Unusual size dependent strengthening mechanisms of Cu/amorphous CuNb multilayers

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Abstract:

Nanostructured crystalline/amorphous metallic multilayers have been increasingly studied due to their high strength and potential enhancement of plasticity in amorphous metals. Here we report on mechanical behaviors of Cu/amorphous CuNb multilayers that were prepared by magnetron sputtering with equal individual layer thickness (h) varying from 1 to 200 nm. A medium-range-order amorphous CuNb layer formed between Cu and amorphous CuNb layers. This intermediate layer facilitates transmission of plasticity from Cu to amorphous layers by preventing the smear of dislocation core on the interface. The maximum hardness of Cu/amorphous CuNb multilayers is achieved when $h \leq 50$ nm, and is much lower than the hardness of single-layer amorphous CuNb films. Molecular dynamics simulations show that, comparing with single-layer amorphous CuNb, the pile-up of dislocations in Cu layers lowered the stress for the activation of shear transformation zones in amorphous CuNb layers in multilayers.

Key words: crystalline/amorphous multilayers; intermediate layer; hardness; deformation mechanisms

1. Introduction

Amorphous metallic alloys, or the so-called metallic glasses (MGs), show extraordinary yield strength, elastic strain, and wear resistance [1-6]. But their poor ductility and catastrophic failure associated with the formation and rapid extension of shear bands hinder their structural applications. Intrinsically, better ductility/toughness can be achieved by optimizing composition and structure (coordination) of MGs [7, 8]. Mechanical behaviors of BMGs can be altered by processing conditions and thermal history [9-11], free volume [12-15], composition and structural inhomogeneity [16-20]. In addition, the deformation behaviors of MGs appear to be size dependent [21-23], which is also a subject of interest in this study. Homogeneous deformation (under uniaxial compression) has been observed [24] in amorphous PdSi pillars with diameters of 400 nm or less, in comparison to the shear band formation in pillars with larger diameters. Similarly the variation of deformation mode was also reported during tension tests of amorphous pillars [25]. Extrinsically, second phases can also enhance the ductility/toughness of MGs [26-28]. Previous studies showed [29] that ZrTi-based bulk metallic glass composites (BMGcs) may have extraordinary tensile ductility (more than 10%) without loss of their high strength because the plastically deformed “soft” phases become sites that promote more shear bands, which would then be stalled by the “hard” surrounding regions that require larger stress to be deformed. The strategy of using ductile crystalline phases to improve ductility of metallic glass matrix has also been applied to Zr-, Mg-, and Ti-based MGc [30-34].

To significantly enhance plasticity of crystalline/amorphous (C/A) composites, it is essential to control the dimension and volume fraction of each phase, and investigate the influence of interphase interfaces on plasticity of these composites. Thus thin film metallic glass composites (TFMGc) consisting of alternating C/A layers have been investigated recently. It is well known that mechanical properties of crystalline metallic materials are tied with nucleation

and propagation of dislocations, whereas MGs typically deform through shear bands or shear transformation zones (STZ) [35-39]. The mechanical strength of C/C (crystalline/crystalline) multilayers can be tailored by varying individual layer thickness and types of layer interfaces (e.g. coherent vs. incoherent) [40-46], and the strengthening mechanisms in these multilayers have been intensely investigated [47-54]. Comparing with the extensive studies on C/C multilayer films, the studies on mechanical behavior of C/A multilayer films are limited [55-63]. Previous studies show when the thickness of amorphous layers is sufficiently thin, crystalline layers can accommodate plasticity and counteract the shear deformation of amorphous alloys (or constrain the formation or propagation of shear bands), and increases the ductility of the C/A multilayer composites [64-67]. Prior studies also suggest a transition of plastic deformation modes from pronounced shear banding to homogeneous co-deformation of C/A layers when layer thickness reduces [68-74]. Most previous studies show that the peak hardness of C/A multilayers approaches or even exceeds the hardness of single layer amorphous metal films [55, 56, 69, 72, 73].

In spite of these previous studies, numerous aspects remain to be investigated in C/A multilayer composites. First, most prior studies focus on amorphous systems (a-CuZr and a-PdSi) wherein the constituents (elements) have negative heat of mixing. There are few studies on amorphous systems consisting of elements with positive heat of mixing. Second, the C/A interfaces require further investigation. As the deformation modes of crystalline and amorphous layers are drastically different, the co-deformation of the multilayers, if accomplished, is largely dominated by the C/A interfaces. In fact, Cu/a-CuZr multilayer films with gradient C/A interfaces have better strength and ductility compared with sharp interfaces [75].

