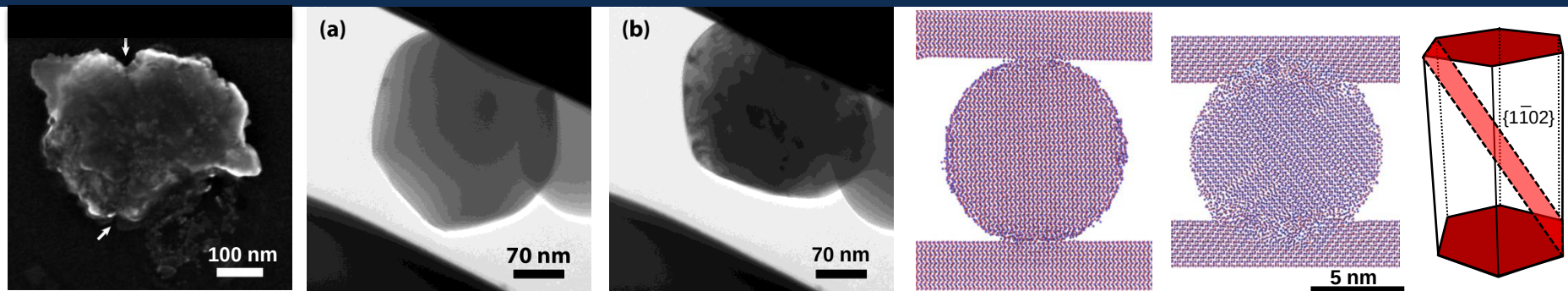


Exceptional service in the national interest



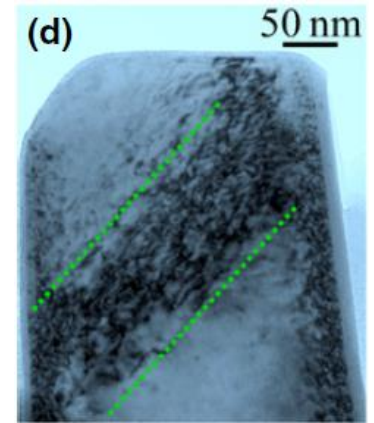
Atomistic Simulations and *In Situ* TEM Compression of Sapphire Particles

**Pylin Sarobol, Michael Chandross, Daniel C. Bufford, Khalid Hattar, Paul G. Kotula,
Brad L. Boyce, Jay D. Carroll, Aaron C. Hall, and William M. Mook**

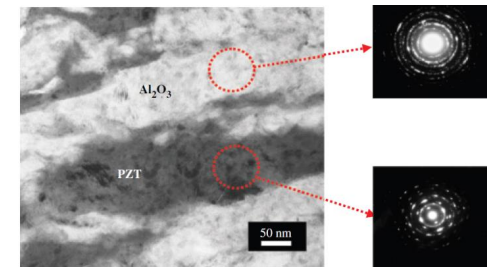
The Rio Grande Symposium on Advanced Materials. October 2, 2015. Albuquerque, NM

Motivation

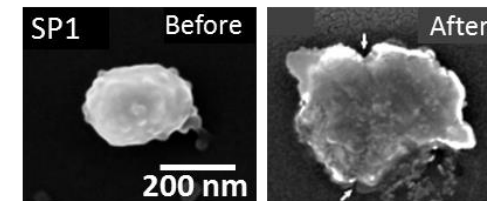
- Bulk materials with high degrees of covalent/ionic bonding, e.g. ceramics, typically undergo brittle fracture when strained.
 - a combination of limited fracture toughness and preexisting flaws.
 - The role of pre-existing flaws and defects can evolve as the characteristic length scale of materials decrease (e.g. micro-pillars and particles) [1-14].
 - In bulk ceramics → crack initiation sites.
- **At small length scales, significant plasticity observed in ceramic single crystals at room temperatures.**
 - Low strain rates → dislocation slip and shape change
 - compressed sapphire micro-pillars [10], particles [16], and confined zones underneath an indenter [36] at RT.
 - High strain rates → aerosol deposition (AD)
 - < 2 μm particles are accelerated to high velocity (200-600 m/s) by pressurized gas, impacted, deformed, and consolidated on the substrates under vacuum [16-24].
 - These sub-micron sized ceramic particles undergo plastic deformation, partly amorphize [25], and break into small crystallites (20-75nm), which bind together to form films [16-19].
- The focus of this study is to better understand the deformation behavior observed in small-scale, compressed ceramic particles, specifically sapphire.



Dislocations on {001} planes in compressed ZrC pillar from S. Kiani, et al. *J. Am. Ceram. Soc.*, 2015:98:2313



AD Al₂O₃ and PZT composite film from J. Akedo. *J. Am. Ceram. Soc.*, 2006:89:1834

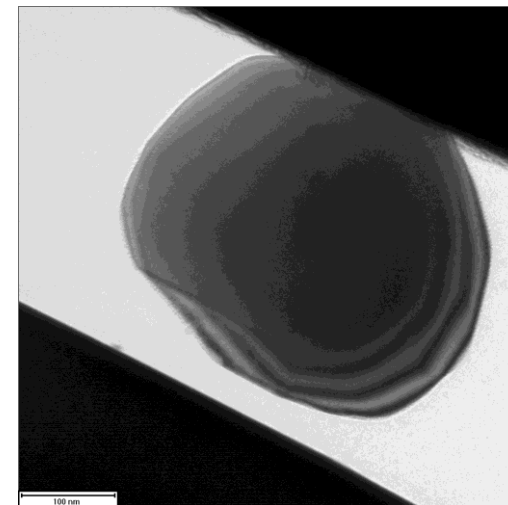
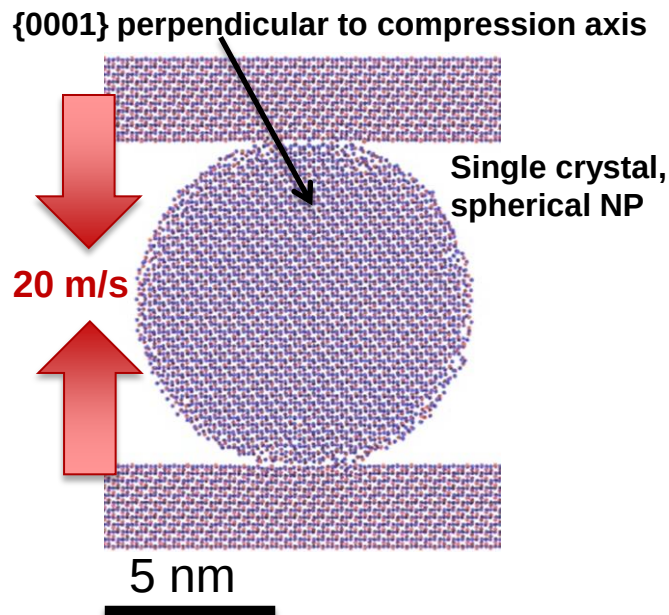


Compressed sapphire particle from P. Sarobol, et al., *JTST.*, 2016:25

Simulated Particle Compression

Molecular Dynamics Simulations – 10 nm nanoparticles (NPs)

- MD allows identification of dislocations, slip planes, and particle fracture.
- Long computing time to simulate size > 50 nm (~36 million atoms)
- **Simulating 10 nm sapphire nanoparticle (NP) (~300,000 atoms)**
- A force-field for ceramics, developed by Garofalini⁸.
- NPs were compressed (by ~1/3 of the initial diameter) between sapphire (single crystal α -Al₂O₃) walls at a constant velocity of **20 m/s**. “Displacement control”.



