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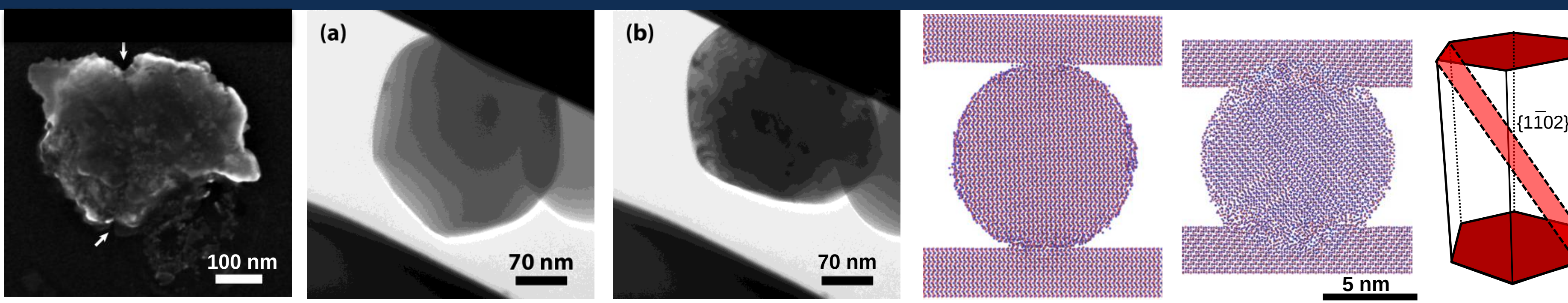

Room Temperature Deformation Mechanisms of Alumina Particles Observed from *in situ* Micro-compression and Atomistic Simulations

<u>Pylin Sarobol</u>, Michael Chandross, Jay D. Carroll, William M. Mook, Daniel C. Bufford, Brad L. Boyce, Paul G. Kotula, Bonnie B. McKenzie, Khalid Hattar, and Aaron C. Hall

International Thermal Spray Conference. May 11, 2015. Long Beach, CA

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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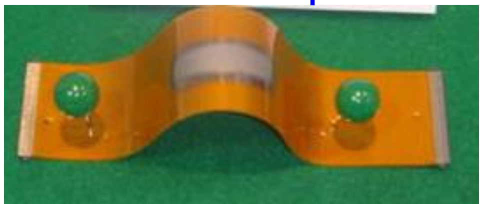
Building Block for Aerosol Deposited Coatings

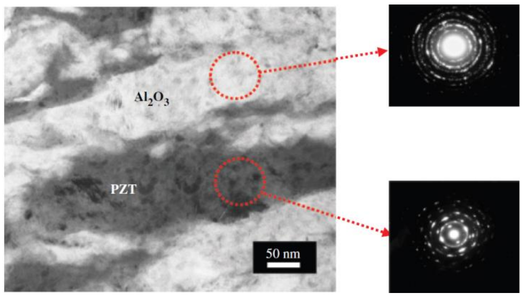
Aerosol Deposition (AD) enables materials integration.

- AD process at room temperature (RT) in vacuum
  - sub-micron particles accelerated to high velocity by pressurized gas, impacted, consolidated to form a film.
- Similar AD ceramic film microstructures
  - sub-micron particles undergo *plastic deformation*
  - break up into *small crystallites* (20-75 nm)[1-3]
  - planar *defects* and *amorphous regions*[4].

Solid-state Deposition



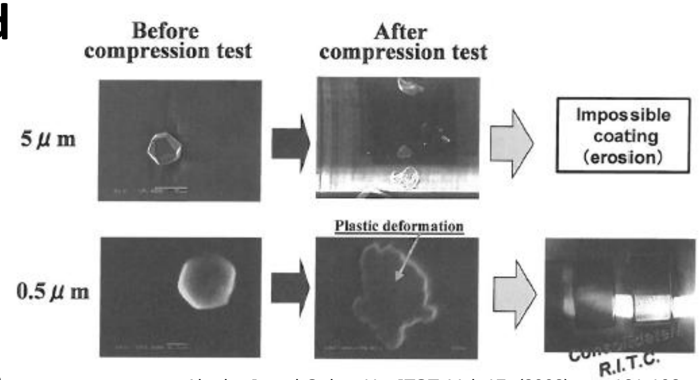
AD Flexible electronics from J. Akedo. *JTTEE5.*, 2007:17:181



Images from J. Akedo. *J. Am. Ceram. Soc.*, 2006:89:1834

Particle deformation/bonding not well understood

- Common deformation mechanisms exist.
- Examine sub-micron ceramic particles RT deformation as a building block for AD coatings.
- Particle compression experiments via molecular dynamic (MD) simulations & *in situ* compression



Akedo, J. and Ogiso, H., *JTST*, Vol. 17, (2008), pp. 181-198.

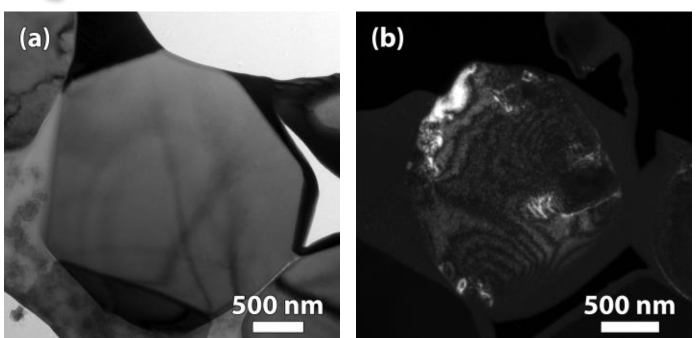
[1] Akedo, J. and Ogiso, H., *JTST*, Vol. 17, (2008), pp. 181-198.
[2] Akedo, J., *JTTEE5*, Vol. 17, (2007), pp. 181-198.
[3] Akedo, J. *J. Am. Ceram. Soc.*, Vol. 89, (2006), pp. 1834-1839.
[4] Park, H. *et al*. Scripta Materialia, 2015.

Ceramic Particle RT Deformation - Alumina

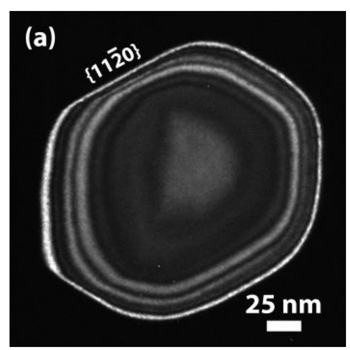
- Deformation behavior influenced by *number of internal defects*, temperature, crystal orientation/size. Numbers of pre-existing (immobile) defect scale with size.
- In situ SEM/TEM micro-compression and Molecular Dynamics Simulations

Proposed

	Micron	Sub-micron	Single Crystal Nano	Bicrystal Nano
# Pre-existing Defects	High	Moderate	None	Grain Boundary
Energy Density Input	Low	Moderate	High	Low
Governing Mechanism(s)	Fracture	Plasticity + Fracture	Plasticity	Fracture
Response to Compression	Crack initiation & Propagation	Dislocation nucleation, slip, crack initiation & propagation	Dislocation nucleation, Slip	Crack initiation & propagation
Compression Testing	SEM	SEM and TEM	MD Simulation	MD Simulation

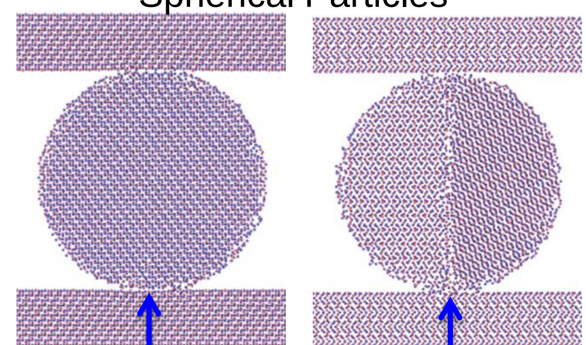


3.0µm Highly Defective



0.3µm Nearly Defect Free

Spherical Particles



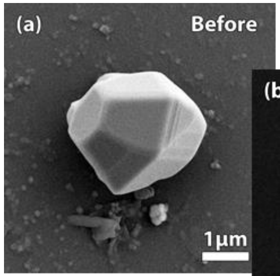
10 nm Defect Free

10 nm with a GB

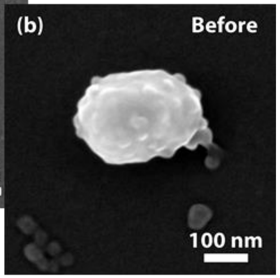
Alumina Particle Compression

In Situ Micro-Compression[5] – 0.3 µm & 3.0 µm particles

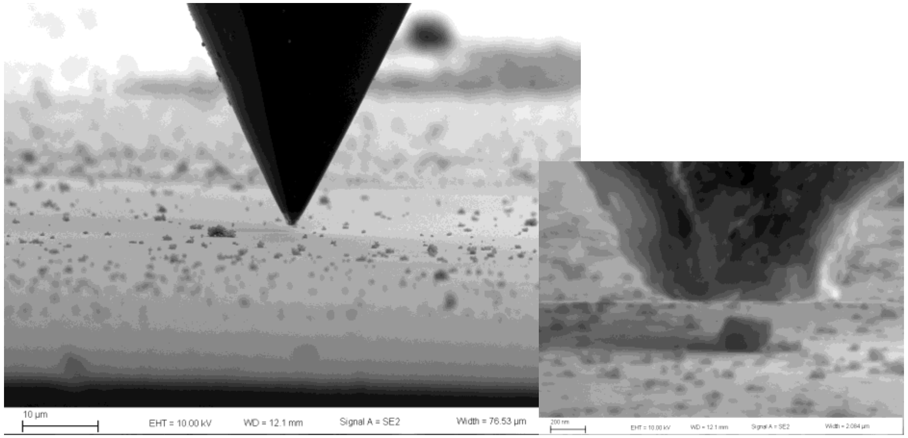
- Single crystal, ultra pure 0.3µm & 3µm, α-Al_2O_3 particles.
- A Hysitron PI85 SEM Picoindenter[6] and the SEM at 5.0 kV were used. Compression done in a ***displacement control*** mode.
  - 0.3 µm particles → 3 µm Ø flat punch tip, **15 nm/s** displl rate.
  - 3.0 µm particles → 6 µm Ø flat punch tip, **8 nm/s** displ rate.
- A Hysitron PI95 TEM Picoindenter with a 1 µm diameter flat punch tip and the a JEOL 2100 LaB_6 TEM[7] at 200 kV were used. Compression done in ***open loop*** mode with the loading rate of 10 µN/s (approx. **< 2 nm/s** displ rate).