In this paper, we investigate the size-dependent strengthening mechanisms in Cu/a-CuNb

multilayers for the following reasons. On the one hand, a-CuNb contains elements with positive heat of mixing (ΔH^{mix} is 3 kJ/mol for Cu-Nb, compared with -23 kJ/mol for Cu-Zr [76]). On the other hand, the strengthening mechanisms of Cu/a-CuNb have not been investigated before, and can be compared to the intensively studied Cu/Nb and Cu/a-CuZr systems. Detailed microscopy and nanoindentation studies show that the maximum strength of Cu/a-CuNb multilayers is much lower than that of Cu/a-CuZr and single layer a-CuNb. Such large difference arises from the formation of an intermediate a-CuNb layer (with semi-crystalline nature) along interfaces. Furthermore MD simulations show that dislocation pile-ups in Cu layer significantly reduce the barrier strength of the C/A interface by facilitating the activation of STZs in a-CuNb. This study sheds light on the design of C/A multilayers by tailoring the amorphous structure along interfaces, and highlights the needs to investigate plasticity of amorphous systems consisting of elements with positive heat of mixing.

2. Experiments

Cu/a-CuNb multilayers were deposited on Si substrates by direct current (DC) magnetron sputtering at room temperature. The multilayers were designed with identical individual layer thickness (h) ranging from 1 to 200 nm. The chamber was evacuated to a base pressure lower than 1×10^{-7} Torr, and $1-3 \times 10^{-3}$ Torr Ar was used during deposition. a-CuNb layers were deposited by co-sputtering Cu and Nb to achieve a composition of Cu 50 at.% and Nb 50 at.% ($\text{Cu}_{50}\text{Nb}_{50}$). The total thickness of Cu/a-CuNb multilayers ranges from 1 to 3.2 μm and the a-CuNb layer is always the cap layer for all the multilayer films. Single layer Cu and a-CuNb films were also deposited as references. Specimens for cross-section transmission electron microscopy (XTEM) studies were prepared by grinding, polishing, followed by low energy Ar ion

milling/polishing. An FEI Tecnai G2 F20 microscope operated at 200 kV was employed to study the microstructure and chemistry of the films. Scanning transmission electron microscopy (STEM) and energy dispersive X-ray (EDX) analysis were conducted using a Fischione ultra-high resolution high angle annular dark field (HADDF) detector with 0.23 nm spatial resolution in the STEM imaging mode, and an Oxford Instruments detector with a spatial resolution of ~ 1 nm attached to the Tecnai F20. X-ray diffraction (XRD) patterns were acquired on a diffractometer (Empyrean 2, PANalytical, Almelo, NL). The hardness and elastic modulus of the specimens were determined by using the instrumented nanoindentation technique [77] on a Fischerscope 2000XYp nano/micro indenter. A minimum of 25 indents was used to obtain an average hardness value at various indentation depths. The hardness of the specimens was determined as the hardness plateau in the plots of hardness vs. indentation depth [78, 79]. A Hysitron TI 950 TriboIndenter was also employed to perform partial loading/unloading indentations to obtain the hardness and modulus at various depths, and probe pop-in events during indentation. Both methods confirm the hardness trend in this study.

3. Results

3.1 Microstructure

The XRD profiles of Cu/a-CuNb multilayers with different h are compared to that of a-CuNb films in Fig. 1a. The amorphous peak in single layer a-CuNb is at $\sim 39^\circ$. The interplanar spacings of Cu (111) and Cu (200) in Cu/a-CuNb multilayers match that of bulk Cu (dashed lines) when $h > 50$ nm. The intensity of Cu (111) (Cu (200)) peak gradually increases (diminishes) with decreasing h . A slight left shift of Cu (111) peaks was observed, corresponding to a moderate in-plane compressive stress in multilayers. When $h = 10$ nm, the Cu (200) peak

disappears. When $h = 1$ and 2.5 nm, a broad peak was observed as shown in Fig. 1b, which can be decomposed into three peaks, corresponding to the a-CuNb, Cu (111), and a middle peak with the d-spacing of $1/2(d_{\text{a-CuNb}} + d_{\text{Cu(111)}})$.