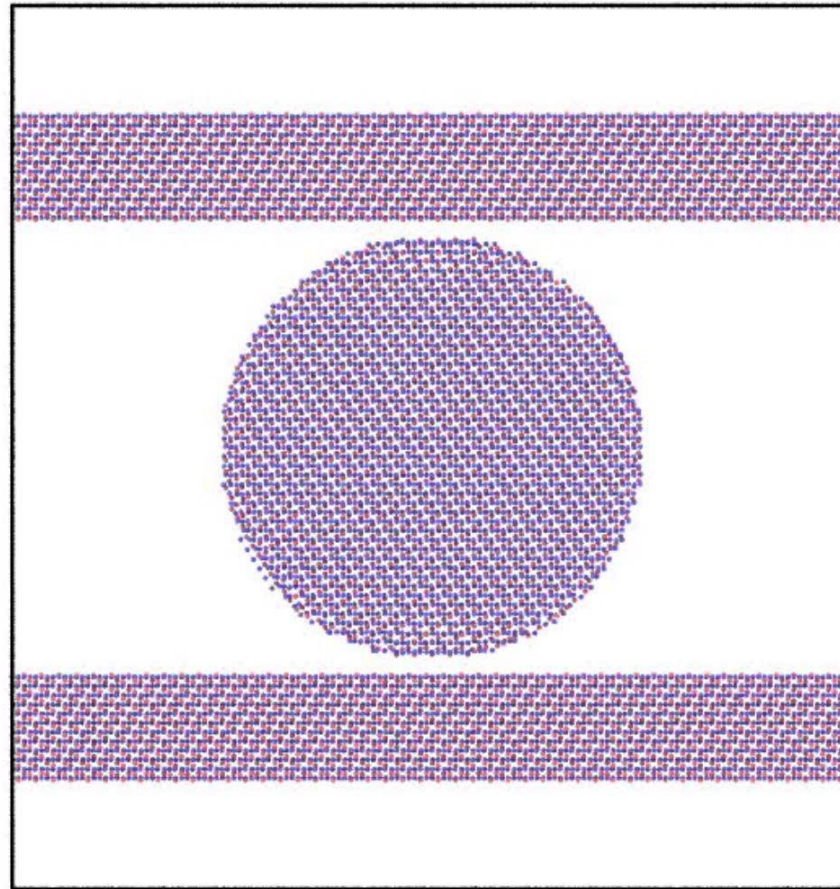
Single crystal,
faceted, 300 nm
diameter particle

In situ TEM micro-compression on 0.3 μ m particle

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

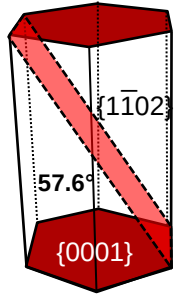
MD Simulation Results

10 nm diameter, defect-free, single crystal α -alumina, compression axis $\perp$ (0001)
20 m/s $\rightarrow$ dislocation nucleation and glide on Rhombohedral planes then fracture

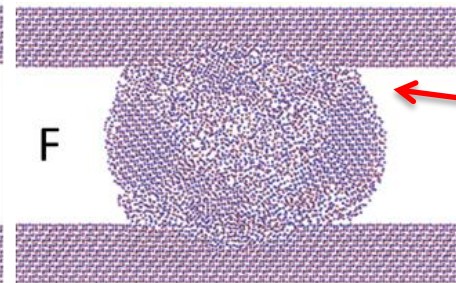
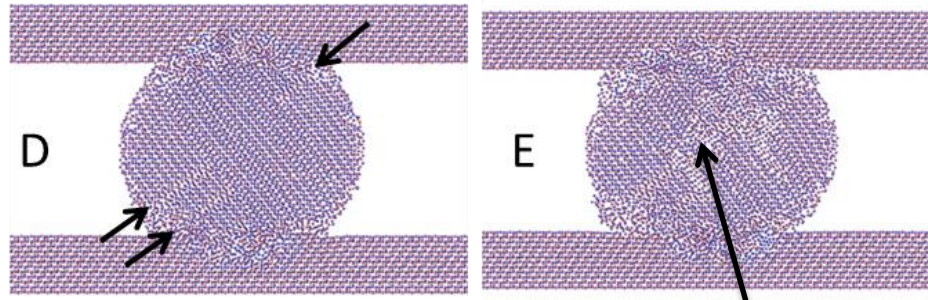
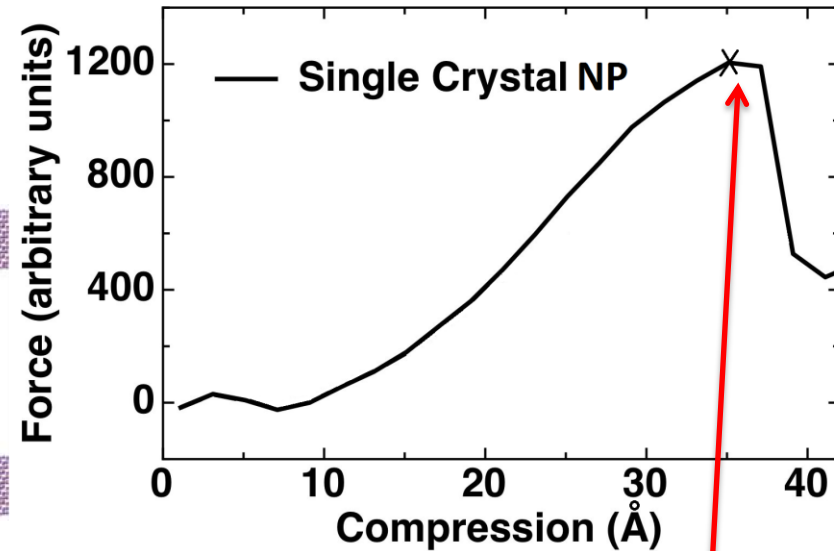
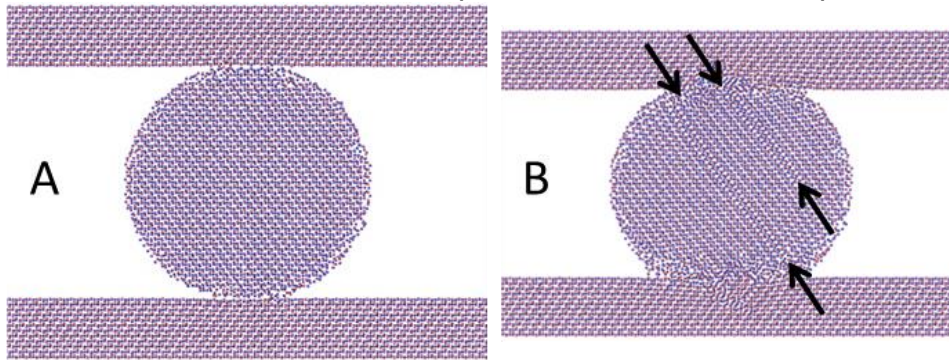


