Size-dependent deformation mechanisms and strain-rate sensitivity in nanostructured Cu/X (X = Cr, Zr) multilayer films

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Abstract

Hardness, activation volume and strain-rate sensitivity of Cu/Cr (face-centered cubic (fcc)/body-centered cubic) and Cu/Zr (fcc/hexagonal close-packed) nanostructured multilayer films have been systematically measured as a function of modulation period (L) and modulation ratio (η), respectively. Significant size effects were found for all the three plastic deformation characteristics, i.e. enhanced hardness and activation volume but reduced strain-rate sensitivity with decreasing the dimension length L. Microstructure evolution was statistically examined to rationalize these size dependences. It was crucially observed that abundant nanotwins existed in the Cu grains, though nanotwin formation was depressed with smaller L. This inverse size-dependent nanotwin formation is responsible for the reduction in strain-rate sensitivity, because the negative effect induced by the decreased nanotwins predominates over the positive effect coming from the raised interfaces/boundaries. A mechanistic model is modified to account for the interface effect as well as the nanotwin effect, which yields calculations of strain-rate sensitivity in broad agreement with the experimental results when L is larger than about 20 nm. Below this critical length size, there are discrepancies between the calculations and the experimental results, due to the change in deformation mechanism from dislocation nucleation/slip in confined layers to dislocation crossing interfaces. A confined layer slip model is also modified by considering the nanotwin strengthening to quantitatively describe the L-dependent hardness. In addition, the effects of constituent phases and their relative content on the activation volume and strain-rate sensitivity of NMFs are discussed with regard to variation in η.

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Keywords: Multilayer films; Deformation mechanisms; Strain-rate sensitivity; Size effect

1. Introduction

Nanocrystalline (NC) metals and alloys have appealing mechanical characteristics of potential significance for structural applications, including ultrahigh yield and fracture strengths, superior wear resistance, and possibly superplastic formability at low temperatures and/or high strain rates [1–5]. Compared with conventional coarse grained materials, the deformation mechanisms derived from nanostructuring are also radically different, as plasticity at the nanoscale will be mediated mostly by grain-boundary deformation processes [6–8]. These have stimulated widespread interest in the mechanical properties and novel deformation mechanisms of nanostructured materials over the past two decades. The understanding of plastic deformation characteristics in NC metals, i.e. flow stress, activation volume (V*) and strain-rate sensitivity (m), has been one of the major objectives in the investigations of such materials [3,5,9,10].

The two rate-sensitive parameters, strain-rate sensitivity m and activation volume V*, are usually used to provide quantitative measures of the sensitivity of flow stress to loading rate, and also give insights into the deformation mechanisms [3,5,11,12]. Recent experimental observations have led to the discovery that NC metals exhibit m and

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that are highly sensitive to the loading rate when the average grain size \(d\) or nanotwin thickness \(\lambda\) is less than 100 nm [9,10,12–15]. It has also been found that the size dependence of the rate-sensitive parameters is closely related to the lattice structure of the metals. Some of the experimental results available on \(m\) vs. \(d\) (or \(m\) vs. \(\lambda\)) are summarized in Fig. 1, classified by the lattice structure of face-centered cubic (fcc), body-centered cubic (bcc) and hexagonal close-packed (hcp) metals, respectively. The data of three representative fcc metals, Cu [12,13,16,17], Al [18–20] and Ni [10,21,22], show a consistent trend for the value to increase with decreasing grain size from the micron to the submicrometer scale, followed by an obvious “take-off” when the grain sizes are reduced to below a couple of hundred nanometers (Fig. 1a).

In contrast to fcc metals, bcc metals exhibit a considerable reduced strain-rate sensitivity in the submicrometer regime (Fig. 1c), as commonly observed in bcc-type Fe [26–28], Ta [12,29], W [30] and V [31]. It has been claimed [12] that this is related to the peculiar plastic deformation mechanisms of bcc metals (especially to the low mobility of screw dislocations), as well as the increasing prevalence of GB strengthening in the smaller size regime. Of special interest is that the \(m\) value of bcc metals is only about \(\sim 0.04\) when the grain size is below 100 nm, which is 5- to 10-fold smaller than that of the fcc metals having the same grain size (Fig. 1a vs. c). For hcp metals, only a limited number of papers [32–37] addressing the grain size effect on \(m\) have been published. No convincing conclusion can be drawn for hcp metals due to the scattering of the limited data (see Fig. 1d).

The aforementioned investigations focused exclusively on single-phase metals. Metallic nanostructured multilayer films (NMFs), composed of alternating nanoscale layers of two different single-phase metals, have attracted much attention for their promising mechanical properties and significant theoretical interest [38–40]. A remarkable enhancement in hardness has been generally observed [40–44] in NMFs with the reduction in layer thickness. Some strengthening models have been proposed (refer to Ref. [41] and the references therein), and the large number of interfaces is widely believed to determine the plastic deformation and the flow stress (or hardness) in the NMFs. Particularly in fcc/bcc and fcc/hcp NMFs with non-coherent interfaces, the interactions between dislocations and interfaces exhibit unique characteristics, as revealed from

Fig. 1. Strain-rate sensitivity of fcc metals (a) and (b), bcc metals (c) and hcp metals (d) as a function of grain size \(d\) or twin thickness \(\lambda\), summarized from available literatures. The curve in (b) is calculated by using GDAS model [25]; all the other curves are visual guides.
recent atomistic simulations [45,46]. A conclusion has been drawn from these studies that it is the layer thickness (equivalent to the interface number) rather than the grain size that becomes the dominant microstructural parameter controlling the strengthening mechanisms in NMFs. Nevertheless, the strain-rate sensitivity of NMFs and its size dependence are far from clear, and should be much more complicated than those of single-phase metals due to the coexistence of two different constituent phases. At present, the relative fundamental questions that are still open include: (i) the competition or cooperation effect between the two constituent phases (e.g. fcc vs. bcc or fcc vs. hcp) at nanoscale size, considering their radically different size (equivalent to the interface number) rather than the grain size or twins, that may have an effect equal to or greater than that of the interfaces; and (iv) the size-dependent dominant mechanisms of the strain-rate sensitivity in NMFs.

