Buckling behaviors and adhesion energy of nanostructured Cu/X (X = Nb, Zr) multilayer films on a compliant substrate

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Abstract

Two sets of Cu/Nb (face-centered cubic (fcc)/body-centered cubic) and Cu/Zr (fcc/hexagonal close-packed) nanostructured multilayer films (NMFs) have been prepared on a flexible polyimide substrate, with a wide range modulation period (λ) from 250 down to 5 nm. The mechanical properties of the two NMFs have been measured upon uniaxial tensile testing and the buckling behaviors have been systematically investigated as a function of λ. A significant difference in the buckling behaviors was found between the two NMFs, with the buckles in the Cu/Nb NMF being mostly cracked, while the buckles were nearly crack-free in the Cu/Zr NMF. The different buckling behaviors, dependent on the constituent phases, are rationalized in the light of the disparity in mechanical properties. The criteria to characterize buckle cracking have been discussed with respect to the mechanical properties (e.g. yield strength, ductility and fracture toughness) of the NMFs. A modified energy balance model has been employed to estimate the adhesion energy of the NMFs on the polyimide substrate. Within the λ regime below a critical size (λ_{crit}) of ~50 nm a λ-independent adhesion energy of about 1.1 and 1.2 J m$^{-2}$ has been determined for the Cu/Nb and Cu/Zr NMFs, respectively, which agrees well with previous reports on the metal film/polymer substrate systems. Within the λ regime greater than λ_{crit}, however, the measured adhesion energy exhibit a strong size effect, i.e. increasing with increasing λ. The λ dependence of the evaluated adhesion energy is discussed in terms of the size-dependent deformation mechanism in NMFs. A micromechanics model has been utilized to quantify the critical modulation period of ~50 nm, where the deformation mechanism changes from dislocation pile-up to confined layer slip.

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1. Introduction

The use of thin films has proliferated in the fields of electronic, engineering, optical, biomedical, nuclear, space, and other applications [1]. This widespread use is attributed to the fact that materials in monolithic form are often unsuitable for the diverse and special requirements, and thin films provide the answer. Thin films are used for many and varied purposes [1]: to provide resistance to abrasion, erosion, corrosion, galling, tarnishing, wearing, radiation damage, or high temperature oxidation; to reduce friction or electrical resistance, provide lubrication, prevent sticking; to provide special magnetic or dielectric properties. Inorganic films on polymer foils have recently become ubiquitous in a variety of applications, e.g. flexible electronics and sensors [2–6]. Whatever their intended use, the properties, structural or functional characteristics, and performance all depend on adhesion between the film and the substrate [7–10]. Thus the estimation of interfacial adhesion is not only scientifically interesting but also critically important for many engineering applications.

Many experimental methods have been proposed to determine the interfacial adhesion between films adherent on rigid substrates such as Si. These methods include indentation tests, stressed overlayers, scratch tests, four point
bending, etc. [11–15], suggesting that interfacial adhesion is material, geometry and even industry specific. However, the aforementioned methods are difficult and unsuitable for examining film adhesion to flexible substrates, due to the viscoelastic behavior of the polymer substrate [16,17]. Since the polymer substrates are stretchable attempts have been made to evaluate film adhesion by uniaxial tensile testing of the film/polymer systems [18–23]. The relevant theoretical frameworks are mainly divided into two kinds of models: the shear lag model based on quantitative calculations of interfacial shear strength from the statistical analyses of crack density at saturation [9,24]; a model based on the elastic buckling of films, as proposed by Hutchinson and Suo [25]. Most recently there has been increasing interest [26–28] in buckling behavior and methods utilizing buckling to characterize the interfacial adhesion of film/polymer systems, owing to the rapid development of stretchable electronics.

In stretching the film/polymer systems the metal film will first develop cracks perpendicular to the tensile direction at lower strains. During further straining of the film compressive transverse stresses arise in the film strips due to a Poisson’s ratio mismatch between the substrate and the film. The compressive stresses will cause buckling and delamination of film strips transverse to the tensile direction. Buckling of films is mainly studied within the framework of the Föppl and von Kármán (FvK) theory of plates [29,30], which has been proven to still be applicable on the microscale for thin films deposited on a substrate with a thickness usually of the order of hundreds of nanometers [31]. In particular, buckles with different types of morphologies have been analyzed and verified, such as straight sided wrinkles and worm-like and circular blisters [32–37].

The measurement of buckled structure dimensions can be used to estimate the interfacial adhesion energy. By developing a new energy balance model that involves the parameters of buckle geometry and film thickness Cordill et al. [21] quantified the adhesion energy of Cr films on polyimide substrate and obtained a value of about 4.5 J m⁻², which is comparable with previous reports on metal/polymer systems. However, they claimed that their model was only applicable to films with a thickness of less than about 100 nm [21]. In thicker films the buckle shape became triangular rather than rectangular, making it hard to measure the eligible buckle dimensions. On the other hand, the determination of critical stress for buckling can be also used to estimate the interfacial adhesion energy. Pundt et al. [38] produced buckles in polycarbonate-supported Nb thin films by hydrogen absorption rather than tensile testing. They measured the critical stress for buckling and subsequently obtained the adhesion energy value (~1 J m⁻²) using a simple model that assumed an energy balance between the adhesion energy and the released elastic energy. These methods and relevant models, however, have only been applied to single layer thin films. Similar studies have not been reported for multilayer thin films on compliant substrates.