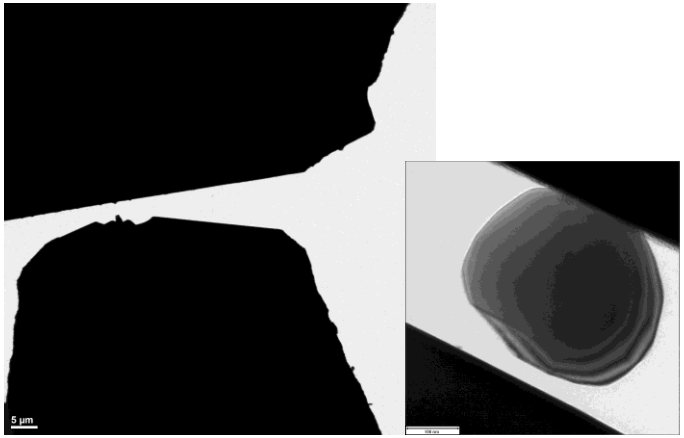
3.0 µm Particle



0.3 µm Particle



In situ SEM micro-compression on 0.3µm particle

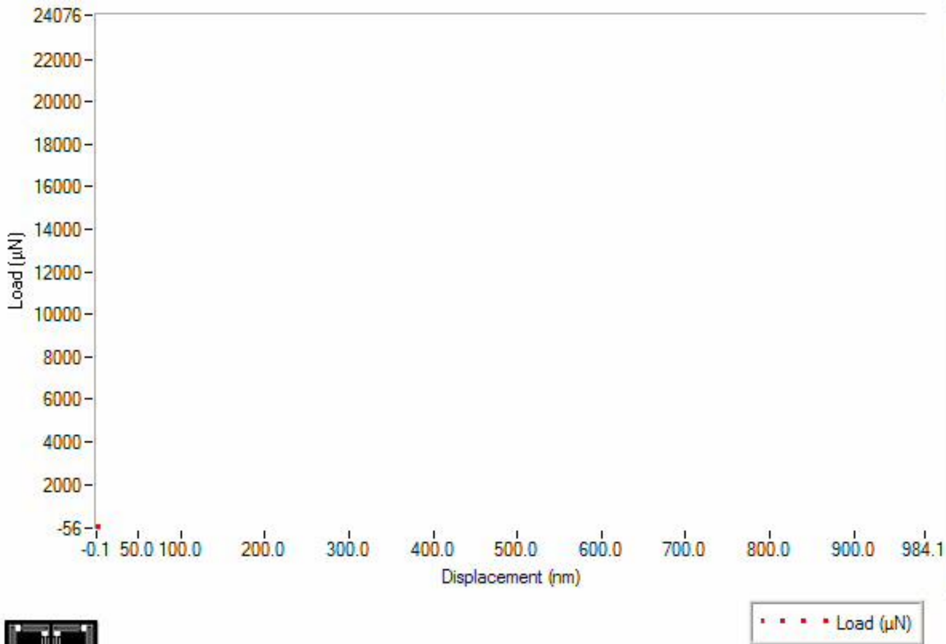


In situ TEM micro-compression on 0.3µm particle

[5] Sarobol, P., *et al.*, *SAND2014-18127*, (2014).
[6] Hysitron I (2013) SEM Picoindenter User Manual. Revision 9.3.0913 edn.
[7] Hattar, K., et al., Nuclear Instruments and Methods in Physics Research B. Vol. 338, (2014), pp. 56–65.

In Situ SEM micro-compression – 3.0 µm

Displacement control, Strain rate ~ 0.003 s^{-1}



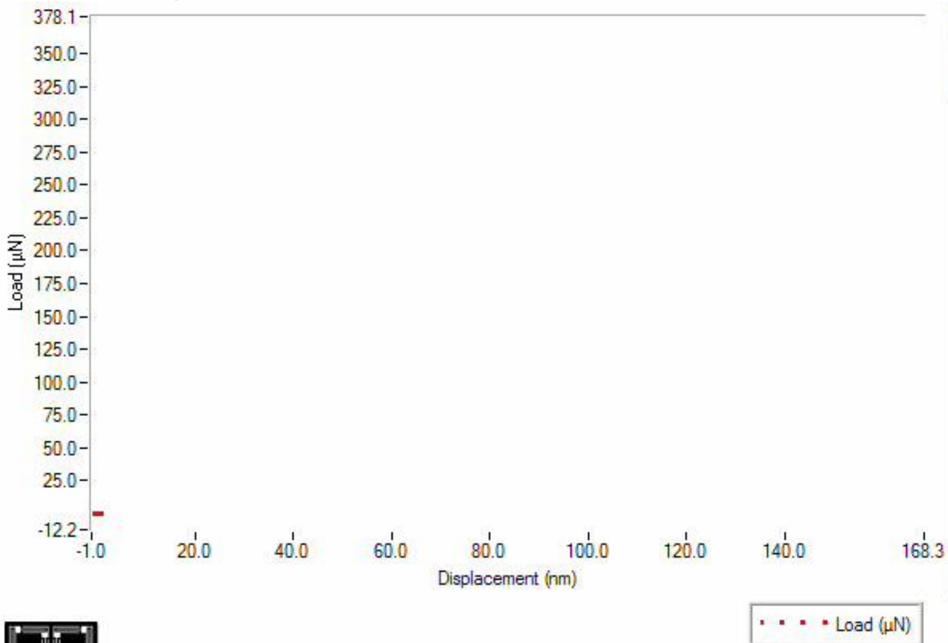
HYSITRON™

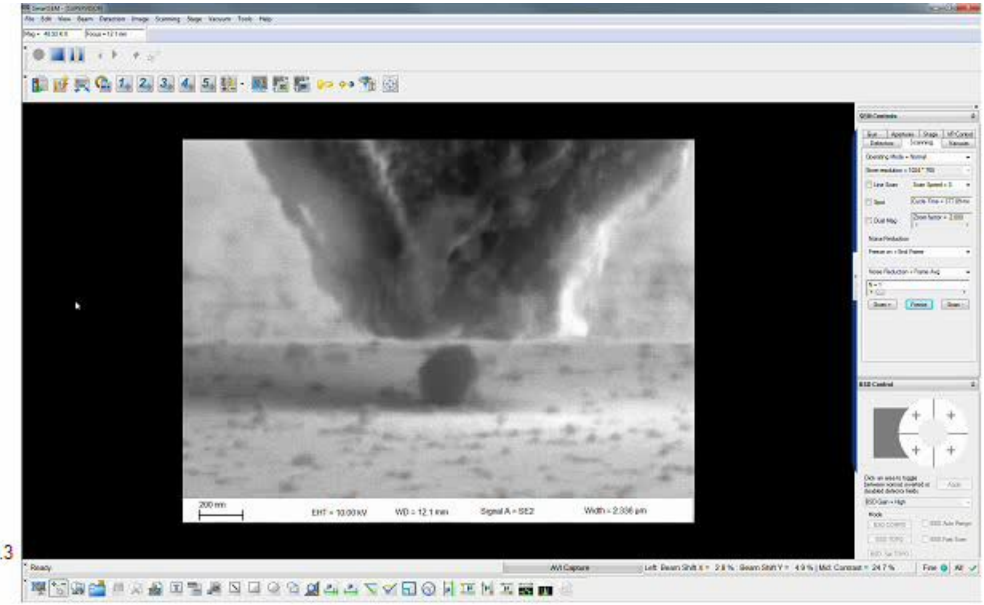
- Compressed 4 particles
- No observable shape change prior to fracture and fragmentation
- Displacement excursion corresponded to a fast fracture event
- Strain Energy Density before Fracture ~203 MJ/m^3
- Strain at fracture ~7%

Tip could not keep up with large displacement gained during fracture.

