DESIGNING NOVEL METALLIC MULTILAYER NANOCOMPOSITES THROUGH ATOMIC ENGINEERING OF INTERFACES – INFLUENCE OF HEAT OF MIXING

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Abstract

Metallic multilayered nanocomposites have observed varying flow strength and indentation moduli values for the same type of interface. The enhanced mechanical properties from these nanocomposites have been attributed to their interfaces. The heat of mixing of the interface determines how much the two different layers have an affinity with each other and the resultant amount of shearing of the interface or transmission of dislocations through the interface. Nanoindentation of thin films on substrate technique is performed on five different metallic multilayer systems with a combination of FCC/FCC, BCC/BCC, and FCC/BCC interfaces to understand the effect of heat of mixing on its mechanical properties of hardness and indentation modulus of the films. In situ scanning probe microscopy (SPM) was done before and after each indentation. From the analysis, it is found that the heat of mixing has significant influence only in the hardness or flow strength values of the FCC/BCC multilayered nanocomposites due to dislocation plasticity mechanisms where the interface shear strength decreases with the change of heat of mixing from negative to positive values. The difference in the mechanical properties of FCC/FCC and BCC/BCC coherent multilayers are mainly due to either their lattice misfit or shear moduli differences, not the heat of mixing.

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Keywords

Nanolayer; nanoindentation; hardness; indentation modulus

Introduction

Metallic multilayer nanocomposites are known for their ultra-high flow strength and deformability [1,2] such that they are being considered as potential nuclear radiation protective coatings [3–5] and online strain monitoring sensors [6]. These remarkable mechanical properties have been attributed to their interfaces [7–9]. Some multilayer materials have observed enhanced hardness and indentation modulus values compared to their counterparts when their individual layer thicknesses [10–19]. Hall-Petch grain size relationship [20,21], Orowan strengthening [22–24], coherency and misfit stress [25–27], confined layered slip [28,29], plasticity in confined volume [30–32] and interface crossing [33,34] have been proposed to account for this, depending on the layer thickness and crystallographic orientation of the individual layers.

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Assuming all the nanocomposites are made by the same process of physical vapour deposition, there is another factor on top of the crystallographic orientations that influence the mechanical strength of the multilayers. This property is the heat or enthalpy of mixing ($\Delta H_{\text{mix}}$) between two individual constituents. It determines whether the constituents would like to create intermetallic alloys or remain distinct at the interface. Multilayers with a positive $\Delta H$ are observed to have sharp interfaces without intermixing between constituent layers [35,36]. Through first principle and atomistic calculations, multilayers with a negative $\Delta H$ observe a reduced hardness due to the reduction of effectiveness of the interface as a dislocation blocking layer [37,38]. A good example is Cu/Nb FCC/BCC multilayers which observed a sharp distinct interface with no intermixing between Cu and Nb layers [28,39–41] as Cu and Nb are immiscible with a small positive $\Delta H_{\text{mix}} = +3$kJ/mol [42]. However, little intermixing of multilayers was observed for another type of FCC/BCC, Al/Nb multilayers from HRTEM images [17,43] due to large negative $\Delta H_{\text{mix}} = -18$kJ/mol [42].

In this paper, we will be looking into the effect of heat of mixing on the mechanical properties of multilayers through nanoindentation of five material systems – Cu/Ni, Fe/W, Cu/Nb, Al/Nb and Cu/Mo. They were specifically chosen to cover the different type of crystallographic orientations (FCC/FCC, BCC/BCC and FCC/BCC) and the range of enthalpy of mixing. Table 1 summarises the established material properties of these five multilayer systems. Properties such as hardness, indentation modulus and the indentation pileup area will be compared and discussed. Hardness in nanoindentation is defined as load divided by the residual area upon nanoindentation. Indentation modulus is calculated using the slope of the unloading curve where it is considered to be an elastic affair with no reverse plasticity.

