalline films, TFMGs exhibit superior mechanical properties such as high strength, high toughness, large elastic limits, and high wear and corrosion resistances [2,4]. TFMGs have been demonstrated to be potentially useful for a number of applications including biomedical, mechanical, electrical, optoelectronic, and magnetic [2–5]. In particular, TFMGs have been utilized as a protective coating to improve fatigue properties of 316L stainless steel [6,7] 7075-T6 aluminum alloy [8], and Ti6Al4V [9]. These protective coatings are in a form of monolayer.

There have been several studies investigating the mechanical properties of multilayers consisted of TFMGs [10–12]. For instance, Donohue et al. have studied the characteristics of Cu/amorphous Pd$_{0.77}$Si$_{0.23}$ multilayer and found that the shear band instability could be suppressed in nanometer-scale metallic glasses constrained by ultrafine crystalline layers [10]. Huang et al. have also reported that the ductility and plastic strain of amorphous Zr$_{45}$Cu$_{55}$ thin film could be enhanced by introducing metallic underlayer to form amorphous/nanocrystalline multilayer [11,12].

On the other hand, mechanical properties of metal oxide thin films such as Cr$_2$O$_3$ and Al$_2$O$_3$ have been investigated in a number of studies [13–15]. Owing to their high hardness, they are considered to be promising candidates to replace transition metal nitrides as protective coatings [13]. However, the major drawback of the metal oxides compared to the generally softer transition metal nitrides is the low toughness and transverse rupture strength [13,16]. In our previous works [17,18], we have found HoScO$_x$ (HSO) thin film to be potentially beneficial for microelectronic applications. In this study, an amorphous HSO is selected because it is one of the rare-earth based oxides having good thermal stability without crystallization up to 800 °C [19]. It would be interesting to characterize the mechanical properties of HSO and then use it to form a new kind of amorphous multilayer.

We have fabricated a multilayer consisting of alternating layers of amorphous Zr-based TFMG and HSO. The motivation of this study is to combine the high hardness of metal oxide and high toughness of TFMG. TFMG/HSO multilayer is then employed as a protective coating for four-point bending fatigue property improvements of 316L stainless steel substrate.

2. Experimental procedures

A quaternary system of ZrCuAlNi alloy and holmium scandium
oxide were prepared as the sputtering targets for Zr$_{58}$Cu$_{24}$Al$_{11}$Ni$_7$ (in at%) TFMG and HSO layer depositions, respectively. More details about HSO sputtering target preparations are given in our previous works [17,18]. A multilayer consisting of ten alternating layers of TFMG and HSO (TFMG/HSO) was deposited on Si wafer and 316L stainless steel substrates using a direct current (DC) and radio frequency (RF) magnetron sputtering system with sputtering power of 100 W, base pressure of $2 \times 10^{-6}$ Torr, working pressure of 10 m Torr, and working distance of 100 mm. The deposition rates were measured to be 6.7 and 0.8 nm/min for TFMG and HSO, respectively.

Mechanical properties including hardness and Young’s modulus were obtained using a nanoindenter system (Hysitron™ Ti 950 Tribolindenter) with a Berkovich indenter. The maximum load ($\mu$N)/load rate ($\mu$N/s) were 1200/240 for the hardness measurement, while those were 2000/400 for the deformation observation. The dwell time for both cases was 5 s at the maximum load. X-ray diffraction (XRD, Bruker D8 Discover) was used for crystallographic analysis with a glancing angle of 0.5°. A transmission electron microscopy (TEM, Philips Technai G$^2$ F20) was used for microstructural characterization. A dual-beam focused ion beam (FIB, FEI Quanta 3D FEG) was used for the TEM sample preparation.

Material test system MTS 370 was used for four-point bending fatigue test. The samples were loaded at various stress levels with a ratio of $\sigma_{\text{min}}/\sigma_{\text{max}} = 0.1$, where $\sigma_{\text{min}}$ and $\sigma_{\text{max}}$ were minimum and maximum applied stress, respectively. A sinusoidal waveform at a frequency of 10 Hz was applied during bending fatigue test. More details about the four-point bending fatigue test were described elsewhere [6].