We further characterized microstructures of Cu/a-CuNb multilayers using TEM. The XTEM micrograph of Cu/a-CuNb 50 nm multilayers in Fig. 2a shows clear layer interfaces, and the average columnar grain size of Cu is comparable to layer thickness. In addition, nanotwins and stacking faults are frequently observed in Cu layers. The selected area diffraction (SAD) pattern of Cu/a-CuNb 50 nm in Fig. 2b shows an amorphous ring arising from a-CuNb, and the continuous diffraction ring due to the formation of nanocrystalline Cu. Similarly XTEM micrographs of Cu/a-CuNb 10 nm and Cu/a-CuNb 100 nm multilayers in Fig. 2c and 2d show abrupt layer interfaces and the formation of alternating a-CuNb and Cu layers. The columnar grain size of Cu in Cu/a-CuNb 10 nm multilayers is slightly greater than layer thickness, and the grain size of Cu is comparable to layer thickness in Cu/a-CuNb 100 nm multilayer.

Fig. 3 shows the HRTEM micrographs of Cu/a-CuNb 2.5 nm, 10 nm, and 50 nm multilayers. The amorphous CuNb in the interfacial regions appears to contain extremely fine semi-crystalline structures, implying the emergence of a medium-range-order (MRO) type of structure, as marked by the arrows. The fraction of interfacial layer with MRO increases with decreasing h . For the Cu/a-CuNb 2.5 nm multilayer, the thickness of interfacial MRO layers is comparable to h .

3.2 Mechanical behaviors of Cu/a-CuNb multilayers

The size dependent evolution of indentation hardness (H_{IT}) of Cu/a-CuNb multilayers (squares) in Fig. 4 shows that when h decreases from 200 to 50 nm, the hardness of multilayers increases monotonically, following the Hall-Petch relation as indicated by the dashed line. When

$h < 50$ nm, the hardness of Cu/a-CuNb multilayers reaches a plateau, ~ 4.5 GPa, and is independent of h .

For comparison, the hardnesses of Cu/Nb [47] and Cu/a-CuZr [56] multilayers as a function of layer thickness are also shown in the same plot. Cu/Nb multilayers have the highest peak strength (~ 6.9 GPa) among the three multilayer systems, followed by a peak strength of 6.3 GPa in Cu/a-CuZr multilayers. It is noted that the peak hardness of Cu/Nb and Cu/a-CuZr approaches the hardness of single layer a-CuNb and a-CuZr respectively, while Cu/a-CuNb multilayer has a much lower peak hardness compared with the hardness of single layer a-CuNb.

When $50 \text{ nm} < h < 200 \text{ nm}$, the hardness of multilayers can be well fitted by a linear line, consistent with the Hall-Petch relation. The Hall-Petch slope can be described by using the following equation [47]

$$k = \left(\frac{\tau^* \mu b}{\pi(1-\nu)} \right)^{0.5} \quad (1),$$

where τ^* is the C/A interface barrier strength for slip transmission, k can be obtained from the measured Hall-Petch slope for indentation hardness ($k = k_{\text{Hall-Petch}}/3.1/2.7$), μ is the shear modulus, b is the Burgers vector of the crystalline layer (Cu), and ν is the Poisson's ratio. The measured Hall-Petch slope for Cu/a-CuNb from the hardness plot is $14.5 \text{ GPa} \sqrt{\text{nm}}$, thus k equals to $1.734 \text{ GPa} \sqrt{\text{nm}}$. By using $\mu = 48 \text{ GPa}$, $b = 0.25 \text{ nm}$, and $\nu = 0.3$ for Cu, *the barrier strength is calculated to be 0.55 GPa, corresponding to a maximum hardness of 4.6 GPa, which agrees well with the measured peak hardness of Cu/a-CuNb multilayers.* Hardness and modulus were also measured by partial loading/unloading indentation (the detailed method and results can be found in Supplementary Fig. S1), and the summary of reduced moduli of single layer and multilayer films were shown in Table 1. The reduced modulus of single layer a-CuNb, Cu/a-CuNb multilayers, and single layer Cu is $\sim 136 \text{ GPa}$, $119\text{-}126 \text{ GPa}$, and 113 GPa , respectively.

