Tensile behaviors of amorphous-ZrCu/nanocrystalline-Cu multilayered thin film on polyimide substrate

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A B S T R A C T
The tensile behaviors of the monolithic ZrCu thin film metallic glass, monolithic crystalline Cu thin film, and the ZrCu/Cu multilayered thin films with various individual layered thicknesses deposited on the polyimide foil have been investigated. The modulus and strength of the multilayered thin films are demonstrated to be consistent with the theoretical Rule of Mixture values. As the individual layer thickness decreases from 100 to 10 nm, the Young’s moduli are varied slightly. However, the maximum tensile stress exhibits a highest value for the 25 nm layer thickness. The higher crack spacing, or the lower crack density, of this 25 nm multilayer film leads to the highest strength.

1. Introduction

Metallic glasses (MGs) with unique atomic structures and excellent mechanical properties are becoming more and more attractive. They have become potential materials for Micro Electro-Mechanical Systems (MEMS) and other applications owing to their high strength, good corrosion resistance, and great forming ability in the viscous state. However, due to the ductility problem, bulk metallic glasses (BMGs) are not easy to be formed or processed into MEMS components. Recently, sputtering techniques have been employed to manufacture MGs into thin film metallic glasses (TFMGs) [5–7]. Nevertheless, the inherent drawback of tension brittleness for such monolithic TFMGs at room temperature still restricts their applications.

In previous researches, many investigators have demonstrated that BMGs with two coexisting phases can influence the movement of shear bands and thus improve the plasticity, such as the works by Das et al. [8] on the Zr50Cu50 (in atomic percent, at.%) BMGs, by Liu et al. [9] on the Zr-based BMGs, and by Lee et al. [10] on the Cu-based BMGs. For TFMGs, there have been much fewer reports on the tensile properties at room temperature. In 1999, Nieh et al. [11] demonstrated that the tensile elongation of a free-standing nanocrystalline Cu laminate coupled with the thin amorphous Cu₃Zr layer can reach high tensile strength. Nieh and Wadsworth [12] and Wang et al. [13] also illustrated that the nanocrystalline/amorphous Cu/ZrCu multilayered laminate with individual thickness of 35/5 nm could display the remarkable plasticity of ~4%. But the volume fraction of the amorphous ZrCu is rather low, only 12.5%. The shear-band movement in the amorphous layer can be suppressed by the nano-scaled crystalline layer, as demonstrated by Donohue et al. [14]. According to these results, it is implied that the shear bands in the amorphous layers were constrained because of their thin thicknesses, and the dislocations in the crystalline layers were disrupted by the amorphous layers. Consequently, integration of the ductile crystalline and the brittle amorphous layers in appropriate thickness and composition can improve the tensile properties of the multilayered systems.

In addition to the researches of the freestanding multilayered systems, the as-deposited thin films on the substrates have been investigated under bending or tensile loading. The soft substrate of polyimide with the benefits of good flexibility, flat surface, low strength, and large strain capability was chosen for comparable investigation [15–17].

In our previous studies, the microcompression testing on the amorphous/nanocrystalline multilayered thin film with different metallic layers has been studied by Liu et al. [18,19]. Then, Pei et al. [20] illustrated that the tensile properties of Cu-foil-supported amorphous/nanocrystalline ZrCu/Cu multilayered thin film were greater than the tensile properties of monolithic ZrCu thin film. Recently, Lee et al. [21] have reported the improved tensile strain in the freestanding ZrCu/Cu multilayered thin film with individual layered thickness of 25 nm. In this study, the tensile behaviors of the amorphous/nanocrystalline ZrCu/Cu multilayered thin films, deposited on the 50-μm-thick polyimide, are systematically examined.

2. Experimental details

The 1-μm-thick ZrCu/Cu multilayered thin films (equal volume fractions, i.e., both 50 vol.%) were prepared by a magnetron sputtering system with a Cu target on the radio frequency (RF) gun and a Zr target on the direct current (DC) gun. The diameter of the target is 101.6 mm and the working distance between the holder and the RF/DC gun is 150 mm. During the deposition process, the holder was set at a rotation...
speed of 10 rpm and it could result in uniform distribution of the film thickness. The base pressure of chamber was pump down to less than 6.7 × 10−4 Pa by a turbomolecular pump and the working gas of pure argon gas was maintained at the rate of 30 standard cubic centimeters per minute. The amorphous ZrCu layers were deposited by the co-sputtering process with the DC and RF guns, and the nanocrystalline Cu layers were deposited by the RF gun. The deposition rates of amorphous ZrCu and nanocrystalline Cu layers are 0.34 nm/s and 0.27 nm/s, respectively. The multilayered specimens were layer-by-layer deposited with alternative amorphous and nanocrystalline thin films.

Moreover, the monolithic crystalline Cu and monolithic ZrCu TFMGs, also with the total thickness of 1 μm, were separately fabricated for parallel study. All the films were deposited on the 50-μm-thick Kapton polyimide (PI) foils. In order to avoid the crimp of specimen, the films were deposited through a dog-bong-shape stainless square-patterned mask. Then, the coated area on the polyimide foils would be taken out by knife cutting and the deforming area is located in the gauge area of 12 mm × 3 mm.