Developing an understanding of these issues would provide valuable insights into the mechanical deformation features of a variety of engineering nanolaminates. Such an understanding would also offer helpful information for microstructure design of NMFs, which can be achieved by artificially tailoring the modulation period ($L$; the thickness of two constituent layers) and/or the modulation ratio ($\eta$; the ratio between the thicknesses of the two constituent layers). In this paper, we report a series of systematic experiments that demonstrate the size-dependent strain-rate sensitivity in non-coherent NMFs, reveal its underlying deformation mechanisms and explore the respective contributions of the constituent phases. For this purpose, two kinds of NMFs, fcc/bcc-type Cu/Cr and fcc/hcp-type Cu/Zr, were chosen as the study materials. Modulation of the structure of the two NMFs is tailored within wide ranges of $L$ and $\eta$, respectively, in order to investigate the size effect and constituent-phase effect on the strain-rate sensitivity. Based on microstructural analyses, the possible mechanisms contributing to these effects are discussed and a mechanistic model is modified to quantitatively describe the size-dependent strain-rate sensitivity in the NMFs.

2. Experimental procedures

2.1. Materials

Silicon-supported Cu/X ($X = \text{Cr, Zr}$) NMFs were prepared by using direct current (DC) magnetron sputtering at room temperature. The chamber was evacuated to a base pressure of $4 \times 10^{-7}$ torr, and $1-3 \times 10^{-3}$ torr Ar was used during deposition. The target purities of Cu, Cr and Zr were 99.99%, 99.95% and 99.95%, respectively. Two kinds of modulation structure were artificially tailored: one kind had a constant modulation ratio $\eta$ of 1 ($\eta$ defined as the ratio of the X layer thickness $h_X$ to the Cu layer thickness $h_{\text{Cu}}$, $\eta = h_X/h_{\text{Cu}}$) but with a wide range of modulation period $L$ ($L = h_{\text{Cu}} + h_X$) from 10 to 250 nm; the other kind had a constant $L$ of 50 nm, with a wide range of $\eta$ from 0.11 to 1.0. In multilayer deposition, the first layer on the substrate was X and the topmost layer was Cu. The total thickness of all the NMFs was about 1.5 $\mu$m. Without a break in the vacuum, all the as-deposited NMFs were annealed at 150 °C for 2 h to stabilize the microstructure and eliminate any residual stress.

2.2. Microstructure characterization

X-ray diffraction (XRD) was carried out using an improved Rigaku D/max-RB X-ray diffractometer with Cu K$\alpha$ radiation and a graphite monochromator to determine the crystallographic texture, the out-of-plane interplanar spacing and the residual stress of the multilayers using the “$\sin 2\theta$ method” [47,48]. Transmission electron microscopy (TEM) was performed on a JEOL-2100 high-resolution electron microscope with a 200 kV accelerating voltage, for which the cross-section samples were thinned by using dimpling and ion-milling. The modulation and interface structures of the NMFs were carefully observed, and the grains and twins were characterized. At least 500 grains were examined within each constituent layer for all the NMFs. The average grain size, $d$, and the percentage of Cu grains containing twins, $N_T$, were statistically evaluated following the procedures in Ref. [49].

2.3. Nanoindentation test method

Nanoindentation measurements were performed at room temperature using a TI950 TriboIndenter (Hysitron, Minneapolis, MN) with a standard Berkovich tip. The displacement and load resolutions of the instruction are 0.04 nm and 1 nN, respectively. The creep properties of the NMFs were characterized under a constant load rate $\dot{P} = 1000 \mu$N s$^{-1}$, with a holding load of 3000 $\mu$N. Choice of the maximum load is based on two requirements: the indentation depth should be controlled below 1/10 of the film thickness in order to avoid any substrate effect, and the indentation depth should be larger than the layer thickness even in the $L = 250$ nm NMFs in order to make sure two constituent layers are both indented. The holding time was kept for 60 s in order to minimize the possible influence of grain growth during creep [50]. The hardness was determined by the following traditional method. In all cases, at least nine measurements were repeated at each sample with the aim of reducing the noise of the creep curves.

The indentation strain rate $\dot{\epsilon}$ is expressed as [51]:

$$\dot{\epsilon} = \frac{1}{h} \left( \frac{dh}{dt} \right)$$

(1)

where $h$ is the indentation depth and $t$ is the time. $dh/dt$ is calculated by first fitting the $h$ vs. $t$ curve during the holding time using the empirical law [52]

$$h = h_0 + x(t - t_0)^y + zt$$

(2)
where \( h_0, x, y \) and \( z \) are fitting constants, and \( t_0 \) is the time of the creep process started. An example of an experimental result (Cu/Cr NMFs with \( L = 250 \, \text{nm} \) and \( \eta = 1 \)) and fitting curve is shown in Fig. 2a. Fig. 2b shows the fitting curves of Cu/Cr NMFs with modulation period \( L \) being varied.

