Hot Nanoindentation of Nanocrystalline Ni-W Alloys

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>As Published</td>
<td><a href="http://dx.doi.org/10.1016/j.scriptamat.2009.08.026">http://dx.doi.org/10.1016/j.scriptamat.2009.08.026</a></td>
</tr>
<tr>
<td>Publisher</td>
<td>Elsevier</td>
</tr>
<tr>
<td>Version</td>
<td>Author's final manuscript</td>
</tr>
<tr>
<td>Accessed</td>
<td>Mon Jan 14 02:07:24 EST 2019</td>
</tr>
<tr>
<td>Citable Link</td>
<td><a href="http://hdl.handle.net/1721.1/69220">http://hdl.handle.net/1721.1/69220</a></td>
</tr>
<tr>
<td>Terms of Use</td>
<td>Creative Commons Attribution-Noncommercial-Share Alike 3.0</td>
</tr>
<tr>
<td>Detailed Terms</td>
<td><a href="http://creativecommons.org/licenses/by-nc-sa/3.0/">http://creativecommons.org/licenses/by-nc-sa/3.0/</a></td>
</tr>
</tbody>
</table>
Hot Nanoindentation of Nanocrystalline Ni-W Alloys

Jason R. Trelewicz and Christopher A. Schuh
Department of Materials Science and Engineering, Massachusetts Institute of Technology,
77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA

Abstract
High temperature nanoindentation experiments are conducted to assess the activation enthalpy for deformation of nanocrystalline Ni-W alloys, for grain sizes between 3 and 80 nm. Thermal softening becomes less pronounced at finer grain sizes, and the activation enthalpy has an apparent inflection at a grain size near ~10-20 nm, in the vicinity the Hall-Petch breakdown. This inflection is related to that observed in the activation volume for deformation, and is associated with a shift to grain boundary-mediated deformation at the finest grain sizes.

Keywords: nanocrystalline materials; nanoindentation; mechanical properties; thermally activated processes

1 schuh@mit.edu
The past several years have seen a significant advance in understanding the mechanisms of deformation in ultrafine and nanocrystalline metals [1-4]. This is due in large part to studies that systematically vary strain rate and temperature, permitting assessment of the kinetic activation parameters for plastic flow [5-12]. Such studies have revealed a reduction in the apparent activation volume and energy for deformation at nanocrystalline grain sizes (below about 100 nm), which is in line with a shift in mechanism to grain boundary-mediated dislocation activity. Despite the increasing prevalence of these measurements, however, most studies provide data points for isolated grain sizes; trends are revealed primarily by comparing across different studies and materials. What is more, data are very scarce for the finest nanocrystalline grain sizes (i.e., below ~15 nm) where the Hall-Petch breakdown occurs and mechanisms shift to resemble those of amorphous metals. At these grain sizes, we have recently conducted indentation tests at various strain rates on FCC Ni-W alloys [3, 13], and revealed an inflection in the activation volume for flow that coincides with the breakdown of Hall-Petch strength scaling. Our purpose in this letter is to provide new experimental data on the temperature dependence of deformation of nanocrystalline Ni-W alloys with grain sizes ranging from 3 to 80 nm. Specific emphasis is placed on the extraction of the activation enthalpy for flow from high-temperature nanoindentation tests, across the range of the Hall-Petch breakdown.

The samples used in this study were nanocrystalline Ni-W alloys, electrodeposited according to the procedures of Ref. [14], and subsequently baked at 300° C for 24 hours in Ar to relax the grain boundaries without inducing significant grain growth or chemical configuration changes (following Ref. [15]). The films were all 40-60 µm thick, and their compositions were measured to within ±1 at.% via energy dispersive spectroscopy (X-ray Optics/AAT#31002) using a LEO 438VP scanning electron microscope. A Rigaku RU300 x-ray diffractometer (XRD) operating at 50 kV and 300 mA was used to quantify grain size to ±25% by applying the integral breadth method to the \{111\} family of peaks, which was further confirmed with transmission electron microscopy using a JEOL 2010 (Tokyo, Japan); for the smallest grain sizes only the (111) peak was available, so the single-peak Scherrer analysis was used instead. Representative
micrographs and electron diffraction patterns are shown in Figure 1 for two of the Na-W specimens, with XRD grain sizes of 80 and 18 nm. Further TEM and characterization of various other Na-W samples produced by our group can be found in Refs. [3, 14, 15]. Table I compiles the composition and grain size data for each of the nanocrystalline Na-W samples employed in the present study.