Metallic nanostructured multilayer films (NMFs) have attracted much attention for their promising mechanical properties and significant theoretical interest [39–42]. The microstructures of NMFs are characterized by (i) alternate nanoscale layers of two different single phase metals (modification structure) and (ii) a large number of interfaces. The effects of a modulation structure and constitutive phases on hardness, strength, ductility, and toughness have been extensively investigated [43–47]. Strengthening models have been proposed (Misra et al. [48] and references therein) to account for the length scale-dependent hardness/strength of NMFs. In addition, micromechanical models [49] have been developed to describe the fracture behavior. Nevertheless, the buckling behavior of NMFs on flexible substrates is poorly understood and evaluations of interfacial adhesion are still unavailable. In this paper we report a series of systematic experiments to reveal the effects of modification structure and constituent phases on the buckling behavior of NMFs. For this purpose two kinds of NMFs, i.e. face-centered cubic (fcc)/body-centered cubic (bcc) type Cu/Nb and fcc/hexagonal close-packed (hcp) type Cu/Zr, were chosen as the model materials, tailored with a wide range of modulation period λ. After stretching the buckle dimensions were measured and utilized to quantitatively estimate the adhesion energies of the NMFs, based on a modified energy balance model. Moreover, the buckling behavior and determined adhesion energy will be discussed with respect to the mechanical properties and deformation mechanisms of the NMFs.

2. Experimental procedures

2.1. Materials

Two sets of Cu/X (X = Nb, Zr) NMFs with modulation periods spanning 5–250 nm were deposited on a 125 μm polyimide substrate by means of direct current magnetron sputtering at room temperature. The chamber was evacuated to a base pressure of ~5 × 10⁻⁸ torr prior to sputtering, and a pressure of 1–3 × 10⁻³ torr Ar was used during deposition. In multilayer deposition the first layer on the polyimide substrate was X and the topmost layer was Cu. The total thickness was about 1000 nm for the two NMFs. Without break in vacuum all the as-deposited Cu/X NMFs were annealed at 150 °C for 2 h to stabilize the microstructure and eliminate residual stress.

2.2. Microstructure characterization

X-ray diffraction (XRD) experiments were carried out using an improved Rigaku D/max-RB X-ray diffractometer with Cu Kα radiation and a graphite monochromator to determine the crystallographic texture and the residual stress using the “sin²ψ method” [49–51]. High resolution transmission electron microscopy (HRTEM) observations were performed to observe the modulation structure using a JEOL-2100F microscope. Atomic force microscopy
AFM) measurements were performed on a 1 × 1 μm² scan area to examine the surface roughness of as-deposited NMFs using a Bruker Dimension Icon.

2.3. Mechanical properties testing

Uniaxial tensile testing was performed in a Micro-force Test System (MTS® Tytron 250) at a constant strain rate of 1 × 10⁻³ s⁻¹ at room temperature. All the samples had a gauge section of 30 mm length and 4 mm width. During tensile testing the force and displacement were automatically recorded by machine and a high resolution laser detecting system, respectively, which can be subsequently converted into stress–strain curves for the NMFs [52,53]. The yield strength (σ_y) was determined as the 0.2% offset. The critical macroscopic strain (ε_cri) characterizing micro-crack formation on the microscopic level, rather than rupture strain or elongation, can be used to represent the deformation capability or ductility of this kind of film. Tensile tests combined with the electrical resistance change method (ERCM) was recently developed [53] to determine ε_cri of polymer-supported NMFs in situ, which is simple to perform but precise. Fracture toughness (KIC) was subsequently calculated, following the method given in previous publications [49–51].

2.4. Buckle observations

Scanning electron microscopy (SEM) was carried out to observe the morphologies of the cracks and buckles. Atomic force microscopy (AFM) experiments were performed at room temperature to determine the buckle dimensions, including buckle height and width. At least 60 rectangular buckles were measured for each NMF. Buckles with large crack openings at the top and/or base were omitted from the adhesion calculation. In order to analyze the interfacial failure mechanism and ensure that the multilayer/substrate interface was failing some buckles in the Cu/X NMFs were cross-sectioned and characterized by dual beam focused ion beam/scanning electron microscopy (FIB/SEM) using an FEI microscope.

3. Results

3.1. Microstructure

The XRD spectra for Cu/X NMFs revealed a strong {1 1 1} out-of-plane texture in the fcc Cu layers and a strong {1 1 0} out-of-plane texture in the bcc Nb layers (Fig. 1a), and (0 0 0 2) out-of-plane texture in the hcp Zr layers (Fig. 1b). The in-plane orientations were random in the constituent layers. The residual stress was determined to be ~200 ± 100 MPa for all the Cu/X NMFs with different λ, which is far less than the NMF strength (presented later). Representative cross-sectional TEM images of some Cu/X NMFs are displayed in Fig. 2, where one can see clear modulated layer structures with columnar grains in the Cu layers and ultrafine nanocrystals in the X layers. No significant intermixing between the Cu and X layers was observed, as proved by the interface HRTEM (Fig. 2 e and f). In addition, Fig. 2g and h shows that there is no obvious intermixing between X (X = Zr and Nb) and the polyimide substrate and no significant metal diffusion into the polymers. The X/substrate interfaces are clear and independent of modulation period. Measurements on surface roughness show that the average root mean square (RMS) roughness of the Cu/Nb and Cu/Zr NMFs are in the range 2.1–5.3 and 1.9–4.2 nm, respectively. The slight difference in RMS roughness indicates that the two NMFs have almost the same surface smoothness.