The strain-rate sensitivity \( m \) is experimentally defined as the slope of the double logarithmic plot of hardness \( H \) and \( \dot{\varepsilon} \) under isothermal conditions [53–55]

\[
m = \frac{\partial \ln(H)}{\partial \ln(\dot{\varepsilon})}
\]

while the activation volume is determined following the expression as

\[
V^* = \frac{2.7 \times \sqrt{3}kT}{H} \left( \frac{\partial \ln(\dot{\varepsilon})}{\partial \ln(H)} \right)
\]

where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. Note that the yield strength of NMFs is assumed to be roughly 1/2.7 of its nanoindentation hardness [41].

3. Results

3.1. Microstructural results

High-angle XRD spectra for Cu/Cr NMFs show a strong Cu-(111) and Cr-(110) texture. The spacing of atomic planes of Cu-(111) is very close to that of Cr-(110) so that their peaks overlap with each other in the XRD pattern at small \( L \). The residual tensile stresses were determined to be \( 200 \pm 30 \, \text{MPa} \) for all the annealed Cu/Cr NMFs, which is far less than the strength/hardness of the NMFs [48,56]. Representative cross-sectional TEM images of the Cu/Cr NMFs are displayed in Fig. 3, including different \( L \) (\( L = 250 \) and 100 nm respectively in Fig. 3a and b with \( \eta = 1 \)) and different \( \eta \) (\( \eta = 1.0 \) and 0.33 respectively in Fig. 3c and d with \( L = 50 \, \text{nm} \)). One can see clear and sharp interfaces between the Cu and Cr constituent layers, with columnar grains in the Cu layers and ultrafine nanocrystals in the Cr layers. The corresponding selected area diffraction patterns (SADPs) indicated that the NMFs exhibited a strong Kurdjumov–Sachs orientation relationship in the growth direction, \{111\}Cu//{110}Cr; \{110\}Cu//{111}Cr, supporting the XRD results.

With regard to the Cu/Zr NMFs, the XRD results show a polycrystalline structure with a (111) texture in the Cu layers and with a (0002) texture in the Zr. At smaller \( L \), the Cu (111) and the Zr (0002) peaks broaden. In addition, neither the Cu (111) peak nor the Zr (0002) shift were comparable to the equilibrium state, indicative of opaque interfaces in the Cu/Zr NMFs that are incoherent. Representative cross-sectional TEM images of the Cu/Zr NMFs are displayed in Fig. 4, including different \( L \) (\( L = 250 \) and 100 nm respectively in Fig. 4a and b with \( \eta = 1 \)) and different \( \eta \) (\( \eta = 0.33 \) and 0.11 respectively in Fig. 4c and d with \( \eta = 1 \)).

![Fig. 2. (a) An example of experimental and fitted creep curve of Cu/Cr NMFs with \( L = 250 \, \text{nm} \) and \( \eta = 1 \). (b) Fitting creep response for Cu/Cr NMFs with different \( L \). Example of the experimental method to determine \( m \) (c) and \( V^* \) (d).](image-url)
L = 50 nm). Similarly, columnar grains are found in the Cu layers, with nanocrystals in the Zr layers. No significant intermixing between Cu and Zr was observed in any of the Cu/Zr NMFs, and there was no evidence of amorphization along the interface. The SADP also shows strong Cu (111) and Zr (0002) textures.

Careful microstructure examinations show that both the Cr grain size in the Cu/Cr NMFs and the Zr grain size in the Cu/Zr NMFs change slightly within the studied ranges of both L and η. They are about 10 ± 5 nm for the Cr grains and 12 ± 4 nm for the Zr grains. Therefore, the Cr layers and the Zr layers can be simply considered to have constant microstructures, regardless of the variation in either L or η. The Cu grain size is also found to be insensitive to η, being almost unchanged at 20 ± 5 nm, when the L of the Cu/Cr and Cu/Zr NMFs is kept at 50 nm. However, the Cu grain size varies remarkably with L.

Given in Fig. 5a and b is the Cu grain size histograms of the Cu/Cr and Cu/Zr NMFs, respectively, with different L but a constant η = 1. In general, the grain size distribution narrows and shifts to a smaller size with reducing L or layer thickness \( h_{Cu} = \frac{1}{2}L \). The average Cu grain size \( d_{Cu} \) scales roughly with L in the Cu/Zr NMFs, but does so in the Cu/Cr NMFs only when L is below 100 nm, as shown in Fig. 5c. Growth nanotwins with a high density are also observed within the Cu grains (indicated by arrows in Figs. 3 and 4). The nanotwin thickness is 7 ± 2 and 8 ± 3 nm in the Cu/Cr and Cu/Zr NMFs, respectively. In the Cu/Cr NMFs with L = 250 nm, over 70% of the Cu grains contain twins. With reducing L, however, the percentage of Cu grains containing nanotwins \( (N_T) \) is linearly decreased (see Fig. 5d).

The present finding that nanotwin formation decreases with reducing L or \( d_{Cu} \) is similar to recent experimental observations that deformation twinning propensity decreases with grain size when the grain size is below about 80 nm in NC Cu [49] and below about 35 nm in NC Ni [57]. A possible reason for this phenomenon is related to the size-dependent “promotion-to-the next-layer” probability for twin formation [49]. The nucleation of one partial, while accounting for the stacking faults, is a necessary but not sufficient condition for twins. Uncorrelated random emissions of individual partials cannot accidentally form a twin several of atomic layers thick. The emissions of partial dislocations, from grain boundaries or interfaces, need to be spatially, and likely temporally, correlated. This layer-by-layer promotional effect may well be due to the inertia of a plane n partial dislocation, which can accumulate huge kinetic energy and move very fast after emission, driven by the high stress in the grain interior, with a total energy several times the stationary dislocation self-energy as it hits the GB/interface, thus satisfying the energy conservation for the creation of a partial dislocation on the plane \( n + 1 \). The “promotion-to-the next-layer” probability
is proportional to the grain size \([49]\), i.e. the smaller the grain, the less the probability of forming twins. The \(L\)-dependent nanotwin formation will have a notable effect on the deformation and mechanical responses of the NMFs.