In Situ SEM micro-compression – 0.3 µm

Displacement control, Strain rate ~ 0.05 s^{-1}

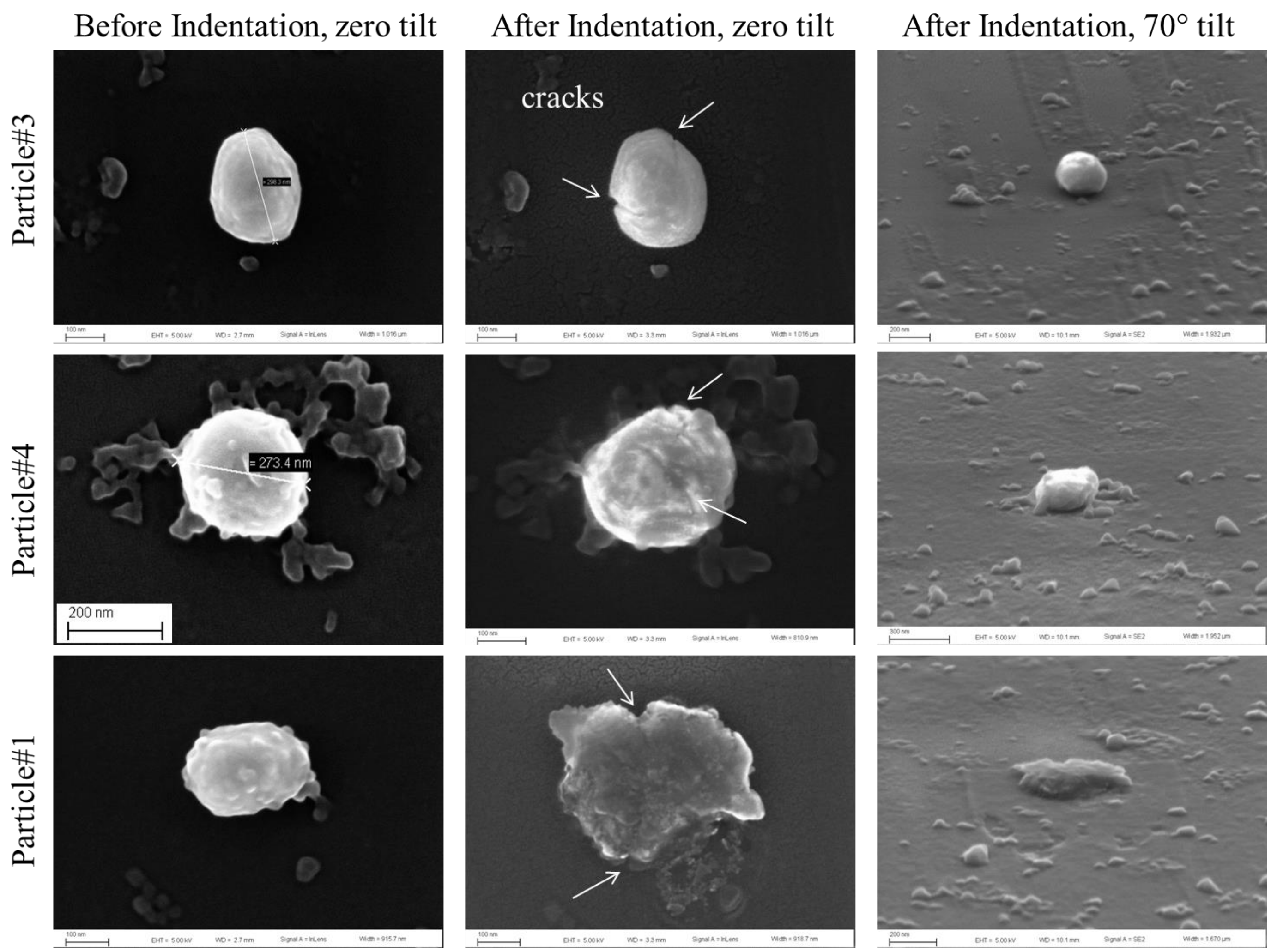




- Compressed 4 particles
- Significant plastic deformation/ shape change and stayed intact
- Displacement excursion corresponded to??? *Ex situ* observation
- Strain Energy Density before displacement excursion ~675 MJ/m^3
- Strain at displacement excursion ~16%

Tip could not keep up with large displacement gained during fracture.

Ex Situ SEM observation – 0.3 µm



~307 µN Max load

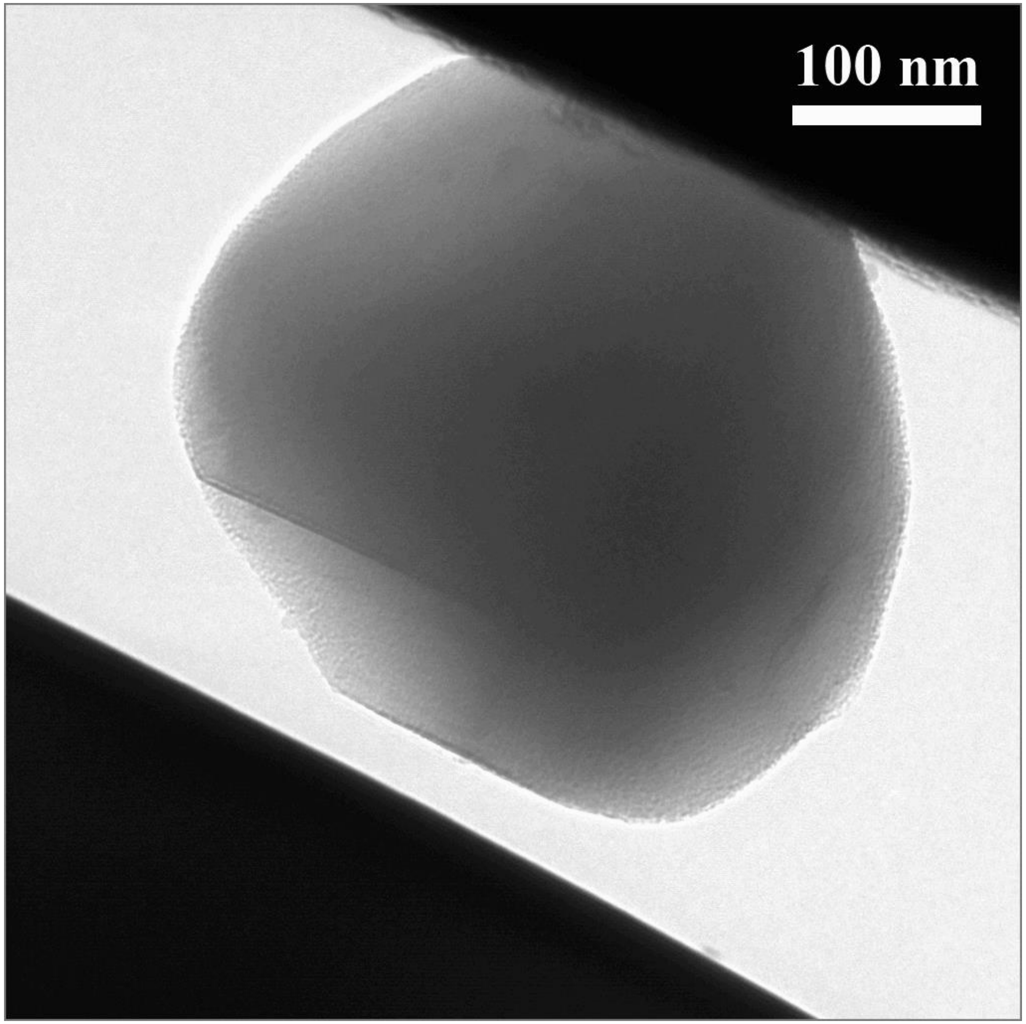
~420 µN Max load

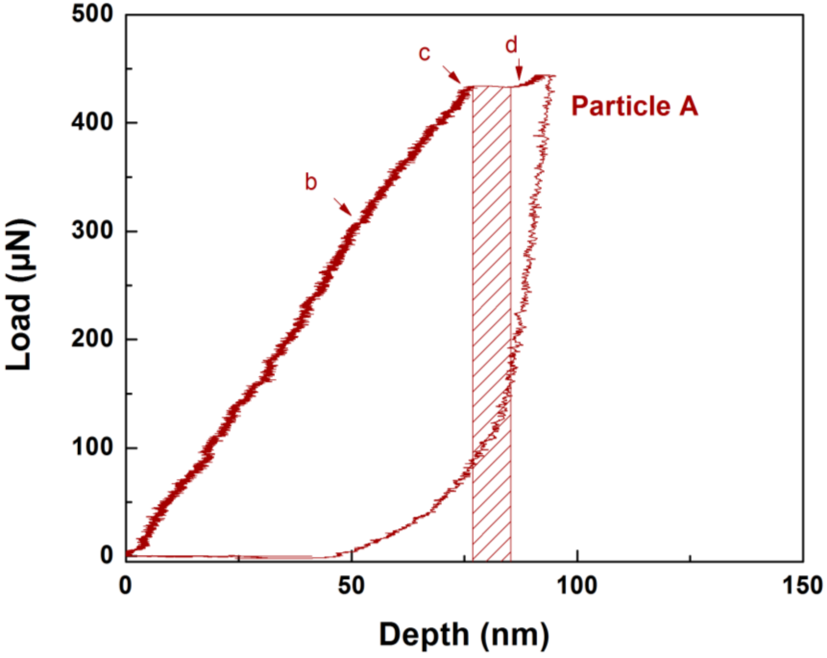
Extreme Loading

Different deformation behavior and load at first fracture may differ from particle-to-particle due to orientation differences and different pre-existing defect densities. However, overall, the sub-micron sized alumina particles exhibited significant plastic deformation before fracture.

In Situ TEM micro-compression – 0.3 µm

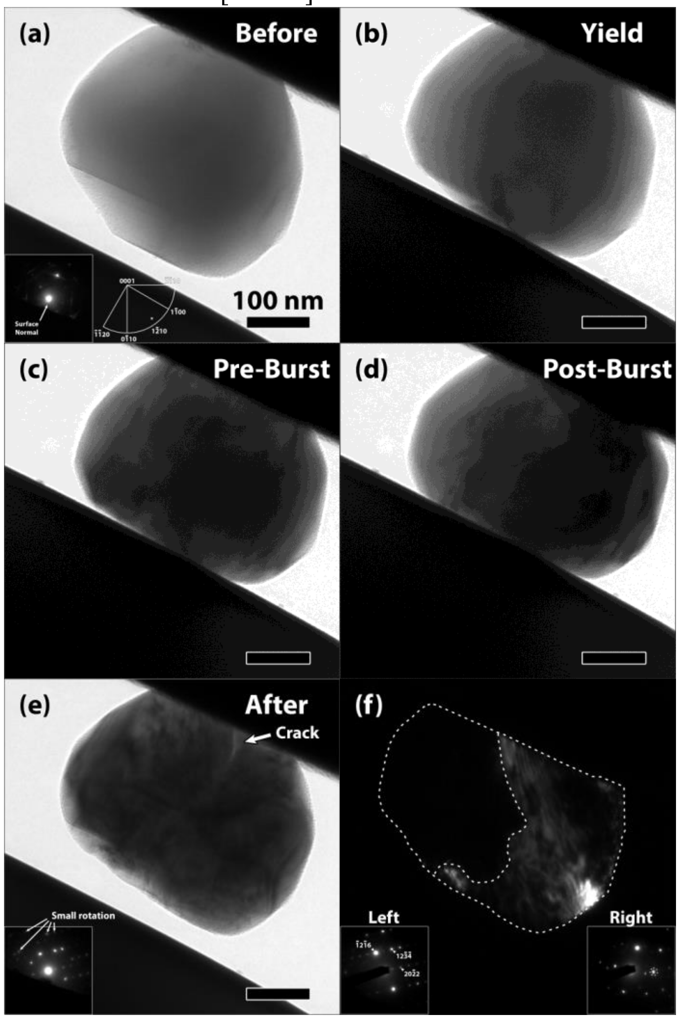
Diameter ~ 0.38 µm, Open loop, Strain rate ~0.005 s^{-1}