MD Simulation Results

Dislocation plasticity precedes fracture.



Primary dislocations nucleate at contact points. Then, move through particle on rhombohedral planes



Force drop
corresponds to
particle fracture

Secondary dislocations nucleate and move through particle on rhombohedral planes, terminating at the primary dislocation planes

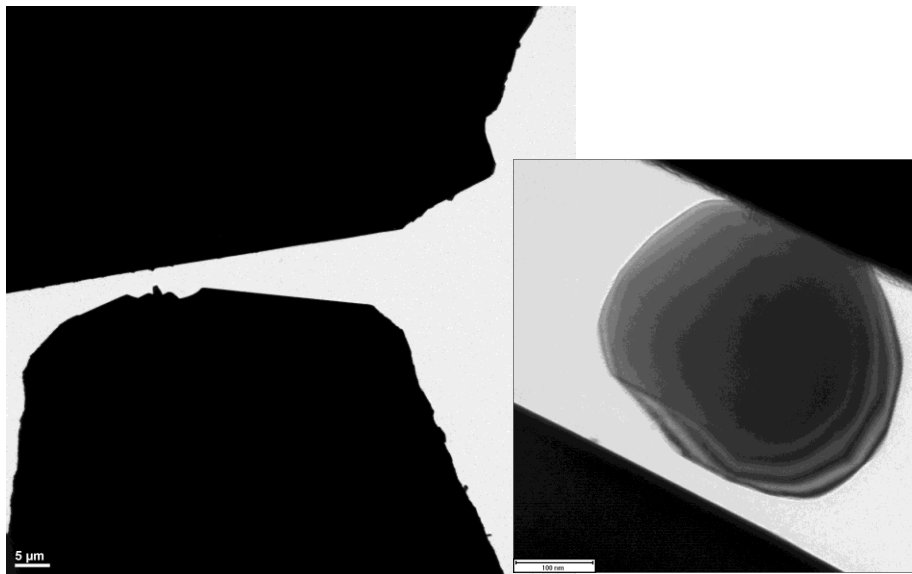
Void Initiation

Fracture

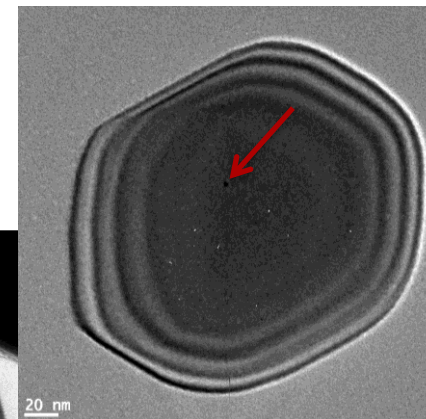
In Situ TEM Compression

In Situ Micro-Compression⁵ – 300 nm particles

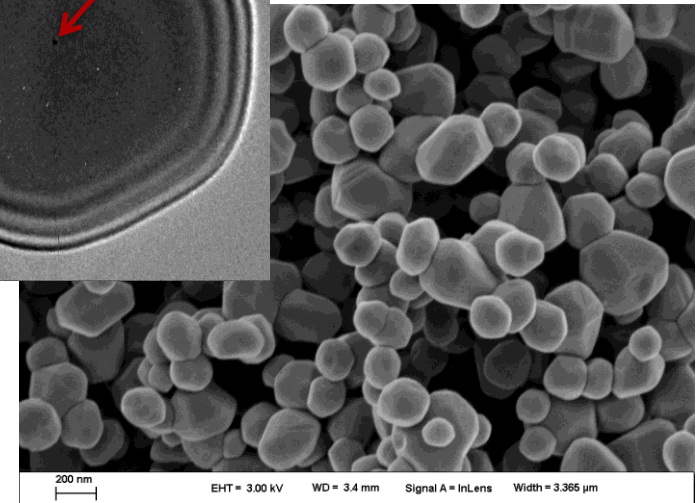
- Single crystal, ultra pure 300 nm sapphire ($\alpha\text{-Al}_2\text{O}_3$) particles.
- A Hysitron PI95 TEM Picoindenter with a 1 μm diameter flat punch tip and the a JEOL 2100 LaB₆ TEM⁷ at 200 kV were used.
- Compression done in **open loop** mode with the loading rate of 10 $\mu\text{N/s}$ (approx. $\leq 2 \text{ nm/s}$ displ rate). Images taken at 15 fps.



In situ TEM micro-compression on 0.3 μm particle



Bright field TEM image of a 300 nm particle oriented on the [001] zone axis.