3.2. Nanoindentation results of the NMFs with variation in \(L\)

Hardness of the Cu/Cr and Cu/Zr NMFs with different \(L\) is summarized in Table 1. One can see that the hardness increases with decreasing \(L\), which is consistent with general observations (e.g. \([41]\)) and thus indicative of \(L\)-dependent deformation behaviors in the NMFs. The hardening effects in the present NMFs resulted not only from the interface constraint but also from the twin strengthening. Details of the analyses of deformation mechanisms and the modeling of \(L\)-dependent strength/hardness will be presented in Section 4.

To reveal the rate-controlling deformation mechanisms, the activation volume \(V^*\) and strain-rate sensitivity \(m\) of the Cu/Cr and Cu/Zr NMFs are respectively plotted as a function of \(L\) (see Fig. 6a and b). The trend of \(V^*\) changing with \(L\) is similar to that of hardness, from \(\sim 13b^3\) at \(L = 250\) nm to \(\sim 23b^3\) at \(L = 10\) nm (Cu/Cr NMFs) and \(L = 25\) nm (Cu/Zr NMFs). It has been suggested \([58]\) that, when \(V^*\) has a large value exceeding \(100b^3\), the dominant deformation mechanism is dislocation, cutting the forest dislocations observed in bulk fcc metals. When \(V^*\) reduces to several \(b^3\) on the order of atomic volume, Coble creep and GB sliding are the dominant deformation mechanisms \([58,59]\). Both dislocation gliding and GB diffusion/gliding can be excluded as the dominant mechanism of present NMFs, in which \(V^*\) has the value between \(10b^3\) and \(30b^3\).

On the other hand, dislocations emission from GBs/interfaces and dislocation interaction with GBs/interfaces can also be thermally activated processes, which have been demonstrated by molecular dynamics simulation and TEM observations \([60,61]\). In addition, twin boundaries (TBs) are also found to affect the thermally activated process via dislocation nucleation in TBs and interacting TBs \([9]\). Consequently, it is believed that the interaction between dislocations and GBs/interfaces/TBs is the dominant deformation mechanism in the present NMFs, which should be responsible for all the size-dependent mechanical properties observed here.

Both kinds of NMFs display reduced \(m\) with deceasing \(L\) or \(d_{Cu}\) (Fig. 6b), which is contrary to the general observations of enhanced \(m\) in fcc NC metals (see Fig. 1a). Several possible reasons for this trend include (i) the negative effect of bcc Cr layer/hcp Zr layer, (ii) the influence of crossed interface number and (iii) the influence of \(L\)-dependent twin formation. Let us first consider the influence of constituent X layers, i.e. the bcc Cr layer in the Cu/Cr NMFs and the hcp Zr layer in the Cu/Zr NMFs.
Considering the NMFs simply as composites, the properties of the composites are affected by any constituent phases. Consistent results in Fig. 1b show that the bcc metals have a reduced $m$ in the NC regime. If the $m_{\text{Cr}}$ (or $m_{\text{Zr}}$) value of the Cr (or Zr) layers decreases with reducing $L$ and dominates over the increased $m_{\text{Cu}}$ of the Cu layers, this may explain the results depicted in Fig. 6b. However, the Cr (Zr) grain size has been found to change only slightly with $L$, which will cause no striking decrease in $m_{\text{Cr}}$ (or $m_{\text{Zr}}$). Therefore, the influence of the fcc Cr layers (or hcp Zr layers) can be excluded as the dominant mechanism.

The second possible reason is the influence of crossed interface number. Recent simulation results [45,46] have shown that the glide dislocations entrapped in the incoherent interface can move along the interface plane through glide and climb, which may lead to annihilation of dislocation content. In this consideration, the smaller the $L$, the more interfaces will be crossed under the indentation (note that the indentation depth differs by less than 20 nm between the maximum $L = 250$ nm and the minimum $L = 10$ nm samples). Because it is easier for the dislocations to climb along the increasing interfaces and subsequently to meet other dislocations of the opposite sign, more dislocations will be annihilated, causing less strain-rate sensitivity. However, we performed further indentation experiments by elevating the maximum load (5000, 7000 and 9000 N) and concomitantly changing the numbers of crossed interfaces, and found no apparent change in the determined $m$ value (Fig. 6c). This actually eliminates the second possible reason.

The influence of self-diffusion along the indenter/sample interface can also be excluded as the main reason. The critical indentation depth for self-diffusion along the indenter/sample interface has been experimentally determined [62].

Table 1

<table>
<thead>
<tr>
<th>NMFs/parameter</th>
<th>$L$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>$H$ (GPa) (Cu/Cr)</td>
<td>9.16 ± 0.35</td>
</tr>
<tr>
<td>$H$ (GPa) (Cu/Zr)</td>
<td>–</td>
</tr>
</tbody>
</table>

Fig. 5. Cu grain size histograms of (a) the Cu/Cr NMFs and (b) the Cu/Zr NMFs with different $L$. (c) The average Cu grain size, $d_{\text{Cu}}$, and (d) the percentage of Cu grains containing nanotwins, $N_T$, as a function of $L$ in the Cu/Cr and Cu/Zr NMFs, respectively. Lines are visual guides.
curves are visual guides. The characteristic microstructures, the constituent phases and their relative content. In particular, the size-dependent nanotwin formation induces an unusual evolution of $m$ with $L$. In this section, the size-dependent strengthening mechanisms and the $L$-dependence sensitivity. For example, the introduction of nanotwins within ultrafine crystalline fcc Cu was observed to increase $m$ by almost an order of magnitude [9]. This noticeable enhancement can be interpreted by the dislocation–nanotwin interactions. Deformation induces displacement of coherent nanotwin boundaries, forming jogs and steps along the nanotwin boundaries. Subsequently, the displaced twin boundaries may serve as barriers to dislocation motion and also provide sources for dislocation nucleation, like grain boundaries. In the present NMFs, the nanotwin percentage is linearly decreased with reducing $L$ (see Fig. 5d), which should be responsible for the reduction in $m$.

