Nanolaminates Utilizing Size-Dependent Homogeneous Plasticity of Metallic Glasses

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Homogeneous plasticity in metallic glasses is generally only observed at high temperatures or in very small structures (less than ≈100 nm), so their applications for structural performance have been very limited. Here, nanolaminates with alternating layers of Cu$_{50}$Zr$_{50}$ metallic glass and nanocrystalline Cu are synthesized and it is found that samples with an optimal composition of 112-nm-thick metallic-glass layers and 16-nm-thick Cu layers demonstrate a maximum strength of 2.513 GPa, a value 33% greater than that predicted by the rule-of-mixtures and 25% better than that of pure Cu$_{50}$Zr$_{50}$ metallic glass. Furthermore, ≈4% strain at fracture is achieved, suppressing the instantaneous catastrophic failure often associated with metallic glasses. It is postulated that this favorable combination of high strength and deformability is caused by the size-dependent deformation-mode transition in metallic glasses, from highly localized plasticity, leading to immediate failure in larger samples to homogeneous extension in the smaller ones.

1. Introduction

For the last 20 years, metallic glasses have been deemed to revolutionize structural materials due to their superior wear and corrosion resistance, excellent hydrogen-storage capabilities, high electrical conductivity, good soft magnetism and superior mechanical properties.[1–6] These attractive characteristics of metallic glasses have shown promise in small-scale applications, such as coatings and chemical and biological nano- and micro-electromechanical systems (NEMS and MEMS).[7–9] However, despite all of these beneficial features, metallic glasses are not being widely utilized in these applications due to their propensity for catastrophic failure in tensile loading by the instantaneous propagation of shear bands. Recently, it was shown that the introduction of an additional either crystalline or amorphous phase into a metallic-glass matrix is capable of suppressing such shear failure, thereby dramatically increasing the global plasticity by forming multiple shear bands and shear-band patterns.[10–12] Another approach that has been shown to induce ductility in metallic glasses is to reduce their dimensions to 100 nm and below, whereupon room-temperature deformation occurs via homogeneous flow, giving rise to enhanced tensile strength and/or ductility compared with their larger counterparts.[13–18] Despite these promising findings, utilizing nanosized metallic glasses – either as stand-alone structures or as part of a composite – in real-life applications remains challenging due to the difficulties associated with microstructure control and microfabrication processing. For example, a common method for inserting a secondary crystalline phase into an amorphous matrix is by annealing it above the glass-transition temperature, which is particularly onerous at small scales due to the highly metastable nature of metallic glasses. Furthermore, while metallic glasses with dimensions of ≈100 nm and smaller suppress immediate tensile failure, forming or patterning them into such small features using conventional microfabrication techniques is quite challenging.[19] These impediments render the insertion of metallic glasses into useful small-scale applications impractical.

Here, we demonstrate the attainment of a superior tensile strength of 2.513 GPa and a non-trivial extension of ≈4%, exhibited by nanolaminates with alternating layers of Cu$_{50}$Zr$_{50}$ metallic glass and nanocrystalline Cu. We attribute this enhanced mechanical performance to the emergence of homogeneous plasticity in the metallic glass below a critical thickness of ≈120 nm. Such nanolaminates may facilitate utilizing metallic glasses in technological applications because: 1) they are 25% stronger and ≈3 times more deformable in terms of plastic strain than pure Cu$_{50}$Zr$_{50}$ metallic glass; 2) they have a high strength-to-weight ratio compared to widely used small-scale structural materials; 3) they retain the metallic glass’s merits, such as enviable wear and corrosion resistance; 4) they are synthesized and patterned via conventional microfabrication processing; and 5) their sizes and properties are highly tunable by controlling the layer thickness and the number of layers.