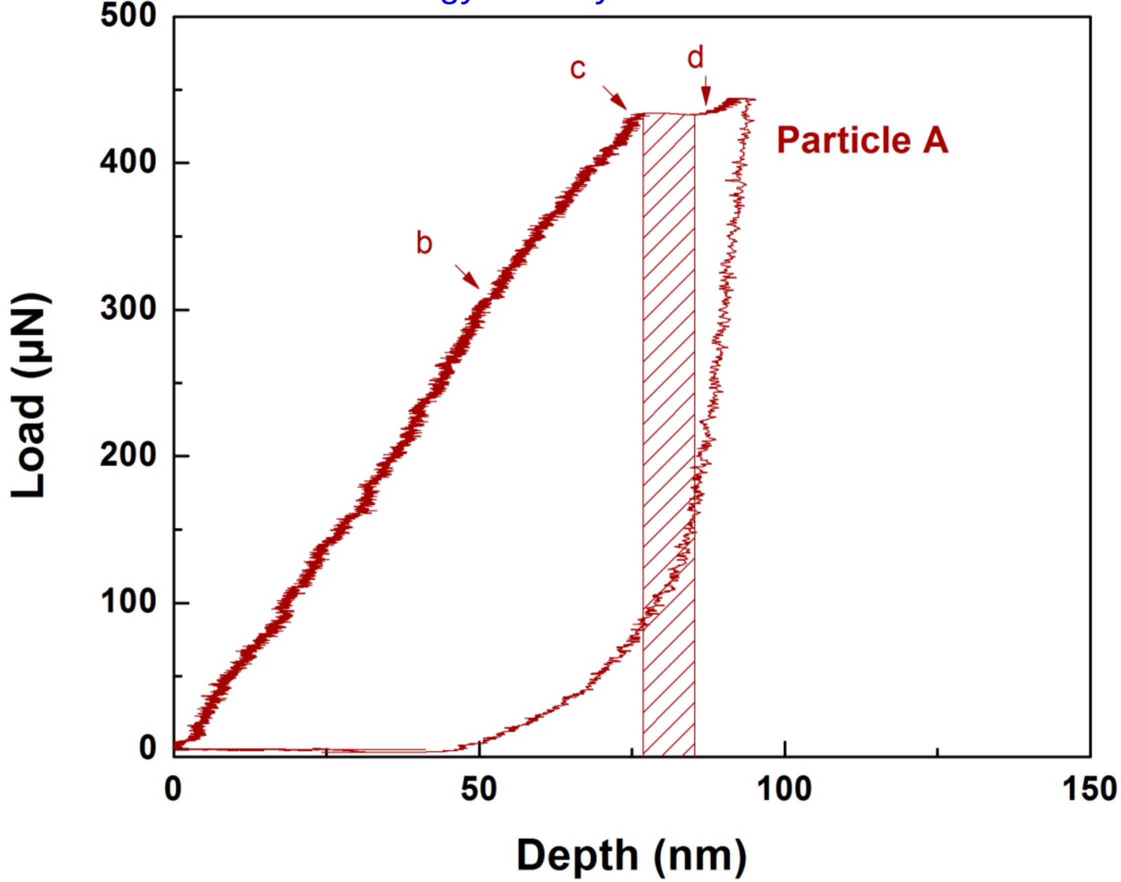
In Situ TEM micro-compression – 0.3 μm

Zone axis near [$\bar{2}$ 5 $\bar{3}$ 2]



Two halves related by slight rotation, both near [$\bar{1}$ 2 1 6] zone axis

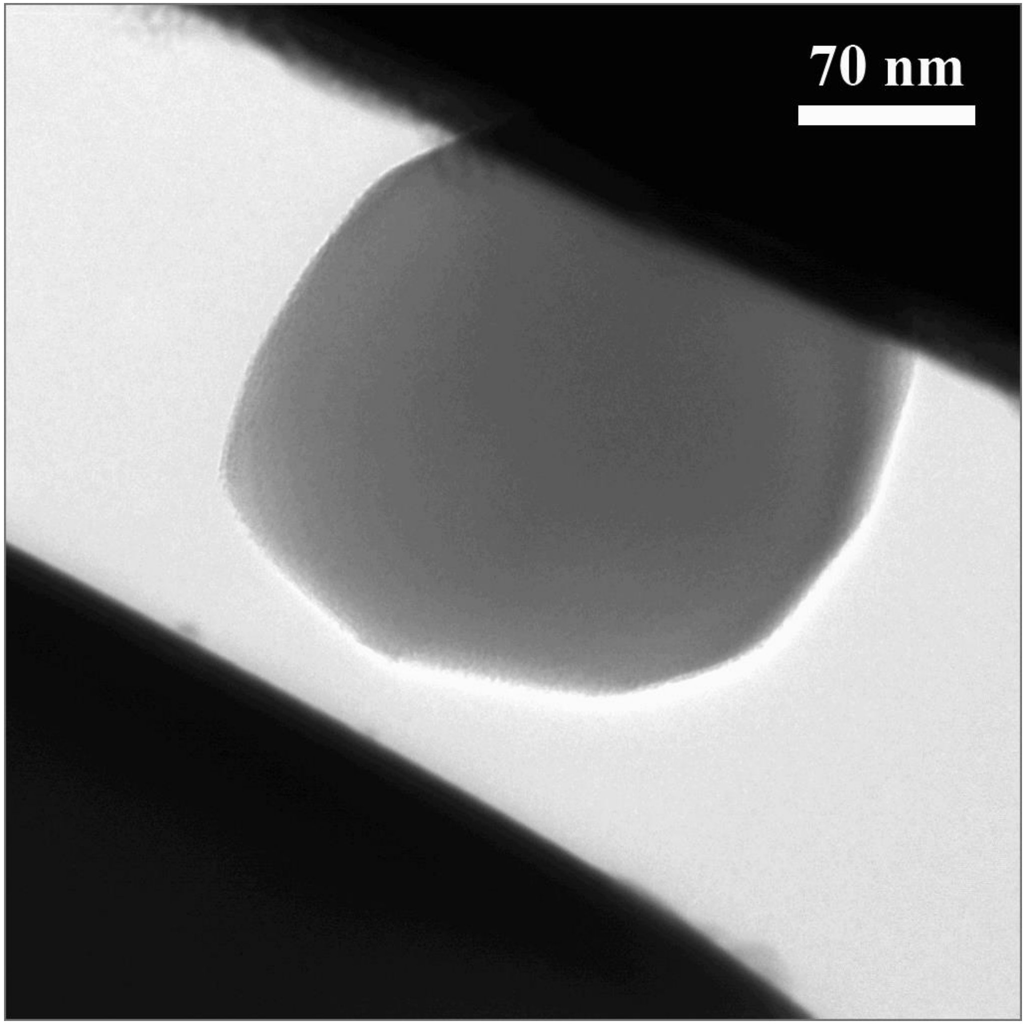
- Stored Energy Density Before Fracture = 573 MJ/m^3

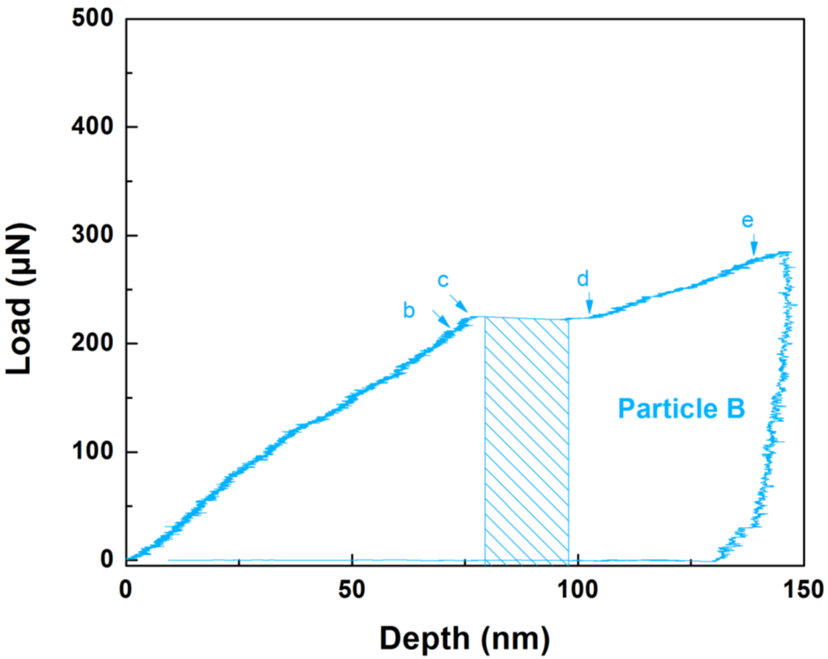


- Pre-burst plasticity: large regime with **high dislocation activity** (nucleation and moving through particle).
- **Crack nucleation and propagation** leading to through-particle fracture.

