SIZE MATTERS

Mechanical Properties of Nano-sized Single Crystals

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But really it’s the work of graduate student A.T. Jennings and post-doc Ju-Young Kim

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In nanocrystals (quantum dots, nanowires, nanotubes, etc.) size modification tunes a variety of properties: optical, electronic, plasmonic, thermal, acoustic, etc. which brings into question material structural integrity.
Background: Nanoindentation

Disadvantages: Strain gradients, complex stress-strain calculations, limited plasticity information
Advantages: Elastic properties, hardness, deformation volume control

Great need for experimental techniques testing mechanical deformation at nano-scale without strain gradients!
Nanoindenter Agilent G200

- Flat punch indenter tip
- Constant displacement rate

Nano-pillar fabrication: Mainly Focused Ion Beam (FIB)

Load-Displacement Data

- Diameter: 100 ~ 900 nm

Image after compression
In-situ tension and compression SEM: SEM with Nanoindenter.

Single Crystal Au

Tension-compression grips 500 nm

Nanocrystalline Ni

Single crystal Cu
Nano-pillar Fabrication Methods

Focused Ion Beam

- Nanocrystalline Ni-4% W nano-pillar
- 100nm metallic glass nano-pillar
- Single crystalline Au tensile nano-pillar
- Single crystalline Mo anti-pillar

FIB-less

- Cu nano-pillar with twin boundaries
- Single crystalline Cu tensile pillar
FIB-less fabrication: E-beam Litho => Electroplating

1. E-beam patterning
2. Electroplating
3. Pillars in PMMA Matrix
4. Free-standing pillar array
Nanotwinned Cu bi-crystalline and twinned FIB-less Cu pillar

Nanocrystalline Au single crystalline pillars for tension and compression testing

"Nano candy canes": Cu with occasional twin boundaries


Microstructure Control through Novel Synthesis
Single Crystals: Ubiquitous Size Effect

Dislocation Nucleation-controlled plasticity

\[ \sigma_f \propto D^{-n} \]
“Smaller is Stronger” and Strain Bursts

Pre-deformation

Size effects with stochastic stress-strain signature and size effects are identical to FIB-fabricated pillars.

Post-deformation
Dislocation starvation and nucleation: source-controlled plasticity

In a nano-pillar (deeply in sub-micron regime) with non-zero initial dislocation density.

Force

Under compression dislocations leave the crystal faster than they multiply.

New dislocations have to be nucleated WHERE?

Coined hardening by dislocation starvation, occurs only in small volumes and not in bulk crystals.

Insights into Deformation mechanisms: TEM

How do we TEM the same nano-pillars before and after deformation???

We test them directly on TEM grid!
Single Crystalline (FIB-less) Pillars are NOT dislocation-free

Dislocation Density:

$$\rho = \frac{L}{\pi R^2 h}$$

$$\rho = 1.46 \times 10^{14} \text{ m}^{-2}$$

Relatively high!

**BUT** important to recognize: the lowest attainable non-zero dislocation density is $1 \times 10^{12} \text{ m}^{-2}$

(corrresponds to a 7-atom loop in 121nm x 188 nm cylindrical volume)

Dislocation Nucleation Sources

FRANK-READ Source
(a.k.a. conventional)
($\Omega \sim 100-1000b^3$)

"Truncated" or
SINGLE ARM Source
(micron-sized pillars)
($\Omega \sim 50-500b^3$)

SURFACE Source
($\Omega \sim 1-10b^3$)

Activation volume can be experimentally determined by varying strain rate:

$$\Omega_{\text{SAS}} = \frac{\Omega_{F-R}}{2}$$

Parthasarathy et al. Scripta Mat (2007)
Weinberger et al. Scripta Mat (2010)

Dislocation Nucleation Sources

Single-arm source

(SAS TEM movie courtesy M. Legros)

Surface source

MD movie courtesy of C. Weinberger

(SS TEM movie courtesy J. Huang)

Surface vs. Single-Arm Sources

Deviation from Power-Law
Small Pillars & Slow Strain Rates

\[
\sigma = \sigma_{\text{ath}} - \frac{k_B T}{\Omega} \ln \frac{k_B T N \nu_0}{E \dot{\varepsilon} \Omega}
\]


Atomistics of Dislocation Motion in Pillars: Molecular Dynamics Simulations

18nm-diameter Au pillar
Constant load = 500 MPa

24nm-diameter Mo pillar
Constant Load = 9 GPa

Mechanical Properties of [001] bcc nano-pillars

1. Stress-strain signature is stochastic, with intermittent strain bursts
2. Power-law size effects present in bcc nano-structures
3. Tension-Compression asymmetry is present and is more pronounced in samples with larger diameters than smaller ones

Overcoming Peierls potential is KEY in BCC Plasticity

- Dislocations propagate by kink-pair nucleation
- Must overcome Peierls potential → requires high stresses or T
- Screw dislocations are much slower than edge dislocations → dominate deformation below T_c

Origins of Different Size Effects

Critical temperature (K)
- W: 760
- Mo: 472
- Ta: 440
- Nb: 290

Movie courtesy: S. Roberts

1. **Intrinsic effect of BCC structure**
   - Shear stresses in positive and negative ⟨111⟩ are not equivalent (except on {110} planes)
   - Twinning vs. Anti-twinning on {112} planes (not mirror)

2. **Extrinsic effect of BCC structure**
   - Non-planar screw dislocation cores
   - Non-Schmid behavior: Importance of shear stress components perpendicular to slip direction:
     “+” for tension \( \tau_p \downarrow \rightarrow \text{CRSS} \downarrow 
     “-” for compression \( \tau_p \uparrow \rightarrow \text{CRSS} \uparrow 

Effects of Crystallographic Orientation: [001] vs. [011]

Effect of Orientation: [001] vs. [011]

Tension-compression asymmetry is more pronounced in flow stress (rather than in yield strength) and in samples with larger diameters (rather than smaller ones).