3.2. Mechanical properties

Fig. 3 shows the evolution of σ_y, ε_cri, and KIC with modulation period λ for the Cu/Nb and Cu/Zr NMFs, respectively. The two NMFs exhibit a similar trend in the evolution of σ_y, which increases monotonically with decreasing λ, ε_cri and KIC first increase, then subsequently decrease, with a maximum value at a critical modulation period of about 50 nm. The increase in σ_y is mainly arises from interface strengthening, according to the model of Misra et al. [48]. The unexpected change in ε_cri and KIC with λ can be explained by a constraint effect that is exerted

![Fig. 1. XRD spectra of (a) Cu/Nb and (b) Cu/Zr NMFs with different modulation periods (λ).](image-url)
Fig. 2. Representative TEM images showing the microstructure and modulation structure of the Cu/Nb NMFs for (a) $\lambda = 50$ nm and (c) $\lambda = 250$ nm, and the Cu/Zr NMFs for (b) $\lambda = 25$ nm and (d) $\lambda = 100$ nm, respectively. (Inset) The corresponding selected area diffraction (SAD) patterns. (e, f) HRTEM images to show the clear Cu/$X$ interface in the Cu/Nb and Cu/Zr NMFs, respectively. (g, h) Representative cross-sectional TEM images to show the clear $X$/substrate interface in the Cu/Nb and Cu/Zr NMFs for $\lambda = 250$ nm, respectively.
Fig. 3. Variation in yield strength ($\sigma_y$), ductility ($\varepsilon_{\text{crit}}$), and fracture toughness ($K_{IC}$) with $\lambda$ in the (a) Cu/Nb and (b) Cu/Zr NMFs, respectively.

by the relatively soft Cu layers on the brittle microcrack-initiating $X$ layers. For details of the underlying mechanisms refer to our previous paper [50], they will not be repeated here.

A comparison between the two NMFs demonstrates that the Cu/Zr NMFs display $\varepsilon_{\text{crit}}$ and $K_{IC}$ values about 50% greater than the Cu/Nb NMFs, although the strengths are close to each other. This indicates that the Cu/Zr NMFs have a superior deformation capability to the Cu/Nb NMFs. In other words, the ductility and toughness of the NMFs are closely dependent on the constituent phases, which can be used to rationalize the different buckling behaviors between the two NMFs, as presented and discussed later.

3.3. Cracking and buckling in NMFs

In uniaxially tensile testing of the NMFs channel cracks perpendicular to the loading direction ($x$-direction) will be induced when the tensile strain is greater than $\varepsilon_{\text{crit}}$. The crack density will further increase upon increasing the applied strain, up to a plateau of about 20–25%. As the film fragments a compressive transverse stress arises due to the mismatch in Poisson ratio between the substrate and the film, which results in buckling perpendicular to the channel cracks. Buckles are initiated at approximately 10–15% tensile strain for Cu/Nb and 12–20% for Cu/Zr NMFs, respectively. SEM images in Fig. 4a and b respectively show typical fracture patterns obtained from the Cu/Nb and Cu/Zr NMFs ($\lambda = 250$ nm) stretched to the same strain of 15%. Cracks and buckles are clearly seen and distinguished in the two NMFs, as separately marked by open and filled arrows. Since careful observations of non-strained specimens did not reveal any cracking or buckling of the NMFs such a regular pattern is a consequence of uniaxial tension in the NMFs. The cracks in the Cu/Nb NMFs are straight, while those in the Cu/Zr NMF are zigzag. In addition, the crack spacing $L$ is obviously greater in the Cu/Zr than in the Cu/Nb NMFs. Quantitative comparison between the statistical results on $L$ (Fig. 4c vs. d) reveals an approximately twofold difference in magnitude. This is consistent with the aforementioned experimental results on ductility that the Cu/Zr NMFs have a higher ductility or deformation capability.

Note that approximately 90% of the crack spacing falls within a narrow range, i.e. ~12–30 $\mu$m in the Cu/Nb NMFs and 30–65 $\mu$m in the Cu/Zr NMFs, respectively. Similar results have been observed [24,54] in single layer films adherent to flexible substrates. There have been some reports [9,24,55] on the theoretical modeling of the crack spacing distribution in single layer films. In particular, predictions showed [24,56] a distribution range from $L_{\text{min}}$ to $L_{\text{max}}$, where the minimum spacing $L_{\text{min}}$ is roughly half of the maximum spacing $L_{\text{max}}$. The present results for NMFs appear to be $L_{\text{max}} \approx 2L_{\text{min}}$, as well, in broad agreement with the predictions. This means, to some extent, that the elastic model for cracking in single layer films may be also applicable to NMFs, as is consistent with the results for Cu/Cr NMFs [51].

In both of the NMFs most of the buckles are rectangular, which means the buckle footprint is a rectangle. However, a distinct difference in buckling behavior exists between the two NMFs. A large number of buckles in the Cu/Nb NMFs are cracked at the apex of the buckles. In contrast, almost all of the buckles in the Cu/Zr NMFs are free of cracks. For example, statistical results revealed that the percentage of cracked buckles was up to 90% in the $\lambda = 250$ nm Cu/Nb NMF strained to 15% (Fig. 4e), with only about 6% in the Cu/Zr counterpart (Fig. 4f). Representative magnified SEM images are shown in Fig. 5a and b to demonstrate a cracked and faultless buckle, respectively, taken from the two NMFs. FIB cross-sectioning of the buckles showed that the buckles in the Cu/Nb NMF crack not only at the top but also at the base (Fig. 5c, marked by arrows). In the Cu/Zr NMF the buckles were symmetrical and perfect and the film/substrate interface had truly failed (Fig. 5d), which can ensure the accuracy of the measurements.
3.4. Buckle dimensions

Fig. 6 shows AFM height images of buckles from \( \lambda = 25 \text{ nm} \) Cu/Nb (Fig. 6a and b) and Cu/Zr (Fig. 6c and d) NMFs, respectively, strained to 15%. Three measurements were performed on each rectangular buckle, i.e. one at the middle and the other two close to the two edges (see Fig. 6a and c). The three profiles are coincident with each other for most of the buckles in the Cu/Zr NMF, as typically demonstrated in Fig. 6d. This is well understood because these buckles have a uniform and smooth convex morphology. In the Cu/Nb NMF, however, only the buckles with a tiny crack at the top exhibit three similar profiles, e.g. the buckle in Fig. 6a and its profiles in Fig. 6b. When a large crack is formed at the apex of the buckle, as in Fig. 5c, the three profiles are very different. Moreover, some profiles are even broken off at the top, due to the large detached crack faces. These buckles with large cracks were ignored in measuring the buckle dimensions of the Cu/Nb NMFs.