2. Results

The freestanding, tensile nanolaminate samples, shown in Figure 1, were prepared by depositing each layer via radio-frequency (RF) magnetron sputtering into a single stack, followed by top-down patterning by a focused-ion-beam (FIB)
microhardness $\approx 5.1$ GPa for nanolaminates of 35 nm nanocrystalline-Cu and 23 nm amorphous-Cu-Zr layers,[22] UTS $\approx 1090$ MPa for nanolaminates of 35 nm-thick nanocrystalline Cu and 5 nm-thick amorphous Cu$_{55}$Zr$_{45}$[23] and UTS $\approx 900$ MPa for nanolaminates of 90 nm nanocrystalline Cu and 10 nm amorphous PdSi.[24] In all of these studies, the nanolaminates did not exhibit any improvement in strength compared with the monolithic metallic-glass constituents, likely due to the relatively low fraction of metallic glass. While the addition of metallic-glass layers into nanocrystalline composites has previously been shown to increase the strength and enhance the ductility compared with pure nanocrystalline metals, the metallic-glass layers in these composites were very thin, $\approx 20$ nm and below, a size small enough to prevent deformation via shear-band propagation.[9, 23, 24] More recently, multilayered nanopillars with diameters of $\approx 1$ $\mu$m, composed of alternating $\approx 600$ nm-thick Cu$_{55}$Zr$_{45}$ metallic-glass layers and $\approx 200$ nm-thick crystalline metallic layers (Zr, Cu, and Mo), resulting in a higher relative fraction of the metallic glass, were tested in uniaxial compression perpendicular to the interfaces.[25, 26] These researchers found that their strengths were comparable to those predicted by the rule-of-mixtures and remarked that the thickness of the crystalline layer had to be sufficiently thick to absorb the shear bands transferring from the amorphous layer to attain the enhanced ductility of the composites. Furthermore, to assess the ductility, it is critical that tensile rather than compressive experiments be conducted, because a component under tensile stress tends to initiate failure in terms of instability when the nanocomposites are under complex stress. The key distinction of this work is that the nanolaminates containing alternating 112 nm-thick metallic-glass layers and 16 nm-thick nanocrystalline layers attained a 33% higher strength than that predicted by the rule-of-mixtures, which was also 25% higher than that of

Figure 1. Schematic of the freestanding tensile samples. a–b) Bright-field TEM images for cross-sections of the nanolaminates with $t_a$ of 17 nm (a) and 128 nm (b). c–d) SEM images of the freestanding tensile samples before (c) and after (d) tension.

method, and undercutting the Si substrate via dry-etching. We prepared seven different nanolaminate samples with amorphous Cu$_{50}$Zr$_{50}$ thicknesses ($t_a$) of 17, 42, 68, 112, 128, 215 and 301 nm, where the thickness of the nanocrystalline Cu layers ($t_{nc}$) was held constant at 16 nm. We also prepared one 920 nm-thick, monolithic Cu$_{50}$Zr$_{50}$ metallic-glass sample. The overall stack height in all of the samples was $957 \pm 89$ nm. Tensile tests were performed parallel to the interfaces at a constant engineering-strain rate of $1 \times 10^{-3}$ s$^{-1}$ in an in situ nanomechanical tester, SEMeror.[20,21] Figure 2 shows the typical stress–strain curves (Figure 2a) and the ultimate tensile strength (UTS) and the fracture strain ($\varepsilon_f$) as a function of metallic-glass thickness, $t_a$ (Figure 2b). The UTS and $\varepsilon_f$ values shown in Figure 2b are the averages and standard deviations from at least five experiments at each $t_a$. These plots demonstrate a clear change in mechanical behavior of the nanolaminates with metallic-glass thickness between $t_a$ values of 112 and 128 nm. The monolithic amorphous sample and the nanolaminates with $t_a$ greater than 128 nm all show very-similar mechanical behavior: a UTS of $\approx 2$ GPa after a very-limited plasticity ($\approx 0.5\%$). However, the UTS of the nanolaminates with a $t_a$ of 112 nm was 2.513 $\pm$ 0.043 GPa, gradually decreasing for the samples with $t_a$ less than 112 nm. These samples also showed an enhanced plastic strain of $\approx 1.5\%$ compared with those with a $t_a$ of 128 nm and greater. The nanolaminates with a $t_a$ of 112 nm attained the maximum overall strength of 2.513 GPa and a fracture strain of 3.972 $\pm$ 0.203%, both of which represent a significant improvement over the monolithic, 920 nm-thick metallic-glass sample, whose UTS was 2.007 $\pm$ 0.056 GPa and $\varepsilon_f$ was 2.979 $\pm$ 0.171%. These values also appear to be substantially better than those reported for nanolaminates with alternating layers of metallic glass and nanocrystalline metal: UTS = 1123 MPa for nanolaminates of 35 nm nanocrystalline-Cu and 5 nm amorphous-Cu$_{55}$Zr$_{45}$,[9]...
pure Cu$_{50}$Zr$_{50}$ metallic glass, and manifested substantial tensile ductility, compared with the non-existent tensile deformability of the pure Cu$_{50}$Zr$_{50}$ metallic glass.

