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Tensile behavior of amorphous/nanocrystalline ZrCu/Cu multilayered films with graded interfaces

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The microstructure and tensile response of amorphous ZrCu and nanocrystalline Cu multilayered thin films, with sharp or graded interfaces, are examined and analyzed. The extracted tensile properties of the multilayered films can be compared with the predicted values based on the iso-strain Rule of Mixture model. The multilayered films with graded interfaces, each about 50 nm thick, consistently exhibit higher tensile strength and elongation. This can be rationalized by the reduced stress and strain incompatibility along the interfaces.

1. Introduction

Metallic glasses (MGs) have been developed and have attracted attention over the past few decades [1–4] due to their unique mechanical and physical properties, for instance, high strength and hardness, good corrosion resistance, excellent shaping and forming ability in the viscosity state, and so on. Recently, the dimension of MGs can be successfully reduced from bulk to thin film scales by using the sputtering technique [5]. The nano- and micro-scaled thin film metallic glasses (TFMGs) can retain the inherent properties and be utilized as potential materials in the Micro Electro-Mechanical Systems (MEMS) devices [6,7].

However, high strength and good ductility are difficult to coexist in monolithic MGs, especially under tensile testing at room temperature [8]. To solve this problem, the major improvement utilized in BMGs is to incorporate some ductile metallic phases in the amorphous matrix as BMG composites (BMGCs) [9–12]. For TFMGs, the toughening concept has been developed by integrating the amorphous and more ductile metallic layers as multilayered thin films (MLTFs) [13–18].

Nieh et al. [13] and Wang et al. [14] found that amorphous/nanocrystalline Cu_4Zr_3/Cu and CuZr/Cu MLTFs with nano-scaled layer thickness could possess both high tensile strength and good ductility. Donhue et al. [15] indicated that the shear bands could be arrested by the crystalline layer and the dislocations could be annihilated by the amorphous layer. In addition, ductile CuZr/Cu MLTFs with various combinations of layer thickness (10–250 nm) were investigated by Pei et al. [16], Lee et al. [17], and Huang et al. [18]. Recently, Kim et al. [19] systematically examined the tensile deformation of free-standing CuZr/Cu nano-scaled specimens with a very small gage length of 700 nm, prepared by complicated fabrication of dry etching and focused ion beam (FIB) machining. These nano-scaled specimens exhibited high tensile strength of 2.5 GPa and ~4% strain, approaching the intrinsic theoretical properties of CuZr/Cu.

Although the tensile properties of TFMGs could be improved by the multilayered structure, the stress concentration, interface debonding, or interface sliding, etc, could induce unsatisfactory premature failure along the interfaces. The sharp interfaces between the connected amorphous and nanocrystalline layers might often induce stress and strain incompatibility due to the mismatch of elastic modulus and strength levels. Consequently, the concept of graded (or gradient) interface utilized in metallic or ceramic thin films for decades is employed in this study for the amorphous/nanocrystalline ZrCu/Cu MLTFs.

From 1991, extensive efforts of graded structures have been investigated to improve the intrinsic properties in several metal/ceramic or ceramic/ceramic thin films, such as the Al/AlN [20],

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diamond/metal [21], Si_3N_4/Al_2O_3 [22], AlN/GaN [23], and so on. Moreover, in 2011, Fang et al. [24] demonstrated the tensile properties of Cu thin films with graded grain sizes; high tensile yield strength of 129 ± 17 MPa and tensile elongation over 50% could be achieved. Inspired by these results, the amorphous/nanocrystalline multilayered system might have a chance to enhance their tensile properties.

2. Experimental procedures

The MLTFs were deposited on the 10-μm-thick Cu foils by a direct current (DC) magnetron sputtering system. This sputtering system has been rebuilt and the sputtering rates and sputtered films are different from our previous work [16]. The Cu foils as the substrate for tensile testing were cut into the dog-bone-shape by the laser patterning process with a pulse ultraviolet laser before sputtering processes. The length and width in the gauge section of dog-bone-shape specimens are 4.8 and 1.3 mm, respectively. In this research, it should be noted that the complicated dry etching and FIB machining techniques were not employed to produce the nano-scaled tensile specimens as did by previous researches [17,19]. Instead, the Cu-foil-supported multilayered thin films in mini-scale were fabricated and tested under tension. Therefore, the resulting tensile properties are not expected to achieve the theoretical level, but might represent the typical properties and tendencies that most MEMS devices would exhibit.

In the sputtering system, a $Zr_{50}Cu_{50}$ (in atomic percent, at%) alloy target and a pure Cu target were used. In all the multilayered systems, the deposited bottom layer facing the Cu foil is always the nanocrystalline Cu and the top surface layer is ZrCu TFMG. To fabricate the ZrCu/Cu multilayered thin films with graded interface, the powers of $Zr_{50}Cu_{50}$ and Cu guns were adjusted between 50–200 W and 5–50 W, respectively. In this study, a pair of amorphous ZrCu and nanocrystalline Cu layers is referred as two layers (2L) or one period. For tensile testing, the graded multilayered specimens with one, three, and four periods were prepared and these multilayers are denoted as G2L, G6L, and G8L, respectively. Meanwhile, the ZrCu/Cu MLTFs with sharp interfaces of the one and five periods, namely, S2L and S10L, were prepared for comparison.

