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Coherent Interfaces Increase Strain-Hardening Behavior in Tri-Component Nano-Scale Metallic Multilayer Thin Films

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Strain-hardening in tri-component nano-scale metallic multilayers was investigated using nanoindentation and micro-pillar compression. Cu/Ni/Nb films were made in tri-layer structures as well as bi-layers consisting of an alloy of Cu–Ni/Nb. Strain-hardening increases as the layer thickness decreases, with 5 nm layers exhibiting higher strengths and hardening coefficients than 30 nm layers. The experimental evidence is described in light of the confined layer slip model, and supports the hypothesis that coherent interfaces with a modulus mismatch in the tri-layer system are responsible for additional deformation mechanisms that can lead to hardening in excess of that found in bi-layer systems.

Keywords: Multilayers, Nanoindentation, Micro-Pillar Compression, Strain-Hardening

Computational simulations of tri-layer nano-scale metallic multilayer (NMM) systems having a combination of coherent and incoherent interfaces have suggested that these systems will possess significant strain-hardening ability above that of their bi-layer counterparts.[1–4] However, the experimental validation of the strain-hardening behavior [2] has only been carried out at a single tri-layer thickness period. With significant evidence in bi-layer NMMs that layer thickness plays a substantial role in controlling the deformation processes in the confined layer slip (CLS) regime,[5–7] this effect of layer thickness on tri-layer systems needs to be evaluated. Briefly, as described in [1], the presence of two adjacent FCC layers with different elastic moduli causes shear stresses to develop at the chemically distinct, but coherent, interface as a threading dislocation moves through the FCC layers. This shear stress can lead to cross-slip at higher stresses, assisted by the high strength imparted by the incoherent interface at the FCC/BCC layers. The cross-slip process, which in a bulk material would weaken the system through additional deformation at a fixed stress, leads to additional dislocation debris within the FCC layers blocking the motion of subsequent threading dislocations and leading

to additional hardening. As the density of interfaces increases, the density of potential cross-slip sites also increases; therefore, it may be expected that reducing layer thickness in the CLS regime of a tri-layer system would increase both the strength- and strain-hardening behavior for these materials systems.

Multiple experimental techniques can be used to investigate a material's relative strain-hardening ability including tensile, compression, and nanoindentation testing. Indentation testing is a high-throughput method which leads to a large test population and provides valuable statistics as opposed to testing limited numbers of samples in thin film compression or tensile testing; however, the indentation results require a more complex and less determinant analysis. The most common indentation technique used to probe the strain-hardening relationship in a material compares the hardness measured using tips with different included angles that create different local strains in the material directly beneath the contact.[8] The Berkovich and cube-corner indenter geometries, corresponding to equivalent cone angles of 70.3° and 42.3°, result in effective strains of approximately 8% and 22%, respectively.[9] A material that exhibits strain-hardening between 8% and 22% strain will show larger

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hardness values with the cube-corner tip over the hardness measured with a Berkovich tip, whereas an elastic-perfectly plastic material should have the same hardness values regardless of indenter geometry.

Micro-pillar compression testing provides a close to uniaxial stress state which allows for a more accurate determination of the strain-hardening exponent of these NMMs, but requires sample preparation techniques which both limit the number of experiments which can be performed as well as adding the concern that milling with Ga ions can alter the subsequent material properties. Additionally, micro-pillar compression tests can access the strain regime from initial yield to the 8% value probed by a Berkovich tip. A limitation of micro-pillar compression testing is that shear often is initiated at the edge of the punch/pillar contact, leading to the inability to generate uniaxial stress-strain conditions past 10% in many materials. Therefore, the combination of indentation and compression testing will allow a more complete study of strain-hardening in these novel multi-component multilayers.