The indentation experiments were conducted with a Hysitron Ubi1 nanoindenter, modified for elevated temperature indentation testing as described in Ref. [16]. Specimens prepared with standard metallographic techniques to a roughness of < 10 nm were clamped to a heated copper stage. An extended zero thermal expansion shaft affixed with a standard diamond Berkovich tip was used in testing. The area function was calibrated on fused silica at room temperature, and its consistency was verified at 150 °C, representing the highest temperature test condition. A maximum load of 10 mN and constant indentation strain rates were employed in all of the tests reported here. Two series of experiments were conducted:

- In the first series, all five of the specimens in Table I were tested at room temperature, at various different strain rates spanning the range $1.5 \cdot 10^{-2} – 15 \text{ s}^{-1}$. The procedures and analysis of this data followed exactly those from Ref. [3] (although the present data are all new). The activation volume for deformation was determined from this series of experiments.

- In the second series, three samples (with grain sizes of ~3, 18, and 80 nm) were tested at a single indentation strain rate of $1.5 \text{ s}^{-1}$, but at temperatures over the range 25 – 150 °C in 25 °C increments. While the samples were exposed to these modest temperatures for extended time periods (> 1 week), hardness and grain size were evaluated at ambient temperature both prior to, and immediately following the elevated temperature nanoindentation experiments, to confirm that structural evolution was absent during testing (as expected based on the thermal stability studies in Ref. [15]). This series of experiments permitted extraction of the activation energy for flow.

For every data point presented in this paper, a minimum of 25 nominally identical indentation tests were used to calculate the average hardness, and the error bars we
present are reflective of the standard deviation of these measurements. It is also important to emphasize that valid hot nanoindentation measurements on nanocrystalline metals, such as described under the second series of experiments, specifically require a material that does not coarsen or undergo other structural changes. It is a unique feature of these Ni-W specimens that in the tested condition, they do not evolve at the temperatures we investigated [15], in stark contrast to all pure nanocrystalline metals and many other nanocrystalline alloys [17-19].

The major results of our experiments are presented in Table I and Figs. 2-4. Before discussing these, it is useful to establish a framework for the analysis. We consider a simple constitutive law for thermally-activated plastic flow, in which the shear strain rate, \( \dot{\gamma} \), follows an Arrhenius temperature dependence governed by the Gibbs activation energy for deformation, \( \Delta G \) [9]:

\[
\dot{\gamma} = \dot{\gamma}_o \exp\left(-\frac{\Delta G}{kT}\right)
\]

(1)

where \( \dot{\gamma}_o \) is a pre-exponential constant. The Gibbs activation energy can be expanded in terms of an effective stress, \( \tau_e \), apparent activation volume, \( V \), and Helmholtz free energy for deformation, \( \Delta F \) [6]:

\[
\Delta G = \Delta F - \tau_e \cdot V
\]

(2)

\( V \) represents the characteristic volume over which the effective stress acts to overcome local barriers to deformation:

\[
V = k \cdot T \left( \frac{\partial \ln(\dot{\gamma}/\dot{\gamma}_o)}{\partial \tau} \right)_T
\]

(3)
In addition to the form of Eq. (2), \( \Delta G \) can also be expanded as an enthalpy and entropy for deformation; it is often assumed that \( \Delta G \) is simply equal to the activation enthalpy for deformation, \( \Delta H \), which amounts to neglecting entropy. Conrad developed the following form for \( \Delta H \) for the case where there are no long-range internal stresses in the specimen [20]:

\[
\Delta H = -kT^2 \left( \frac{\partial \tau}{\partial T} \right)_\gamma \left( \frac{\partial \ln(\dot{\gamma}/\dot{\gamma}_0)}{\partial \gamma} \right)_T
\]  

(4)

In Eq. (4), the first bracketed term quantifies the temperature dependence of the yield stress at a constant strain rate, and is proportional to the slopes presented in Figure 3; hardness is converted to shear yield stress by dividing out the proportionality constant \( 3\sqrt{3} \). The second bracketed term describes the change in yield stress with strain rate at a constant temperature, which we relate to the activation volume given by Eq. (3), giving:

\[
\Delta H \approx -T_o V \left( \frac{\partial \tau}{\partial T} \right)_\gamma
\]  