In Situ TEM micro-compression – 0.3 µm

Diameter ~ 0.24 µm, Open loop, Strain rate ~ 0.009 s^{-1}





In Situ TEM micro-compression – 0.3 µm

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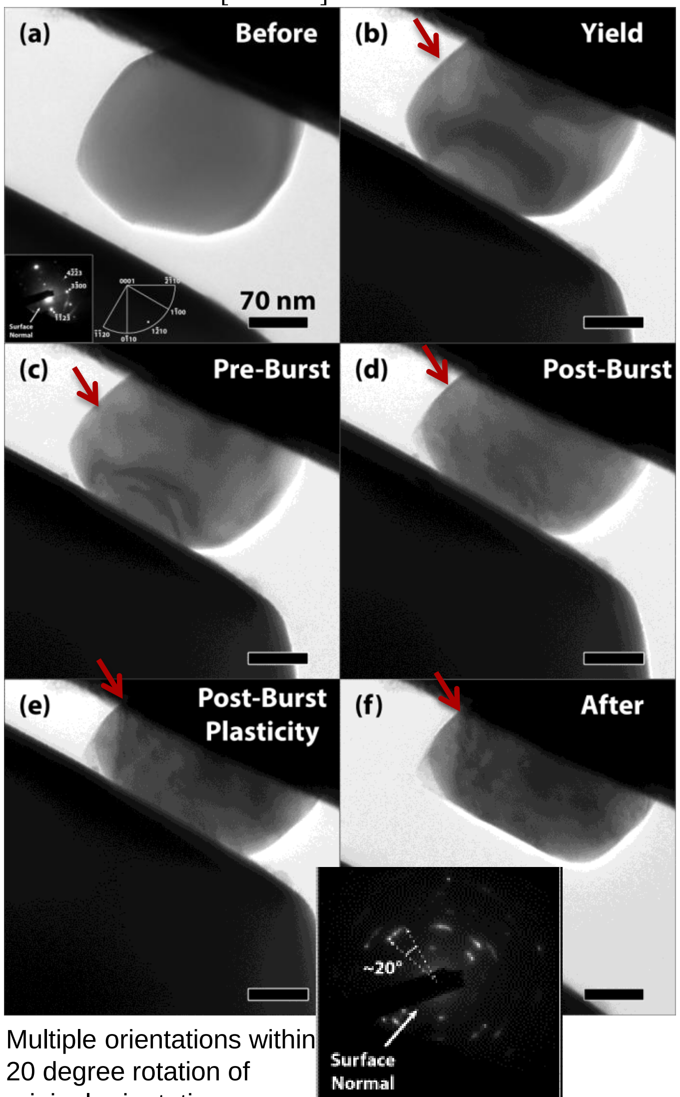
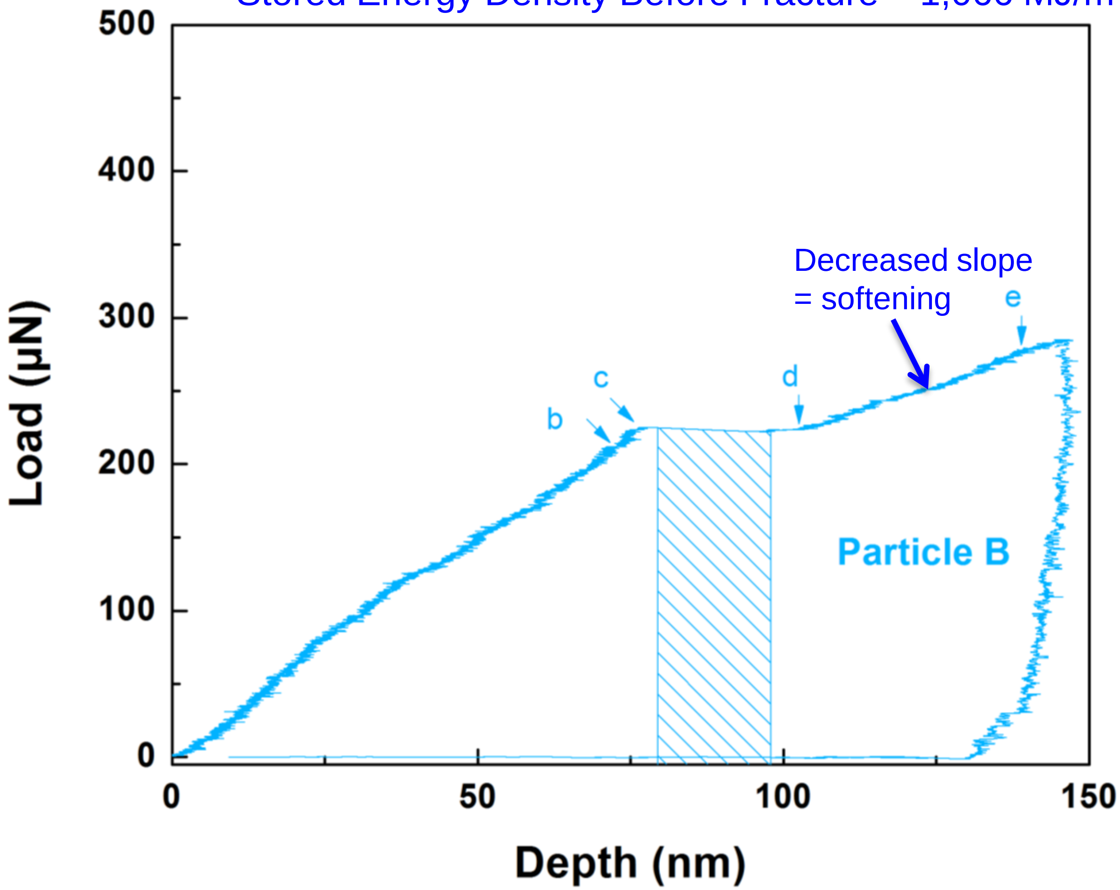
Zone axis near $[\bar{9}\,\bar{9}\,18\,6]$



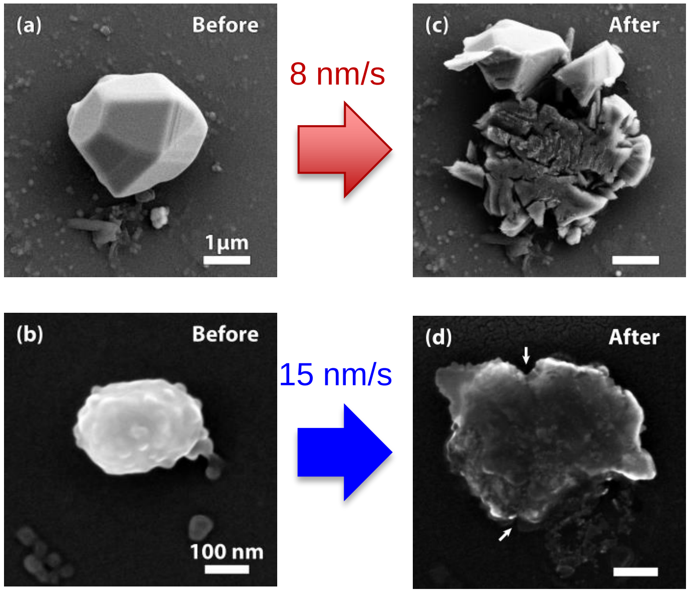
Multiple orientations within 20 degree rotation of original orientation.

- Stored Energy Density Before Fracture = 1,066 MJ/m^3



- Pre-burst plasticity: small regime with low dislocation activity.
- **Coordinated shear deformation**.
- Post-burst plasticity: high dislocation activities, change in deformation mechanism as indicated by lower slope.
- **Polycrystalline** with orientations spread within 20 degree rotation.

Micro-compression Summary



Particle Identifier	Diameter (μm)	Nominal Strain Rate (s^{-1})	Strain Energy Density Before Displacement Excursion (MJ/m^3)	Strain at displacement excursion (%)
Large Particles				
SEM-LP1	2.9	0.03	47	5
SEM-LP2	2.6	0.006	106	5
SEM-LP4	2.9	0.005	70	5
SEM-LP5	2.9	0.003	203	7
Avg Large Particles	**2.8**	-	**106±69**	**5.5 ± 1**
Small Particles				
SEM-SP2	0.17	0.09	494	11
SEM-SP3	0.29	0.05	366	12
SEM-SP4	0.28	0.05	607	13
SEM-SP5	0.29	0.05	675	16
*TEM-SA2	0.38	*0.005	573	32
*TEM-SB1	0.24	*0.009	1066	27
Avg Small Particles	**0.26**	-	**630±238**	**18 ± 9**

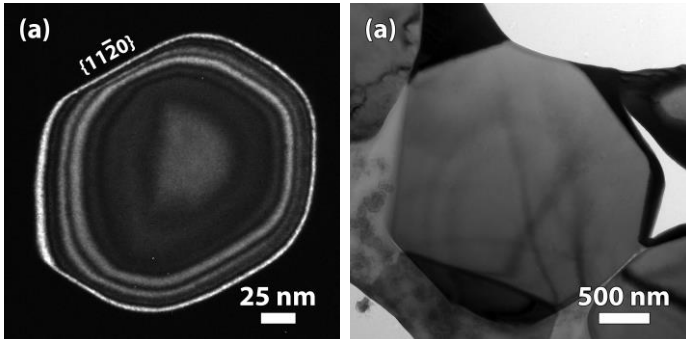
	Micron	Sub-micron
# Pre-existing Defects	High	Moderate
Energy Density Input	Low	Moderate
Governing Mechanism(s)	Fracture	Plasticity + Fracture
Response to Compression	Crack initiation & Propagation	Dislocation nucleation, slip, crack initiation & propagation

- Micron sized particles - brittle fracture
- Sub-micron sized particles - substantial plastic deformation before fracture and/or coordinated shear deformation.
  - **6x** higher strain energy density input
    - dislocation nucleation
  - **3x** higher accumulated strain
  - In some cases, became polycrystalline.

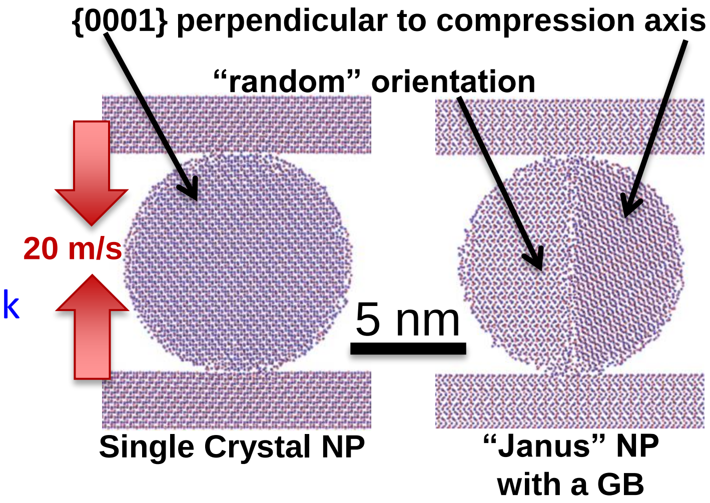
Simulated Particle Compression

MD Simulations – 10 nm nanoparticles (NPs)

- Infeasible (long computing time) to simulate size >0.05µm
- TEM examination showed that 'smaller' particles (0.3µm) are nearly defect-free, and 'larger' particles (3.0µm) contain immobile defects.
- Circumvented the size limitation of our models by simulating similar sized (10 nm) nanoparticles (NPs) that were either single crystal or contained an internal grain boundary (GB) as an initial immobile defect.
- Hypothesis: Pre-existing defects influence behaviors
  - The defect-free single crystal NP will require higher energy density input to nucleate and glide dislocations.
  - The NP with a grain boundary (GB) as immobile defect will require less energy density input for crack initiation at the GB.
- A force-field for ceramics, developed by Garofalini[8].
- NPs were compressed (by ~1/3 of the initial diameter) between single crystal α-Al_2O_3 walls at a constant velocity of **<u>20 m/s</u>**.