Tri-component films consisting of Cu (lattice parameter = 3.61 Å), Ni (lattice parameter = 3.52 Å), and Nb (lattice parameter = 3.30 Å) are the basis of this study. Cu/Ni/Nb NMM films used in this study were deposited using magnetron sputtering on (100) oriented Si starting with the Nb layer and ending with the Ni layer to a total thickness of 3 µm with equal individual layer thicknesses of 5 and 30 nm. Preliminary transmission electron microscopy investigations of the 30 nm multilayers show a mixture of coherent FCC/FCC boundaries as well as some grains which show renucleation at the boundary. A second set of samples was fabricated to investigate the specific role of the FCC/FCC interfaces while maintaining the same overall chemistry of the tri-layer; these samples began with a 5 or 30 nm Nb layer, but then used co-sputtering to create a 10 or 60 nm thick FCC alloy layer. The alloy system was deposited to a total thickness of 1.6 µm, the repeating period of layers was constant between the alloy and tri-layer system. X-ray diffraction characterization of these films shows very strong textures with Nb predominantly (110) and Cu and Ni (and CuNi alloy) predominately (111) orientation. Since Cu and Ni are both FCC materials and the lattice constants are within 3% of each other, this combined effect can promote epitaxial growth across the interface, leading to the desired coherent interface. Previous studies have also shown that epitaxial growth is possible between Cu/Ni multilayers deposited using magnetron sputtering,[10–13] further supporting the assumption that these layers are deposited with coherent interfaces.

Micro-pillars with aspect ratios of 1:3 were fabricated using a focused Ga ion beam at an accelerating voltage of 30 keV in a Tescan Vela FIB instrument. Initially, currents of 4 nA were used to mill rough pillar shapes; exact dimensions were achieved

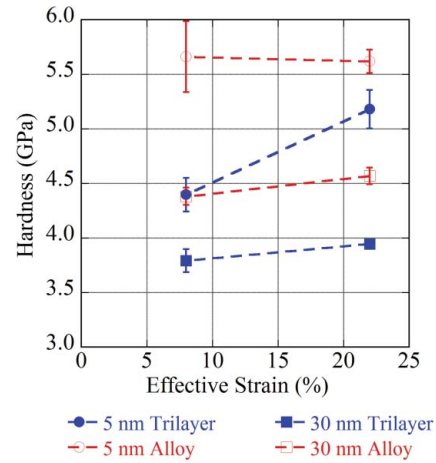


Figure 1. Hardness measurements from nanoindentation experiments conducted using a Berkovich tip (effective strain 8%) and cube-corner tip (effective strain 22%), approximating the hardening response of multilayer films with mixed interfaces (tri-layer) and incoherent interfaces (alloy).

after low current polishing to help minimize irradiation damage with currents ranging from 1 nA to 100 pA. The micro-pillars were imaged using a Hitachi S4800 high-resolution scanning electron microscope (HRSEM) to determine the taper due to FIB milling. These particular milling conditions resulted in a taper angle of 3.25°, the effects of which were subtracted from initial load-displacement curves using a first-order correction.[14]

Nanoindentation was performed using a Hysitron UBI indenter using the load-controlled partial unload technique to a maximum load of 10 mN. Hardness values were determined from similar contact areas, corresponding to depths of approximately 140 nm for the Berkovich and 400 nm for the cube-corner, to suppress differences due to indentation size effects. No less than 20 indents were obtained on each sample to ensure statistical reliability. Figure 1 shows the nanoindentation hardness results obtained from the two different tips on all four multilayers. All eight sets of experiments showed similar modulus values of approximately 140 GPa ensuring the variations in hardness are not due to tip calibration errors. The substantial increase in hardness for the tri-layer samples with a 5 nm layer thickness indicates a significant strain-hardening ability, whereas little to no strain-hardening is observed in the 5 nm bilayer alloy. However, due to the large deviation in the Berkovich values for the 5 nm alloy film, this result is inconclusive. Both samples with a 30 nm layer thickness show a small increase in hardness for both the tri-layer and alloy film, which indicates some strain-hardening has occurred. Prior results by our group and collaborators [15] on similar films (but grown under different conditions) showed similar change in hardness of 0.6 GPa between 5 and 30 nm layer thickness tri-layers,