Our analysis indicates that the observed trends in the strength and fracture strain in these nanolaminates as a function of \( t_a \) shown in Figure 2b were due mainly to the size-dependent mechanical behavior of the metallic glass, rather than the role of nanocrystalline Cu or of the amorphous-crystalline interfaces. If the mechanical behavior of the metallic glass were independent of sample thickness, the thin metallic-glass layers in all of the nanolaminates would exhibit a similar UTS (\( \approx 2 \) GPa) and fracture strain (\( \approx 3\% \)) to the monolithic metallic-glass sample. While we did not measure the tensile properties of the monolithic, 16 nm-thick nanocrystalline Cu sample, its strength, as inferred from the literature, was between 340 and 1080 MPa.\[27–29\] Since the volume fraction of metallic glass decreases as \( t_a \) decreases, the rule-of-mixtures predicts that the UTS should gradually decrease with decreasing \( t_a \), which is contrary to our observations. Alternatively, if the interfaces were to act as a strengthening or softening mechanism, the UTS of the nanolaminates likely initiates in the metallic-glass layer; 3) an absence of any crystalline phases in the amorphous layers was observed; 4) there was no evidence of multiple shear bands, implying that macroscopic fracture likely occurred by the propagation of a single primary shear band; and 5) obstruction of the nanocrystalline layers to shear-band propagation from the amorphous phase was observed. This TEM-based analysis supports our hypothesis that the enhanced strength and ductility here arose from the thickness-dependent deformation of the metallic glasses rather than any other mechanism such as the formation of multiple shear bands.

### 3. Discussion

Transmission-electron-microscopy (TEM) images of the nanolaminates’ through-thickness cross-sections are shown in Figure 3. To perform this TEM analysis, we extracted the remaining gauge sections after tensile fracture for the nanolaminates with \( t_a = 42, 68, 128 \) and 215 nm using a micromanipulator (AutoProbe200, Omniprobe Inc.), transferred them onto TEM grids and thinned the cross-sections in the FIB. We summarize our observations based on TEM analysis here:

1) there was no interfacial delamination or fracture, implying good adhesion between the layers prior to fracture;
2) there were no traces of fracture or microcracks in the nanocrystalline Cu layers, implying the macroscopic fracture of the nanolaminates likely initiates in the metallic-glass layer;
3) an absence of any crystalline phases in the amorphous layers was observed;
4) there was no evidence of multiple shear bands, implying that macroscopic fracture likely occurred by the propagation of a single primary shear band; and
5) obstruction of the nanocrystalline layers to shear-band propagation from the amorphous phase was observed. This TEM-based analysis supports our hypothesis that the enhanced strength and ductility here arose from the thickness-dependent deformation of the metallic glasses rather than any other mechanism such as the formation of multiple shear bands.

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**Figure 2.** a) Typical true-stress–strain curves for the nanolaminates. b) The ultimate tensile strength and fracture strain of the nanolaminates as a function of the thickness of the amorphous layer. These plots demonstrate a clear change in mechanical behavior of the nanolaminates with metallic-glass thickness between 112 and 128 nm.