4. Discussions

4.1. Evolution of microstructure with layer thickness

Cu/a-CuNb multilayers consist of alternating amorphous CuNb layers and nanocrystalline Cu layers were synthesized. Although the calculated Gibbs free energy vs. concentration diagram suggests that the a-CuNb phase could form in a wide window (if Cu concentration is between 35-80 at. % [80]), our studies show that the structure of a-CuNb could be tailored by changing the individual layer thickness of a-CuNb and Cu. When h equals 1 or 2.5 nm, the broad peaks can be decomposed into an amorphous peak (a-CuNb), a Cu (111) peak, and a middle peak with the d-spacing of $\frac{1}{2} (d_{a-CuNb} + d_{Cu(111)})$. The formation of middle peak implies the possible structural change of a-CuNb along interfaces in these very fine multilayers. The formation of the middle peak has been frequently observed in crystalline/crystalline metallic multilayers, such as Cu/V [78], Ag/Ni [81] and Fe/W [82] and such phenomena were ascribed to the interface constraint between the adjacent layers. The observation of this similar phenomenon in the current Cu/a-CuNb is somewhat unusual, because a-CuNb does not have a regular crystal lattice. Consequently one would not anticipate the prominent interfacial constraint between Cu and a-CuNb, which could affect the plasticity transfer between layers. The amorphous hump corresponds to the average nearest neighbor distance (NND) in the amorphous structure, and the formation of a middle peak in the Cu/a-CuNb thus may indicate a slight variation of NND in a-CuNb.

On the other hand, as shown in Fig. 3, interfacial MRO layers with semi-crystalline nature exist along the C/A interfaces. As there is no mutual solubility between Cu and Nb at room temperature (due to positive heat of mixing) [76], Cu (Nb) atoms may have the tendency to

stay in extremely fine nanoclusters (< 1 nm) instead of the ideal random distribution of Cu and Nb atoms in typical amorphous metals. Atomic resolution STEM images may be needed in future studies to further confirm this hypothesis. While depositing the first few monolayers of a-CuNb on Cu layers, there is a tendency for Cu atoms in a-CuNb to segregate (into sub-nanometer clusters) due to the influence of underlying Cu layers. Such an arrangement could reduce the mismatch between NND of a-CuNb and Cu (reduce mismatch strain energy) and may consequently leads to the formation of MRO layers that lattice parameters equivalent to the average of a-CuNb and Cu (111) as evidenced by XRD and TEM-SAD studies. The formation of these MRO layers could lead to softening of a-CuNb in multilayers comparing to the single layer a-CuNb. MD simulations on Cu/a-CuZr system show that a finite width (~ 1 nm) transition layer (both structurally and compositionally) between crystalline and amorphous layers can be formed at C/A interface and the corresponding interface shear strength (1.3 GPa) for the nanolayered composites is lower than the shear stress (1.5-2 GPa) to yield pure BMGs [83].

4.2 ‘Weak’ strengthening effect in Cu/a-CuNb multilayers

The unusual size dependent variation of hardness for Cu/a-CuNb multilayers is intriguing compared with other C/A multilayers such as Cu/a-CuZr. Previous studies on several C/A multilayers show that the peak hardness of multilayer approaches the hardness of the single layer amorphous films [56, 72, 73]. For instance, the peak hardness of Cu/a-CuZr is similar to the hardness of single layer a-CuZr (Table 2). This is expected as the one would anticipate that the maximum hardness of C/A multilayers is ultimate determined the stress required to yield the single layer metallic glass. If the same hypothesis holds for other systems with C/A interfaces, then one would anticipate that the peak hardness of Cu/a-CuNb should be similar to that of a-CuNb, ~ 7 GPa. However the peak hardness for Cu/a-CuNb multilayer in our study is merely 4.5

GPa, much lower than the hardness of the single layer a-CuNb. In fact, as shown in Table 2, the rule-of-mixture hardness (H_{rom}) value, calculated as $H_{rom} = 1/2(H_{a-CuNb} + H_{Cu})$, is very close to the peak hardness of Cu/a-CuNb multilayers as shown in Fig. 5. Such a drastic difference between the current study and prior studies on C/A multilayers suggest unusual strengthening mechanism in Cu/a-CuNb multilayers. Notice in Table 1, the moduli of Cu/a-CuNb multilayers are similar to the rule-of-mixture modulus of single layer a-CuNb and Cu.