3.3. Nanoindentation results of the NMFs with variation in $\eta$

Table 2 summarizes the measured activation volume $V^*$ and strain-rate sensitivity $m$ of the two kinds of NMFs with different $\eta$ but a constant $L$ of 50 nm. The constant $L$ means the same interface numbers. In addition, the grain sizes of all the constituent layers of Cu, Cr and Zr, as well as the $N_I$, are almost unvaried with changing $\eta$ from 1.0 to 0.11. It is the relative content of the two constituent layers that becomes the changing parameter. Fig. 7a and b displays the dependence of $V^*$ and $m$ on the volume fraction of the Cu layer ($h_{Cu}/(h_{Cu}+h_X)$), respectively. An approximately linear relationship is found between $m$ and $h_{Cu}/(h_{Cu}+h_x)$. Considering the NMFs as nanolaminates and assuming the effective medium theory is still operative in the NC regime, one can derive the strain-rate sensitivity $m$ as [63]

$$m = \frac{h_X}{h_{Cu}+h_X} \times m_X + \frac{h_{Cu}}{h_{Cu}+h_X} \times m_{Cu}$$

(5)

where $m_{Cu}$ and $m_X$ are the strain-rate sensitivity of the NC Cu layer and X layer, respectively, which are considered as constant due to the almost unchanged grain size with the variation in $\eta$. Retrogression of the two curves in Fig. 7b leads to results of $m_{Cu} \approx 0.012$ and $m_Z \approx 0.003$, which will be used in following calculation of the $L$-dependent strain-rate sensitivity. This is reasonable because the aforementioned experimental results have shown that both the Cr and Zr layers have grain sizes that are insensitive to $L$ and $\eta$. From Fig. 7, it is also found that the thermally activated process of NMFs is dependent not only on the interfaces and other characteristic microstructures such as NC grain and nanotwins, but also on the relative content of the constituent layers.

4. Discussion

In the previous section we presented experimental results showing that the strain-rate sensitivity of NMFs is closely related to the interfaces, the characteristic microstructures, the constituent phases and their relative content. In particular, the size-dependent nanotwin formation induces an unusual evolution of $m$ with $L$. In this section, the size-dependent strengthening mechanisms and the $L$-dependence
The curves are visual eyes.

Table 2
Summary of \( V^* \) and \( m \) of Cu/Cr and Cu/Zr NMFs with different \( \eta \).

<table>
<thead>
<tr>
<th>NMFs/parameter</th>
<th>( \eta )</th>
<th>0.11</th>
<th>0.25</th>
<th>0.33</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Cr ( V^<em>(b^</em>) )</td>
<td>11.57 ± 0.6</td>
<td>12.36 ± 0.9</td>
<td>13.24 ± 0.7</td>
<td>15.20 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>Cu/Cr ( m )</td>
<td>0.031 ± 0.001</td>
<td>0.028 ± 0.002</td>
<td>0.026 ± 0.002</td>
<td>0.022 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>Cu/Zr ( V^<em>(b^</em>) )</td>
<td>14.35 ± 0.5</td>
<td>15.22 ± 0.7</td>
<td>16.59 ± 0.9</td>
<td>22.13 ± 1.1</td>
<td></td>
</tr>
<tr>
<td>Cu/Zr ( m )</td>
<td>0.025 ± 0.002</td>
<td>0.022 ± 0.002</td>
<td>0.019 ± 0.002</td>
<td>0.012 ± 0.001</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7. Experimental results of (a) \( V^* \) and (b) \( m \) as a function of the Cu content, \( h_{Cu}/(h_{Cu}+h_{X}) \), for the Cu/Cr and Cu/Zr NMFs, respectively. The curves are visual eyes.

of \( m \) will be intensively analyzed and theoretically modeled, respectively, focusing on the contribution of nanotwins.

4.1. Nanotwin contribution to the size-dependent strengthening effect

Extensive researches \([40-44]\) have been performed to investigate the effect of length scale, from the micrometer to the nanometer range, on the strengthening mechanisms in NMFs. Some strengthening mechanisms have been proposed to explain the high strengths of these materials as their characteristic dimensions shrink toward the nanoregime, e.g. (i) the Hall–Petch-like strengthening relationship \([38,40,44]\), applicable at the submicrometer length scale, (ii) the confined layer slip (CLS) mechanism \([41,64,65]\), applicable at a few tens to a few hundreds of nanometers length scale, and (iii) the interface barrier strength (IBS) mechanism \([41,66]\), at a few to a few tens of nanometers length scale. The CLS model involves the glide of a single dislocation loop in the soft phase bounded by two interfaces, while the IBS model considers the interface cutting by a single dislocation. When the CLS stress (\( \sigma_{CLS} \)) to drive the dislocation glide exceeds the IBS stress (\( \sigma_{IBS} \)) to drive the dislocation cross the interface, the strengthening mechanism will change from the CLS to the IBS model.