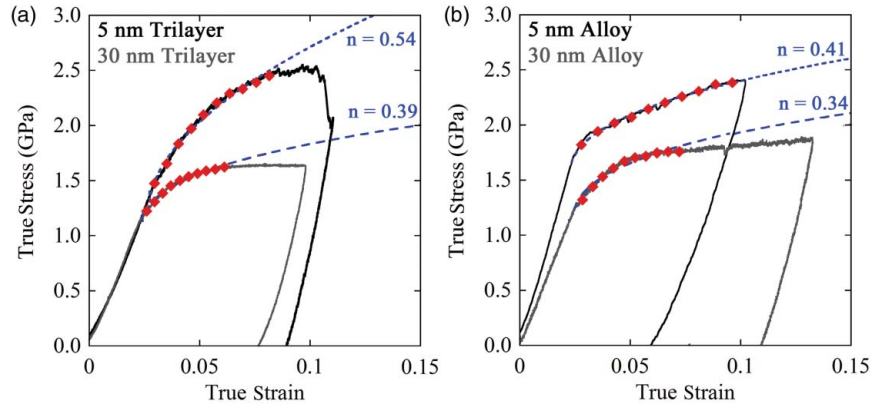


Figure 2. Representative stress–strain curves from micro-pillar compression testing of NMMs for (a) tri-layer (mixed interfaces) and (b) the bi-layer alloy (incoherent interface only) films.

though the measured hardness in the current study is lower than those prior published values.

To gain a more accurate measurement of the strain-hardening response at lower strains, micro-pillar compression tests were conducted in a Zeiss DSM 962 SEM with a modified Alemnis *in situ* indenter first developed by Rabe et al.,[16] modified and improved by Wheeler and Michler,[17] using displacement control at strain rates of approximately $1\text{e}-3/\text{s}$. The taper corrections previously described were applied to the load–depth curves and resulted in the true stress–true strain curves shown in Figure 2. While the first-order taper correction is more accurate than using no correction at all, there are still limitations to this simplified correction. First and foremost, this correction assumes elastic–perfectly plastic deformation which, in the case of samples which exhibit strain-hardening behavior, is a gross over correction. Additionally, since the deformation behavior of these pillars is different (5 nm tri-layers do not deform to a taper-free pillar before shearing while the alloy films barrel significantly), the relative taper correction of those conditions would only show a stronger trend than the one reported here, with tri-layers hardening more than alloy films and thinner layers (specifically for the tri-layer samples) hardening more than thicker layers.

Slight differences in the initial loading slope or rounding at the initial contact in Figure 2 are likely due to slight misalignment of the pillar with the tip,[18,19] different roughness or roundness of the top of the pillar which would alter the initial contact, or different amounts of residual stresses.[20] Due to these issues, the elastic modulus in micro-pillar testing is more often taken from an unloading slope, where the initial contact is not as strong of an effect.[21] In this case, the substrate stiffness was sufficiently high, so that the effect of pillar sink-in into the substrate compliance was found to be negligible.[22] To address any non-linear loading due to rounding of the top of the pillar from FIB milling, the

curves are offset so that the extrapolated elastic portion crosses the origin.

Uniaxial strain-hardening behavior follows the well-known Ludwik relationship between stress and strain, as shown in other compression tests on nanolaminates [23]:

$$\sigma = \sigma_{ys} + K\varepsilon_p^n, \quad (1)$$

where σ_{ys} is the yield strength, K is the strength index, and n is the strain-hardening exponent. The portion of each curve used in curve fitting is emphasized in red diamonds and overlaid over the stress–strain curve with the curve fits shown as dashed lines. All curve fits have R -values of at least 0.98, suggesting these reasonably describe the strain-hardening relationship of the films during the initial strain-hardening (up to $\approx 8\%$). A summary of the mechanical properties extracted from micro-pillar compression tests is listed in Table 1.

The trend seen from the indentation study follows closely with that observed in the compression results, with thinner layers exhibiting stronger strain-hardening behavior than thicker layers. The stress–strain curves shown in Figure 2 indicate that by 8% strain, both 30 nm films have reached their maximum flow stress, while 5 nm films continue to harden until approximately 11% strain. This explains why the 30 nm films do not show significant increases in the hardness values when indented using Berkovich and cube-corner tip geometries (Figure 1). Since the 5 nm tri-layer film continues to harden up until the pillar shears at 11% strain, the increased hardening is reflected in the higher hardness values observed when using the sharper tip in the indentation study. The only discrepancy in the strain-hardening behavior between the two techniques is seen in the 5 nm alloy film, which shows obvious hardening in the compression results, but not in the indentation results. However, since the Berkovich indentation results (Figure 1) show a large spread (0.7 GPa) for the 5 nm alloy film, the hardening could likely

be masked by the scatter in the data. Additionally, since the alloy films exhibit some barreling in the post mortem images (Figure 3), some of the additional strain-hardening observed in compression testing could be an artifact of the increasing cross-sectional area.