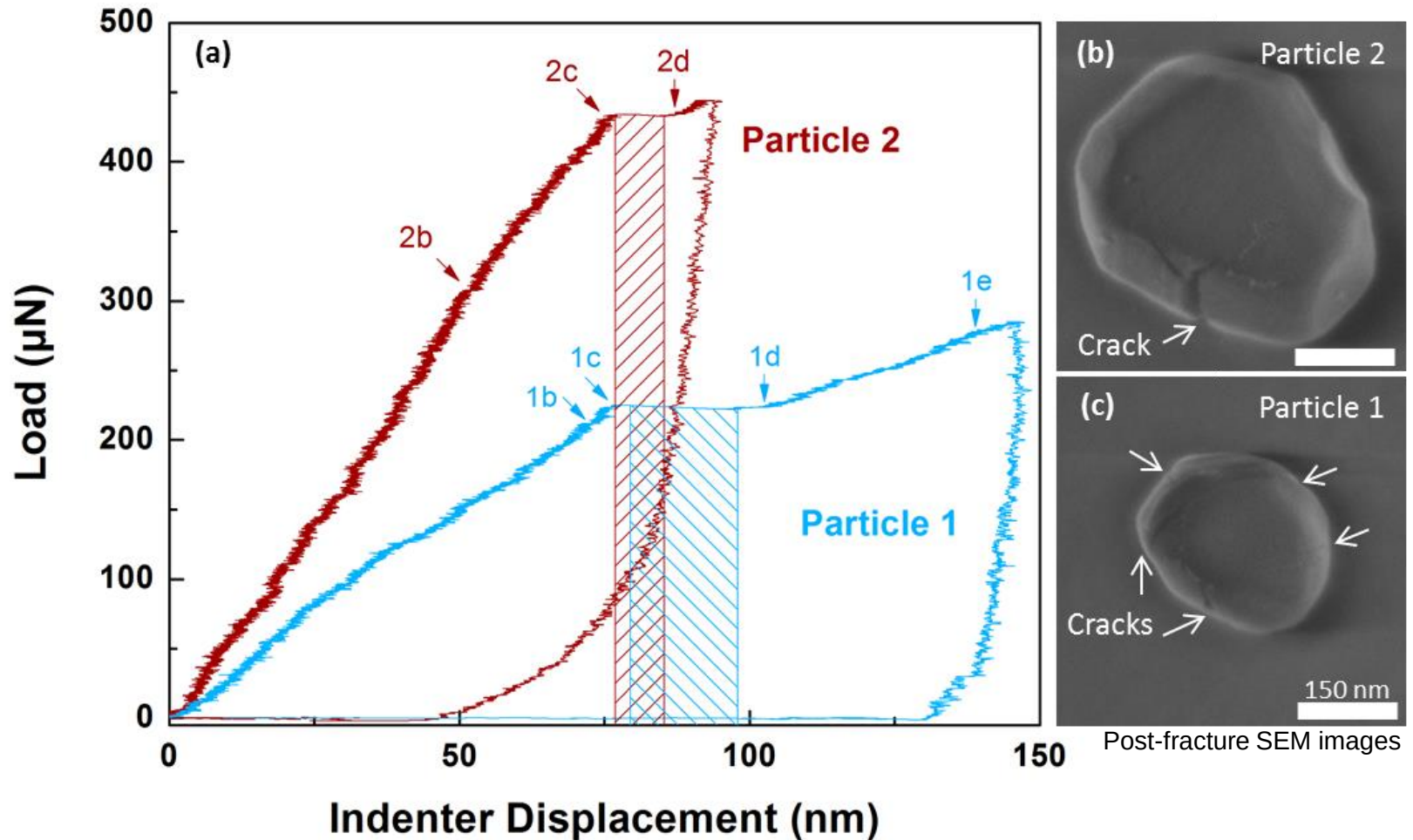
SE SEM image of the 300 nm

[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.

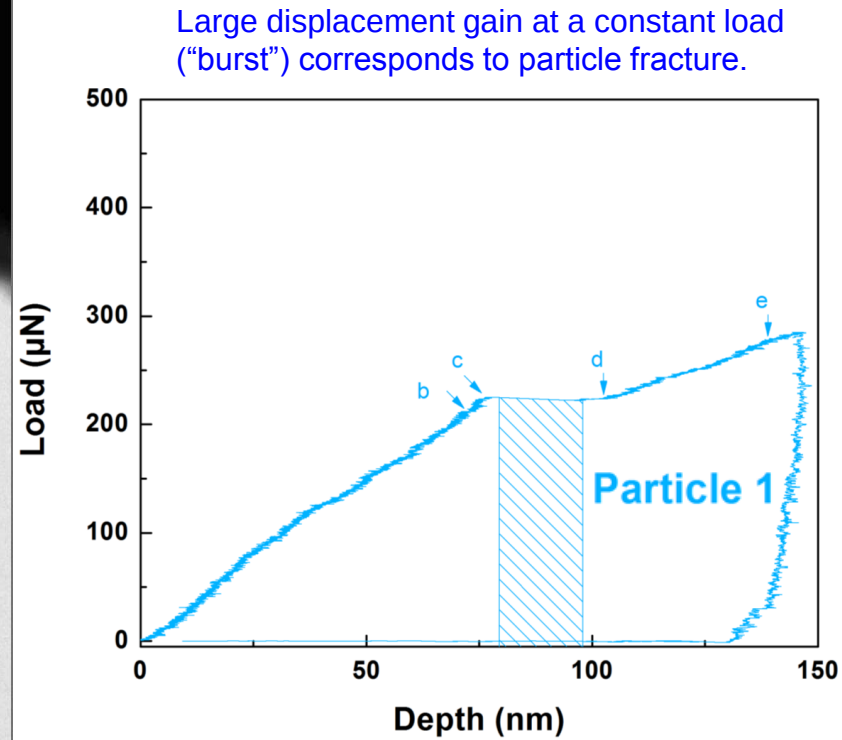
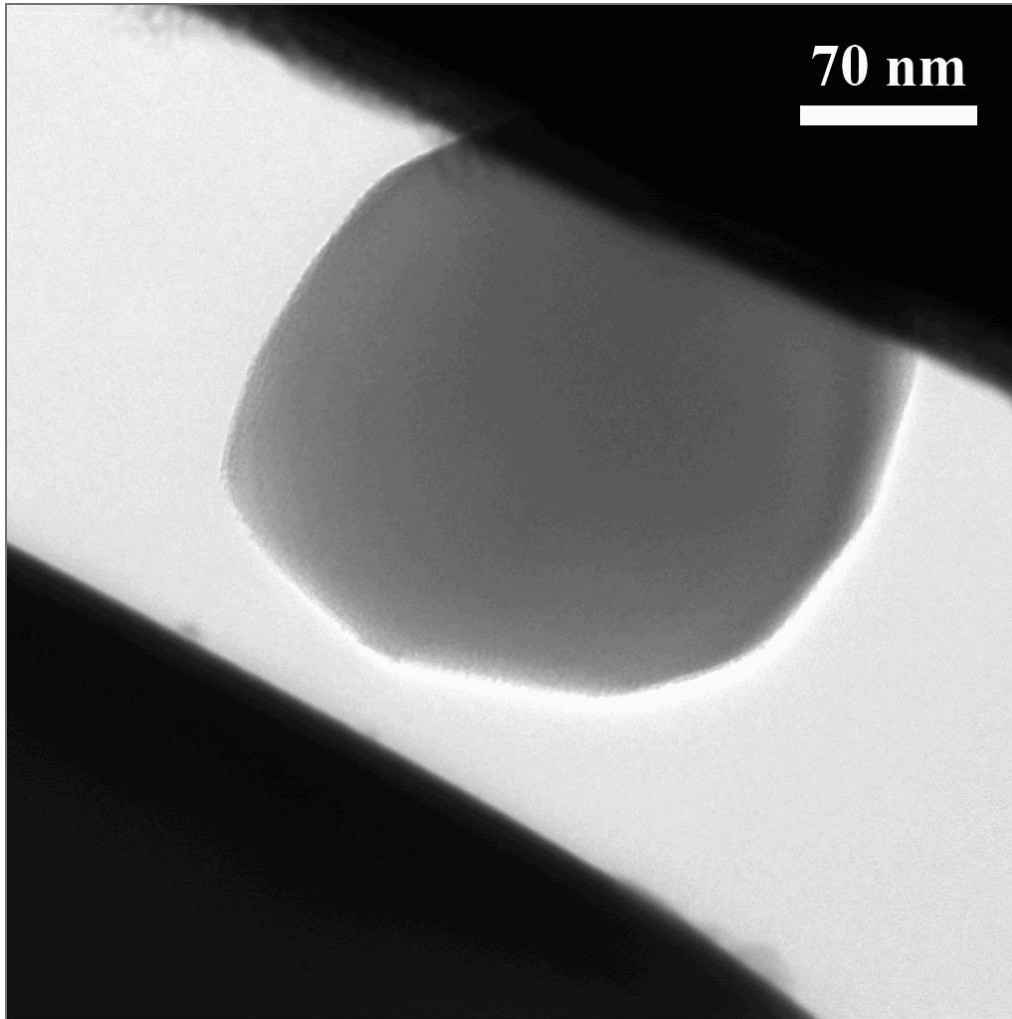
In Situ TEM Compression