**Figure 3.** a,b) Nanolaminates with \( t_a \) of 42 nm (a) and 128 nm (b). The TEM observations support the idea that the enhanced strength and ductility here arise from the thickness-dependent deformation of metallic glasses rather than any other mechanism, such as the formation of multiple shear bands and the generation of a crystalline phase in the amorphous layers.
The critical stress required for shear-band propagation is generally given by the Griffith theory.\cite{13,16,18,30} By equalizing the elastic-strain energy and the crack-like-shear-band-propagation energy, the critical stress for shear-band propagation can be represented by \( \sigma = \sqrt{2I/\pi E} \), where \( I \) is the energy per unit area of the shear band, \( E \) is the elastic modulus and \( h \) is the gauge length, as shown in Figure 4. This type of modeling implies that the critical stress for shear-band propagation in our metallic-glass layers (all of which had the same gauge length) is a constant, rather than a function of \( t_a \). It is important to note the Griffith theory is valid in brittle fracture, which is the behavior we observed in the nanolaminates with \( t_a \) above the critical thickness. We invoked Griffith's theory to explain the mechanical behavior only for \( t_a \) above the critical thickness. Recent observations for Zr-based metallic-glass nanopillars with diameters of 100 nm revealed that they deform by homogeneous flow at room temperature and attain a higher UTS than that for larger samples of the same glass, which deform by shear-band propagation.\cite{31} These authors predicted the UTS of metallic glasses that deform by homogeneous flow below a critical size of \( \approx 100 \) nm to lie between the ideal strength (\( \approx E/30 \)), as an upper bound, and the stress required to induce homogeneous plasticity at room temperature, as a lower bound.\cite{31} Since shear-band propagation is the energetically favored process in large metallic-glass samples, it is reasonable to assume that the UTS resulting from shear-band propagation is lower than that arising from homogeneous plasticity. Therefore, a useful representation of the UTS as a function of \( t_a \), consisting of upper and lower plateaus below and above the critical thickness, respectively, is:

\[
UTS = \left( \sigma_{\text{hom}} + \sigma_{\text{local}} \right) - \left( \sigma_{\text{hom}} - \sigma_{\text{local}} \right) \text{erf} \left( \frac{t_a - t^*}{w} \right)
\]  

In Equation 1, \( \sigma_{\text{hom}} \) and \( \sigma_{\text{local}} \) are the UTS values of a metallic glass deformed by homogeneous flow and localized shear-band propagation, \( t^* \) is the transition thickness and \( 4w \) is a measure of the extent of the transition region, and erf is the error function defined by \( \text{erf} \left( x \right) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} dt \). For perfectly bonded layers subjected to isostrain, the average axial stress in the nanolaminates can then be calculated by the rule-of-mixtures:

\[
UTS_{\text{NL}} = \frac{UTS_t}{t_a + \sigma_{\text{local}}} + \frac{\sigma_{\text{nc}}}{t_a + \sigma_{\text{nc}}}
\]

In Equation 2, \( \sigma_{\text{local}} \) is the flow stress of nanocrystalline Cu at the fracture strain. Fitting this functional form with 4 variables to the experimental data shown in Figure 2b, while maintaining \( t_a = 16 \) nm and \( \sigma_{\text{local}} = 2.007 \) GPa (as measured for the 920 nm-thick metallic-glass sample), yields \( \sigma_{\text{hom}} = 2.838 \) GPa, \( \sigma_{\text{nc}} = 905.5 \) MPa, \( t^* = 121.9 \) nm, and \( w = 11.7 \) nm. As shown in Figure 5b, the analytical model agrees with the experimental data very well. \( \sigma_{\text{hom}} \) of 2837.8 MPa is comparable with the ideal strength of Cu_{50}Zr_{50} of 2817 MPa, as evaluated by \( E/30 \).\cite{12} The strength of the 16 nm-thick nanocrystalline Cu, 905.5 MPa, evaluated by the model is also within the range reported previously.\cite{37,26} The 46.8 nm width (4\( \alpha \)) of the strength-transition region is narrow, indicating that this transition is abrupt rather than gradual, (i.e., it occurs at some critical thickness rather than via an intermediate deformation mode), which is in agreement with the existing literature.\cite{13–18} Our model predicts an optimal metallic-glass thickness, \( t_a \), of 94 nm, attaining the maximum strength of this system of 2.555 GPa.