The length scale of the present NMFs mainly falls into the CLS regime. The \( \sigma_{CLS} \) required to propagate a glide loop of Burgers vector \( b \) confined to the Cu layer is given as \([41,48]\)

\[
\sigma_{CLS} = \frac{M \mu' b \sin \varphi}{8 \pi h_{Cu}} \ln \left( \frac{2h_{Cu}}{b \sin \varphi} \right) + \frac{F}{h_{Cu}} + \frac{\mu' f \nu}{B(1-\nu)}
\]

where \( M \) is the Taylor factor, \( \varphi \) is the angle between the slip plane and the interface, \( v \) is the Poisson ratio of Cu, \( \mu' = \left( \frac{\mu_{Cu} \mu_X}{\mu_{Cu} + \mu_X} \right) \) is the mean shear modulus of Cu/X NMFs, which can be estimated by the shear modulus \( \mu_{Cu} \) and volume fraction \( f_{Cu} \) of Cu layer and those of the X layer, \( \nu \) represents the core cut-off parameter, \( F \) is the characteristic interface stress of multilayer, which has a typical value of \( \sim 2 \text{ J m}^{-2} \) in NMFs with incoherent interfaces \([41]\), \( \nu \) is the in-plane plastic strain and \( B \) is a strain resolution factor of the order of 0.5 for the active slip systems. The second and third terms in Eq. (6) represent the contribution of the interface stress and the dislocation–dislocation interaction, respectively \([41]\). Putting \( m = 3.06 \), \( \mu'_{Cu} = 48.3 \text{ GPa} \), \( \mu'_{Cr} = 115.4 \text{ GPa} \), \( \mu'_{Zr} = 33.0 \text{ GPa} \), \( v = 0.343 \), \( b = 0.2556 \text{ nm} \), \( \nu = 0.2 \), \( F = 2 \text{ J m}^{-2} \), \( \nu = 1 \% \) and \( \varphi = 70.5^\circ \) into Eq. (6), the \( \sigma_{CLS} \) of the Cu/Cr and Cu/Zr NMFs (both with \( \eta = 1 \)) can be respectively calculated as a function of \( L \) (see the dashed curves in Fig. 8a and b). Experimental results \((H/2.7 \text{ [41]}\) are also depicted in the corresponding figures for comparison. While the CLS model predicts strength increase with decreasing \( L \), it does not fit the experimental data very well. Overall, this model predicts strengthening at a much faster rate with decreasing \( L \) than that observed experimentally, resulting in the under-prediction of strength at large \( L \) and over-prediction at low \( L \).
vital refinement to the CLS mode, Eq. (6), is to incorporate the contribution of nanotwins. It is well known
[2,3,9,13,15,16,67–69] that nanotwins have a significant strengthening effect, especially in ultrafine and NC Cu. In
the present NMFs, we also found a large number of nanotwins in the NC Cu layers. The contribution of nanotwin
strengthening should be included in the modified CLS model, to yield

$$
\sigma_{CLS} = \frac{M \mu^* b \sin \varphi}{8\pi h_{Cu}} \left( \frac{4 - \nu}{1 - \nu} \right) \ln \left( \frac{\varphi h_{Cu}}{b \sin \varphi} \right) + \frac{F}{h_{Cu}} \\
+ \frac{\mu^* f_{Xe}}{B(1 - \nu)} \frac{N_T}{100} k_T^{-1/2}
$$

(7)

where \( k_T \) is a constant having the value of \( \sim 3400 \) MPa nm\(^{1/2} \) [70] and \( N_T \) is a function of \( L \) (Fig. 5d). Eq. (7) yields calculations in better agreement with the experimental data (see the solid curves in Fig. 8). This indicates that the nanotwins make remarkable contributions to the strength of both Cu/Cr and Cu/Zr NMFs, and nanotwin strengthening should be an indispensable strengthening mechanism in the NMFs that contain a high density of nanotwins.

When the layer thickness decreases down to a few tens of nanometers, the CLS stress may exceed the IBS stress, i.e. \( \sigma_{CLS} > \sigma_{IBS} \). The strengthening mechanism will thus change from the CLS to the IBS model, and a peak strength will be achieved that is determined by the stress needed to transmit a single dislocation across the interface. Recent atomic simulation results [45,46] have shown that the peak strength is closely dependent on the shear strength of interface or the atomic structure of the interface. The peak strength of Cu/Nb NMFs was experimentally determined by Misra et al. [41] to be 2.6 GPa below \( L_{cri} \sim 6 \) nm. In the present experiments, the peak strength is evaluated as \( \sigma_{IBS} \approx 3.35 \) GPa for the Cu/Cr NMFs and 2.25 GPa for the Cu/Zr NMFs, both below \( L_{cri} \sim 20 \) nm. The difference in \( \sigma_{IBS} \) may be ascribed to the different interface atomic structure between the NMFs, while the increase in \( L_{cri} \) may be an anomaly, caused by the sparse experimental data.

4.2. Competing effect on the \( L \)-dependent strain-rate sensitivity

Our experimental results have demonstrated a competing effect between NC grains and nanotwins on the size-
dependent strain-rate sensitivity in both Cu/Cr and Cu/
Zr NMFs. On the one hand, the Cu grain size decreases
with reducing \( L \), which will cause an increase in \( m_{Cu} \) and hence in \( m \). On the other hand, the nanotwins that will signifi-
cantly enhance \( m_{Cu} \) are gradually depressed with reduc-
ing \( L \). Interaction of the two opposite influences leads to a competing effect on \( m_{Cu} \) and \( m \). This is much more compli-
cated than what should be observed in NC metals with
grain size larger than \( d_{cri} \). This is defined as the critical
grain size below which the nanotwin formation will be sup-
pressed and above which the nanotwin formation will be pro-
moted, and is about 80 nm in NC Cu [49] and about
35 nm in NC Ni [57]. In the present NMFs, the average Cu grain size is decreased with reducing \( L \), all less than
\( \sim 80 \) nm.