### Table 1: A comparison of the mechanical properties and heat of several multilayer systems

<table>
<thead>
<tr>
<th>Material System</th>
<th>Crystal Type</th>
<th>Lattice Mismatch$^a$/%</th>
<th>Average Shear Stress, $G_c$ (GPa)</th>
<th>Elastic Modulus of Composite (GPa)$^b$</th>
<th>Heat of Mixing, $\Delta H_{\text{mix}}$ [42] (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Ni</td>
<td>FCC/FCC</td>
<td>2.5</td>
<td>61</td>
<td>141.9 E isotress 155</td>
<td>+4</td>
</tr>
<tr>
<td>Fe/W</td>
<td>BCC/BCC</td>
<td>9.9</td>
<td>117</td>
<td>266.7 E isotress 300</td>
<td>0</td>
</tr>
<tr>
<td>Cu/Mo</td>
<td>FCC/BCC</td>
<td>6.5</td>
<td>83</td>
<td>157.1 E isotress 192.5</td>
<td>+18</td>
</tr>
<tr>
<td>Al/Nb</td>
<td>FCC/BCC</td>
<td>0.05</td>
<td>72.5</td>
<td>83.3 E isotress 87</td>
<td>-18</td>
</tr>
<tr>
<td>Cu/Nb</td>
<td>FCC/BCC</td>
<td>11.2</td>
<td>42</td>
<td>107.4 E isotress 107.5</td>
<td>+3</td>
</tr>
</tbody>
</table>

$^a$ For the FCC/BCC materials, the lattice spacing is between the FCC {111} and BCC {110} interplanar spacing

$^b$ Calculations based on bulk elastic modulus values. Isostress modulus of composite: $E_{\text{isostress}} = \frac{E_1 E_2}{V_2 E_1 + V_1 E_2}$

Isostrain modulus of composite: $E_{\text{isostrain}} = V_1 E_1 + V_2 E_2$ [19,44]
Material and Methods

Cu/Nb, Al/Nb, Cu/Mo, Fe/W and Cu/Ni metallic multilayers with individual layer thicknesses ranging from 1nm to 50nm respectively were deposited at room temperature on Si (100) substrates for all except Cu/Nb multilayers on a sapphire substrate by dc magnetron sputtering technique. A base pressure of 6.67 x 10^{-6} Pa is reached prior to deposition. The total multilayer film was kept between 1 to 2µm for all the nanolayers. The growth and characterization of Cu/Nb [40], Al/Nb [17], Cu/Mo [45], Fe/W [11] and Cu/Ni [46] can be found in literature. The resulting films are polycrystalline with a strong \{111\} FCC Cu/Al //\{110\} BCC Nb texture for Cu/Nb, Al/Nb and Cu/Mo. Cu/Ni observed a strong \{111\} FCC // \{111\} FCC texture and Fe/W observed a strong \{110\} BCC // \{110\} BCC texture.

The hardness and indentation modulus of films were measured by means of an indentation load and depth sensing apparatus, Hysitron Triboindenter TI950 using a Berkovich tip in continuous stiffness measurement mode. The instrument has a displacement resolution of 0.1 nm and a loading resolution of 50 nN. The tests were performed in displacement control of 10nm/s with a hold time of 5s with individual spacing between two indents of 30µm. Maximum indentation depth was kept at about 10% of the total film thickness for all experiments to avoid the substrate effect [47]. These steps were done in accordance to ISO 14577-4:2016 [48]. In situ scanning probe microscopy (SPM) was done before and after each indentation. An average of 5 out of 10 indentation points was chosen to calculate the hardness and indentation values.

For any thin films on substrate nanoindentation measurement, the effect of substrate on the film’s indentation modulus is inevitable. This is especially so for the silicon and sapphire substrates being used. One way is during nanoindentation measurements, the maximum indentation depth is kept at about 10% of the total film thickness to minimize the substrate effect [47] followed by Oliver-Pharr method of extraction [49]. This works for most film-substrate systems. Another way to extract the approximate the indentation modulus of the composite is to take a series of measurements at different indentation depths and extrapolating a linear fit to indentation modulus to zero vs. ratio of indentation depth over film thickness [48]. However, this method does not work well with stiff coatings with compliant substrates [50] and was not adopted.

To extract the film-only indentation modulus without the influence of the substrate, there have been a number of empirical models that have been developed – Gao et al. [51], Mencik et al. [52], Doerner and Nix [53], Bec et al. [53,54] and Bull [50]. For this paper, the model by Hay et al. was used to evaluate the indentation modulus of the thin films from the reduced indentation modulus values [55]. An extension of Gao et al. [51] and Mencik et al. [52] papers, her model allows for extraction of film modulus for both compliant films on stiff substrates and stiff films on compliant substrates. This is essential based on the moduli of multilayers being studied.
Results

The indentation-derived hardness and reduced Young’s modulus of the multilayer were obtained from the Oliver-Pharr method of analysis [49]. The Young’s modulus and Poisson’s ratio of the Si substrate are taken to be 130GPa and 0.218 respectively. The Young’s modulus and Poisson’s ratio of the Sapphire substrate for the Cu-Nb multilayers are 300GPa and 0.21 respectively. The Young’s modulus and Poisson’s ratio of the diamond indenter are 1141GPa and 0.07 respectively.