We now examine the correlation between peak hardness and H-P slope of several multilayer systems, including Cu/Nb [47], Cu/a-CuZr [56], and Cu/a-CuNb. It has been established that using the Hall-Petch slope, one can estimate the peak hardness of multilayers by using equ. (1). As shown in Table 2, the calculated peak hardnesses of Cu/Nb and Cu/a-CuNb both match well with the measured peak hardnesses. In contrast the hardness calculated from the H-P slope for Cu/a-CuZr is significantly lower than the measured peak hardness.

Since the H-P slope can correctly predict the peak hardness of Cu/a-CuNb multilayers, we hypothesize that the peak hardness of Cu/a-CuNb multilayers could be limited by the inherently low hardness of a-CuNb in multilayers, which is ~ 4.6 GPa, similar to the barrier strength predicated by H-P slope. The prediction that the hardness of a-CuNb layer in multilayers may be inherently lower than that of the single layer a-CuNb is somewhat surprising and will be discussed again in the next sections. Nonetheless if the assumption is correct, the modified ROM hardness, H_{rom}^{mod} , can be calculated as $\frac{1}{2} (H_{a-CuNb}^{ML} + H_{Cu}) = 3.2$ GPa, close to the lower bound hardness of Cu/a-CuNb multilayers at large h . Similar trend is observed in both Cu/Nb and Cu/a-CuZr multilayers as shown in Fig. 4 and Table 2.

According to the models proposed by Nix [84] and Misra [47], when the layer thickness of multilayers is small enough (tens of nm or so), the Hall-Petch relation cannot explain the size

dependent strengthening well. Instead, the confined layer slip (CLS) model works much better for numerous crystalline metallic multilayers. In contrast to crystalline multilayers and Cu/a-CuZr multilayers, there is not a thickness range corresponding to the CLS strengthening mechanisms in the current Cu/a-CuNb multilayers, as when $h = 50$ nm, the strength of multilayers has already reached a plateau. CLS models cannot describe the hardness plateau observed in our study, indicating a “weak” strengthening effect from the Cu/a-CuNb layer interfaces (Fig. S2).

The fundamental mechanisms that lead to such discrepancy between the current system and the Cu/a-CuZr system could be related to the formation of interfacial MRO layers in a-CuNb. Binary CuZr BMGs were successfully fabricated and studied because of the good glass forming ability [85, 86], in contrast the glass forming ability of CuNb system is not ideal. Bulk CuNb amorphous has been prepared by mechanical alloying or heavy cold-rolling, but the as-received CuNb is not completely amorphous [80, 87, 88] similar to the MRO a-CuNb layer observed at layer interface in our study. The formation of such an MRO interfacial layer equivalently reduces the thickness of amorphous layer which can be seen in the extensive HRTEMs of Cu/a-CuNb 2.5 nm. In Cu/a-CuNb multilayer, the interfacial MRO layer could prevent incoming lattice dislocations from smearing the stress/strain concentration at the interface, thus facilitating slip transmission into amorphous layers and weakening the barrier strength of amorphous layer. Therefore this interfacial MRO layer in a-CuNb could reduce the peak hardness of Cu/a-CuNb multilayers.

The H_{IT} of Cu/a-CuNb multilayers reaches a plateau at the peak value of 4.6 GPa, which is much lower than the hardness of single layer a-CuNb (~ 7 GPa). To address this “weak” strengthening effect, we examined plastic deformation modes of single layer amorphous and the

multilayers with h of 50 nm or less. Fig. 6 shows load-displacement curves and surface morphologies of films after nanoindentation. Single layer a-CuNb shows a load-displacement curves with multiple pop-ins (a1), which matches well with the shear bands (local terrace-like pile-ups around the indent indicated by arrows) revealed by the SPM images in (a2 and a3); in contrast, the Cu/a-CuNb 20 nm multilayers have smooth load-displacement curves (b1), consistent with the homogeneous surface morphology (no clear step-like pile-ups) in (b2 and b3). The absence of step-wise pile-up after indenting to a greater depth is also confirmed for Cu/a-CuNb 5 nm multilayer. These studies show that the single layer a-CuNb (1 μ m) and Cu/a-CuNb multilayers ($h < 50$ nm) have different plastic deformation modes. The a-CuNb deforms inhomogeneously by forming shear bands, but the multilayers could deform homogeneously by formation of clusters of STZs. It should be noted that strain rate was kept similar during nanoindentation tests of all specimens in order to eliminate the influence of strain rate on deformation mode of amorphous metals [89-91]).

