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ORIGINAL REPORT



Suppression of shear banding in high-strength Cu/Mo nanocomposites with hierarchical bicontinuous intertwined structures

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ABSTRACT

The microstructures and mechanical behavior of high-temperature co-sputtered Cu/Mo nanocomposites were investigated and compared with Cu/Mo multilayers. The co-sputtered nanocomposites present hierarchical architectures with bicontinuous intertwined Cu/Mo phases, the feature size of which can be tuned from 35 to 3 nm by changing the deposition parameters. After indentation, shear bands were found in the multilayers but not in the hierarchical nanocomposites. *In situ* nanocompression tests in Transmission electron microscopy showed that the hierarchical nanocomposite containing fine-length-scale intertwined Cu/Mo phases has very high strength. The hierarchical structure is proposed to play an important role in suppressing shear band formation.



IMPACT STATEMENT

Cu/Mo nanocomposites with novel hierarchical architecture containing bicontinuous intertwined structures were fabricated through co-sputtering. High strength and good deformability were achieved in the nanocomposites through *in situ* nanomechanical testing.

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Metallic nanocomposites;
co-sputtering; deformability;
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1. Introduction

Metallic nanocomposites (MNCs) have received broad attention due to their exceptionally high strength [1], good fatigue and radiation resistance [2,3] and thermal stability [4]. Most studies on MNCs have focused on multilayers, where layers of different metals are stacked sequentially [1,5,6]. The high strength of multilayer MNCs was attributed to the ability of the bimetal interface to block slip transmission [7–10]. The evolution of composite strength as a function of the distance between interphase boundaries, λ , has been investigated and different deformation mechanisms have been proposed [1,11]. In a Cu/X system, where X is the other constituent metal, the Hall-Petch law prevails at micron to submicron length scale. Dislocation pileup at the interface is the major deformation event, resulting in a yield strength, σ , proportional to $\lambda^{-1/2}$. When λ is in tens

of nanometers, confined layer slip (CLS)—glide of single dislocation loops bounded by the interfaces, becomes dominant which leads to a $\sigma \propto \ln(h)/h$ relationship. When λ is reduced to a few nanometers, dislocation glide of individual dislocations across interfaces is the key unit mechanism and the peak strength of the multilayer is defined by the interface barrier stress to slip transmission. However, the multilayer nanocomposites have very limited uniform deformability due to the formation of localized shear bands. Three modes of shear banding have been reported, including dislocation cutting through the interface [5,12], sliding of columnar grains [13,14] and localized rotation of interfaces that are weak in shear [7,8]. Since the slip directions may be aligned in a multilayer system, the shear bands tend to propagate across the entire thickness of the thin film, resulting in premature failure.

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This article presents results on the synthesis and nanomechanical characterization of hierarchical nanocomposites with bicontinuous intertwined Cu and Mo phases. After significant plastic deformation, shear bands were not observed. Very high flow stresses were measured in the nanocomposite with fine-length-scale Cu/Mo phases during *in situ* nanocompression test. The results provide insight on producing materials with high strength and good deformability through morphological design.

2. Experimental

Cu/Mo nanocomposite with a nominal 50/50 atomic ratio were deposited at high temperatures by direct current magnetron sputtering. Transmission electron microscopy (TEM) and scanning TEM (STEM) characterizations were performed on a JEOL2010 and a Cs-corrected JEOL3100. The TEM samples were prepared by focused ion beam (FIB) in FEI Nova200 scanning electron microscope. The nanocomposites were indented using a Berkovich tip in a Hysitron PI950 Triboindenter with indentation depth up to 350 nm. *In situ* nanocompression experiments in TEM were conducted using a Hysitron PI95 Picoindenter. Load and displacement were measured during the experiments to estimate stress-strain curves assuming uniform cylindrical cross-section of the nanopillars.