The maximum strength ($\sigma_{\max}$) of the two different interface systems follows the expected strength trend with the 5 nm films showing higher strengths than the 30 nm films.[1] The yield strength of the films is more

similar between samples, with the average strength of the 5 nm layers being only slightly higher than the 30 nm layers. Since the initial yield of the composite signifies the strength required to initiate dislocation motion in the softest layer, and thus is an inherent material property, it is not surprising that the yield strength is not as strongly affected by the layered structure. This was also seen by Abdolrahim et al.[24] The alloy films also have additional solid solution strengthening component, which is on the order of 60 MPa for the CuNi alloy.[25,26] This is on the order of the increase observed in the hardness and yield strength for the alloy system in Table 1. Differences in layer thickness in the FCC layers between the alloy (60 nm) and the tri-layer (30 + 30 nm) make an exact comparison difficult, but it appears that there is a measurable impact from solid solution strengthening in the alloy systems. While a few of the tri-layer compression strength values are larger than the alloy samples, this is an issue of statistics as opposed to a physical relationship. With only two pillars for each compression test, the observed variations could be caused by misalignment, errors in taper correction, or actual differences found in point to point positions in the films (i.e. the observed scatter in the nanoindentation data). Nonetheless, in all cases, the ranking of hardness and flow stress follow between the indentation and compression testing, with the acknowledgement that the limited statistics in the compression testing means that there may not be statistically significant results in the compression testing. For instance, the average maximum stress for the 30 nm tri-layer is less than that of the 30 nm alloy, but not to a level that would be significant; however, when taken in light of the indentation testing the different testing methods do appear to support each other.

In general, these results show that the strain-hardening exponents of 5 nm films are larger than the 30 nm films in both material systems. Additionally, the higher strain-hardening exponents observed in the tri-layer samples indicate that the presence of the

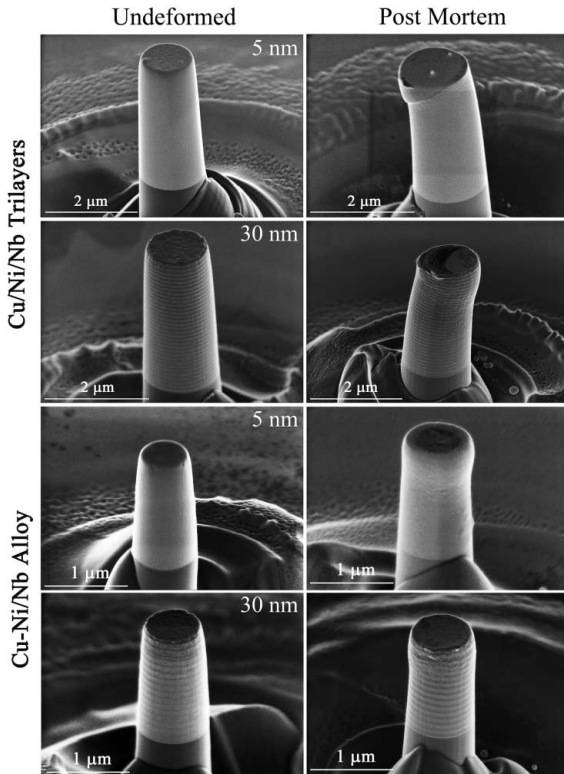


Figure 3. Undeformed (left) and post mortem (right) pillars of mixed interface tri-layer films and incoherent interface alloy films showing difference in deformation as a result of interface type and layer thickness.

Table 1. Strength- and work-hardening summary for tri-layer and alloy films tested using micro-pillar compression and nanoindentation.