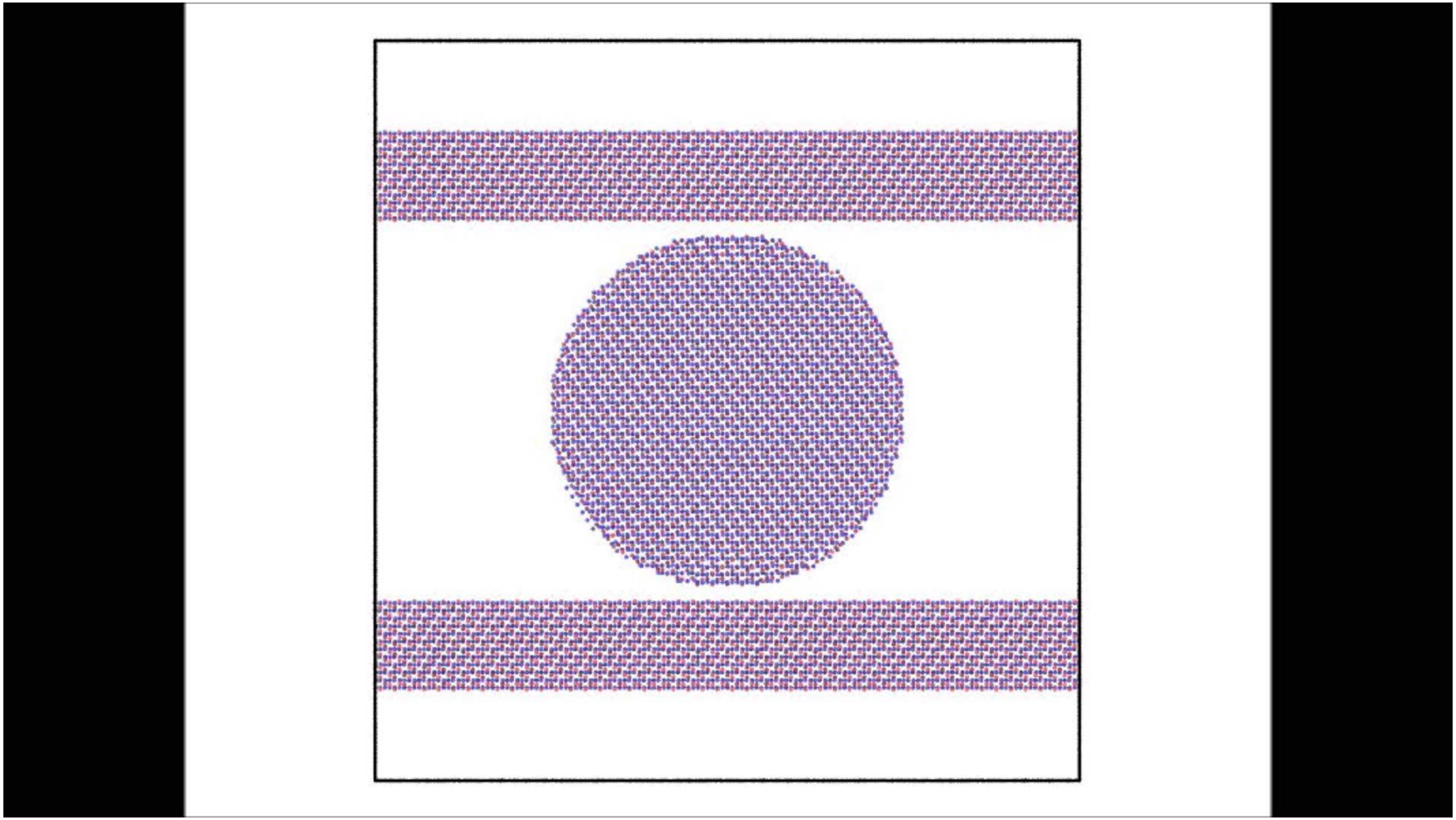
0.3µm Nearly Defect Free **3.0µm with GB**



[8] Blonski, S. and Garofalini, S. H., *J. Phys. Chem.*, Vol. 100, (1996), pp. 2201-2205.

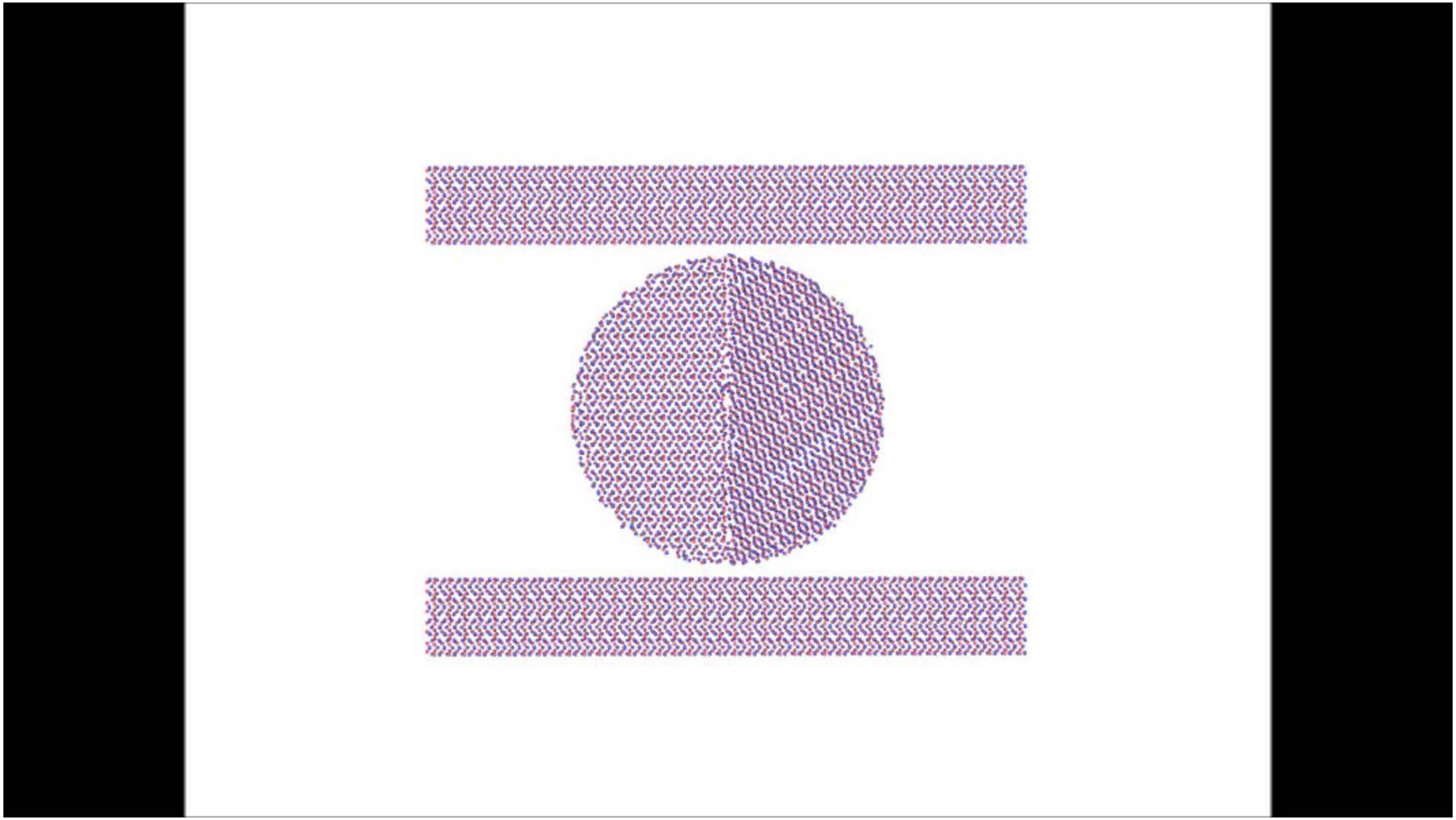
MD Simulation Results

10 nm diameter, defect-free, single crystal α-alumina, compression axis ⊥ (0001)
20 m/s → dislocation nucleation, coordinated shear, fracture



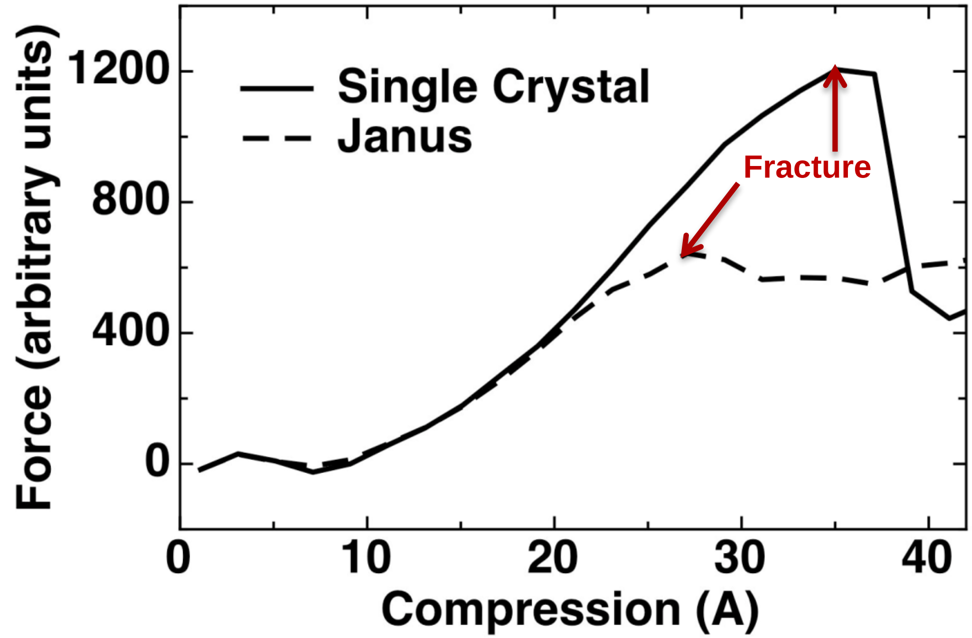
MD Simulation Results

10 nm diameter, contain a GB, ‘Janus’ α-alumina,
20 m/s, left side randomly oriented and right side compression axis ⊥ (0001) → Fracture