3. Microstructure and mechanical behavior

3.1. Cu/Mo multilayer

A Cu/Mo multilayer was synthesized by depositing 3 nm Cu and 3 nm Mo sequentially at room temperature. The cross-sectional TEM image of the sample is shown in Figure 1(a) with the selected area diffraction pattern (SADP) in the inset indicating an Mo(110)//Cu(111)//interface fiber texture. Through fitting the electron diffraction intensity around Mo(110) and Cu(111) spots into Gaussian profiles, it could be estimated that more than 60% of Cu atoms take body centre cubic (BCC) structure, assuming the same texture effect for Cu and Mo. Figure 1(b) shows high-resolution-TEM image (left) and annular bright field atomic image (right) at two Cu/Mo interfaces. They indicate that Cu may exist as an face centre cubic (FCC) structure with Cu(111)//Mo(110)//interface or be coherent with the BCC Mo. The energy difference between BCC and FCC Cu is quite small, in a range of 7–48 meV/atom based on first principle calculations [15,16]. Therefore BCC Cu can be energetically favorable when it provides a better fit to the substrate lattice, until a critical

thickness is reached where the energy gained from lattice fit becomes smaller than the increase of volume energy of the strained film [17]. The STEM image of the multilayer after 8% maximum indentation is shown in Figure 1(c). Mo appears brighter because of its higher *z*-number. A shear band is visibly emanating from near the tip of the indent, indicated by the dashed lines. Significant instability is observed, which can be traced down from the red arrows. The lack of deformability was also observed during nanopillar compression testing, the result of which is shown as the orange curve in Figure 1(e). Only 2.5% of plastic strain was recorded before the load drop, after a maximum flow stress of 2.8 GPa was reached. The STEM image of the pillar after the test in Figure 1(d) suggests that the load drop was due to the shearing of top region of the pillar along the dashed line.

3.2. Nanocomposite with coarse-length-scale bicontinuous zones

Figure 2(a) shows the cross-sectional STEM images of the 550 nm thin film prepared by depositing both Cu and Mo at 0.3 nm/s on a MgO substrate at 750°C. Due to their positive heat of mixing (+19 kJ/mol), Cu and Mo phase separated during deposition [18]. This is further confirmed by the energy dispersive spectroscopy maps on top of the image. The SADP in the inset indicates a BCC Mo(110)//FCC Cu(111) texture. It can be observed that the composite spontaneously formed a hierarchical modulated structure with alternating 100–200 nm thick Mo and Cu-rich layers. The top Mo-rich layer is bicontinuous with interpenetrating Mo and Cu nano-scale phases. Figure 2(b) shows a plan-view STEM image confirming the bicontinuous intertwined morphology. The Mo grains have average size of 35 nm × 110 nm, with interpenetrating copper phase having a ligament size of ~10 nm. Figure 2(c) shows that there are nano-scale Mo particles (5.2 ± 2.6 nm in diameter) in the Cu-rich layers. The inset is an atomic image of a Mo particle. It shows that the smaller Mo particles are coherent with the surrounding Cu, presenting an FCC structure. A schematic showing this hierarchical architecture can be found in Figure 2(d). Because of the high temperature and long deposition duration, extended bulk diffusion could produce this coarse structure with length scale over 100 nm. At the top of the thin film, the bicontinuous structure was conserved because the material here was exposed to high temperature for shorter time.

Figure 2(e) shows a STEM image of the sample after indentation. After a total indentation depth of 350 nm, shear band formation was not observed. In region I, the Cu layers deformed first at lower strain. In region II, the thickness of the Mo-rich layer also reduced, indicating