The AFM results (Table 1) show that the average buckle height and width generally increased with increasing modulation period \( \lambda \), which is common to the two NMFs. At the same \( \lambda \) the Cu/Zr NMFs have buckle dimensions greater than the Cu/Nb NMFs. Jin et al. [57] found that in single layer Cr films on a flexible polyethylene terephthalate substrate both the buckle width and height markedly increased when the film thickness was varied from 15 to 140 nm. Similar results were observed by Pundt et al. [38] for polymer-supported Nb films, with the buckle width increasing from 5.7 to 11.4 \( \mu \text{m} \) with a film thickness increase from 50 to 200 nm. Here in the NMFs the buckle dimensions increased with modulation period rather than film thickness. It seems that the length scale dependence of buckling behavior in the NMFs is in principal analogous to that in the single layer films, but the variable is modulation structure size rather...
than film thickness. Another characteristic of NMFs, as distinct from single layer films, is that the buckle dimensions are dependent not only on the length scale but also on the constituent phases. The greater buckle dimensions in the Cu/Zr NMFs than in the Cu/Nb NMFs may be related to superior ductility or crack resistance in the former. Since

![Fig. 5. Respective SEM images showing (a) a cracked buckle in the Cu/Nb NMFs and (b) a faultless buckle in the Cu/Zr NMFs. (c, d) FIB cross-sectioning of buckles in the two NMFs reveals that film/substrate interface had failed. (c) The buckles in Cu/Nb NMFs crack not only at the top but also at the base (marked by arrows). (d) In contrast, the buckles in Cu/Zr NMFs are symmetrical and have a smooth arch shape.](image)

![Fig. 6. AFM height image of a rectangular buckle with three measurements in (a, b) Cu/Nb and (c, d) Cu/Zr NMFs. (b, d) Buckle profiles corresponding to (a) and (c), respectively.](image)
\[ \frac{h_{E}}{\Delta} + \frac{e}{\Delta} = 1 \text{ and } l \]
\[ \frac{1}{C_{0}} + \frac{1}{\Delta} = 1 \text{ and } \frac{h_{E}}{C_{0}} \]
are the elastic modulus and Poisson’s ratio, respectively, with a definition of some important parameters for modeling. The coordination system is also shown.

The buckling mode can be regarded as a “Euler mode”. A model unit is considered that contains the buckled part (2l width, Fig. 7) and the remaining unbuckled part (B - 2l in width B is the buckle spacing). The energies involved in the energy balance thus include the strain energy of the buckled film region \( (U_{bu}) \), the strain energy of the remaining adherent region \( (U_{re}) \), and the interfacial adhesion energy \( (U_{ad}) \). The total energy \( U_T \) is written as:

\[ U_T = U_{bu} + U_{re} + U_{ad} \]  

(1)

Referring to the buckle cross-sectional diagram and relevant parameters (Fig. 7a), the expressions for \( U_{bu} \), \( U_{re} \), and \( U_{ad} \) are:

\[ U_{bu} = \frac{h_{E_f}}{1 - v_f^2} (2\nu_{re}\nu_c - \nu_c^2) \]  

(2)

\[ U_{re} = \frac{(B - 2l)h_{E_f}}{2(1 - v_c^2)} \nu_{re}^2 \]  

(3)

\[ U_{ad} = 2\Gamma \]  

(4)

where \( \nu_f \) and \( E_f \) are the elastic modulus and Poisson’s ratio of the film, respectively, \( \Gamma \) is the specific value of the interfacial adhesion energy, and \( \nu_c \) is the critical buckling strain, having the value \[ \nu_c = -\frac{3\pi^2}{12} \left( \frac{h}{l} \right)^2 \]  

(5)

\( \nu_{re} \) is the average strain in the unbuckled region, given by

\[ \nu_{re} = \nu_c - \frac{3\pi^2}{16l^2} \text{ and } \nu_{re} = 1 + \frac{3}{4} \left( \frac{\delta}{h} \right)^2 \]  

(6)

where \( \delta \) is the buckle height. The thermodynamic force for interface decohesion \( F \) follows:

\[ F = -\frac{\partial U_T}{\partial l} = \frac{h_{E_f}}{1 - v_f^2} (\nu_{re}^2 + 2\nu_{re}\nu_c - 3\nu_c^2) - 2\Gamma \]  

(7)

Considering the equilibrium condition \( F = 0 \) and \( l = 0 \), there is a critical value \( \Gamma_{cri} \) for the debonding energy (adhesion energy):

\[ \Gamma^* = \frac{2\Gamma_{cri}(1 - v_f^2)}{h_{E_f}} = \nu_{re}^2 + 2\nu_{re}\nu_c - 3\nu_c^2 \]  

(8)

Insertion of Eq. (6) in Eq. (8), with some analysis, results in

\[ \sqrt{\frac{\delta}{h}} = (2\pi)^{1/4} \left[ 1 + \sqrt{1 + \frac{3\pi^2}{4} \left( \frac{\delta}{h} \right)^4} \right]^{-1/4} \]  

(9)

with an introduced dimensionless value

\[ \alpha = 2\Gamma^* \left( \frac{2}{\pi} \right)^4 = \frac{4\Gamma_{cri}(1 - v_f^2)}{h_{E_f}} \left( \frac{2}{\pi} \right)^4 \]  

(10)

Eqs. (9) and (10) relate the interface energy directly to the buckle dimensions, especially to the combined parame-
ters $\sqrt{\delta/h}$ and $l/h$. The value of $x$, which will be used to evaluate the adhesion energy through Eq. (10), can be experimentally calibrated by plotting $\sqrt{\delta/h}$ as a function of $l/h$.

