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Mechanical properties of crystalline Cu/Zr and crystal–amorphous Cu/Cu–Zr multilayers

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ABSTRACT

We compare the indentation hardness of crystal/crystal (C/C) Cu/Zr multilayers and the crystal/amorphous (C/A) Cu/Cu–Zr multilayers with equal individual layer thicknesses spanning from 1 to 200 nm. Both systems show similar layer thickness dependent evolution of hardness. At smaller layer thickness the C/C multilayers show softening, while no softening is observed in the C/A multilayers. The layer thickness dependent hardness is quantitatively estimated by using dislocation models. The significance of crystalline (Zr) layer and amorphous (Cu–Zr) layer on plastic deformation mechanisms is discussed.

1. Introduction

Metallic glasses (MGs) are amorphous metals that do not have long range atomic order like crystalline materials do, but have pronounced short- and medium-range order at the atomic scale. Correspondingly MGs exhibit localized deformation in form of shear transformation zones (STZs) in lieu of abundant plasticity carriers – dislocations in crystals [1–5]. Strain hardening in crystalline metals, which leads to stable and uniform elongation and tensile ductility, is rendered possible by mechanisms such as dislocation multiplication and interactions. In MGs, however, the carrier of plasticity – STZ is a small cluster of closely packed atoms that spontaneously and cooperatively rearrange to accommodate the applied shear strain [3]. On average, the activation energy and activation volume of shear transformations are usually much larger than that for a mobile dislocation in crystals [2,4]. Moreover, a dislocation leaves a recovered lattice behind, while the STZ is often excited to a more energetic state (i.e., softened) upon shear transformation, via local volume dilatation together with topological transitions and/or chemical alienation [2]. Finally, when a dislocation runs into a grain boundary or other dislocations, it encounters an elevated activation barrier. This mechanism is absent in MGs considering that the STZs are not mobile defects. Due to the above characteristics of STZ, once plastic deformation starts in MGs, it quickly localizes via linked STZs in an autocatalytic manner, resulting in narrow shear bands. This plastic instability in turn triggers catastrophic fracture, significantly undercutting their structural applications [6–8]. Cu–Zr thin film MGs (TFMGs) as lucrative engineering material, also rarely show tensile ductility at room temperature and are considered quasi-brittle materials. Therefore, the approach to improve the ductility continues to be a significant issue. For MGs, the improvements of plasticity under tension and/or compression employ the concept of design of MG composites (MGCs), by incorporating deformable metal phases into the metallic glassy matrix [9–11]. In parallel, the integration of amorphous and crystalline layers by adjusting their constituent has been regarded as a potential method for improving the ductility of metallic multilayer [12–15].

Wang et al. [12] reported that a Cu/Cu–Zr crystalline/amorphous (C/A) nanolaminate with respective thickness of 35/5 nm reliably showed high tensile strength (~1.2 GPa) and large tensile elongation (~14%) before failure. The results indicated that the shear bands formation could be suppressed by the nanocrystalline layer and the dislocations could be disrupted by the amorphous layer, which act as high-capacity sources and sinks for dislocations, enabling absorption of free volume and free energy transported by dislocations; the amorphous–crystalline interfaces (ACIs) exhibit unique inelastic shear (slip) transfer characteristics, fundamentally different from those of grain boundaries (GBs) and crystalline–crystalline interfaces (CCIs). It has been demonstrated that the energy of a CAI is, in general, lower than the energy of a CCI [16]. Further investigations showed that the interplay of crystalline

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and amorphous layers not only suppressed the propagation of shear bands and dislocation pile-ups but also provided the high defects absorption capacity [13,14]. Liu et al. [15] systematically reported the results of micropillar compression tests on A/C multilayer with 3 constituents of Zr–Cu/Cu, Zr–Cu/Mo, and Zr–Cu/Zr with various layer thicknesses. The plastic compressive strain can achieve over 50% as a result of the multilayered structures.

Unlike single-layer films, interface can play a decisive role in strengthening crystalline/crystalline (C/C) and C/A metallic multilayers. A clear layer thickness (h)-dependent strengthening phenomenon is often observed in C/C multilayers, such as Cu/Ni [17,18], Cu/Cr [19,20], Cu/Nb [21,22], and Cu/Zr [23,24]. When the equal individual layer thickness, h, is larger than 50 nm, film hardness increases linearly with $h^{-1/2}$, consistent with the Hall–Petch (H–P) dislocation pile-up model [25]. When h is less than 50 nm, the size dependent strengthening behavior is non-linear, and deformation can be described by the confined layer slip (CLS) mechanism [21]. When h is a few nanometers, the strength of metallic multilayers reaches saturation and no significant strengthening (even softening) is observed as h further decreases. The peak strength of multilayers is affected by coherency stress [26] and moduli differences [27].

In spite of success in understanding deformation mechanisms in crystalline metallic multilayers, little is known about the length scale-dependent hardening in C/A multilayers, such as Cu/Cu–Zr multilayers. In this paper, the mechanical behavior of the C/A Cu/Cu–Zr multilayers was investigated and compared to that of C/C Cu/Zr multilayers.