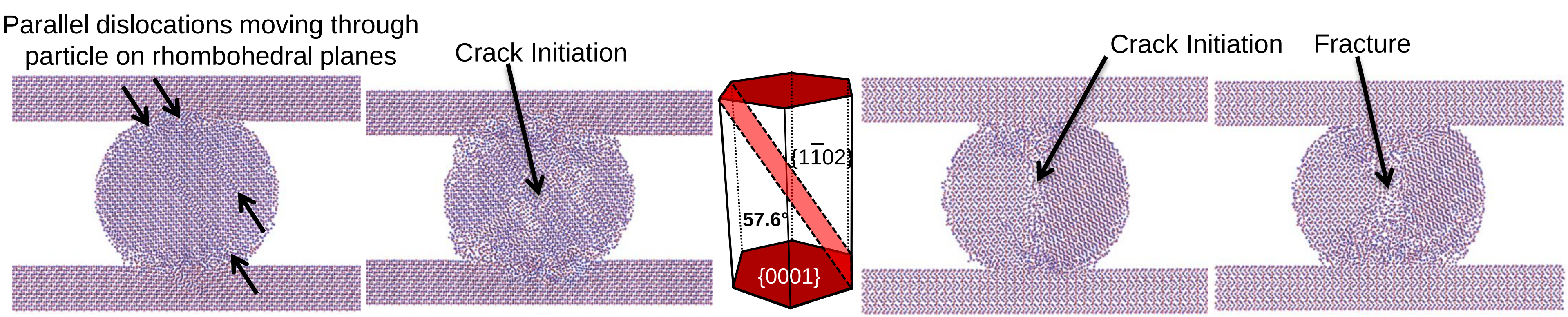


MD Simulation Results

- The energy to fracture is larger for single crystal NP by a factor of **2.9x**.
  - ➢ Energy for both dislocation nucleation/movement *and* fracture
  - ➢ factor of **6x** from experiment.
- The strain to first fracture is larger for single crystal NP by a factor of **1.5x**
  - ➢ factor of **3x** from experiment.
- We have qualitative and quantitative agreement between experiments and simulations.



Defect-free single crystal NP **'Janus' NP containing a grain boundary**



Ceramic Particle RT Deformation - Alumina

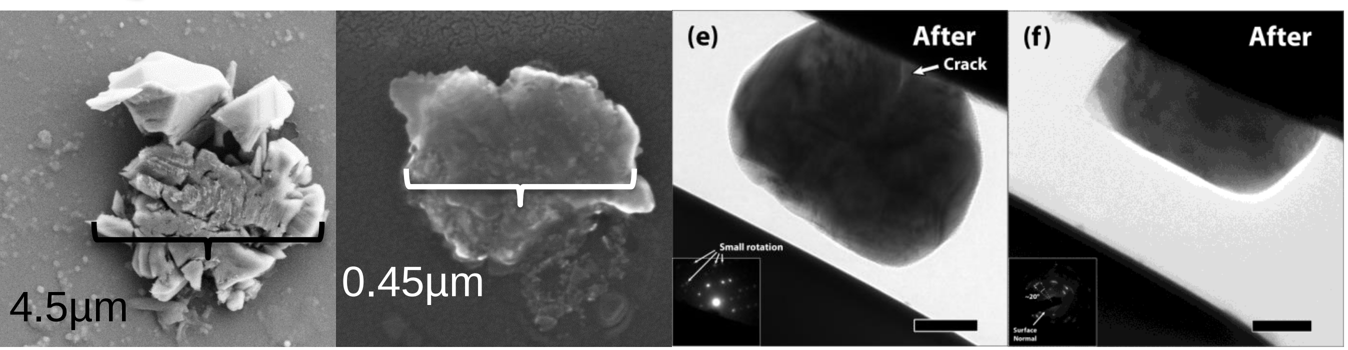
- Deformation behavior influenced by numbers of internal defects, orientation, size.

Verified

	Micron	Sub-micron
# Pre-existing Defects	High	Moderate
Energy Density Input	Low	Moderate
Governing Mechanism(s)	Fracture	Plasticity + Fracture
Response to Compression	Crack initiation & Propagation	Dislocation nucleation, slip, crack initiation & propagation
Compression Testing	SEM	SEM and TEM

Implications:

- Large particles contain large density of *immobile* defects. Sub-micron size particles needed for AD.
- Mobile dislocations needed to provide extensive plastic deformation.
- Deforming pre-compressed particles took less load for larger displacement.
- **Feedstock treatment by pre-deforming particles will**
  - **induce numerous *mobile* dislocation density**
  - **Reduce energy density input for more plastic deformation**
  - **increase deposition efficiency.**
  - **Ball-milling!!!**



3.0µm - Fracture and Fragmentation

0.3µm – plastic deformation, shape change, cracking

0.3µm - Dislocation Plasticity & through particle fracture

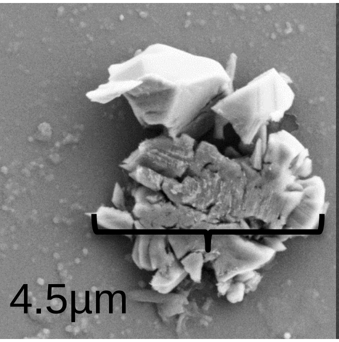
0.3µm - Coordinated Shear Deformation - Polycrystalline

Ceramic Particle RT Deformation - Alumina

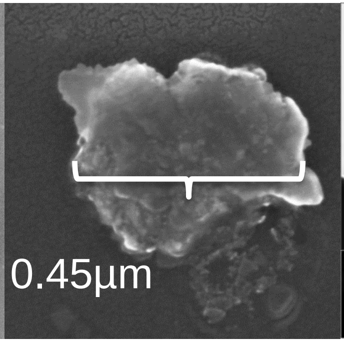
- Deformation behavior influenced by numbers of internal defects, orientation, size.

Verified

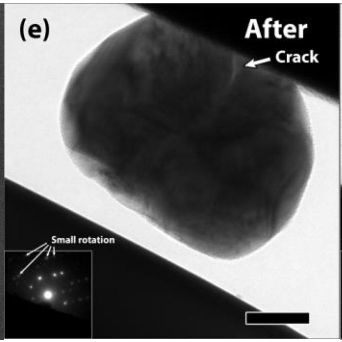
	Micron	Sub-micron	Single Crystal Nano	Bicrystal Nano
# Pre-existing Defects	High	Moderate	None	Grain Boundary
Energy Density Input	Low	Moderate	High	Low
Governing Mechanism(s)	Fracture	Plasticity + Fracture	Plasticity	Fracture
Response to Compression	Crack initiation & Propagation	Dislocation nucleation, slip, crack initiation & propagation	Dislocation nucleation, Slip	Crack initiation & propagation
Compression Testing	SEM	SEM and TEM	MD Simulation	MD Simulation



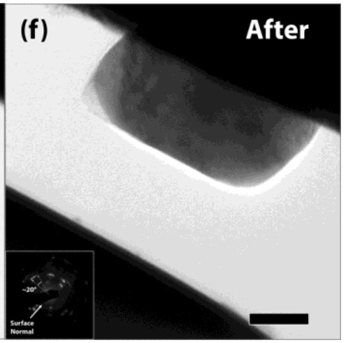
3.0µm - Fracture and Fragmentation



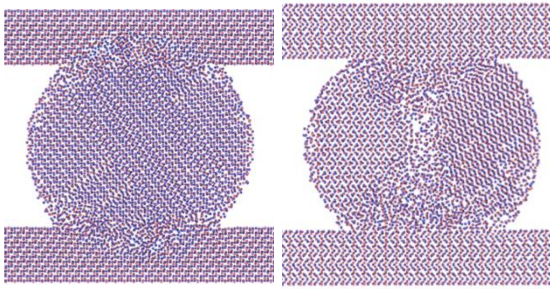
0.3µm – plastic deformation, shape change, cracking



0.3µm - Dislocation Plasticity & through particle fracture



0.3µm - Coordinated Shear Deformation - Polycrystalline



10 nm - Coordinated Shear Deformation

10 nm - Fracture

Conclusions

- Pre-existing defects (type and #) highly influence deformation behaviors.
- The findings from the *in situ* micro-compression experiments agree with those from atomistic simulation qualitatively and quantitatively:
  - Defective micron sized Al_2O_3 particles exhibit brittle fracture in compression.
  - Nearly defect-free, sub-micron sized Al_2O_3 particles exhibit plasticity & fracture
    - Higher strain energy density input needed. Higher accumulated strain before fracture.
    - Responses include dislocation nucleation, slip, significant shape change, coordinated shear deformation, becoming polycrystalline, cracking.
    - Ball mill sub-micron particles to induce mobile dislocations

      → reduce energy needed for deformation → increase deposition efficiency
- Use info to inform feedstock preparation and coating deposition parameters and particle-particle bonding in the consolidated coatings.