The model and above equations are now applied to the present NMFs, with the aim of determining the adhesion energy. Typical $\sqrt{\delta/h}$ vs. $l/h$ figures for the Cu/Nb NMFs for $\lambda = 50$ and 250 nm, respectively, are shown in Fig. 8a and b. The buckle values can be fitted as a function of $x$ using Eq. (9). The three values of $x$ used are the maximum, average, and minimum fits to the data. It was suggested [21] that the minimum $x$ corresponds to smaller buckles (lower buckle height), which are usually in the incipient debonding condition and thus devoid of mechanically induced faults. Therefore, the minimum $x$ will result in the minimum adhesion energy that is closer to the intrinsic value [21]. In the present work a similar treatment was employed to evaluate the adhesion energy by using the minimum $x$. The measured adhesion energy is plotted as a function of $\lambda$ for the Cu/Nb and Cu/Zr NMFs, respectively, in Fig. 9a. It was disappointing to find that the determined values are generally one or two orders greater than those (about several J m$^{-2}$) found in the literature for metal films on polymer substrates [16,21,38,58,59]. The values also change with the modulation period, in conflict with the principle of invariable adhesion energy. Since all the NMFs were produced in the same way and the layer firstly adherent to the substrate was always Nb (or Zr) the same adhesion energy should be measured for the Cu/X

![Fig. 8](image-url)

**Fig. 8.** The buckle dimensional data for Cu/Nb NMFs ((a, c) $\lambda = 50$ nm; (b, d) $\lambda = 250$ nm), fitted to (a, b) the original model of Cordill et al. and (c, d) the present modified model, respectively. Note that $\lambda$ has replaced film thickness $h$ in the present model ((c) vs. (a) and (d) vs. (b)). Three different $x$ values are shown in each figure.

![Fig. 9](image-url)

**Fig. 9.** Variation in the evaluated adhesion energy with $\lambda$. (a) Derived from the Cordill et al. original model; (b) derived from the present modified model. The evaluated adhesion energy is invariable in (b) when $\lambda$ is smaller than about 50 nm.
(X = Nb or Zr) NMFs regardless of the modulation period. The discrepancy between the calculated and theoretical values suggests that the single layer film model cannot be applied directly to NMFs and some modifications should be made.

The characteristics that distinguish NMFs from single layer films include the modulation structure, numerous interfaces, and constraints between the hetero-layers. It has been generally accepted [60] that the dislocation activities in NMFs are constrained by the large number of interfaces and, hence, the modulation period, rather than the total film thickness is the microstructural length controlling the deformation behavior. The present experimental results also indicate that the buckling dimensions are closely dependent on the modulation period at the same total film thickness. These motivate us to assume that a modeling unit in the NMFs should be the modulation structure or the bilayer structure composed of the constituent phases. Referring to Fig. 7b, the model for NMFs has the same parameters and definitions as in the model of Cordill et al., but the modulation period \( \lambda \) becomes the size variant rather than film thickness \( h \). Following similar procedures for derivation, Eqs. (9) and (10) are, respectively, modified

\[
\sqrt{\frac{\delta}{\lambda}} = (2\pi)^{1/4} \left[ 1 + \sqrt{1 + \frac{3}{4} \left( \frac{1}{\lambda} \right)^4} \right]^{-1/4}
\]

\[
\alpha = 2G^f \left( \frac{2}{\pi} \right)^4 = \frac{4G^f \left(1 - v^f\right)}{\lambda E_f} \left( \frac{2}{\pi} \right)^4
\]

Similarly to the above data analysis procedures, \( \sqrt{\delta/\lambda} \) was plotted with respect to \( h/\lambda \) (as represented in Fig. 8c and d). The minimum \( \alpha \) was also determined, and finally the adhesion energy was re-evaluated. Fig. 9b shows the new adhesion energy after modification. For both the Cu/Nb and Cu/Zr NMFs two regimes in the evolution of adhesion energy with \( \lambda \) were identified. When \( \lambda \) is greater than about 50 nm the evaluated adhesion energy decreases with decreasing \( \lambda \), showing an apparent size effect. This is particularly so for the Cu/Nb NMFs, the evaluated adhesion energy of which decreases from \( \approx 50 \) to \( \approx 1.1 \text{ J m}^{-2} \) as \( \lambda \) decreases from 250 to 50 nm. In comparison, the Cu/Zr NMFs undergo a decrease from \( \approx 3 \) to 1.2 J m\(^{-2} \) for the same change in \( \lambda \). When \( \lambda \) is less than \( \approx 50 \) nm, however, the evaluated adhesion energy of the NMFs are both \( \lambda \)-independent and reach a constant value, i.e. \( \approx 1.1 \text{ J m}^{-2} \) for the Cu/Nb NMFs and 1.2 J m\(^{-2} \) for the Cu/Zr NMFs. These values agree well with previous reports on metal/polymer systems, such as \( \approx 1 \text{ J m}^{-2} \) for Au on polyimide [16], \( \approx 1 \text{ J m}^{-2} \) for Nb on polycarbonate [38], \( \approx 1 \text{ J m}^{-2} \) for Pd on polycarbonate [58], \( \approx 4.5 \text{ J m}^{-2} \) for Cr on polyimide [21], and \( \approx 6.3 \text{ J m}^{-2} \) for Ni on polycarbonate [59]. The comparisons prove that the modified model provides meaningful adhesion energy estimates for NMFs.

Replacing film thickness by modulation period \( \lambda \) in the energy balance model yields credible adhesion energies for NMFs. This modification may be understood from the view that the incoherent Cu–X interfaces have a relatively low shear strength and can be regarded as “weak” interfaces [61–63]. Therefore, NMFs composed of Cu/X layers can readily shear on each other and act as freestanding individual films with limited dislocation activity between the two layers during NMF buckling. Since the thickness of each layer is half of the modulation period (i.e. \( \lambda/2 \)), \( \lambda \) becomes the characteristic length scale parameter in the new energy balance model. Nevertheless, more sound explanations are required in the next work.