It has been shown [24] that the critical stress σ for shear band formation in amorphous alloys can be expressed as $\sigma = \sqrt{2^{3/2}\Gamma E/h}$, where Γ is the energy per unit area of shear band, E is the Young's modulus, and h is the height of the column (thickness of the film). This equation shows that the critical stress for shear band formation increases with the decrease of film thickness at a rate of $h^{-1/2}$. According to this formula, the critical stress for shear band formation in the 50 nm thick a-CuNb in the Cu/a-CuNb 50 nm multilayers is more than 7 GPa (using $\Gamma = 10 \text{ J/m}^2$ and $E = 100 \text{ GPa}$), much larger than the stress for the formation of shear bands in 1 μ m thick a-CuNb film ($\sim 1.7 \text{ GPa}$). As the hardness of Cu/a-CuNb 50 nm multilayer is merely 4.5 GPa, the a-CuNb in the multilayers (when $h < 50 \text{ nm}$) may accommodate the plasticity by nucleation of numerous shear transformation zones (STZs), which requires a much lower stress

and is an indication of more homogeneous deformation in amorphous metals. Similar softening phenomenon due to homogeneous deformation has been observed during nanoindentation studies of amorphous PdSi pillars with various diameters [24]. The average flow stress at 5% strain for homogeneous deformation of a-PdSi pillars is ~1.6 GPa for pillars with diameter of 400 nm or less, but above 2 GPa for inhomogeneous deformation of pillars with larger diameters [24].

The intriguing phenomenon that hardness of Cu/a-CuNb multilayers ($h < 50$) reaches a plateau is closely tied to the microstructure of C/A interface and the dimension of h . As illustrated in Fig. 7, the interfacial a-CuNb with MRO leads to an interface affected zone, which may facilitate the transfer of plasticity from the soft Cu layers into the much stiffer a-CuNb layers at a lower stress (Fig. 7b). Also the reduction of h in multilayers promotes the transition of deformation mode in a-CuNb and thus reduces the barrier stress for transmission of plasticity across layer interfaces.

4.3. MD simulation studies of plastic deformation in Cu/a-CuNb multilayers

To understand the plastic deformation and strengthening mechanism of Cu/a-CuNb multilayers, we conducted a series of molecular dynamic simulations of Cu 5 nm/a-CuNb 2.5 nm multilayers under uniaxial compression at a temperature of 10 K. Empirical interatomic potentials for Cu and Nb and their cross-pair have been widely used in our previous studies [92-94]. The compression strain rate is $10^8/\text{s}$. The simulation cell contains 5 bilayers as shown in Fig. 8a (See supplementary Video 1). The in-plane dimensions for Cu are 10.5 nm along the $\langle 112 \rangle$ direction and 11.5 nm along the $\langle 110 \rangle$ direction. Periodic boundary conditions are applied in all three directions. Dislocations are characterized using common neighbor analysis.

MD simulations demonstrated the transfer of plasticity across the Cu/a-CuNb layer interfaces. Plastic deformation commences in Cu layers via the nucleation and propagation of