- Elastic to Plastic transitions are unclear. Seemed to happen much earlier in the loading (first 5-10 nm displacement). Absence of concavity and linearity of the curves were surprising.
- G_C values for Particle 1 and 2 are 45 J/m² and 17 J/m², respectively. Values within the calculated range of orientation-dependent G_C of single crystal alumina of 16 - 65 J/m² [47].

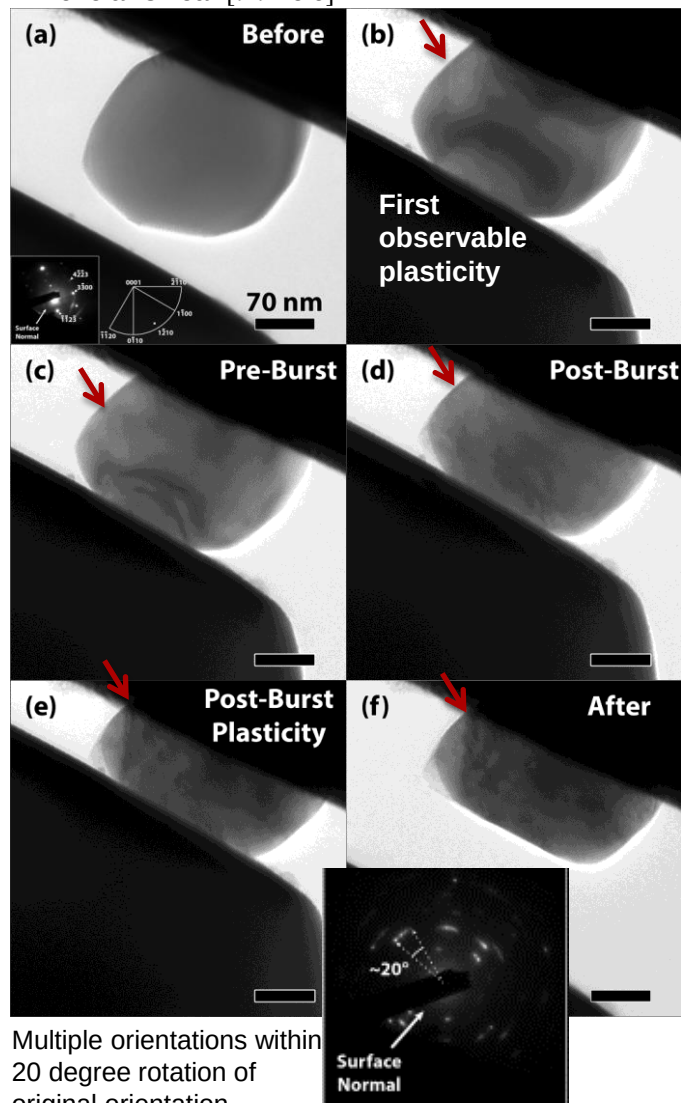
In Situ TEM Compression – P1

Diameter $\sim 0.24\ \mu\text{m}$, Open loop, Strain rate $\sim 0.009\ \text{s}^{-1}$