4. Discussions

In the previous section we presented experimental results showing that the buckling behavior is closely dependent on the constituent phases. The buckles in the Cu/Nb NMFs are mostly cracked, while in the Cu/Zr NMFs the buckles are almost free of cracks. The adhesion energy evaluated from a modified model, although size-independent at \( \lambda \) less than about 50 nm, is remarkably sensitive to \( \lambda \) when greater than 50 nm. In this section the constituent-dependent buckling behavior will be discussed with respect to the mechanical properties, and the evolution of adhesion energy will be intensively analyzed in the light of the size-dependent deformation mechanisms in NMFs.

4.1. Dependence of buckling behaviors on the mechanical properties

Buckle cracking or not is controlled by competition between externally applied loads and the intrinsic deformation/fracture resistance. NMFs with diverse constituents have different mechanical properties, which are essentially responsible for the dissimilar buckling behaviors reported here. Some limited investigations [64–68] have looked at the subject of buckle cracking. Jia et al. [68] proposed that, once the strain at the top surface of the buckled film \( (\varepsilon^{\text{top}}) \) exceed the fracture strain of the film material, the buckles will crack. However, Faulhaber et al. [65] claimed that buckle cracking should be controlled not only by the local stress and moment but also by other factors such as film toughness. Similarly, Strawbridge and Evans [66] suggested that the \( K_{\text{IC}} \) criterion dominates buckle cracking. In this paper the two possible criteria, i.e. critical stress/strain and fracture toughness, will both be discussed in characterizing buckle cracking and explain the differences between the two NMFs.

4.1.1. Critical strain criterion

Although buckling is a relaxation mechanism responsible for a decrease in the average stress in the film, it contributes to heterogeneous stress in the buckle. The associated bending deformations cause tensile stress in the buckled film. A variation in strain takes place through the thickness of the buckled film. The stress component in the buckled film along the \( \gamma \)-axis is expressed as [69]:
\[ v_y = v_c - z \frac{\partial^2 w}{\partial y^2} = v_c + z \left( \frac{\pi}{2} \right)^2 \frac{\delta}{\lambda} \cos \left( \frac{\pi}{2} \right) \]  

(13)

where \( w(y) \) is the displacement along the z-axis:

\[ w(y) = \frac{\delta}{2} \left( 1 + \cos \frac{\pi}{2} \right) \]  

(14)

where \( z = 0 \) coincides with the undeflected midplane of the film [1] and \( y = 0 \) corresponds to the middle point of the symmetric buckled part (Fig. 7). Eq. (13) shows that \( v_y \) is maximum in tension at the upper surface of the buckle top, i.e. \( y = 0 \) and \( z = \lambda/2 \) (or at \( y = \pm \lambda \) and \( z = -\lambda/2 \), see Fig. 7). The maximum tensile strain is given by

\[ \varepsilon_{yN}^m = \frac{\pi \delta^2}{4 l^2} \left( \frac{\delta}{\lambda} - \frac{1}{3} \right) \]  

(15)

The dependence of \( \varepsilon_{yN}^m \) on has been calculated and plotted in Fig. 10a as a function of \( l \). For comparison experimentally measured \( \varepsilon_{cr,y} \) values for the \( \lambda = 250 \) nm Cu/Nb and Cu/Zr NMFs, respectively, which is independent of \( l \), are also presented in this figure. \( \varepsilon_{yN}^m > \varepsilon_{cr,y} \) means that the local strain at the top surface of the buckle exceeds the deformation capability of the NMFs, which will result in buckle cracking. Since the Cu/Zr NMFs have a higher \( \varepsilon_{cr,y} \) value than Cu/Nb NMFs, buckle cracking is much more likely to occur in the Cu/Nb NMFs. This can qualitatively explain the experimental phenomenon that the buckles in the Cu/Nb NMFs are mostly cracked.

4.1.2. Fracture toughness criterion

On the basis of the fracture mechanics and critical microcrack length we propose a new parameter \( (\varepsilon_{cr,y}) \) to more intuitively characterize buckle cracking. This parameter, having the physical meaning of the critical strain required to nucleate microcracks, can be approximately used to represent the cracking tolerance of films. The combined parameter is related to the fracture toughness, yield strength, and film thickness of NMFs:

\[ \varepsilon_N = \frac{\varepsilon_{yN}^m}{\varepsilon_0^m} \]  

(17)

\( \varepsilon_N \geq 1 \) indicates buckle cracking, and vice versa. Fig. 10b shows the variation in \( \varepsilon_N \) with \( l \) at different \( \delta \) for both the Cu/Nb and Cu/Zr NMFs. Within the range of \( l \) from \(~7\) to \(17\) \(\mu m\) and \( \delta \approx 2.5 \) \(\mu m\) (Table 1) \( \varepsilon_N \) is always below 1 for the Cu/Zr NMFs. In contrast, \( \varepsilon_N \) for the Cu/Nb NMFs is much greater than 1 within the range of \( l \) from \(~3\) to \(8\) \(\mu m\) and \( \delta \approx 2.5 \) \(\mu m\) (Table 1). These quantitative comparisons are coincident with the aforementioned experimental results on the cracking probability of buckles. It is thus suggested that the parameter \( \varepsilon_N \) could be utilized to characterize the probability of cracking in buckles. The greater \( \varepsilon_N \) the greater the possibility that the local strain at the buckle top is above the cracking tolerance of the films. Since the elastic energy dissipation in buckling is insufficient to release the local stored energy, cracking accompanies buckling. The predictions from Eqs. (16) and (17) suggest that NMFs with a higher \( KIC/\sigma_y \) value of may be prone to form faultless and smooth buckles.