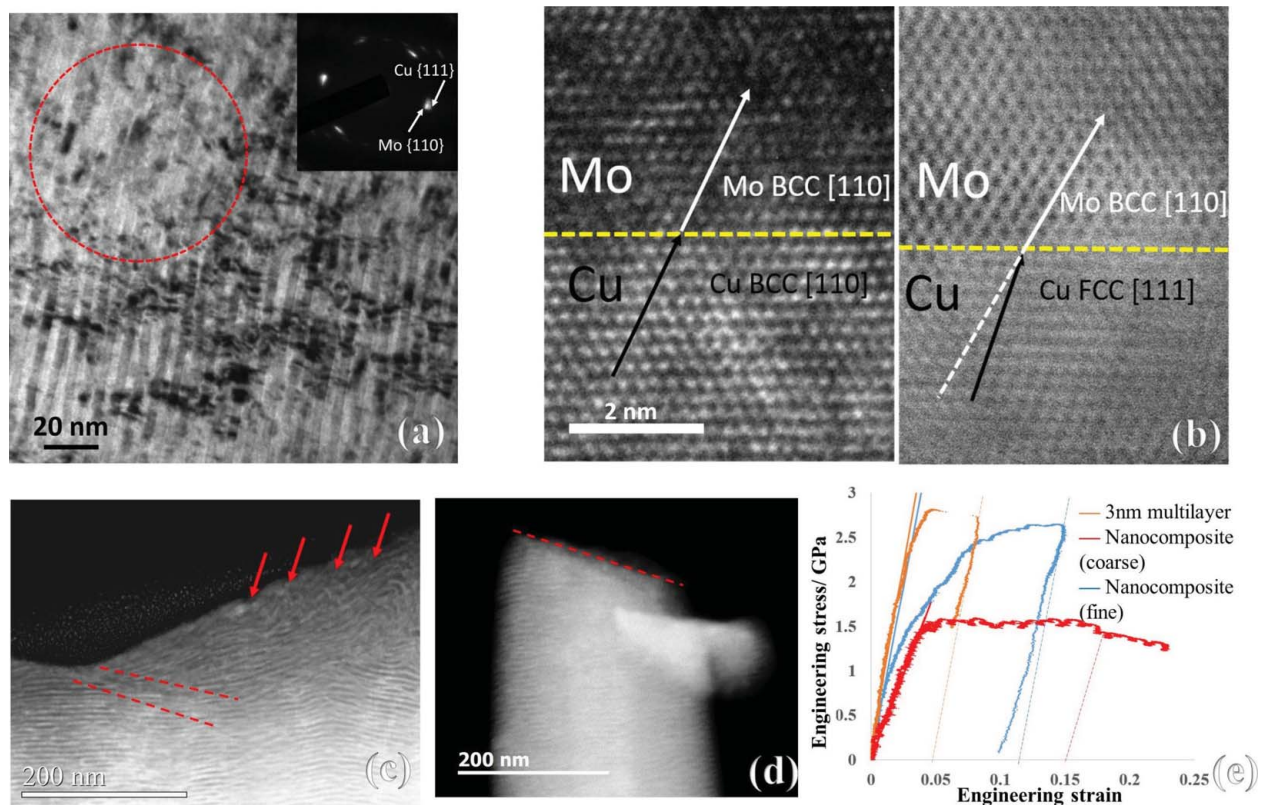


Figure 1. (a) TEM image of the Cu/Mo multilayer; inset: SADP of the circled area. (b) Atomic images showing Cu layer having BCC (left) and FCC (right) structures. (c) STEM image of indented multilayer. (d) STEM images of the top region of a multilayer nanopillar after the compression test. (e) Engineering stress-strain curves from the compression tests on 3 nm multilayer (orange), nanocomposite with coarse-length-scale bicontinuous zones (red) and nanocomposite with fine-length-scale zones (blue).

co-deformation of the Mo-rich and Cu-rich zones. In region III, where the material encounters the largest strains, the Mo grains are flattened in the horizontal direction and a Mo/Cu layered structure can be observed. The vertical dimension of the Mo grains was reduced by 73%.

Nanopillars with a diameter of 250 nm were FIBed to conduct *in situ* compression tests in the TEM. An engineering stress-strain curve is shown as the red curve in Figure 1(e). Figure 2(f) shows TEM images of the pillar at different plastic strains. The maximum flow stress was measured as 1.6 GPa and softening started at 15% plastic strain. During the compression, the thickness of the Cu layers was reduced with Cu extruding out, as indicated by the red arrows. The thickness of the Mo layers did not have a measurable change.