![Figure 1: Comparison of hardness vs h^0.5 plots for various metallic multilayer systems including Cu/Ni (FCC/FCC), Fe/W (BCC/BCC), Cu/Mo, Al/Nb and Cu/Nb (all FCC/BCC) where h is individual layer thickness.](image)

The hardnesses of Cu/Nb, Al/Nb, Cu/Mo, Fe/W and Cu/Ni are plotted as a function of h^{1/2} as shown in Figure 1. The experimental points are compared with existing literature (Cu/Ni [56], Fe/W [11], Cu/Mo [57], Al/Nb [17], Cu/Nb [56]) to confirm validity of the measurements made. The measured experimental values are close to the previous reference values and are along the nonlinear increasing slope range of the confined layer slip region. For a particular layer thickness value, the peak hardness value is highest for Fe/W at followed by Cu/Mo, Cu/Nb, Cu/Ni and Al/Nb.
Figure 2: Comparison of the Indentation modulus (with substrate effect removed) versus individual layer thickness plots for various metallic multilayer systems including Cu/Ni (FCC/FCC), Fe/W (BCC/BCC), Cu/Mo, Al/Nb and Cu/Nb (all FCC/BCC).

The indentation moduli of the films are plotted as a function of individual layer thickness, h as shown in Figure 2 at 10% film thickness indentation depth. The initial reduced indentation modulus values observed increased Young’s modulus with increasing indentation depth. The model by Hay et al. was used to evaluate the indentation modulus of the thin films from the reduced indentation modulus values [55]. Her model allows for extraction of film modulus for both compliant films on stiff substrates and stiff films on compliant substrates. The tunable constant used for the results is F = 0.0626, as the constant fits well for the 10% indenter penetration to film thickness. Relatively constant indentation moduli are observed for Cu/Ni, Cu/Mo and Al/Nb multilayers. However, a significant drop in indentation modulus is observed for Fe/W and Cu/Nb multilayers as the individual layer thickness are increased.

In situ scanning probe microscopy (SPM) was used to check and quantify pile-up effect of the multilayer film around the Berkovich indenter to justify the expected Young’s modulus and hardness values. The scan rate of 1Hz with a tip velocity of 20µm/sec and a set point load of 2µN. Figure 3 shows the post indentation SPM images of the indents observed for the films. Average plane background subtraction was applied to all the SPM images. The plastic flow around the indenter is observed. Sink-in is observed for Cu/Ni and Fe/W multilayers.
Pile-up is clearly evident for the FCC/BCC films showing the most significant pile up increasing with increasing misfit strain value. The amount of pile up is independent of the individual layer thickness. The range of pile-up height to indentation depth is between 5nm to 40nm.

**Figure 3:** A set of in situ SPM images of the indents observing the pile-up behaviour around the indent

**Discussion**

*Comparison of hardness of various multilayer systems*

Above individual layer thicknesses of 50nm, hardness is found to be proportional to the layer thicknesses. The Hall-Petch slope, \( k \), can determine the rate of strength increase with decreasing \( h \). Since experimental data was not measured at this length scale, the Hall-Petch slope is calculated for the different systems using the equation,

\[
k = 0.1G\sqrt{\frac{h}{E}}
\]

Considering the Hall-Petch slope value determined by the stiffer phase of the two materials, it is observed that the Fe/W system observed the highest measure of interface barrier strength of 0.464 MPa.m\(^{0.5}\), followed by Cu/Mo (0.357 MPa. m\(^{0.5}\)), Cu/Ni (0.216 MPa.m\(^{0.5}\)), Cu/Nb (0.132 MPa.m\(^{0.5}\)), Al/Nb (0.115 MPa.m\(^{0.5}\)). This initial trend seems to follow with decreasing heat of mixing values. The same trend was
correlated in Zhang et al. recent paper where he establishes the correlation between the Hall-Petch slope and the peak hardness in metallic nanolaminates [58].

At multilayer individual layer thicknesses between 5nm-50nm, dislocation pileups become more and more difficult. The phenomenon of confined layer slip comes into play where the propagation of single dislocation loops occurs parallel to the layers. At this regime, the dislocations tend to dominate in the more compliant layer of the two. For FCC Cu/Ni and BCC Fe/W multilayers, the 5nm-50nm range tends to be dominated by Koehler and coherency stresses [59]. These stresses can be varied based on factors such as shear modulus mismatch and lattice mismatch [60,61]. Liu et al. performed in situ transmission electron microscopy microcompression on FCC/FCC cube-on-cube interface nanopillars at varying tilt angles to determine the interfacial shear strength of the interfaces [62]. The interfacial shear strength decreases with increasing misfit strain (> 5%) and had no relation to the heat of mixing. In the paper, the Cu/Ni multilayered nanopillars which have a lattice mismatch strain of 2.5% deformed uniformly and did not observe any shearing. In comparison, Fe/W multilayers have a much larger lattice mismatch strain of 9.9% due to BCC/BCC crystallographic orientation and zero heat of mixing. Using a similar analogy, Fe/W multilayers observed enhanced hardness but it would be easy to shear along their interface too.