### 3. Results and discussion

In order to determine the optimum condition of TFMG/HSO multilayer, the bilayer repeat length and total thickness were kept at 20 nm and 200 nm, respectively; however, the thickness of TFMG and HSO layers in a period were varied to be 15/5 and 10/10 nm, respectively. Hardness and Young’s modulus measurement results of these multilayers and monolayers are listed in Table 1. The indentation depths were limited to be less than 10% of the film thickness to avoid substrate effects [20]. For TFMG monolayer, the hardness and Young’s modulus are 4.63 ± 0.05 GPa and 160.53 ± 2.96 GPa, respectively. Meanwhile, for TFMG/HSO multilayers, the hardness and Young’s modulus increase with increasing of HSO thickness. Compared to 15/5 nm TFMG/HSO multilayer, the 10/10 nm sample is shown to have higher hardness and Young’s modulus of 7.57 ± 0.08 GPa and 239.25 ± 4.45 GPa, respectively, corresponding to approximately increases of 50%.

Vella et al. [21] proposed a rule to define the hardness of multilayered system based on the isostrain conditions in which each layer is assumed to experience the same strain conditions. According to their equation [21], the hardness of 10/10 nm TFMG/HSO multilayer is calculated to be 7.31 GPa, which is similar to the measured value of 7.57 GPa. Since 10/10 nm TFMG/HSO multilayer shows the highest hardness and Young’s modulus, it is then chosen for further experiments to improve fatigue property.

Fig. 1 shows XRD patterns of TFMG monolayer, HSO monolayer, and TFMG/HSO multilayer deposited on Si substrates. The broad humps, in the 2θ range of 30°–45° for TFMG and 25°–40° for HSO, indicate the presence of amorphous structure. These results confirm the amorphous state of TFMG, HSO, and TFMG/HSO multilayer. Cross-sectional TEM image and diffraction pattern of multilayer grown on Si substrate are presented in the inset of Fig. 1, which show that relatively smooth and uniform layer structures for both TFMG and HSO could be achieved by DC/RF magnetron sputtering system. A Pt protective layer was deposited on the top of multilayer to reduce the ion-induced damages in TEM sample preparation by FIB. The thickness of multilayer is confirmed to be 200 nm. The diffuse holo diffraction patterns in the inset of Fig. 1 show no detectable crystallinity or grain structure in the multilayer due to the amorphous nature, in agreement with the XRD patterns. TEM-EDS elemental line-scan result in Fig. 2 further verifies the chemical composition of TFMG/HSO multilayer.

<table>
<thead>
<tr>
<th>Film</th>
<th>Hardness (GPa)</th>
<th>Young’s modulus (GPa)</th>
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<tbody>
<tr>
<td>TFMG</td>
<td>4.63 ± 0.05</td>
<td>160.53 ± 2.96</td>
</tr>
<tr>
<td>HSO</td>
<td>10 ± 0.06</td>
<td>216.36 ± 2.06</td>
</tr>
<tr>
<td>15/5 nm TFMG/HSO</td>
<td>6.85 ± 0.04</td>
<td>229.99 ± 3.81</td>
</tr>
<tr>
<td>10/10 nm TFMG/HSO</td>
<td>7.57 ± 0.08</td>
<td>239.25 ± 4.45</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns of TFMG monolayer, HSO monolayer, and TFMG/HSO multilayer. Insets are diffraction pattern and cross-sectional TEM image of TFMG/HSO multilayer. The white lines in TEM image are used as a visual guideline for each layer of TFMG/HSO.

Fig. 2. TEM-EDS elemental line-scan result of TFMG/HSO multilayer with the inset revealing where the line scan is performed. The vertical grid dashed lines highlight approximate locations of TFMG/HSO interfaces.
corresponding to the TEM image in the inset. However, the possible ion bombardment during FIB processing might have resulted in intermixing of elements in first top TFMG/HSO bilayer.