3.3. Nanocomposite with fine-length-scale bicontinuous zones

Figure 3(a) shows cross-sectional STEM images of the 1 μm thin film synthesized by depositing both Cu and Mo at 0.63 nm/s on a 650°C ~ 700°C Si substrate. Large

islands of Cu-rich regions are distributed in a Mo-rich matrix. Figure 3(b) shows that the Mo-rich matrix has a fan-like appearance, where the alternating Cu/Mo layers stretch in the direction perpendicular to the growth front of the composite. The average thickness of Mo layer is measured to be ~ 4 nm while that of Cu is ~ 3 nm. The inset shows a SADP of this region. Clear BCC rings of Mo can be observed, with some weak intensity spots of Cu (111) and Cu (200). Figure 3(c) is an atomic image of a few Cu/Mo layers, showing coherent interfaces with Cu taking the Mo BCC structure. This coherency of metals normally having different crystal structures is typical during the early stage of spinodal decomposition [19]. The continuous (110) ring in the SADP indicates that Cu and Mo in this region containing a few tens of layers are in various orientations. Therefore, the coherency only exists in short range order, across one to a few interfaces. A plan-view sample of the Mo-rich matrix exhibits a bicontinuous morphology as shown in Figure 3(d). This morphology is expected when the spinodal decomposition outruns the deposition process [20]. As a fresh layer is deposited, the existing layer has already decomposed, which serves as a template for the decomposition

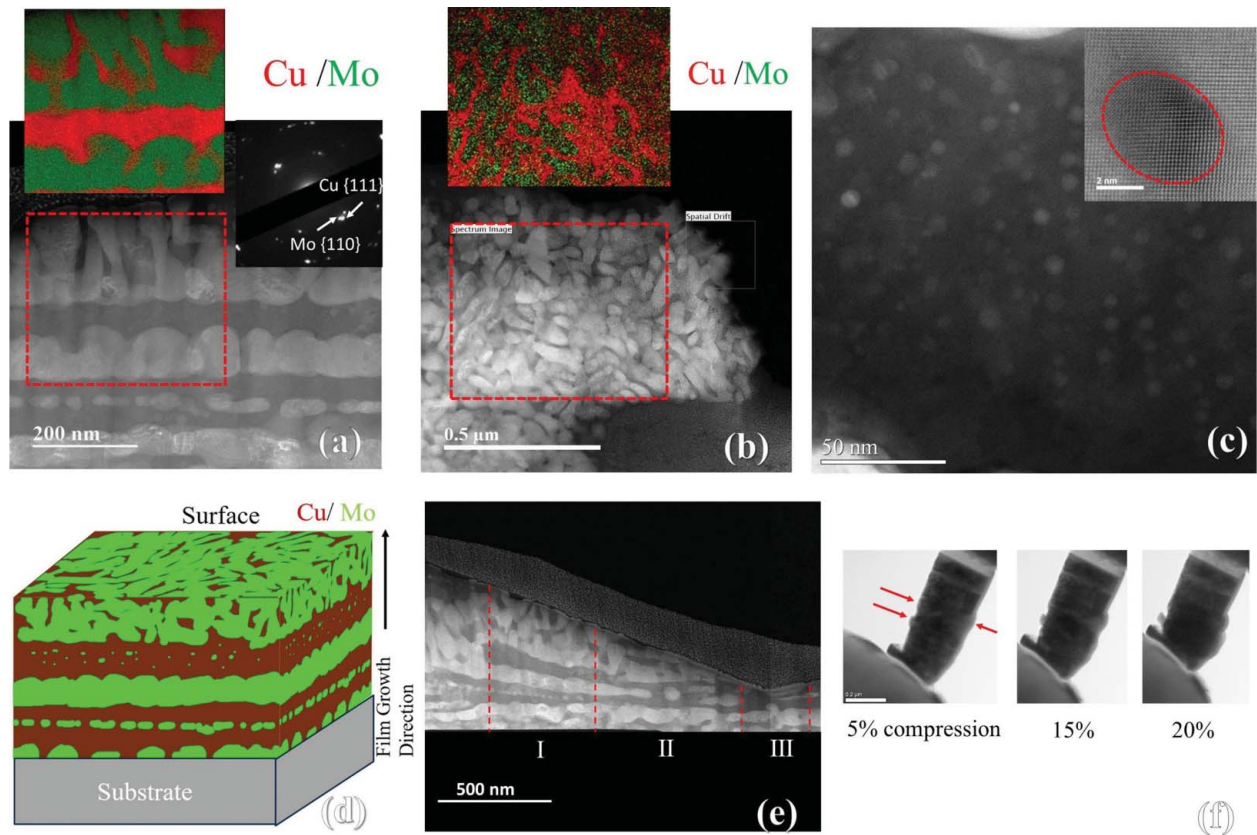


Figure 2. (a) Cross-sectional view STEM image of the nanocomposite with coarse-length-scale bicontinuous zones; inset: SADP of the region. (b) plan-view STEM image of the bicontinuous layer. (c) STEM image of the Cu layer showing Mo particles; inset: atomic image of a Mo particle showing FCC structure. (d) Schematics showing the 3D structure of the nanocomposite. (e) STEM image of the deformed sample. (f) TEM images of the nanopillars at different plastic strains during the *in situ* nanocompression test.