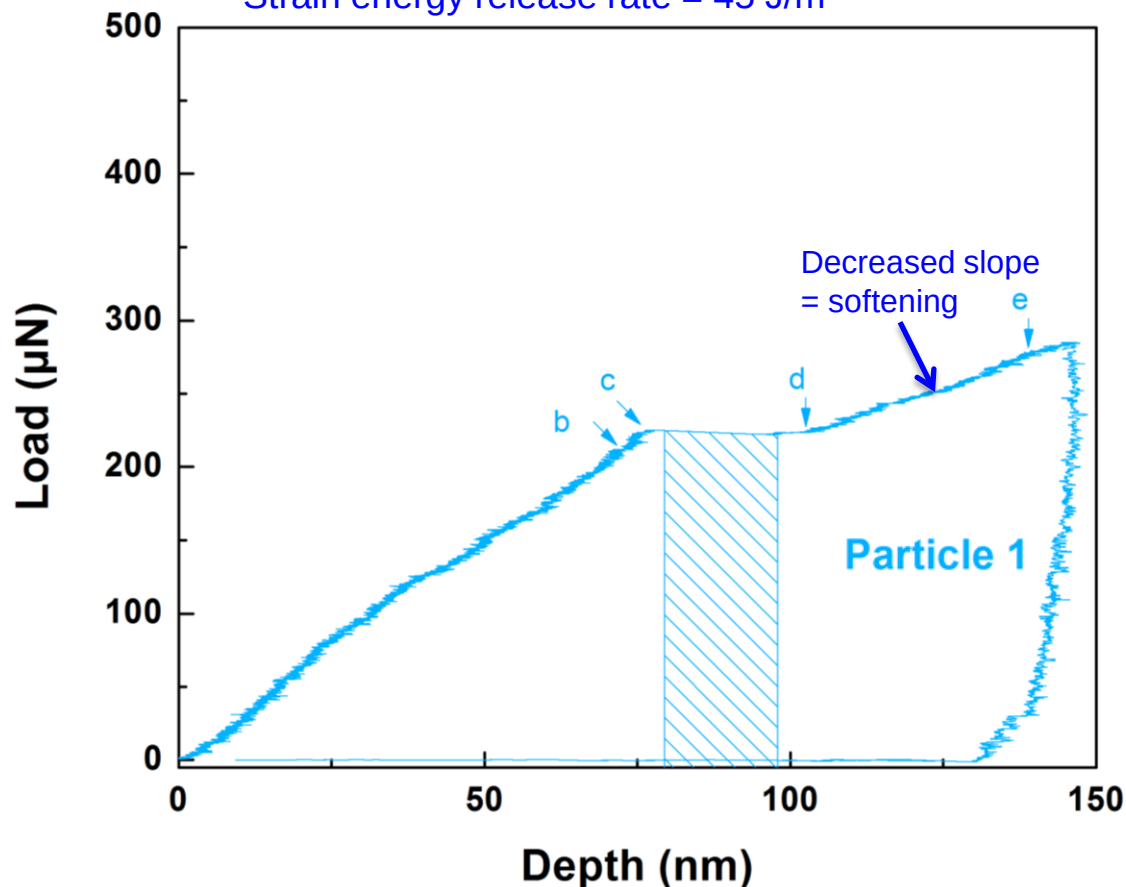


In Situ TEM Compression – P1

Zone axis near $[\bar{9}\bar{9}186]$



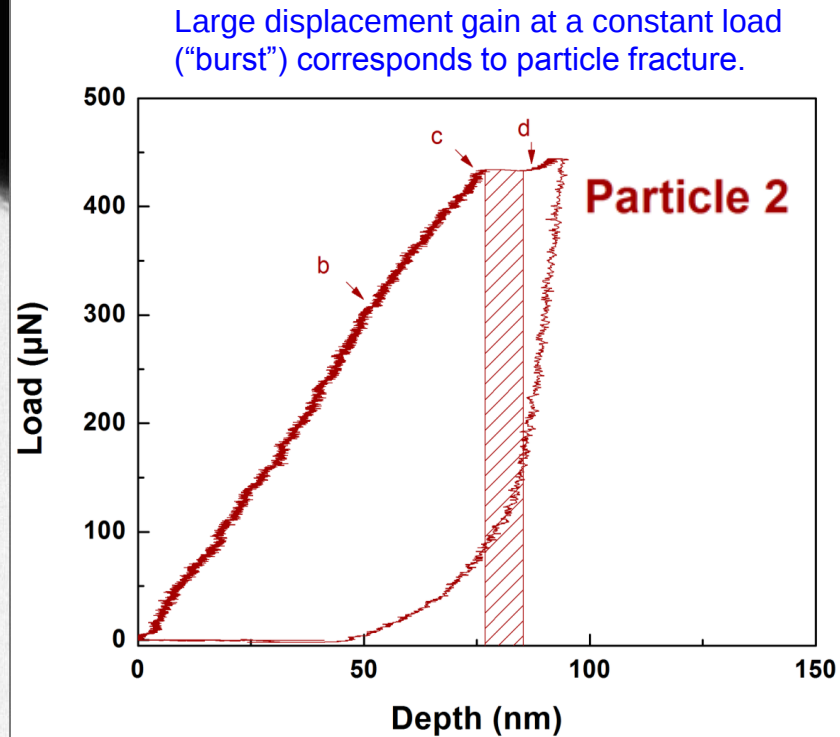
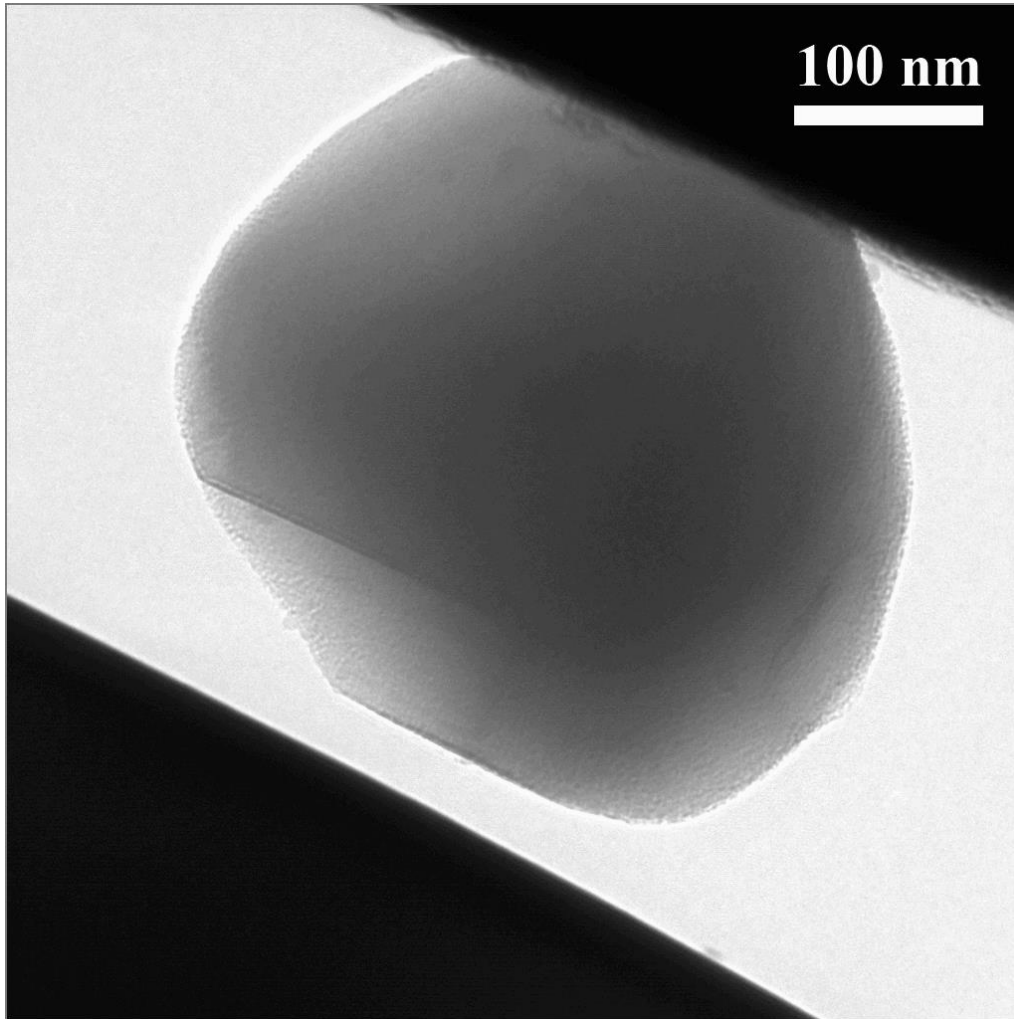
■ Strain energy release rate = 45 J/m²



- Pre-burst plasticity: small regime with low dislocation activity.
- **Crack nucleation and propagation** leading to through-particle fracture.
- Post-burst plasticity: high dislocation activities, change in deformation mechanism as indicated by lower slope.
- **Mosaicity** with a 20 degree orientation spread.