Sample		Micro-pillar compression				Nanoindentation
		σ_{ys} (GPa)	$\sigma_{\max}$ (GPa)	n , Ludwik	Eng. stress at 8% (GPa)	Berkovich-8% (GPa), $H/2.7$ [8]
5 nm Tri-layer	P1	1.48	2.17	0.50	2.01	1.63 ± 0.06
	P2*	1.57	2.32	0.54	2.23	
30 nm Tri-layer	P1	1.44	1.85	0.35	1.83	1.4 ± 0.12
	P2*	1.18	1.53	0.39	1.51	
5 nm Alloy	P1	1.64	2.60	0.42	2.34	2.1 ± 0.04
	P2*	1.82	2.24	0.41	2.15	
30 nm Alloy	P1	1.32	1.75	0.31	1.68	1.62 ± 0.03
	P2*	1.36	1.68	0.34	1.65	

Stress-strain curves shown in Figure 3 are noted with *.

FCC/FCC interfaces adds an additional hardening mechanism, which does not occur in the bi-layer samples. While only a small difference is observed between the strain-hardening exponents in the 30 nm films, the 5 nm tri-layers display significantly more hardening than the alloy film with an increase in the hardening coefficient from 0.4 to 0.5.

The strain-hardening in tri-component multilayers has been previously [27] shown to be a result of increased dislocation content that is deposited along the interface as dislocations propagate through an individual layer. These deposited dislocations act as barriers to further deformation and also can act as nucleation sources for more dislocations, leading to an increase in the dislocation density of the films. Furthermore, a previous study conducted by Abdolrahim et al. [24] indicates decreasing layer thickness should result in an increase in the number of interfacial interactions and dislocation nucleation sites, which would increase strain-hardening in the system as dislocations interact with one another and hinder further deformation. This trend is verified in the current study for both interface structures; however, it is in direct contrast to recent investigations on incoherent and semi coherent interface multilayers. These studies have observed strain-hardening exponents of multilayer films decrease with layer thickness, while the strain-hardening rate increased up to a critical layer thickness before decreasing.[23,28] The decreasing hardening ability of multilayers with decreasing layer thicknesses was attributed to the dislocation storage capacity of the material, with higher strength materials (multilayers with smaller individual layer thicknesses) having a higher probability of dislocations being absorbed by the interface.[23] However, a direct comparison between these studies is difficult due to the significant variation in results possibly due to differences in sample production, mechanical testing apparatus, and data analysis procedures. Further research is needed to elucidate the cause of this disparity.

For this specific tri-layer system, it is believed that deformation is driven by ‘superthreader’ dislocations that have penetrated the coherent interface and propagate through the Cu and Ni layers.[15] Due to the different moduli of the two FCC materials, a coherency stress is created at the boundary that causes the threading dislocation to lag at this interface. Additionally, the portions of the dislocation in each of the two layers propagate at different speeds as a result of the different moduli, which causes instability in the dislocation at the coherent boundary. The addition of a BCC layer adds additional strength to the system as a whole, and provides enough internal shear stress to allow for cross-slip of the superthreading dislocation at the coherent interface. This in turn can act as dislocation pinning sites or a dislocation source, both of which lead to subsequent strain-hardening in this tri-layer NMM. The

defects produced from cross-slip debris have a minimum stable size and therefore will act as a larger relative barrier to dislocation motion in thinner layers, since there is less room to allow for dislocation bowing around the defect. Additionally, as the layer thickness decreases the interface density also increases allowing this mechanism to occur more often in the same volume. Thereby, when the individual layer thickness is reduced there are more dislocation interactions and an increase in both strength and strain-hardening ability.

In summary, complementary measurement techniques have verified that NMM tri-component films with smaller layer thicknesses exhibit a greater strain-hardening ability and a greater hardness than those with larger layer thicknesses in both mixed and incoherent interface structures. Nanoindentation using different indenter tips suggests that strain-hardening of the 5 nm layer thickness sample is significantly larger than that of the 30 nm thickness samples, specifically for the tri-layer sample. Micro-compression testing demonstrated that the strain-hardening exponents of samples with layer thicknesses of 5 nm are $\approx 50\%$ greater than that of the material with layer thicknesses of 30 nm layer. In both layer thicknesses used in this study, the addition of a modulus mismatched FCC/FCC interfaces provides additional strain-hardening over compared with an FCC/BCC bi-layer with an equivalent composition. This provides experimental support of the proposed hardening mechanism based on cross-slip at the FCC/FCC interfaces in these nanolaminate systems.

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