glide dislocations on $\{111\}$ planes in Cu. As shown in Fig. 8b, plastic deformation in Cu layers is carried over by nucleation and glide of lattice dislocations of $\frac{1}{2}\langle 110 \rangle \{111\}$. During compression, abundant dislocations nucleate from layer interfaces, propagate within the Cu layer, and then deposit on the two interfaces that confine the layer. Previous studies show that during deformation of metallic multilayers, such as Cu/Nb, dislocations nucleated within the Cu or Nb layers will accumulate along layer interfaces [47, 92, 93] and the slip transmission of dislocations across layer interface will reduce the dislocation density at layer interfaces. MD simulations for Cu/a-CuZr system have shown similar mechanisms where the dislocations in Cu can directly induce the formation of shear bands in a-CuZr layer (10nm and 5 nm in layer thickness) [95]. Jia et al. [96] showed that formation of shear bands of the Cu/Nb (C/C) metal matrix composite is related to the co-deformation of heterophase alloy, triggered by the stress concentration at the interfaces. However, in the current study, we did not observe the accumulation of dislocations along the Cu/a-CuNb layer interface. Instead, the a-CuNb layers are locally sheared without the generation of shear bands (Fig. S3 and S4). The shear deformation in a-CuNb effectively reduces the dislocation content arrived at the Cu/a-CuNb interfaces, in contrast to the reduction of dislocations at interface via slip transmission in crystalline metallic multilayers. Fig. 9 shows the evolution of atomic structures in a-CuNb layer in the Cu 5 nm/a-CuNb 2.5 nm multilayer before and after loading to a uniaxial compressive strain of 8.0%. The black dotted lines indicate the position of original layer interfaces, and the red dotted lines indicate the location of layer interfaces after 8% compression. Deformation distorted the sharp C/A layer interfaces. More importantly the plastic deformation induces prominent local shears as evidenced by high-density shear deformed regions (denoted by three ellipses) across the a-CuNb layer. MD simulations of the single layer a-CuNb (not shown here) suggest that the shear stress

to nucleate a shear band is ~ 8 GPa under uniaxial compression, and deformation is dominated by a single shear band. In contrast, the shear stress to nuclear shear transformation regions (ellipses) in a-CuNb in the multilayer is ~ 4.8 GPa under uniaxial compression. It is worth pointing out that such high shear stresses associated with the nucleation of shear transformation zones are partially ascribed to the high strain rate and the finite sized model in MD simulations. Nevertheless, the significant difference between 8 GPa and 4.8 GPa indicates that the Cu/a-CuNb layer interface reduces the stress to nucleate shear deformation in a-CuNb, consistent with experimental studies that show the maximum strength of Cu/a-CuNb multilayers is much less than the strength of single layer a-CuNb.

4. Conclusions

The microstructure and mechanical properties of Cu/a-CuNb multilayers have been systematically studied. When $h \leq 50$ nm, the hardness of multilayers reaches a plateau value, which is much lower than the hardness of single-layer a-CuNb. Such a phenomenon is distinctly different from size dependent strengthening reported in Cu/a-CuZr multilayers. Microstructure analyses show that the a-CuNb at interfaces may have MRO that lowers the resistance to activate shear transformation zones in amorphous-CuNb layers. MD simulations suggest that the stress for the activation of STZs in the a-CuNb in multilayers is much less than the stress necessary to trigger shear bands in single-layer a-CuNb. Future works on C/A multilayers with amorphous alloys that have positive heat of mixing are needed to further explore the effect of positive heat of mixing on deformation behaviors of C/A nanolaminates.

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Figure captions

Figure 1. (a) The XRD profiles of Cu/a-CuNb multilayers (with individual layer thickness $h=1-200\text{nm}$) show Cu layers with (111) and (200) texture and amorphous humps from a-CuNb layers. (b) Peak deconvolution of the XRD profiles of Cu/a-CuNb 2.5 nm and 1 nm multilayers. A middle peak emerges with inter-planar spacing identical to the average of a-CuNb and Cu (111).

Figure 2. Cross-sectional TEM (XTEM) micrographs of Cu/a-CuNb multilayers with different individual layer thickness. (a) XTEM image of Cu/a-CuNb 50 nm multilayer shows alternating nanocrystalline Cu and featureless amorphous CuNb layers with clear layer interfaces. (b) SAD pattern of the Cu/a-CuNb 50 nm multilayer shows semi-continuous Cu (111) and (200) diffraction dots and the diffuse halo ring from a-CuNb layer. (c-d) XTEM micrographs of the Cu/a-CuNb 10 nm and 100 nm multilayers with discrete layers and abrupt layer interfaces.

Figure 3. High resolution TEM (HRTEM) images of (a) Cu/a-CuNb 2.5 nm, (b) Cu/a-CuNb 10 nm, and (c-d) Cu/a-CuNb 50 nm multilayers. In the a-CuNb layers, extremely thin (several monolayer thick) semi-crystalline layers are observed as indicated by the arrows.