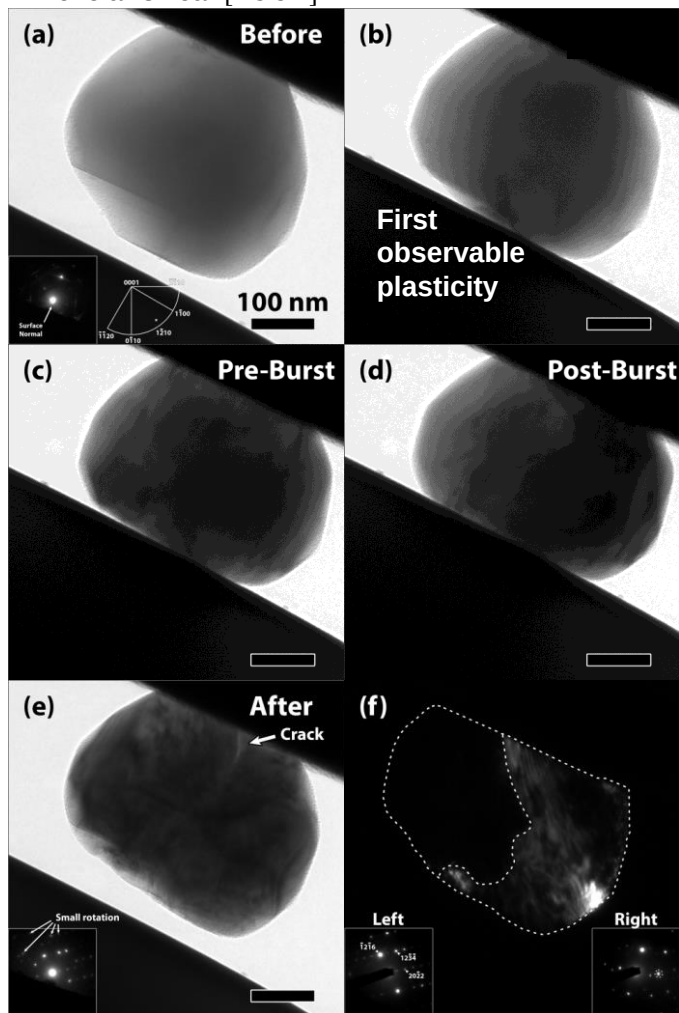
In Situ TEM Compression – P2

Diameter $\sim 0.38 \mu\text{m}$, Open loop, Strain rate $\sim 0.005 \text{ s}^{-1}$



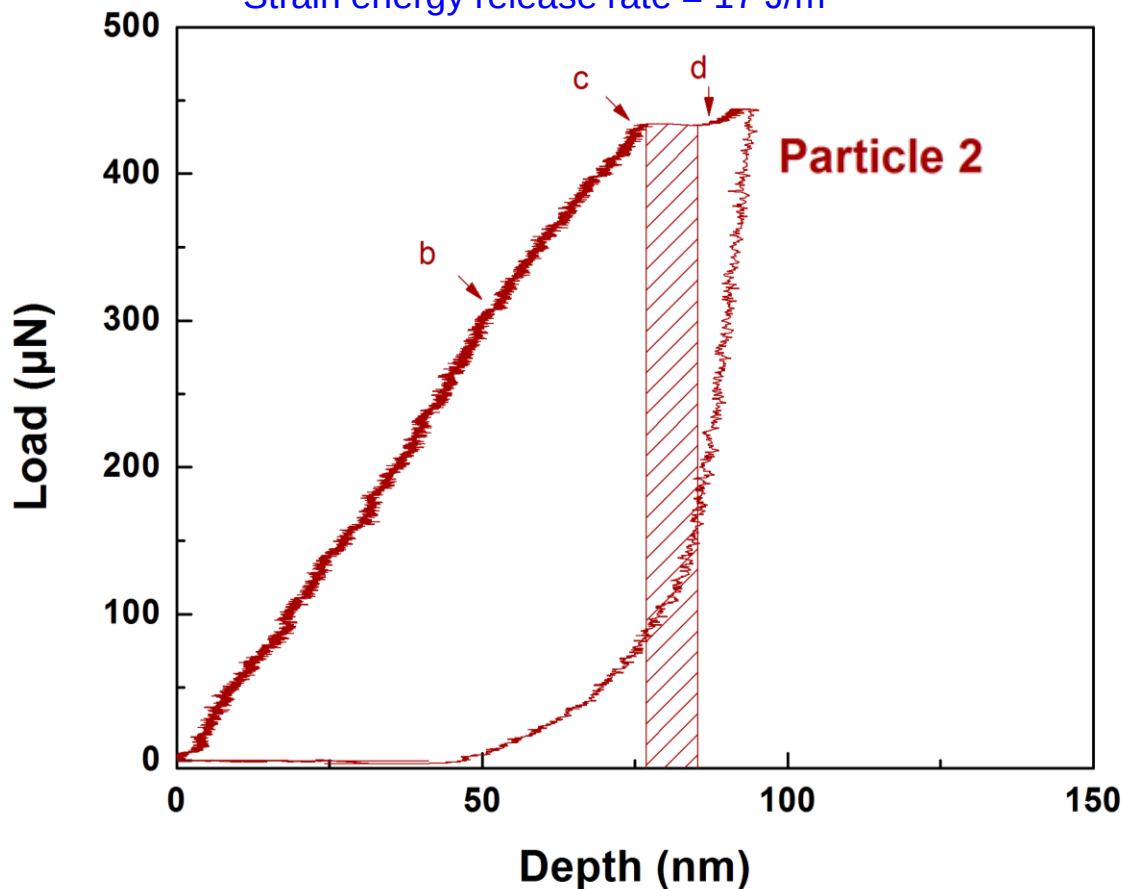
In Situ TEM Compression – P2

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



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

▪ Strain energy release rate = 17 J/m^2



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

Conclusions

- The findings from molecular dynamic simulations and *in situ* TEM micro-compression experiments agree well:
 - Dislocation plasticity precedes fracture in compressed small sapphire particles at RT.
 - Range of responses to compression includes
 - Dislocation nucleation, slip, movement
 - Significant shape change
 - Orientation spread (mosaicity)
 - Fracture
- Room temperature plasticity in ceramics at small length scale gave insights into future development of alternative ceramic forming technology and high strength/high toughness functional ceramics.
- Use info to inform feedstock preparation, aerosol deposition parameters, and particle-particle bonding in the consolidated coatings.