of the fresh layer, resulting in a structure as shown in Figure 3(e). The large Cu-rich islands contain Mo particles with diameters of ~ 2 nm, which tend to align parallel to the upper contour of the island as indicated by the dashed lines in Figure 3(f). The formation of these Cu islands can be attributed to the higher mobility of Cu than that of Mo. Since the films were naturally cooled after deposition, they were exposed to above-ambient temperatures for a few hours. As such, Cu atoms could have sufficient mobility and time to aggregate into large clusters.

Figure 3(g) shows the STEM image of a deformed region, where the indentation proceeded into 30% of film and the formation of a shear band was not observed. Immediately under the indent tip, highlighted in the red rectangle, the thickness of both Cu and Mo laminates increased to 5 nm. Slightly away from the tip, as indicated by the yellow rectangle, the laminate thickness was reduced to ~ 1.5 nm. The direction of the lamellar was also shifted towards the shape of the indent tip, as indicated by the dashed line.

The blue curve in Figure 1(e) shows the result of a nanopillar compression test, from which the maximum

flow stress was measured to be 2.6 GPa. The nanocomposite began to exhibit non-linear behavior at 1 GPa while strain softening was not observed up to 12% plastic strain. Figure 3(h) includes the STEM images of the pillar before and after the test. The diameter of the middle region as indicated by the arrows increased by 16%, while at the top where there is no Cu island, the diameter only increased by 4.6%. The thickening is uniform throughout the top 200 nm of the pillar, indicating that the smaller change in diameter is not a consequence of the constraint imposed by indenter friction.

4. Discussion

4.1. High-strength multilayer with shear banding

An extremely high strength is recorded for the multilayer, which can be explained by the length-scale-dependent deformation discussed previously. At 3 nm layer thickness, dislocations cutting through the interface is supposed to be the dominant deformation event. As demonstrated in Figure 4(a), once the critical stress is reached, multiple dislocation would glide across the