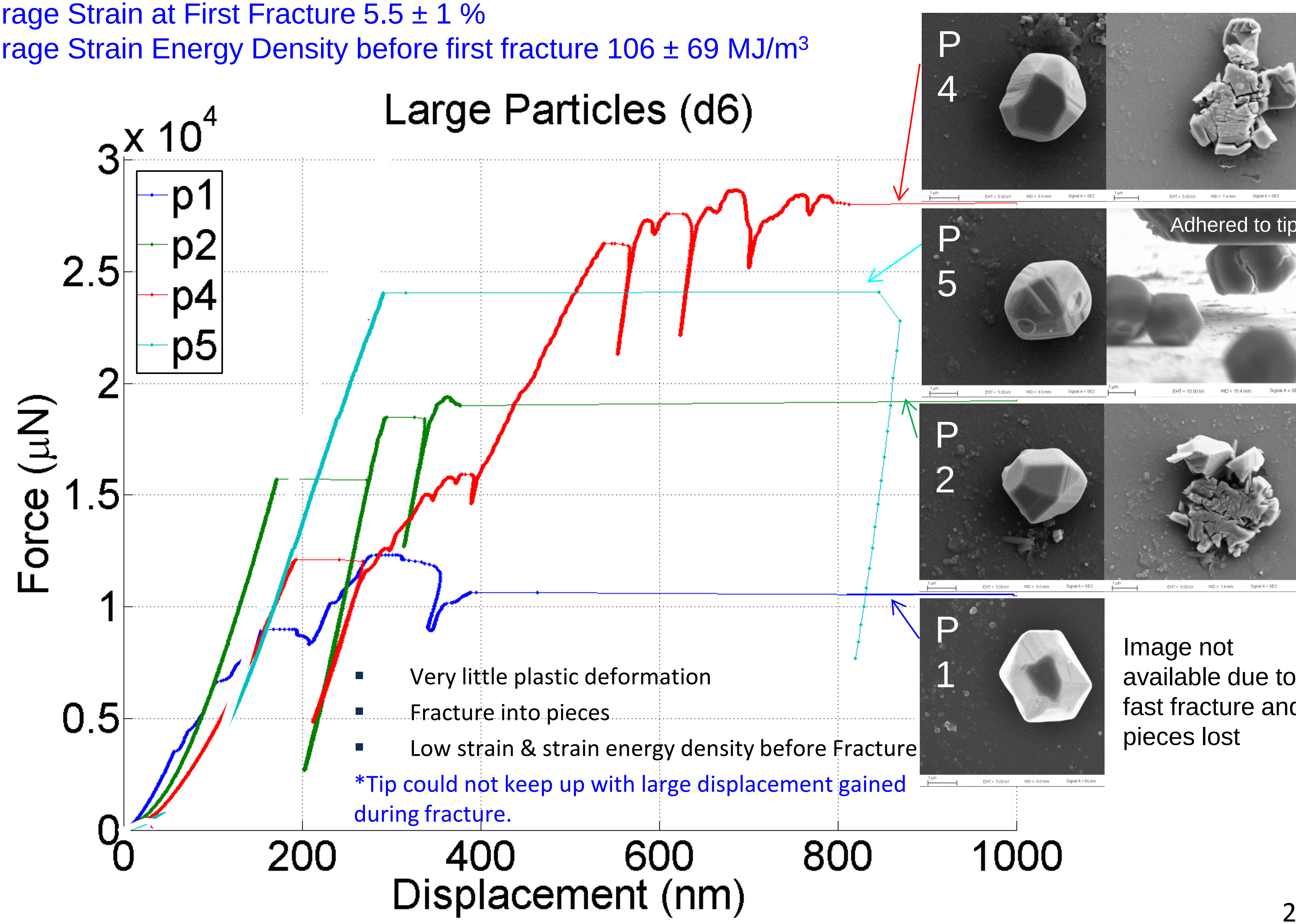
Thank you for your attention.

Pylin Sarobol – psarobo@sandia.gov

BACKUP SLIDES

In Situ SEM micro-compression – 3.0 µm

- Average Strain at First Fracture 5.5 ± 1 %
- Average Strain Energy Density before first fracture 106 ± 69 MJ/m^3



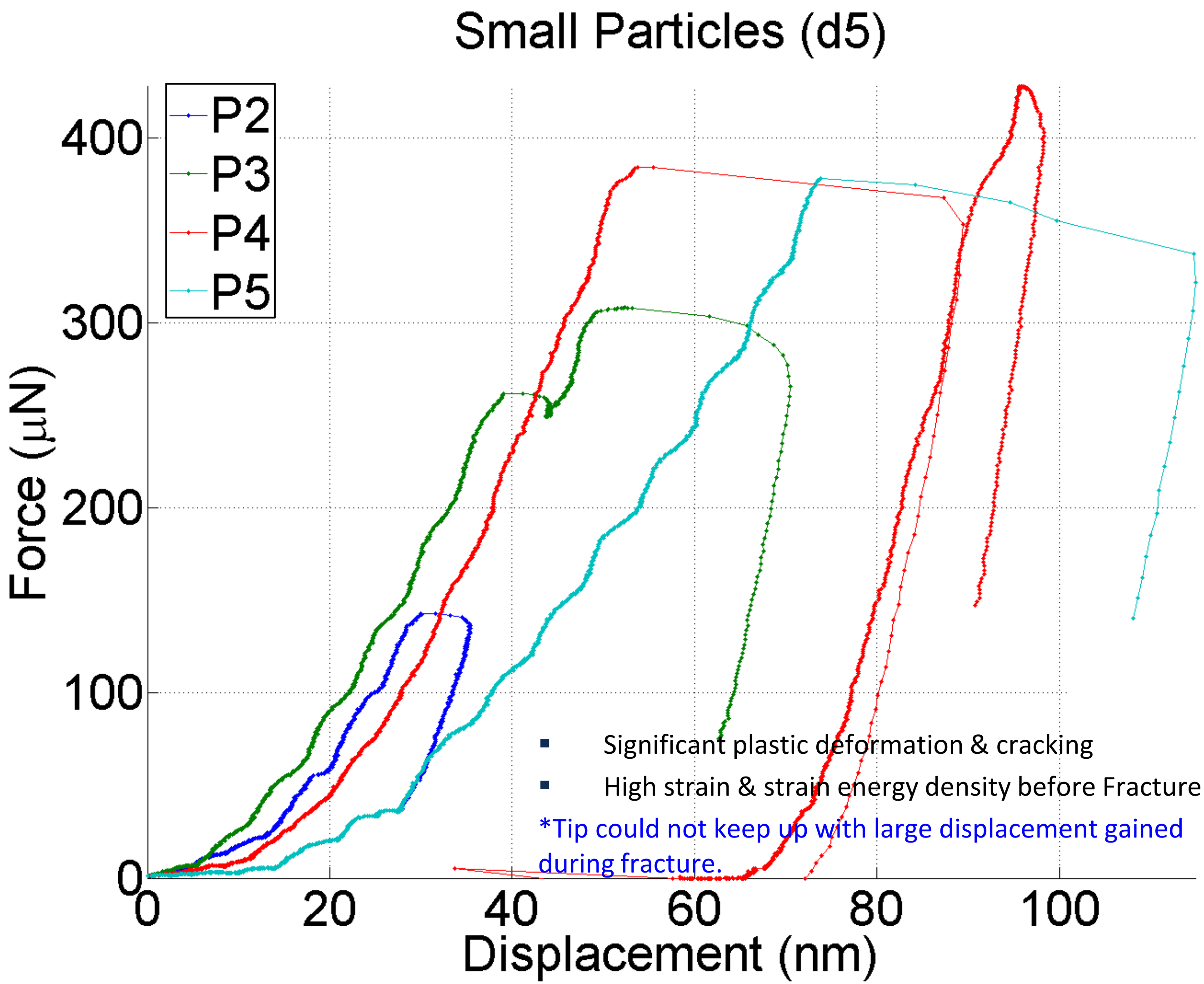
- Very little plastic deformation
- Fracture into pieces
- Low strain & strain energy density before Fracture

*Tip could not keep up with large displacement gained during fracture.

Image not available due to fast fracture and pieces lost

In Situ SEM micro-compression – 0.3 µm

- Average Strain at First Fracture 13 ± 2 % → **2x** that of 3.0 µm particles
- Average Strain Energy Density before first fracture 535 ± 137 MJ/m^3 → **5x** that of 3.0 µm particles



- Significant plastic deformation & cracking
- High strain & strain energy density before Fracture

*Tip could not keep up with large displacement gained during fracture.

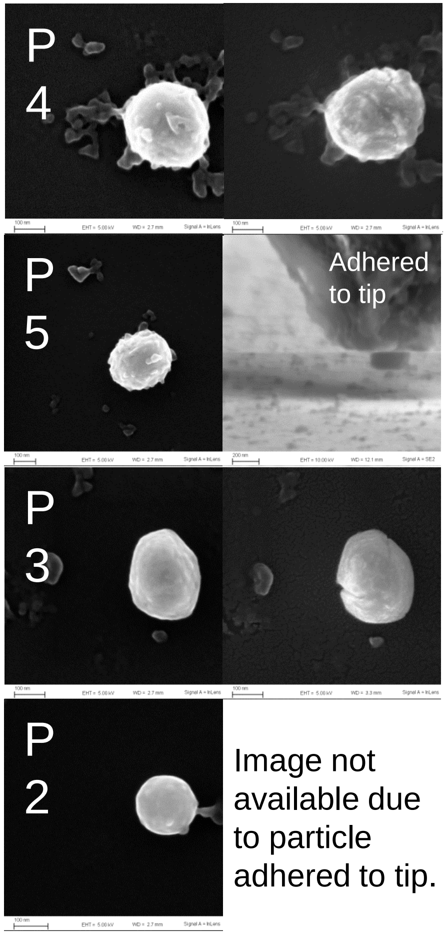
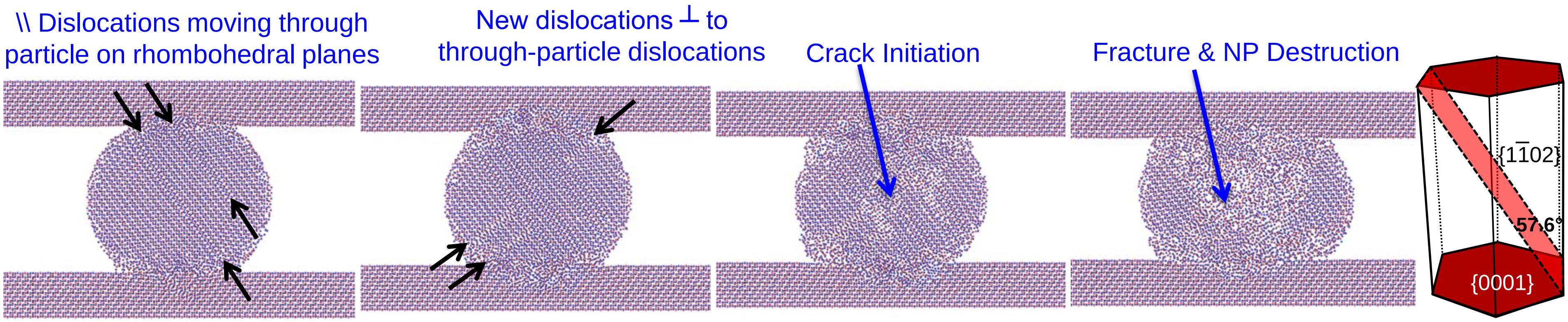


Image not available due to particle adhered to tip.

MD Simulation Results

Defect-free single crystal NP



'Janus' NP containing a grain boundary