2. Experimental details

Cu (99.995%) and Zr (99.99%) targets were used to deposit C/C Cu/Zr and C/A Cu/Cu–Zr multilayers on HF etched Si (1 0 0) substrates by direct current (DC) magnetron sputtering at room temperature. The chamber was evacuated to a base pressure of $\sim 6.0 \times 10^{-8}$ Torr, and $1.0–2.5 \times 10^{-3}$ Torr Ar were used during deposition. The substrate was neither heated nor cooled during deposition. The constituents within the C/A and C/C multilayers have equal individual layer thickness h varying from 1 to 200 nm. First, a 100-nm-thick Cu seed layer is deposited onto the Si substrate, and the cap layer of the multilayer was also Cu. The $Cu_{60}Zr_{40}$ (atom fraction) amorphous layer was prepared by co-sputtering. The total thickness of the C/C Cu/Zr and C/A Cu/Cu–Zr multilayers was $\sim$2 μm for $h < 100$ nm and $\sim$3.6 μm for $h \geq 100$ nm. For comparison, 2 μm-thick single layer Cu, Zr and amorphous $Cu_{60}Zr_{40}$ films were also prepared on Si (1 0 0) substrates. X-ray diffraction (XRD) experiments were performed in a Bruker D8 Discover X-ray powder diffractometer at room temperature to determine the crystallographic texture of films. High resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) analyses were performed on an FEI Tecnai G2 F20 microscope operated at 200 kV, with a Fischione ultra-high resolution high-angle annular dark field (HAADF) detector. The STEM in image mode has a resolution of 0.23 nm and the Oxford instruments EDX detector has a probe size of $\sim$1 nm for chemical analysis.

The indentation hardness (H_{IT}) defined as the plateau region of the plot of hardness vs. indentation depth was determined, at room temperature, by using instrumented nanoindentation technique via a Fischerscope HM2000XYp micro/nanoindentor equipped with a Vickers indenter tip. The indentation depth is typically 75–325 nm. The technique to calculate hardness and elastic modulus was similar to the continuous stiffness measurement (CSM) method described by Oliver and Pharr [28], where the corrected indentation depth was calculated from the tangential intercept of a non-linear unloading curve fitted by the power law method. A minimum of 15–20 indents separated from each other by at least 50 μm were performed on 3–4 specimens of each multilayer to obtain an average hardness value at various indentation depths, following the procedure provided in Ref. [18].

3. Results

3.1. Microstructure of C/C and C/A multilayers

XRD patterns in Fig. 1(a) reveal that Zr film showed a strong (0 0 0 2) texture, whereas Cu film had single crystal-like strong (2 0 0) texture. The $Cu_{60}Zr_{40}$ films had amorphous nature with a broad diffraction hump spreading over 35–45°. The as-deposited C/C Cu/Zr multilayers on Si (1 0 0) substrates (Fig. 1(b)) exhibited strong Cu (1 1 1) and Zr (0 0 0 2) texture when $h \geq 5$ nm. When h decreases, the Cu (1 1 1) and Zr (0 0 0 2) peaks broaden. However, when $h = 2$ nm, the Zr peaks and Cu (1 1 1) peak were not observed in C/C Cu/Zr multilayers.

XRD results revealed that most of the as-deposited C/A Cu/Cu–Zr multilayers on Si (1 0 0) substrates exhibit Cu (1 1 1) and Cu (2 0 0) peaks, and the Cu (1 1 1) peaks broaden with decreasing h (Fig. 1(c)). However, the intensity of Cu (2 0 0) peaks remained the same, which can be contributed to the Cu seed layer. The peak intensity of glassy phase is quite low in all the C/A Cu/Cu–Zr samples (Fig. 1(d)). Unlike the case of C/C multilayers at $h = 2$ nm, the Cu (1 1 1) peak can be found in the C/A multilayers, even when h is 1–2 nm.

Cross-sectional TEM (XTEM) studies were carried out to examine the microstructure of the films in details. A bright field XTEM image of Cu 50 nm/Zr 50 nm (referred to as Cu/Zr 50 nm thereafter) multilayers in Fig. 2(a) shows polycrystalline grains in a modulated layer structure. The inserted selected area diffraction (SAD) pattern reveals strong Cu (1 1 1) and Zr (0 0 0 2) texture. HRTEM micrograph (Fig. 2(b)) displays incoherent Cu/Zr interface with insignificant intermixing. Stacking faults and growth twins were also observed in Cu. A STEM micrograph of the Cu/Zr 5 nm multilayers and the superimposed compositional line scan in Fig. 2(c) also demonstrate a chemically alternating layer structure with some degree of intermixing. Intermixing was also detected in HRTEM micrograph (Fig. 2(d)) as evidenced by slightly thicker Zr in comparison to Cu. Significant intermixing were detected in Cu/Zr 2 nm multilayers as shown in Fig. 2(e) and (f). The compositional line profile in Fig. 2(e) also confirms the intermixing.

XTEM micrograph of the C/A Cu/Cu–Zr 50 nm multilayers (Fig. 3(a)) unveils drastic contrast difference between polycrystalline Cu and amorphous Cu–Zr layers. The inset of SAD pattern also showed a diffuse amorphous ring. Similar amorphous structure was revealed in C/A Cu/Cu–Zr 5 nm films by HRTEM micrograph and the fast Fourier transform (FFT) of region II (RII) in Fig. 3(b). In all C/A multilayers, layer interfaces are clearly distinguishable.

3.2. Hardness of multilayers

The indentation hardness (H_{IT}) of films was determined from the plateau hardness of the depth dependent measurement. A typical example is shown in Fig. 4(a) for C/A Cu/Cu–Zr 10 nm multilayer. Appropriate range of indentation depth was selected to avoid indentation size effect and substrate effect [29,30]. The H_{IT} of monolithic Zr, Cu and amorphous $Cu_{60}Zr_{40}$ films was 5.75, 1.82 and 6.25 GPa, respectively.

From Fig. 4(b), one can clearly see that as h decreases from 200 to 5 nm, the H_{IT} of both C/C and C/A multilayers strongly increases first and then reaches a maximum (i.e., C/A reaches the hardness of amorphous films and C/C reaches the hardness of Zr films). Strikingly, it is found that the H_{IT} of both C/C and C/A multilayers are