(5)

where \( V \) is measured at a reference temperature \( T_o \). We note in passing that the temperature dependence of \( V \) characterizes the entropic effects inherent to \( \Delta F \). However, at low measurement temperatures, these contributions are small compared to \( \Delta H \) [7]. Accordingly, in this work \( V \) is quantified at room temperature, and the subsequent discussion correspondingly refers to the activation enthalpy for deformation at room temperature.

Our experiments on the rate-dependence of strength at room temperature yielded results typical of prior work in this vein on various nanocrystalline FCC metals [3, 5, 21-26]. In particular, hardness was found to increase with indentation strain rate, as captured by Eq. (3), and the slopes aligned well with our prior reports on similar Ni-W alloys from Refs. [3, 13]. For this reason, instead of presenting the raw data, we compile the extracted activation volumes for deformation in Table I. We also provide two normalizations, one
employing the cubed Burger’s vector, $b^3$, and one employing the atomic volume of the FCC Ni-W solid solution, $\Omega$. Both quantities are corrected for the lattice parameter shift with W addition [14]. The activation volume first decreases as grain size is reduced to 10-20 nm, then increases with further grain size refinement, rendering an inflection in $V$ in the vicinity of the Hall-Petch breakdown. This trend is also shown graphically in the upper panel of Fig. 4.

Whereas such measurements of rate sensitivity in nanocrystalline metals are relatively common, temperature-dependence is less frequently studied, and our hot nanoindentation experiments are the first of their kind on nanocrystalline Ni-W alloys. Typical load-displacement data for tests conducted at four different temperatures are shown in Figure 2 for the ~18 nm grain size Ni-W specimen. The curves shift to larger indentation depths with increasing test temperature, reflective of a drop in hardness as expected for a polycrystalline metal. However, the slope of this thermal softening is found to depend upon grain size, as shown in Figure 3.

In Table I and the lower panel of Fig. 4, the extracted values of the activation enthalpy based on Eq. (5) are plotted for the three samples tested at elevated temperatures. Table I also includes a normalization by the shear modulus and cubed Burger’s vector, which is a common form used in the study of dislocation dynamics. At the largest tested grain size of 80 nm, which is in the range of conventional Hall-Petch hardness scaling, the activation enthalpy of 1.8 eV agrees well with literature values for pure nanocrystalline Ni [6] of comparable grain size. A similar value (~1.6 eV) is found at the smallest grain size of 3 nm, which is very close to the amorphous limit and well beyond the Hall-Petch breakdown. At the intermediate grain size of 18 nm, near the nominal Hall-Petch inflection point, however, we find a significantly lower value of just 0.7 eV. These values of activation enthalpy thus appear to exhibit an inflection around the regime of the Hall-Petch breakdown (c.f. Fig. 4) in much the same way as the activation volume. In fact, the trend in $\Delta H$ is a direct consequence of the trend in $V$, which are proportional via Eq. (5); the actual temperature dependence of hardness is monotonic with grain size (cf. Fig. 3).
These measurements offer, we believe, the first experimental assessment of activation enthalpy across the Hall-Petch breakdown. Although we have tested only three grain sizes here, quantitative measurements such as these can shed additional light on the specific mechanisms that control strength in the finest nanocrystalline metals, especially over a range of grain sizes where the mechanisms are changing. For example, for our 80 nm grain size specimen, the values of $\Delta H/(\mu \cdot b^3) \approx 0.15$ and $V/b^3 \approx 34$ are decidedly below the typical range for forest dislocation interactions (0.2–1.0 [27] and 100–1000 [6, 7, 23], respectively). These lower activation enthalpies and volumes have been rationalized as being controlled by the heterogeneous nucleation of dislocations from grain boundary ledges, for which $\Delta H \approx 1–2$ eV and $V/b^3 \approx 1–50$ are expected [28-31].