A mechanistic model has recently been proposed by Gu
and Dao et al. [25,71] and Asaro and Suresh [23] to quan-
titatively describe the size-dependent flow stress and strain-
rate sensitivity for metals with NC grains and nanotwins.
In this model (called the GDAS model below in order to
distinguish it from the CLS model above), the flow stress
is assumed to be controlled by the partial dislocation emis-
sion from the GBs and TBs. Correspondingly, the shear
flow stresses, \( \tau_{GB} \) and \( \tau_{TB} \), are respectively expressed in

terms of the stacking fault energy \( \Gamma \) and parameters to
measure the extension of non-uniform partial dislocation

\( \beta_0, \beta_1 \) and \( \beta_2 \) as [25]

$$
\tau_{GB} = \frac{\Gamma}{\mu_{Cu}} b + \frac{1}{3} \left( 1 - \frac{1}{12\pi\beta_1} \right) b
$$

(8a)

$$
\tau_{TB} = \frac{\Gamma}{\mu_{Cu}} b + \frac{1}{3} \left( 1 - \frac{1}{12\pi\beta_2} \right) b
$$

(8b)

Fig. 8. Flow stress of (a) the Cu/Cr and (b) the Cu/Zr NMFs, estimated as nanoindentation measured hardness divided by a factor of 2.7, as a function of \( L \). Calculations from different models are depicted in the figures. The dash curves are from the traditional CLS model, the solid curves are from the present modified CLS model, which considers the nanotwin strengthening, and the dashed-dotted curves are from the present modified GDAS model, which considers both the interface effect and nanotwin strengthening. For details see the text.
where the parameter $\beta$ is defined as $\beta = \frac{1}{d_{Cu}^2} \int_0^{d_{Cu}} \delta(x)dx$, with the extension distance $\delta(x)$ being related to the grain size. The other two parameters, $\beta_1$ and $\beta_2$, have similar expressions, $\beta_1 = \frac{1}{d_{Cu}^2} \int_0^{d_{Cu}} \delta_1(x)dx$ and $\beta_2 = \frac{1}{d_{Cu}^2} \int_0^{d_{Cu}} \delta_2(x)dx$, respectively, with $\lambda_1 = \lambda/\sin(\theta)$ and $\lambda = \theta_0$ being the angle between the matrix slip plane and the TB. Both extension parameters are related to the geometrical lengths, grain size and twin thickness, as is the flow stress. Evaluation of the three extension parameters is presented in Refs. [25,71] and is not repeated here. Note that Eq. (8a) considers only the partial dislocation emission from GBs, while Eq. (8b) covers the partial dislocation emission from not only GBs but also TBs. Eq. (8) has been successfully applied to NC Cu [71] and nanotwinned Cu [25], where the grains are equiaxial and exhibit equivalent behaviors in three dimensions. The Cu grains in NMFs, however, behave equally only in one dimension and exhibit distinct behaviors in two dimensions. Therefore, it is reasonable to replace $d_{Cu}$ by $\mu_{Cu} = (L/2)$ and consider the influence of interface stress when applying Eq. (8) to the Cu phase in NMFs, i.e.

\[
\frac{\tau_L}{\mu_{Cu}} = \frac{\Omega}{\mu_{Cu} b} + \left( \frac{1}{3} - \frac{1}{12\pi\beta_1} \right) \frac{2b}{L} + \frac{2F}{L} \tag{9a}
\]

\[
\frac{\tau_{TB}}{\mu_{Cu}} = \frac{\Gamma}{\mu_{Cu} b} + \frac{1}{2} \left( \frac{1}{3} - \frac{1}{12\pi\beta_2} \right) \frac{2b}{L} + \frac{1}{2} \left( \frac{1}{3} - \frac{1}{12\pi\beta_2} \right) \frac{b}{x} + \frac{2F}{L} \tag{9b}
\]

Note that the NMFs studied here consist of a two-phase metallic structure, including coherent interfaces and twin boundaries. In the above revision, the first term in Eq. (9a) mainly comes from the contribution of coherent interfaces, while the first term in Eq. (9b) is from the stacking fault. Therefore, the parameter of $\Omega$ in Eq. (9a), defined as the critical energy needed to nucleate partials from coherent interfaces, is different from $\Gamma$ in Eq. (9b). After these revisions, the total stress is then obtained by taking the nanotwin weight into account:

\[
\tau = \left( 1 - \frac{N_T}{100} \right) \tau_L + \left( \frac{N_T}{100} \right) \tau_{TB} \tag{10}
\]

Flow stresses ($= M_T$) calculated from the modified GDAS model (i.e. Eqs. (9) and (10)) are depicted in Fig. 8 as dashed–dotted lines for comparison with experimental data and with the modified CLS model. Both the values of $\Omega$ used in the present calculations fall into the range of 0.02–1.0 J m$^{-2}$, as determined by atomic simulations [72]. The two modified models yield similar calculations, and are both in good agreement with the experimental data. This indicates that the modified GDAS model, after considering the size-dependent nanotwin formation, is applicable to the flow stress of NMFs.