The glassy nature of the as-deposited ZrCu TFMG was examined by X-ray diffractometer (XRD, Siemens D5000) with Cu Kα radiation under the normal couple mode. The composition was identified as Zr78Cu22 by a JEOIL-6330 scanning electron microscope (SEM) system with an energy dispersive X-ray spectrometer (EDS). For the EDS analysis, the specimens were examined several times under the magnification of 500×. Moreover, the operating voltage, probe current, and deriving time for identification were controlled at 10 kV, 1 × 10−10 A, and 120 s, respectively. The microstructure and surface morphology of the manufactured films was also observed by the SEM system at the operating voltage of 10 kV.

For the tensile testing of polyimide-supported multilayered thin films, the individual layer thicknesses of 1-μm-thick ZrCu/Cu multilayered thin films are varied from 10, 25, 50, 75, to 100 nm. The first deposited bottom layer is nanocrystalline Cu and the top one is ZrCu TFMG. Uniaxial tensile testing with a force transducer of 250 N and a strain rate of 3 × 10−3 s−1 was conducted on the coated specimens at room temperature by a minitesteter of MTS Tytron 250 Microforce Testing System. Moreover, a displacement gauge with acquisition rate of 100 Hz was assembled for detecting the tiny displacement during the tensile testing. To confirm the reproducibility, tensile testing for each condition was repeated by more than 10 times.

3. Results and discussion

To identify the structure of multilayered thin films, the representative XRD patterns of polyimide-supported ZrCu/Cu multilayered thin film with individual layered thickness of 100 nm are shown in Fig. 1. The inclined patterns of the XRD results are due to the effect of PI substrates. In Fig. 1, the PI substrate presents a diffused peak at the 2θ diffraction angle range of 30° to 35°. According to our previous works on the ZrCu TFMG, a broad diffraction hump can be observed at the 2θ diffraction angle range of 38° to 46°. Moreover, the nanocrystalline Cu thin film exhibits the peaks of (111), (200) and (220) planes at 43.4°, 50.5° and 74.2°, respectively. The highly textured {111} plane is contributed by the nanocrystalline face-centered cubic Cu layers.

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In this study, all the multilayered specimens have the ZrCu TFMG as the top layer to ensure the initiation of shear bands from this layer. Fig. 2 shows the SEM surface morphology of the PI-supported multilayered thin films. Under low magnifications as shown in the left side of Fig. 2(a) and (b), the as-deposited specimens with various individual layered thicknesses show the smooth surfaces with slight contrast from huge height difference topography. However, at a high magnification of 50,000× as shown in the right side of Fig. 2(a) and (b), there are some inevitable sphere domains on the surface, since the sputtered film was grown and impinged from isolated islands. The morphology is consistent with the observations of Zr-based amorphous films reported by Raible et al. [22].

The mechanical properties were examined by tensile testing and the reported method in reference [23] was utilized in this study. The tensile load of the 50-μm-thick uncoated PI substrates was averaged and fitted with a fourth-order polynomial as follows:

\[ F = 15.88037c - 321.25815c^2 + 4043.95503c^3 - 20346.30584c^4, \]  

where \( F \) is the tensile load and \( c \) is the tensile strain. The result calculated from the polynomial form is regarded as the reference of uncoated PI substrate, as shown in Fig. 3(a). Then, the tensile stress of thin film (\( \sigma_{film} \)) can be extracted by deducting the contribution of the uncoated substrate from the total load:

\[ \sigma_{film} = \frac{1}{w_{film}t_{film}}(F_{total} - F_{PI}), \]

where \( w_{film}, t_{film}, F_{total} \), and \( F_{PI} \) are the width and thickness of the coated film, and the tensile load for the coated specimen and the uncoated PI substrate, respectively [16].
EMultilayer(ROM) as expressed by:

\[\text{constraint effects for the nanoindentation measurement}[24,25].\]

Nanoindentation, are well expected, since there are more size from the micro-scaled minitester, as compared with the moduli from ZrCu and 127 GPa for Cu[19,20]. The slightly lower moduli measured close to the results from nanoindentation, which are 93 GPa for 83 GPa and 104 GPa, respectively. These experimental values are moduli of the monolithic ZrCu TFMG and Cu thin films.

According to Eq. (2), the engineering stress–strain curves of the 1-μm-thick monolithic ZrCu TFMG and monolithic nanocrystalline Cu thin film can be extracted as plotted in Fig. 4(b). The tensile moduli of the monolithic ZrCu TFMG and Cu thin film are determined to be 83 GPa and 104 GPa, respectively. These experimental values are close to the results from nanoindentation, which are 93 GPa for ZrCu and 127 GPa for Cu [19,20]. The slightly lower moduli measured from the micro-scaled minitester, as compared with the moduli from nanoindentation, are well expected, since there are more size constraint effects for the nanoindentation measurement [24,25].