Figure 4. Comparison of indentation hardness of Cu/Nb [47], Cu/a-CuZr [56], and Cu/a-CuNb multilayers. A linear fit for Cu/a-CuNb was made when $h=200-50\text{nm}$, shown as the dashed line. The indentation hardnesses of the single layer Cu, Nb, a-CuZr, and a-CuNb films are also shown. The peak hardness of Cu/a-CuZr approaches that of the a-CuZr; whereas the peak hardness of Cu/a-CuNb is much lower than that of the a-CuNb.

Figure 5. Evolution of indentation hardness (H_{IT}) of Cu/a-CuNb multilayers as a function of $h^{-1/2}$, where h is the individual layer thickness. A linear fit was made when $h=200-50\text{nm}$ shown as the dashed line. The hardness for the single layer a-CuNb and Cu films were added as references. H_{barrier} was converted by the interface barrier strength which was calculated by Hall-Petch slope. H_{rom} is the average of $H_{\text{a-CuNb}}$ and H_{Cu} , while $H_{\text{rom}}^{\text{mod}}$ is the average of $H_{\text{a-CuNb}}^{\text{ML}}$ and H_{Cu} .

Figure 6. Load-displacement curves and images of surface morphology of indents after nanoindentation of single layer a-CuNb and Cu/a-CuNb 20 nm multilayers. (a1) and (b1) show the load-displacement curves of a-CuNb and Cu/a-CuNb 20 nm multilayers respectively. Discrete pop-in events in the a-CuNb are indicated by arrows. (a2-b2) The SPM images of the indent morphology after indentation for a-CuNb (a2) and Cu/a-CuNb 20 nm multilayers (b2). (a3-b3) Comparisons of the 3D SPM images show prominent step-like pile-ups and shear bands (indicated by arrows) for the single layer a-CuNb (a3), as compared to the homogeneous deformation for the Cu/a-CuNb 20 nm multilayers.

Figure 7. A schematic to illustrate the deformation mechanism in the Cu/a-CuNb multilayers. (a) Single layer a-CuNb deforms by shear banding. (b) In Cu/a-CuNb multilayers ($h<50$), deformation is dominated by dislocation pile-ups in Cu layers and the formation of STZs in a-CuNb layers. In the beginning, dislocations in Cu layer accommodate the plasticity; then through the crystalline/amorphous interface plasticity is transferred into a-CuNb layer in the form of shear events (motion of STZs); later, dislocations motion in the adjacent Cu is triggered by the shear events in a-CuNb through another

crystalline/amorphous interface.

Figure 8. Atomic structures of Cu 5 nm / a-CuNb 2.5 nm multilayers, showing (a) initial structure before deformation, and (b) the deformed multilayers containing glide dislocations in Cu layers under uniaxial compression at a strain of 6.5%. Dislocations are characterized according their centro-symmetry parameter. Cu atoms are in blue and Nb atoms are in orange.

Figure 9. Atomic structures around one a-CuNb layer in Cu 5 nm/a-CuNb 2.5 nm multilayers, showing (a) the undeformed structure and (b) the deformed structure at uniaxial compressive strain of 8.0%. The black dotted lines indicate the original interfaces. The red dotted lines indicate the interfaces after 8% compressive strain. The local shears of atomic clusters across the a-CuNb layer are denoted by three ellipses. Atoms are colored according to their excess energy.

Table captions:

Table 1. Measured modulus of single layer and multilayer thin films

	a-CuNb	Cu/a-CuNb 5nm	Cu/a-CuNb 20nm	Cu/a-CuNb 50nm	Cu/a-CuNb 100nm	Cu/a-CuNb 150nm	Cu
Modulus (GPa)	136±3	123±5	126±3	119±5	122±4	120±5	113±9

Table 2. Comparison of hardness of several Cu-based multilayer films

System	H-P slope (GPa√nm)	Measured peak hardness (GPa)	Calculated peak hardness from H- P slope (GPa)	Single layer film hardness (GPa)	ROM hardness (GPa)
Cu/Nb	2.1	6.9	6.8	$H_{Nb}=2.7$	2.2
Cu/a-CuZr	1.05	6.3	1.5	$H_{a-CuNb}=6.2$	3.9
Cu/a-CuNb	1.7	4.5	4.6	$H_{a-CuNb}^{SL}=7.2$	4.5
				$H_{a-CuNb}^{ML}=4.5$	3.2

a-CuNb

Cu/a-CuNb 20 nm

(a)

(b)