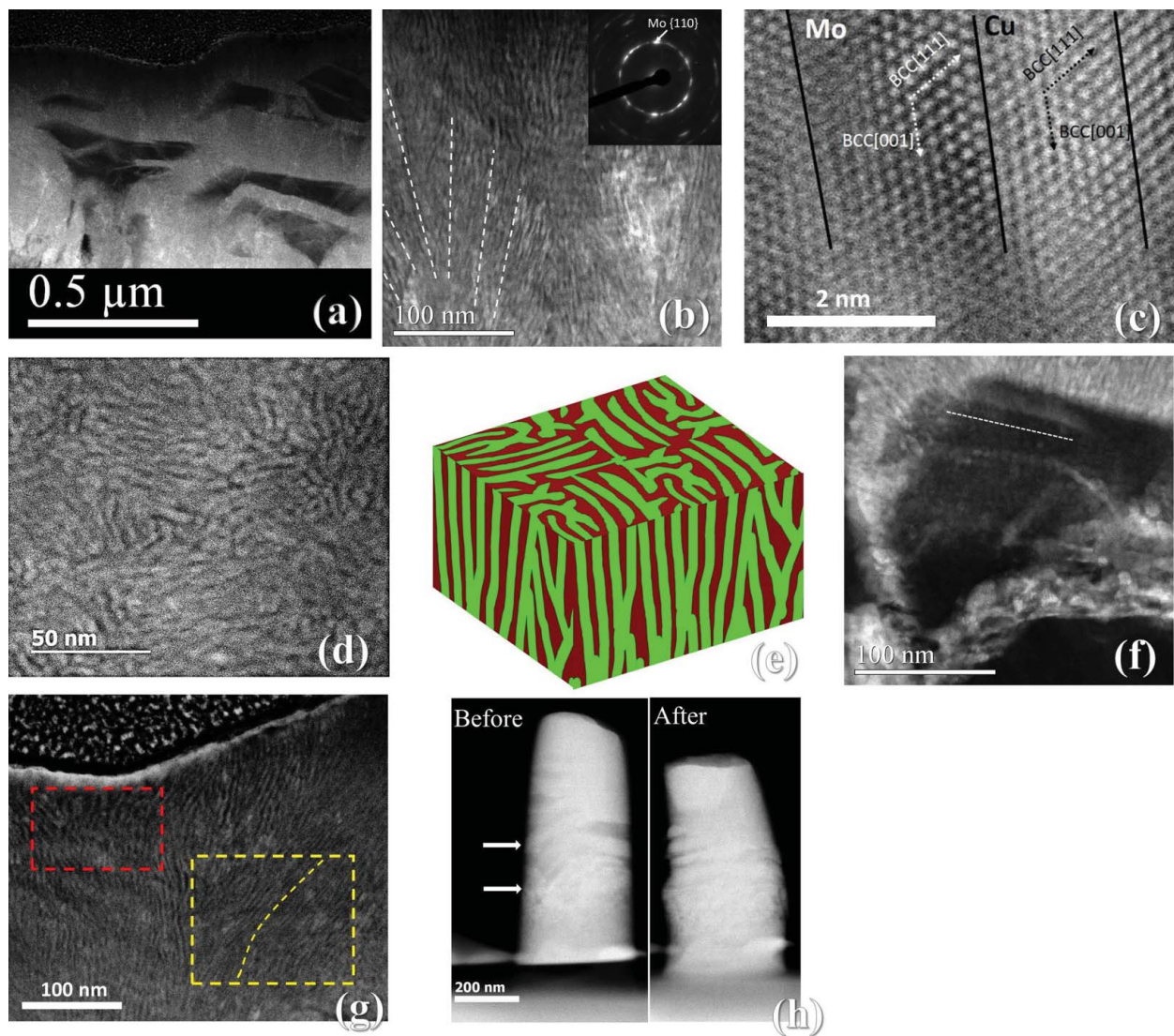


Figure 3. (a) Cross-sectional view STEM image of the nanocomposite with fine-length-scale bicontinuous zones. (b) STEM image showing the fine layered structure; inset: SADP of the region. (c) Atomic image of a few Cu/Mo layers. (d) Plan-view STEM image of the Mo-rich matrix. (e) 3D schematics of the bicontinuous zone. (f) STEM image of the Cu islands. (g) STEM images of the indented area. (h) STEM image of the nanopillar before and after compression test.

interfaces especially for the coherent interfaces, forming shear bands like the ones indicated by red arrows in Figure 1(c). The other type of shear band shown between the dotted lines in Figure 1(c) can be explained by a process depicted in Figure 4(b), which has been discussed in the Cu/Nb system [21]. Because the FCC Cu/BCC Mo interface is weak in shear, the interface is susceptible to slip when there is a load component along the interface. When the indenter is pressed into the multilayer, it causes stress concentration and rotation of the layers. Hence the rotated interface is loaded in shear and slip on the interface plane will be favored over intralayer slip. Continued shear along the interface leads to the onset of shear banding.

4.2. Low-strength hierarchical nanocomposite without shear banding

The absence of shear banding in the nanocomposite with coarse-length-scale bicontinuous zones is expected because the layers are thicker than 100 nm. At this length scale, dislocation pile-up against the interfaces (Figure 4(c)) is expected to be the key unit mechanism resulting in intra-layer slip events. In Region I of Figure 2(e), the Cu-rich zone deforms first because Cu has lower yield strength than Mo. With greater indentation depth, Cu strengthens due to increased dislocation density and reduced layer thickness. In Region II, the strength of Cu reaches that of Mo and co-deformation begins. Under the