We now examine the UTS profile of the metallic glass in the nanolaminates to understand the scientific basis for the proposed model and to justify its possible use as a predictive tool. Above the critical thickness of \( \approx 120 \) nm, it is reasonable to approximate the lower-strength region as a constant, even though some researchers have reported size effects in the strength of metallic-glass nanopillars at the scale where they deform by shear-band propagation.\cite{32–34} The proposed theory to explain the size effect in metallic glass deformed and fractured by shear bands is based on Griffith's crack-propagation

![Figure 4](image1)

**Figure 4.** a) Embryonic shear-band propagation is suppressed below the critical thickness. b) Mature shear bands form in the nanolaminates with a thicker amorphous layer than the critical value.

![Figure 5](image2)

**Figure 5.** a) Suggested UTS profile of amorphous layer as a function of thickness of amorphous layer. b) Model developed for UTS of nanolaminates fitting to experimental data.
theory,[13,16,30] where the critical stress for shear-band propagation is proportional to $\sqrt{t/L}$, with $L$ being the dimension of the monolithic samples, leading to the “smaller-is-stronger” phenomenon. However, utilizing this approach to calculate the critical stress for shear-band propagation in the nanolaminates predicts a UTS that is independent of the metallic-glass thickness. This is probably because when a mature shear band is nucleated, each metallic-glass layer is long and wide enough for the shear band to propagate along the in-plane direction, as shown in Figure 4b. A lower strength independent of $t_b$, based on the Griffith theory, is valid only when shear bands propagate, introducing new surfaces in the metallic glasses, which indicates, in the higher-strength region below the critical thickness, that embryonic shear-band propagation is most likely to be suppressed. This observation agrees well with the theoretical work of Shimizu et al.,[35] who suggested that embryonic shear-band propagation is the critical condition for macroscopic yielding and predicted the incubation length scale for attaining maturity to be $\approx 100$ nm for Zr-based metallic glasses.

4. Conclusions
The demonstration of combined 2.513 GPa tensile strength and $\approx 4\%$ tensile deformability, optimized by tuning the metallic-glass thickness in nanolaminates of amorphous-nanocrystalline metals suggests that this may be a viable route towards developing materials with a superior mechanical performance beyond those achievable by the individual constituents and vastly superior to those predicted by the rule-of-mixtures. Our findings may provide a useful foundation for the application of these types of nanolaminate structures in micro- and nanodevices requiring a robust mechanical performance, as well as for understanding the fundamental scientific principles driving postelastic deformation in small-scale metallic systems.

5. Experimental Section
The nanolaminates were prepared on Si (100) substrates with alternating layers of Cu$_{50}$Zr$_{50}$ metallic glass and nanocrystalline Cu$_{70}$Zr$_{10}$ using RF powers in the magnetron sputtering. The Cu$_{50}$Zr$_{50}$ metallic-glass layers were deposited from separated pure-Cu and Zr targets at RF powers of 56 W and 224 W, respectively, and the nanocrystalline Cu layers were deposited from a pure-Cu target at an RF power of 102 W. The base pressure was $2 \times 10^{-7}$ Torr or lower and the processing pressure was 3 mTorr with pure-Ar gas. We confirmed the composition of the Cu$_{50}$Zr$_{50}$ metallic glass using energy-dispersive X-ray spectroscopy. We also confirmed that the variation in the composition was negligible in an area of 2 cm $\times$ 2 cm at the center of the sample stage in the sputter; samples sputtered only in this area were used to minimize the variation in composition along the position. The Si substrates were undercut by dry-etching in a XeF$_2$ chamber, and the tensile samples were patterned by FIB. The tensile tests were performed parallel to the interfaces at a constant engineering-strain rate of $1 \times 10^{-3}$ s$^{-1}$ in an in situ nanomechanical tester, SEMentor. True-stress–strain curves were calculated from the initial sample geometry measured by SEM and the load–displacement monitored during the tests. To minimize the unnecessary deformation of other parts than gauge during the tests, we used tensile samples with heads much larger than the gauge dimension and dimension tension grips, as shown in Figure 1.

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