Based on the data, the theoretical moduli of multilayered thin films can be obtained from an iso-strain model of Rule of Mixture (ROM) as expressed by:

\[E_{\text{Multilayer}} = (1-f)E_{\text{ZrCu}} + fE_{\text{Cu}}.\]

where \(E_{\text{Multilayer}}, E_{\text{ZrCu}},\) and \(E_{\text{Cu}}\) are the tensile moduli of the multilayer thin film, ZrCu TFMG, and nanocrystalline Cu film, respectively, and \(f\) is the volume fraction of the nanocrystalline Cu layer in the multilayer thin films. In this research, the volume fraction for all the 10 to 100 nm multilayered films is set to be the same, i.e., 50 vol.%. The theoretical value of the modulus can thus be calculated by ROM as 94 GPa. The results from tensile test and nanoindentation are all summarized in Table 1.

The representative engineering stress–strain curves of the ZrCu/Cu multilayered thin films, with individual layer thicknesses of 10, 25, 50, 75, and 100 nm, are presented in Fig. 3(c). The moduli of these samples are all in the range of 87 ± 10 GPa, close to the theoretical ROM prediction of 94 GPa. The modulus with various individual layer thicknesses shows the slight variation and it is barely affected by the layer thickness due to its intrinsic characteristic. These results are considered to be reasonable and predictable.

The maximum stresses of multilayered thin films with various layered thicknesses of 10, 25, 50, 75, and 100 nm are extracted to be 550 ± 20, 765 ± 30, 740 ± 12, 1030 ± 15, and 540 ± 10 MPa, respectively, as plotted in Fig. 4. The variation of the stress as a function of layer thickness can be explained from two aspects. The first one is from the nanocrystalline Cu layers, rationalizing in terms of the Hall–Petch type relationship for multilayered materials [26]. Here the individual Cu layer thickness can be regarded as the grain size in the Hall–Petch equation; the smaller the thickness, the stronger the Cu layers. The second aspect is from the amorphous ZrCu layers. Shear banding predominates over the deformation process, which is less sensitive with respect to the thickness in the range of 25 to 100 nm. Judging from these two aspects, the increasing stress from 100 to 25 nm is logical.

However, as the thickness of nanocrystalline or amorphous layer is reduced to 10 nm, the effects of layer roughness and interface become critical under tension. The uneven layer thickness for the 10/10 nm film, and sometimes incomplete coverage of one layer, would lead to uneven distribution of the local stress. The 10/10 nm multilayered film becomes prone to premature failure and thus a lower maximum stress.

In addition to the stress dependence from the layer thickness, it is noted that the surface crack density is quite different in various multilayered films. As shown by the two examples in Fig. 5(a) and (b), there are microcracks in the deformed films, perpendicular to the tensile direction. Quantitative measurements of the microcrack density and relative microcrack spacing reveal the dependence of the layer thickness, as depicted in Fig. 5(c) and (d). In Fig. 5(d), the average crack spacing at the higher strain of 10% is always smaller than that at 2% strain. Note the similar trend of the average crack spacing in Fig. 5(d) and the maximum stress in Fig. 4. The 25/25 nm film possesses a lower surface microcrack density, higher microcrack spacing, and thus higher maximum tensile stress. The multilayered ZrCu/Cu thin film would exhibit the highest tensile stress when the crack density is the lowest. With the lowest crack density, the multilayered film behaves tougher, and would sustain the applied loading to a higher stress level. Both of these happen in the 25/25 nm ZrCu/Cu multilayer, which is demonstrated to be the optimum layer thickness under tensile loading.

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<tr>
<th>Testing methods</th>
<th>Young's modulus, E (GPa)</th>
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<tr>
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<tr>
<td>Nanocrystalline Cu</td>
<td>104</td>
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<td>Theoretical ROM values</td>
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<tr>
<td>Amorphous ZrCu</td>
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<td>127</td>
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<tr>
<td>Theoretical ROM values</td>
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4. Conclusions

The current study systematically demonstrates the tensile behaviors of PI-supported amorphous/nanocrystalline ZrCu/Cu multilayered thin films. For the morphology observation, it is composed of fine sphere domains, measuring ~30–100 nm, on the surface of as-deposited ZrCu/Cu multilayered thin films. The domain interfaces would lead to stress concentration and reduce the maximum tensile stress. The cracks perpendicular to the tensile direction are seen to propagate along the domain interfaces. Moreover, the moduli extracted from the tensile loading of the monolithic ZrCu TFMG and monolithic nanocrystalline Cu thin films (83 and 104 GPa) are close to the results obtained by nanoindentation (93 and 127 GPa). The moduli and stresses of the multilayered ZrCu/Cu thin films extracted by deducting the contribution of the uncoated PI substrate from the coated samples are also compatible with the values calculated from the theoretical rule of mixture prediction. Furthermore, as the layer thickness going down from 100 nm to 10 nm, the tensile moduli would vary slightly. But the tensile stresses exhibit strong dependence as a function of layer thickness. The 25/25 nm film shows the highest stress to the level of 1030 MPa. It always possesses a lower surface microcrack density, higher microcrack spacing, and thus higher maximum tensile stress. Consequently, the 25/25 nm ZrCu/Cu multilayered film is suggested to be the optimum layer thickness under tensile loading.

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References