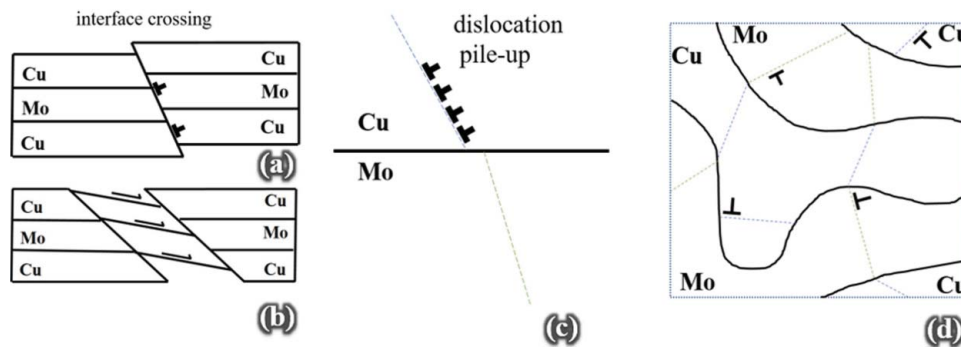


Figure 4. Schematics of (a) interface crossing of dislocations in Cu/Mo multilayers; (b) shear band formation due to interfacial slip; (c) dislocation pile-up in submicron scale Cu and Mo and (d) slip systems in a bicontinuous intertwined morphology.

indent tip (region III), the thickness of both Cu and Mo was reduced to ~ 20 nm. CLS is expected to occur and accounts for further thinning of the layers. *In situ* testing further confirms the individual deformation behavior of Cu and Mo. In the nanopillar, Cu layers have free surfaces, where they could extrude out during compression. Most deformation thus occurred in Cu layers until the final failure of the nanopillar before Mo-rich layers start to yield. As a result, the maximum stress is relatively low as it measures the stress required to deform the Cu grains, rather than both phases in the composite. The 1.6 GPa flow stress is still considered high for Cu. It accounts for the deformation of highly deformed thin Cu layers constrained by Mo layers.

4.3. High-strength hierarchical nanocomposite without shear banding

Figure 3(g) shows the deformed region of the bicontinuous intertwined Cu/Mo phases with fine-length-scale. Immediately under the indent tip as indicated in the red rectangle, the thickness of the alternating layers increases and there are no obvious steps along the interface. CLS is the most probable mechanism to explain this deformation, where the stress is nearly all compressive. As crossing of the interface by dislocations is not involved, continuity of the laminates is preserved. In the area indicated by the yellow rectangle, the thickness of the layers was reduced and the orientation of the layers changed. In this region, the load direction is not parallel to the interface, resulting in both resolved shear and compressive stresses. The compressive stress causes CLS, reducing the layer thickness. The shear stress parallel to the interface activates interfacial slip and thus rotation of the layers. The *post-mortem* characterization did not give information on the deformation of Cu islands because of the irregularity of their shapes. From the *in situ* test, it is shown that the Cu islands exhibited significant plastic deformation. The plasticity starts in the lower-strength

Cu islands, which account for the low yield strength of the composite. The Mo particles in Cu islands increase the composite's strength by precipitate hardening. As the Cu is compressed, vertical distance between the Mo particles reduces, further increase the strength of Cu islands. With strain hardening of the Cu islands, plastic deformation of the bicontinuous Cu/Mo phases begins. The bicontinuous region is expected to have comparable strength with the 3 nm multilayers due to their similar length scale. This explains the high stress measured during the compression test.

The absence of shear banding can be explained by two factors. First the Cu islands contain large grains of Cu. The progression of shear band would be diverted once it encounters a strain hardening Cu grain. The other factor is the bicontinuous intertwined morphology of the Cu/Mo phases. In the bicontinuous region, the interfaces follow a tortuous path. Therefore, interface slip would not sustainably occur in a localized region as shown in Figure 4(b). In addition, the slip systems in the bicontinuous structure are not aligned across multiple ligaments, as depicted in Figure 4(d). The glide of a dislocation across multiple ligaments is thus very difficult, which involves changing slip plane and Burgers vector. Flow localization in multilayers where slip systems are aligned as shown in Figure 4(a) is hence not expected to occur for the bicontinuous morphology.

5. Conclusion

Our results show that a nanocomposite composed of large Cu islands and bicontinuous zones with a few nm length scale possesses very high strength as well as good deformability. After large deformation, shear band formation was not observed in the nanocomposite, as opposed to in the multilayers. The hierarchical structure is proposed to encourage the suppression of shear banding.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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