However, the heat of mixing values do have a dramatic impact on the shear resistance at FCC/BCC interfaces. Liu et al. did some molecular dynamic simulations to explain the effect of heat of mixing on FCC/BCC interfaces using Cu/Nb interface as an example [38]. Kim et al. has also suggested experimental evidence of the effect of heat of mixing in the FCC/BCC interfaces [39,41,43]. He observed that FCC/BCC structure remains intact with the interstitial formation energies at the interfaces decrease significantly with decreasing heats of mixing. The critical shear stress increases and then decreases with decreasing heat of mixing. The shift in the stacking fault energy in the FCC plane causes a change in the active shear plane from the FCC/BCC plane to the FCC/FCC' plane at the interface for reduced heats of mixing. Our experimental result among the FCC/BCC interfaces seem to suggest the behaviour with the Cu/Mo being of high flow strength but easy to shear, followed by Cu/Nb and Al/Nb.

**Comparison of Indentation modulus and pile up area of various multilayer systems**

The multilayered nanostructure is novel in a sense that it is a special case of orthotropic material in particular transversely isotropic along the 13-plane. This is expected because of the lattice misfits at the interfaces among the different components. They possess five independent constants of $E_{11}$, $E_{22}$, $v_{12}$, $v_{13}$ and $G_{12}$. A simple way to compute the magnitudes of $E_{11}$ and $E_{22}$ is to use the isostrain ($E_{11}$) and isostress ($E_{22}$) condition respectively. Work by Tang et al. did a simulation model for metal-ceramic layers on the close estimation of indentation derived modulus to $E_{11}$ and $E_{22}$ stresses and found that the obtained indentation modulus was a good representation of the $E_{22}$ isostress case [63]. Cu/Nb, Al/Nb and Cu/Ni multilayered nanocomposites observed higher indentation moduli values than expected $E_{11}$ and $E_{22}$ cases with Cu/Nb multilayers increasing with decreasing individual layer thickness. The higher indentation moduli results may be due to the reported supermodulus effect from the unique multilayered structure [64–66].
However, Fe/W and Cu/Mo multilayered nanocomposites observed significantly lower indentation moduli values. Elastic Moduli difference of individual Fe and W multilayers, as well as elastic moduli of individual Cu and Mo multilayers, are more significant than of silicon substrate. These two give rise to the soft, compliant multilayers on hard, stiff substrates. It is evident that the Hay’s model used may not have fully account for the effect of the substrate on the multilayers. Future work of considering newer elastic moduli models that take into account multilayered architecture and their individual Young’s modulus value from Bull and Puchi-Cabrera can be considered [50,67]. Based on these results, no significant influence of heat of mixing on the indentation modulus values can be observed.

In the purely elastic contact solution, material always sinks in, while for elastic/plastic contact, the material may either sink in or pile up. The compliant films on stiff substrates exhibit a tendency to pile up. Due to this, the areas calculated from the Oliver-Pharr method are too small, with the severity of the problem increases with the degree of modulus mismatch and indentation depth. The stiff films on compliant substrates exhibit a tendency to sink-in excessively resulting in the areas calculated to be too large. The value of calculated area varies with $1/A$ for hardness and $1/\sqrt{A}$ for indentation modulus. Based on the images in Figure 3, significant pile up tend to be seen at larger layer thicknesses compared to thinner ones for FCC/BCC materials. Besides this, no particular trend can be observed on the influence of heat of mixing.

**Conclusion**

The effect of heat of mixing on the mechanical properties of five multilayer systems Cu/Ni, Fe/W, Al/Nb, Cu/Mo and Cu/Nb were compared through the nanoindentation technique. The heat of mixing has significant influence only in the hardness or flow strength values of the FCC/BCC multilayered nanocomposites due to dislocation plasticity mechanisms where the interface shear strength decreases with the change of heat of mixing from negative to positive values. FCC/FCC and BCC/BCC coherent multilayers did not observe any significant influence of heat of mixing with its hardness or indentation moduli values. The differences in their values are mainly due to either their lattice misfit or shear moduli differences.

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