The fundamental properties of these thin films were characterized by Siemens D5000 X-ray diffraction (XRD), JOEL-6330 scanning electron microscopy (SEM) with energy dispersive X-ray spectrometry (EDS), and FEI Tecnai Field-Emission transmission electron microscopy (TEM). The cross-sectional TEM foils were machined by an SEIKO SMI3050 dual FIB system. The uniaxial tensile testing with a constant strain rate of $1 \times 10^{-3}\ s^{-1}$ was conducted on the Cu-supported ZrCu/Cu multilayered thin films at room temperature by an MTS Tytron 250 Microforce Testing System (mini-tester). For the sake of detecting the precise variation of displacement, an extensometer was assembled in the mini-tester during the tensile testing.

3. Results and discussion

To examine the nature of multilayered structure, all the ZrCu/Cu MLTFs with graded or sharp interfaces deposited on the Si (100) wafer (no Cu foil effect) were prepared and characterized by XRD. According to XRD results, the broad diffraction hump at the 2θ diffraction angle range of 30°–45° corresponds to the amorphous ZrCu. The nanocrystalline Cu layers possess column grains with strong {111} plane texture, different from the previous report with more equiaxed Cu grains [25]. The strength for such Cu layers with columnar grains under tension with tensile axis parallel to the {111} planes tends to be lower than that with more equiaxed grains. The composition of amorphous ZrCu layer was identified as $Zr_{50}Cu_{50}$ by SEM/EDS. The SEM plane-view micrographs under lower magnifications show featureless surface morphology, but the ZrCu sphere domains can be observed on the top surface under high magnifications. The mound-like structure is a result of the isolated islands growing along the perpendicular direction [26]. Moreover, the microstructure of the ZrCu/Cu MLTFs with graded and sharp interfaces were characterized by TEM.

Fig. 1 shows the representative TEM micrographs for the graded interfaces in the G2L and G6L films. Through numerous TEM micrographs, the total thicknesses of the G2L, G6L, and G8L were measured and they are all close to 1000 nm. The individual layer thickness for the monolithic amorphous ZrCu or nanocrystalline Cu varies from ∼470 nm in G2L, ∼120 nm in G6L, down to ∼75 nm in G8L. In contrast, the individual layer thickness is ∼500 nm in S2L and ∼100 nm in S10L. With the similar individual layer thickness, G2L and S2L, as well as G6L/G8L and S10L, can be compared with each other. There is only one graded interfacial layer (or region) in G2L, but there are 5 and 7 interfacial layers in G6L and G8L, respectively. The thickness of graded interface layer (or region) is difficult to be precisely measured, due to its local variation. However, it can be still estimated, to the best judgment based on numerous TEM bright and dark field characterizations, to be 55 ± 10 nm. The white traces parallel to the growth direction in the multilayered structures (Fig. 1) were caused by the Ga ion beams during FIB trimming for preparing the cross-sectional TEM specimens. The grain size in the nanocrystalline Cu layers was also determined to be 40 ± 10 nm and the grains were grown perpendicular to the substrate.

Within the graded interfacial region, about 55 ± 10 nm thick, there are fine Cu particles dispersed in the ZrCu amorphous matrix, as shown in the dark field image in Fig. 2(a). The Cu particles typically measure about 5–10 nm in size, and should be effective strengthening second phases, as discussed below. Such Cu particles were not dispersed uniformly in the graded interfacial layer, being more near the Cu layer and less near the ZrCu layer. For the electron diffraction pattern in Fig. 2(b), the halo is referred to the amorphous ZrCu structure and the rings and spots are corresponded to the d-spacings of Cu {111}, {311} and {222} planes. Furthermore, Fig. 2(b) shows the high resolution TEM lattice image taken from one interface in G8L, showing some nanocrystalline pure Cu particles with the size of about 3–5 nm in the amorphous ZrCu matrix.

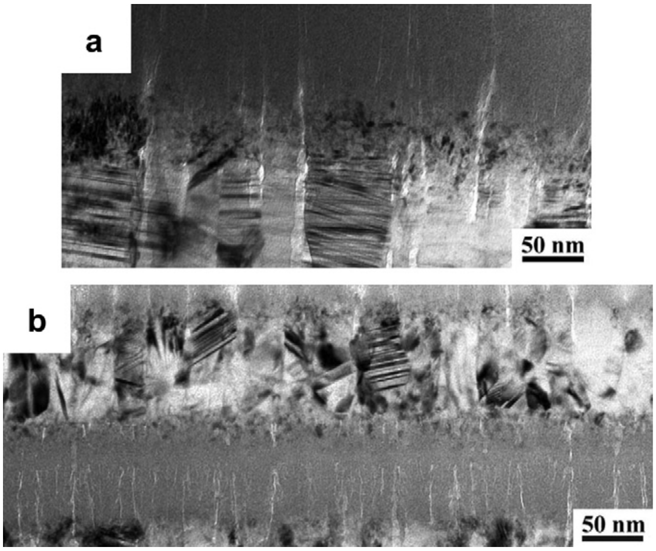

Fig. 1. Cross-sectional TEM micrograph showing the graded interface in the (a) G2L and (b) G6L ZrCu/Cu multilayered thin films.