To examine microstructural changes, Fig. 3 shows cross-sectional TEM images of TFMG/HSO multilayer on a silicon substrate after nanoindentations. Underneath the indent area severe plastic deformation are observed as the arrow indicated in Fig. 3(a). A deeper indentation in Fig. 3(b) was aimed to observe the response of multilayer with indentation depth and loading being 105 nm and 2000 μN, respectively. Fig. 3(b) shows that the pile-up is found around the indent indicating the multilayer is plastically deformed [22].

At the location immediately underneath the indent, the multilayer suffers from severe deformation. When the low loading is applied, the deformed multilayer is still seen clearly with the layer structure. Yet, such layer structure becomes indistinct under the high loading, as shown in Fig. 3(b). The poorly-defined layered structure is presumably resulted from loading-induced intermixing, which is commonly observed in the multilayer upon severe deformation. Chen et al. [23] has reported shear bands formation

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**Fig. 3.** Typical cross-sectional TEM images after nanoindentations with loading of (a) 1200 μN (b) 2000 μN and (c) enlarged image of area marked by a marked area in (b). The marked area in (b) and the arrow in (a) indicate the serration area and catastrophic deformation, respectively. The light and dark layers in the multilayer structure represent TFMG and HSO layers, respectively.

**Fig. 4.** Load-displacement curves of TFMG monolayer (blue), HSO (purple) and TFMG/HSO multilayer (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 5.** S–N curves of uncoated and coated 316L stainless steel after four-point bending fatigue test. Arrows indicate the run-out data of fatigue cycles without failure.
The high hardness and Young's modulus are achieved when the thickness of both TFMG and HSO monolayers is 10 nm. The formation of slip bands in the 316L stainless steel substrate resulting in crack propagation. The fatigue crack initiation is associated with the slip bands piled up due to localized plastic strain. Consequently, the slip bands propagation along with the fatigue cycles govern the degree of local deformation. Then, the movement of slip bands results in a crack nucleation site on the surface as a crack shown in Fig. 6(a) or slip-band ridge in Fig. 6(b). However, the intrusion of slip bands into multilayer indicates the retarding effect of coating on the propagation of slip bands. On the slip-band ridge indicated by the arrow in Fig. 6(b), the ridge drives the adjacent multilayer upward and locally deforms it, causing the multilayer thickness reduction of ~35%. The local deformation characteristics near the slip-band ridge region confirm the good ductility of the multilayer. During the cyclic fatigue loading, the multilayer exhibits high toughness to absorb energy and plastically deform. Nevertheless, the coating reduces crack initiation on surface at the early stage of fatigue failure, thereby improving the fatigue properties. For the TFMG monolayer deposited on 316L stainless steel substrate, Lee et al. [9] have demonstrated that the columnar boundaries, nearly parallel to slip bands in the substrate, are considered as the possible path for the cracks to propagate. Most likely, the columnar structure as radial cracks in TFMG [9] and ceramic monolayers [24] are eliminated when they are formed as a multilayer.

There are three proposed mechanisms of cracks propagation in multilayer systems. These include crack deflection at interface between layers, ductile interlayer ligament bridging, and crack tip blunting due to nanoplasticity at interface which is restricted only for a metal/ceramic multilayer [25]. Further, Zhang et al. [25] have reported that in a metal/ceramic multilayer, the metal layer is deformed plastically by shearing to stop the crack propagation in the ceramic layer. Accordingly, TFMG/HSO multilayer used as the protective layer improves the fatigue properties of 316L stainless steel.

4. Conclusions

In this study, we examined the mechanical properties of amorphous TFMG/HSO multilayer prepared by magnetron sputtering. The high hardness and Young's modulus are achieved when the thickness of both TFMG and HSO monolayers is 10 nm. The
References