Screw dislocations appear to play a more important role in flow stress (rather than yield stress) and in larger (rather than smaller) pillars.

Opposite $\chi$ for \{1 1 2\} and \{2 1 1\} planes => diametrically opposite twinning-antitwinning slip

- \{001\} orientation: \{1 1 2\} shears in the twinning sense => Compression $>$ Tension
- \{011\} orientation: \{2 1 1\} shears in the antitwinning sense => Tension $>$ Compression

Compression $>$ Tension for [100] Mo while Tension $>$ Compression for [110] Mo

Deformation Mechanisms and Size Effects

Plasticity carriers: Dislocations

Low and Trial, *Acta Met.* (1962) Fe-3% Si

Single Crystals (Au, Mo, Nb, etc.)

Plasticity carriers: Dislocations + grain/twin boundaries

{h₁,k₁,l₁} {h₂,k₂,l₂}

Bi-Crystals (Al)

See poster by A. Kunz (Room 31B)

Nanocrystalline Metals (Ni)

Nano-twinned Metals (Cu)

Metallic glasses

See talk by D. Jang on Thursday at 2pm (Bulk Metallic Glasses VIII)

Some of the final bulk metallic glass material

Amorphous/Nanocrystalline Nanolaminates

See talk by J.-Y. Kim on Thursday at 2:20pm (1-D Mechanics)

Increasing disorder (introducing boundaries and amorphous-ness)
Summary and Acknowledgements

• Single crystalline Cu (fcc) nano-pillars fabricated without FIB yet with similar dislocation densities exhibit an identical size effect and stochastic intermittent flow as FIB-produced ones.

• Dislocation starvation followed by surface source nucleation likely dominates plasticity at sizes below ~125nm.

• Dislocation multiplication through single-arm source operation likely governs plasticity in pillars above ~125nm diameters.

• Single crystalline Cu nano-pillars exhibit significant strain rate sensitivity at very small sizes, possibly corresponding to activation of surface sources.

• Body-centered (bcc) nano-pillars also exhibit stochastic behavior, but much more complex size effects and tension-compression asymmetry.

Helpful discussions:
C. Weinberger (Sandia NL)
J. Li (U Penn)

For details/publications: http://jrgreer.caltech.edu/
Introducing multiple boundaries

Single Crystals

Nano-twinned

Nanocrystalline

Nanocrystalline + Nano-twinned

Jang, D, Cai, W., Greer, J.R. Nano Letters (in press, 2011)
Stress vs. strain for each microstructure (D=500nm)

- **Single crystalline**:
  - d=162 nm (grain size)

- **Nano-twinned**:
  - d=8.8 nm (twin spacing)

- **Nanocrystalline**:
  - d=250 nm (grain size)

- **Nanocrystalline/Nano-twinned**:
  - d=6.7 nm (twin spacing)

Jang, D., Cai, W., Greer, J.R. *Nano Letters* (in press, 2011)
Introducing twin boundaries increases strength
Introducing grain boundaries decreases strength

Jang, D, Cai, W., Greer, J.R. Nano Letters (in press, 2011)
Transition to surface source operation may be manifested as deviation from the "athermal" size effect

\[
\sigma = \sigma_0 \dot{\varepsilon}^m
\]

\[
\Omega = k_B T \frac{\partial \ln(\dot{\gamma})}{\partial \tau}
\]

\[
\tau = M \sigma
\]

\[
\dot{\gamma} = M \dot{\varepsilon}
\]

Jennings, A.T., Li, J., Greer, J.R. (submitted, 2011)
Activation Volume for a Single-Arm Source

1/2 of Frank-Read Source:
\[ Q_{SAS} = \frac{1}{2} Q_{FRS}, \quad \Omega_{SAS} = \frac{1}{2} \Omega_{FRS} \]

Activation Volume (\( \Omega \))

\[ \Omega \left( \tau_{athermal} \right) \propto \tau_{athermal}^{-5/3} \]

\[ \frac{\tau_{athermal} - \tau}{\tau_{athermal}} \ll 1 \]

\[ \tau_{athermal} \propto D^{-n} \]

\[ f(\theta) \propto r_0^{-1/3} \]

\[ \Omega_{FR} \propto r_0^{5/3} \]

**References**

Nabarro (1989)
Shemenski (1965)
Estrin et al (2007)
Zhu et al (2010)

Jennings, A.T., Li, J., Greer, J.R. (submitted, 2011)
Moving onto BCC metals: Post-testing morphology

Pronounced shearing-off in tension

Crystallographic slip in compression


TEM Sample Preparation: Phase 1

1. Bring Micromanipulator almost in contact with lamella

2. Attach lamella with Pt bond

3. Severe connection, detach lamella

4. Lift-out lamella

Lamella fabricated for Lift-out

500nm Pt cap

Pt bond

Pillar underneath

Micromanipulator

Pt needle inserted
TEM Sample Preparation: Phase 2

1. Bring in TEM grid

Pt Needle

TEM grid

Cross-section of lamella after some initial thinning

Before the needle
Complex dislocation networks formed in Nb and Mo after compression

⇒ Partial dislocations generated on \{110\}, \{112\}, and \{123\} planes in Nb

⇒ Dislocation segments are straight (rather than wavy) in Nb implying rare cross-slip

⇒ Dislocation density increases in Nb and Mo after compression

Kim, J.-Y., Jang, D., Greer, J.R. *Scripta Mater.* 61, 3 (2009).  TEM images by Dongchan Jang