After the calculation of flow stress, the GDAS model can be further modified to rationalize the $L$-dependent strain-rate sensitivity in the present NMFs. The original GDAS model is applied for single-phase metals, especially for nanosized Cu [23,25,71]. In this paper, the modified GDAS model is similarly applied only to the single Cu layer for calculating $\mu_{Cu}$. The value of $\mu_X$ (X = Cr and Zr) has been calibrated in Section 3.3, and the total $m$ of NMFs can be obtained through Eq. (5). In the modified GDAS model, the critical dislocation half-circular loop size for activation ($r^*_{s}$) in the Cu phase can be given as follows by referring to Ref. [25]:

\[
r^*_{s} = \kappa \left( \frac{\tau_L}{\mu_{Cu}} \right)^{-1} b \left[ \ln \left( \frac{\sqrt{3}\tau_{s}^*}{b} + 1 \right) \right] \tag{11a}
\]

\[
r^*_{TB} = \kappa \left( \frac{\tau_{TB}}{\mu_{Cu}} \right)^{-1} b \left[ \ln \left( \frac{\sqrt{3}\tau_{s}^*}{b} + 1 \right) \right] \tag{11b}
\]

In above equations, $\kappa = 5/(16\sqrt{3}\pi)$, and the core cut-off radius is taken to be $b/(\sqrt{3})$. Since the activation volume is obtained by [25]

\[
V^* = \frac{1}{2} \pi (r^*)^2 b \tag{12}
\]

and $m$ is related to $V^*$ by the expression [12,23]:

\[
m = \sqrt{3kT} \frac{V^*}{V^* \sigma} \tag{13}
\]

the strain-rate sensitivity of Cu related to the dislocation interaction with the interface and the TB, $m_{Cu}^L$ and $m_{Cu}^TB$, is respectively given by

\[
m_{Cu}^L = \frac{2\sqrt{3}kT}{M \pi (r^*)^2 b \tau_{s}^*} \tag{14a}
\]

\[
m_{Cu}^TB = \frac{2\sqrt{3}kT}{M \pi (r^*)^2 b \tau_{s}^*} \tag{14b}
\]

Finally, $m_{Cu}$ can be written in terms of $m_{Cu}^L$ and $m_{Cu}^TB$ as

\[
m_{Cu} = \left( 1 - \frac{N_T}{100} \right) m_{Cu}^L + \left( \frac{N_T}{100} \right) m_{Cu}^TB \tag{15}
\]

The above equations lead to calculations showing that the strain-rate sensitivity of NMF decreases with reducing $L$ down to $\sim 20$ nm, which is in broad agreement with the experimental results (Fig. 9). When $L$ is below $\sim 20$ nm, the calculations change to show an increase, while the experimental results still show a decrease. This discrepancy may be related to the change in deformation mechanism from dislocation emission to dislocation crossing interface, similar to the change from the CLS model to the IBS model below $L_{crit} \sim 20$ nm, as discussed above. In dislocation crossing interfaces, the atomic structure of coherent interface is capable of promoting room temperature climb at the interfaces [45]. The dislocations at interfaces can dissociate into interfacial dislocations with an out-of-plane component Burgers vector, and hence spread widely in the interfaces, which will cause dislocation annihilation upon meeting dislocations with the opposite sign. The notable effect of interfaces is also demonstrated in Fig. 9,
where the variation in $\Omega$ clearly changes the $L$-$m$ curve. The modified GDAS model nevertheless provides satisfactory calculations of the $L$-dependent strain-rate sensitivity in both Cu/Cr and Cu/Zr NMFs, although it fails to reflect the transformation in the deformation mechanism below $L_{cr} \approx 20$ nm. Of importance to note is that the size-dependent nanotwin formation and the contribution of dislocation–nanotwin interaction are effectively taken into consideration in the modified GDAS model, with which we can model the reduction in strain-rate sensitivity with decreasing $L$. In comparison, if the nanotwin contribution is not covered and only the dislocation–interface interaction is considered, i.e. $m_{Cu} = m_{Cu}^{s}$, the predicted trend is of enhanced strain-rate sensitivity with decreasing $L$ (short-dashed curves in Fig. 9, indicated by “No twins”), which is in contrast to the experimental observation.

Finally, we make a comparison between the Cu-based NMFs and NC Cu to demonstrate a radical difference in the size dependence of strain-rate sensitivity. Fig. 10 presents the $h_Cu$-dependent $m$ of the present Cu/Cr NMFs, together with the $d_{Cu}$-dependent $m$ of NC Cu [16]. The NC Cu exhibits an enhanced $m$ at a smaller size, which is attributed to the promoted GB activities. In contrast, the Cu/Cr NMFs display a decrease in $m$. This decrease can be reasonably explained on the basis of the deformation mechanism being controlled by the nanotwin-related dislocation nucleation/slip at regime II, as shown in Fig. 10, and the deformation mechanism of dislocation crossing interfaces at regime I, respectively.

5. Conclusions

(1) Microstructure evolutions in the Cu/Cr and Cu/Zr NMFs are carefully examined by variations in the modulation period $L$ and the modulation ratio $\eta$. Abundant nanotwins are observed in the Cu grains, and the nanotwins content decreases with reducing $L$ or grain size, indicative of a significant size dependence of nanotwin formation.

(2) The strengthening mechanisms of NMFs are elucidated by considering the nanotwin strengthening. The contribution of nanotwins to strength is found to be especially noticeable at large $L$. A modified CLS model, incorporating the nanotwin strengthening, yields calculations that fit well with the experimental results.

(3) The strain-rate sensitivity of Cu/Cr and Cu/Zr NMFs is systematically studied and correlated to the microstructure characteristics of the interface, grains and nanotwins. A reduction in strain-rate sensitivity is experimentally determined with reducing $L$. This trend is closely related to the depressed nanotwin formation, which has a negative effect on the strain-rate sensitivity that predominates over the enhancement effect coming from refined dimensions. Based on the deformation mechanisms, a mechanistic model is modified by involving the effect of size-dependent nanotwin formation, which results in calculations that are in broad agreement with the experimental data.
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