4.2. Effect of size-dependent deformation behavior on the evaluated adhesion energy

A thickness dependence of adhesion energy has generally been reported for substrate-supported single layer metal films [70–72], where the adhesion energy evaluated by different measurement methods (such as four point bending, stressed overlayers, and indentation tests) was commonly found to increase with increasing film thickness. It has been suggested that plastic energy dissipation in thicker films is responsible for an enhancement in the measured adhesion energy [7,8]. In present work the adhesion energy of NMFs evaluated by the buckling method is also dependent on size length when \( \lambda \) is greater than about

![Fig. 10. (a) Dependence of \( \varepsilon_{yN}^m \) on \( \delta \) as a function of \( l \). The experimentally measured \( \varepsilon_{cr,y} \) of \( \lambda = 250 \) nm for the Cu/Nb and Cu/Zr NMFs is shown for comparison. Note that the four curves apply to both the Cu/Nb and Cu/Zr NMFs. (b) Dependence of the strain ratio \( \varepsilon_{yN}^m \) on \( \delta \) as a function of \( l \) for both the Cu/Nb (right two curves) and Cu/Zr (left two curves) NMFs strained to 20%, respectively. The value of \( \varepsilon_{yN} \) is almost less than 1 in the Cu/Zr NMFs within the buckle dimension range. In contrast, \( \varepsilon_{yN} \) of the Cu/Nb NMFs is greater than 1 within the buckle dimension range.](image-url)
50 nm. This will be similarly discussed in the light of the deformation mechanisms in NMFs.

Extensive studies (see Misra et al. [48] and references therein) have been performed to investigate the effect of length scale, from the micrometer to nanometer range, on the deformation behavior of NMFs, as their characteristic dimensions shrink toward the nanoscale regime. Some deformation mechanisms have been proposed: (i) dislocation pile-up (DP) [39,60], applicable at the sub-micrometer scale to a few hundreds of nanometers; (ii) the confined layer slip (CLS) mechanism [41,48], applicable at the few to a few hundreds of nanometer length scales; (iii) the interface barrier crossing (IBC) mechanism [73,74], at the few nanometer length scales. The CLS mechanism involves the glide of a single dislocation loop in the soft phase bounded by two interfaces while the DP mechanism considers the pile-up of dislocations within the thickness space. The modulation period of current NMFs is 5–250 nm. This size range falls mainly in the CLS regime, while a small part may be in the DP regime. Quantitative calculations will be performed to identify the regimes.

Hsia et al. [75] developed a micromechanical model to describe the fracture behavior in laminates consisting of alternating ductile and brittle layers. In this model the deformation capability of the ductile layers can be quantitatively evaluated by deriving an equilibrium number of dislocations that can be accumulated in a single ductile layer. The model assumes that: (i) a crack is initially formed in the brittle layers and blocked by a interface; (ii) dislocations are emitted from the crack tip, piled up in the neighboring ductile layer and against the next interface (see the sketch inserted in Fig. 11a). The cracking of current Cu/X NMFs is initiated in the brittle X layers and blocked by the ductile Cu layer, fitting well with the model. We then employed this model here to understand the deformation mechanisms in NMFs. The dislocations emitted from the crack tip have two effects that are in competition. One is that the emitted dislocations blunt the crack tip and, hence, reduce the tensile stress at the crack tip. The other is that the dislocations piled up at the interface produce a back stress to the crack tip to hinder further dislocation emission. At a given load level the equilibrium number \( n \) of dislocations is [75]

\[
  n = \frac{4\pi(1 - \nu)}{\ln(\lambda/r)} \left( \frac{K_{\text{app}} \sqrt{\lambda}}{A \sqrt{2\pi}} \sin \phi \cos \frac{\phi}{2} - \tilde{\gamma} \right)
\]

where \( \phi \) is the angle of inclination of the slip plane to the interface (chosen to be 45°), \( A \) is a factor slightly greater than unity, \( r \approx 2.7r_0/b \), with \( r_0 \) being the effective core radius and \( b \) the Burgers vector of dislocation in the ductile material, \( K_{\text{app}} \), \( \lambda \), and \( \gamma \) are the normalized values of the far field mode I stress intensity \( K_{\text{app}} = 1.12\sigma_{\text{app}}\sqrt{\pi\lambda/2} \) [76], the maximum distance \( \lambda_{\phi} = \lambda/2\sin\phi \) that the leading

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**Fig. 11.** (a) Dependence of the maximum equilibrium dislocations \( (n_{\text{max}}) \) in the Cu layer on the normalized Cu cohesive strength \( (\tilde{\sigma}_c) \) as a function of \( \lambda \). A critical modulation period \( (\lambda_{\text{crit}}) \) of \( \sim 50 \) nm can be clearly seen, below which \( n_{\text{max}} \) is sharply reduced to a few dislocations. (Inset) A sketch of the micromechanical fracture model, which shows a microcrack initiated in the \( X \) layer and blocked at the interface, causing the emission and pile-up of dislocations in the Cu layer. (b) Variation in the evaluated adhesion energy with \( \lambda \). Two regimes divided by \( \lambda_{\text{crit}} \) represent the \( \lambda \)-independent and \( \lambda \)-dependent ranges, respectively. (Insets) The corresponding deformation mechanisms, i.e. dislocation pile-up (DP) for regime II and confined layer slip (CLS) for regime I. (c, d) Sketches illustrating the deformation gradient caused by buckling and formation of geometrically necessary dislocations to accommodate the gradient in NMFs with smaller and larger \( \lambda \), respectively.
dislocation can travel, and the surface energy $\gamma$, respectively,

$$K_{app} = \frac{K_{app}}{\mu \sqrt{b}}$$

where $\mu$ is the shear modulus of the Cu layers. The tensile stress at the blunted crack tip $\sigma_{tip} = \frac{\sigma_{app}}{\mu}$ is related to $n$ and $K_{app}$ as [75]

$$\sigma_{tip} \sqrt{n} = 2\sqrt{\frac{2}{\pi} K_{app} \left(1 - \frac{3(\sin \phi \cos \phi \frac{3}{2})}{\ln(\lambda/\rho)}\right) + \frac{12A}{2 \lambda \ln(\lambda/\rho)} \gamma \sin \phi \cos \phi \frac{3}{2}}$$