As the grain size decreases, dislocation activity transitions from grain boundary emission of unit to partial dislocations [32, 33], which aligns very well with our measurements of activation enthalpy and volume reducing by about a factor of two as grain size drops from 80 to 18 nm. Finally, for sufficiently small grain sizes, the unit process of deformation has been proposed to transition to local shear transformations of a few atoms in the grain boundary regions [3, 34]. Such shear transformation zones are common in metallic glasses, with activation enthalpies greater than 1 eV (and up to about 5 eV in some cases), and activation volumes so large that they are difficult to measure ($>100 \text{ }\Omega$) [35]. Our observation that both $V$ and $\Delta H$ increase beyond the Hall-Petch breakdown is essentially consistent with the proposed transition to such a local shear transformation mechanism as the rate-limiter for plasticity in the finest nanocrystalline metals [3, 13, 34].

There are many additional complexities involved in inferring specific mechanistic details from these limited measurements. For example, it is important to remember that in the present Ni-W alloys, grain size is controlled via the W addition [14, 36]; changes in grain size are attended by changes in composition (cf. Table I). The role of grain size and composition is therefore convoluted in these data, along with tertiary properties affected by composition such as the stacking-fault energy [37] (which has a significant impact on dislocation emission at grain boundaries [32]). The role of the grain boundary relaxation
state is another significant complexity, which was touched upon in a prior paper from our group [15]. Whereas in the present work we use samples that are relaxed and stable, the role of grain boundary state on deformation mechanisms is apparently quite acute [38, 39].

In light of these complexities, we emphasize that the present work is intended as a first set of observations about the activation parameters for deformation across the Hall-Petch breakdown. Nevertheless, the values we have measured here are broadly in line with the proposed mechanistic transition from full dislocation emission, to partial dislocation emission, to grain-boundary confined shear transformation zones as the grain size reduces across the Hall-Petch breakdown.

Acknowledgements

This work was supported by the US Army Research Office, through the Institute for Soldier Nanotechnologies at MIT, and through contract No. DAAD19-03-1-0235.
Tables

Table 1: Grain size (±25% as measured by XRD), composition (±1 at%) and measured activation parameters for the experimental specimens. For three of the samples hot nanoindentation testing was used to assess the activation energy. Activation volume is normalized by both the cubed Burger’s vector and by the atomic volume. A normalized activation energy (by the shear modulus and cubed Burger’s vector) is also included.

<table>
<thead>
<tr>
<th>Grain Size (nm)</th>
<th>Composition (at% W)</th>
<th>Activation Volume $V/b^3$</th>
<th>$V/\Omega$</th>
<th>Activation Enthalpy $\Delta H/(\mu\cdot b^3)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>3.9</td>
<td>1.65</td>
<td>33.8</td>
<td>1.8</td>
</tr>
<tr>
<td>18</td>
<td>15.2</td>
<td>0.51</td>
<td>14.1</td>
<td>0.7</td>
</tr>
<tr>
<td>10</td>
<td>16.7</td>
<td>0.30</td>
<td>19.0</td>
<td>27.5</td>
</tr>
<tr>
<td>6</td>
<td>19.1</td>
<td>0.22</td>
<td>32.3</td>
<td>46.6</td>
</tr>
<tr>
<td>3</td>
<td>26.6</td>
<td>0.53</td>
<td>105.5</td>
<td>151.0</td>
</tr>
</tbody>
</table>

References

Figure captions

Figure 1: Transmission electron micrographs of two of the nanocrystalline Ni-W alloys used in hot nanoindentation testing. Nominal grain sizes of (a) 80, (b) 18 were assessed by x-ray diffraction, which agree well with the present observations.

Figure 2: Representative nanoindentation load-displacement curves for an 18 nm grain size specimen at four various test temperatures. As the test temperature is raised, the indentation depth increases for the same applied maximum load, indicating that the material softens with temperature.

Figure 3: Measured values of hardness as a function of temperature for three nanocrystalline grain size specimens; error bars on hardness are smaller than the data points themselves, the standard deviation for each point being less than ±0.18 GPa.

Figure 4: Activation enthalpy and volume as a function of grain size for nanocrystalline Ni-W alloys. A minimum is observed in both properties at a grain size of ~10-20 nm. The vertical dashed line denotes the approximate grain size where the hardness scaling exhibits an inflection from classical Hall-Petch (H-P) behavior to a Hall-Petch breakdown regime, as described in Refs.[3, 13].