(20)

Upon increasing the applied load further dislocation emission competes with cleavage at the blunted crack tip. When the microcrack tip tensile stress $\sigma_{tip}$ reaches the normalized cohesive strength of the material $\sigma_c = \sigma_c/\mu$ cleavage occurs in the ductile Cu layer and the microcrack will propagate and form a channel crack. Based on this criterion the maximum number of dislocations emitted from the microcrack tip prior to cleavage ($n_{max}$) can be obtained from Eqs. (18) and (20) at a reasonable value $\sigma_c = 0.2 - 0.4$ that is applicable to ductile metals such as Cu [75].

The predicted $n_{max}$ (see Fig. 11a) apparently shows a size effect. A critical modulation period $\lambda_{crit}$, with a value between 30 and 50 nm depending on the value of $\sigma_c$, is observed, below which $n_{max}$ sharply decreases down to a very low magnitude. Beyond $\lambda_{crit}$ many more dislocations can accumulate within the thickness of the Cu layers. This means that in the regime below $\lambda_{crit}$ the dislocations will be strongly constrained by the interfaces and have to glide individually in-plane within the Cu layers. The critical point $\lambda_{crit}$ thus marks a transition in deformation mechanism from DP to CLS. Evaluation of the evolved adhesion energy is consistent with the deformation mechanism transition (see Fig. 11b, which is essentially the same as Fig. 9b but is colored to show the two regimes I and II, divided by $\lambda_{crit}$). Comparisons clearly demonstrate that the intrinsic adhesion energy is evaluated in the case of the CLS deformation mechanism, while the size-dependent adhesion energy corresponds to the dislocation pile-up deformation mechanism.

At present the determined adhesion energy and its dependence on $\lambda$ can be rationalized in the light of the size-dependent deformation mechanisms in NMFs. The curvature of buckles inevitably causes a local deformation gradient, for which geometrically necessary dislocations are required to accommodate the deformation discrepancy. At $\lambda \approx 50$ nm the deformation mechanism of the NMFs is CLS, i.e. dislocations individually glide in-plane within the constrained layers. The induced geometrically necessary dislocations are limited and only single row arrayed in a buckle-like shape (Fig. 11c). The buckles thus have smaller dimensions and mainly deform elastically. As a result, the determined adhesion energy is close to the intrinsic value and hence exhibits $\lambda$-independence (I regime in Fig. 11b). At $\lambda > 50$ the deformation mechanism changes to DP, i.e. dislocations can be loosely moved both in-plane and out-of-plane within the layers. There are broad three-dimensional spaces available for the generation and accumulation of a large number of geometrically necessary dislocations (Fig. 11d). Since a larger deformation gradient can be accommodated, buckles with greater dimensions can be formed where plastic deformation plays an important role. The introduction of plastic deformation will overestimate the adhesion energy and result in an enhancement in the determined adhesion energy. The thicker $\lambda$ the greater the plastic deformation. A remarkable $\lambda$-dependence of adhesion energy is finally measured, shown as regime II in Fig. 11b. In comparison, the Cu/Nb NMFs have a ductility or deformation capability lower than the Cu/Zr NMFs. Much more plastic deformation is thus expected in the Cu/Nb NMFs. In addition, the buckles in the Cu/Nb NMFs are mostly cracked. These are responsible for the stronger $\lambda$ effect in the Cu/Nb NMFs than in the Cu/Zr counterparts.

The above discussions reveal that at large $\lambda$ within regime II appreciable plastic deformation will inevitably exist during buckling. Since the present models to determine the adhesion energy are simply based on elastic deformation, they seem to be inapplicable to the large $\lambda$ scale. This also indicates that the $\lambda$-dependence of adhesion energy determined in regime II is related to the improper models. More suitable models should be proposed in the future that can take into account plastic deformation and are thus workable at the larger scale.

5. Conclusions

1. Buckling behavior has been systematically investigated and compared in Cu/Nb and Cu/Zr NMFs with a wide modulation period. The dimensions of buckles increased with the modulation period, and were greater in the Cu/Zr NMFs than in the Cu/Nb NMFs. The buckles in the Cu/Nb NMFs are mostly cracked, but almost crack-free in the Cu/Zr NMFs. Buckle cracking is related to the mechanical properties of the NMFs and quantitatively characterized by a combined parameter.

2. A modified energy balance model has been proposed to evaluate the adhesion energy of the NMFs using the buckle dimensions. The adhesion energies were determined to be $\sim 1.1$ and $1.2$ J m$^{-2}$, respectively, for the Cu/Nb and Cu/Zr NMFs, which was constant when the modulation period of the NMFs was smaller than $\sim 50$ nm. Since the measured adhesion energies agree well with previous reports on metal/polymer systems the modified model is applicable for the adhesion energy evaluation of NMFs.
3. When the modulation period of the NMFs was greater than ~50 nm the evaluated adhesion energy of the two NMFs exhibited a strong size effect, i.e. it increased with increasing modulation period. This is rationalized in the light of the size-dependent deformation mechanism in NMFs. A micromechanics model has been employed to identify the critical modulation period of ~50 nm, which represents a critical point for deformation mechanism transition from dislocation pile-up to confined layer slip.

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References