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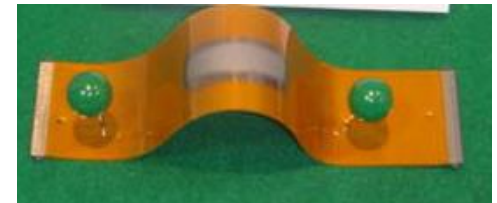
Thank you,
for your attention.

Pylin Sarobol –
psarobo@sandia.gov

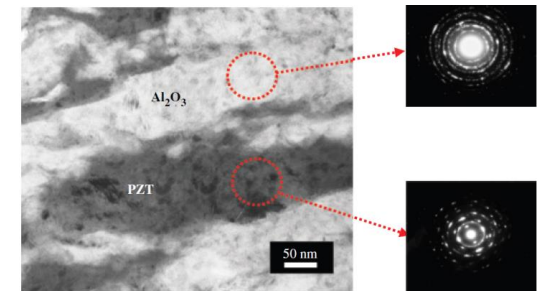
BACK UP SLIDES

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.



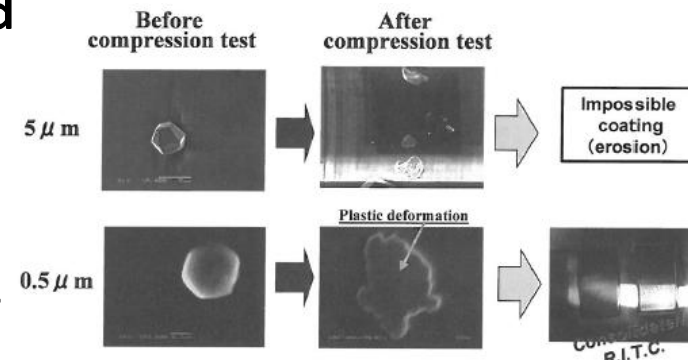
AD Flexible electronics from J. Akedo. *JTTEE5*, 2007:17:181



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.

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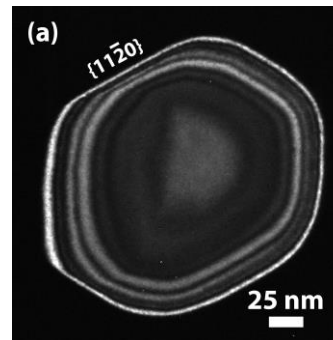
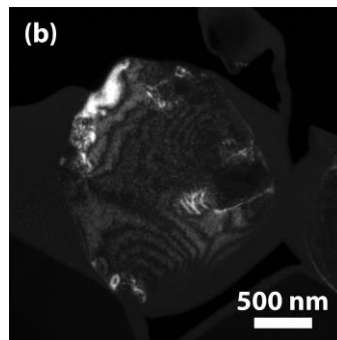
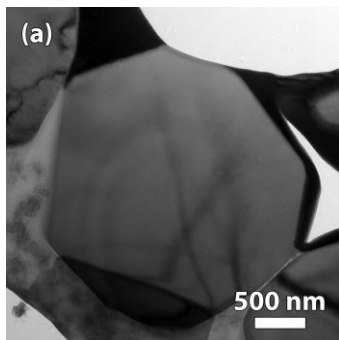
Ceramic Particle RT Deformation - Sapphire

- 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
# 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

- Infeasible (long computing time) to perform molecular dynamics simulations on size $>0.05\mu\text{m}$
- 'smaller' particles ($0.3\mu\text{m}$) are nearly defect-free, and 'larger' particles ($3.0\mu\text{m}$) contain immobile defects that serve as crack nucleation sites.
- Circumvented the size limitation of our models by simulating similar sized (10 nm) nanoparticles (NPs) that were either
 - single crystal
 - contained a grain boundary (GB) as an initial immobile defect.
- This approach still enables the study of NP deformation/fracture in computationally-feasible systems.



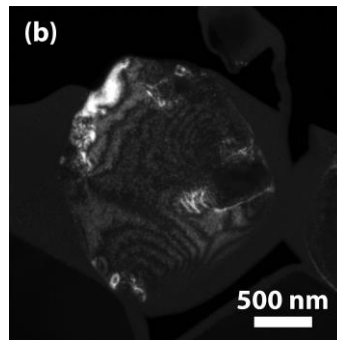
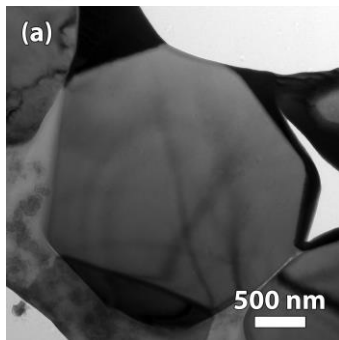
3.0 μm Highly Defective

0.3 μm Nearly Defect Free

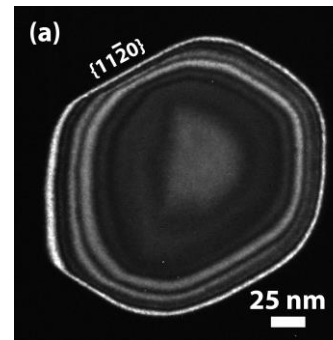
Ceramic Particle RT Deformation - Alumina

- 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*

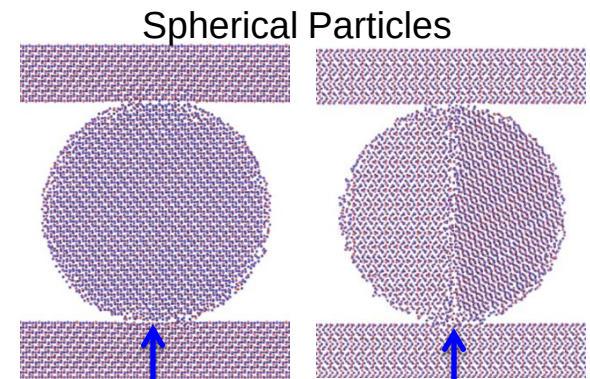
Proposed		Micron	Sub-micron	Single Crystal Nano	Bicrystal Nano
	# Pre-existing Defects	High	Moderate	None	Grain Boundary
	Energy Density Input	Low	Moderate	High	Low
	Governing Mechanism(s)	Fracture	Plasticity + Fracture	Plasticity	Fracture
	Response to Compression	Crack initiation & Propagation	Dislocation 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



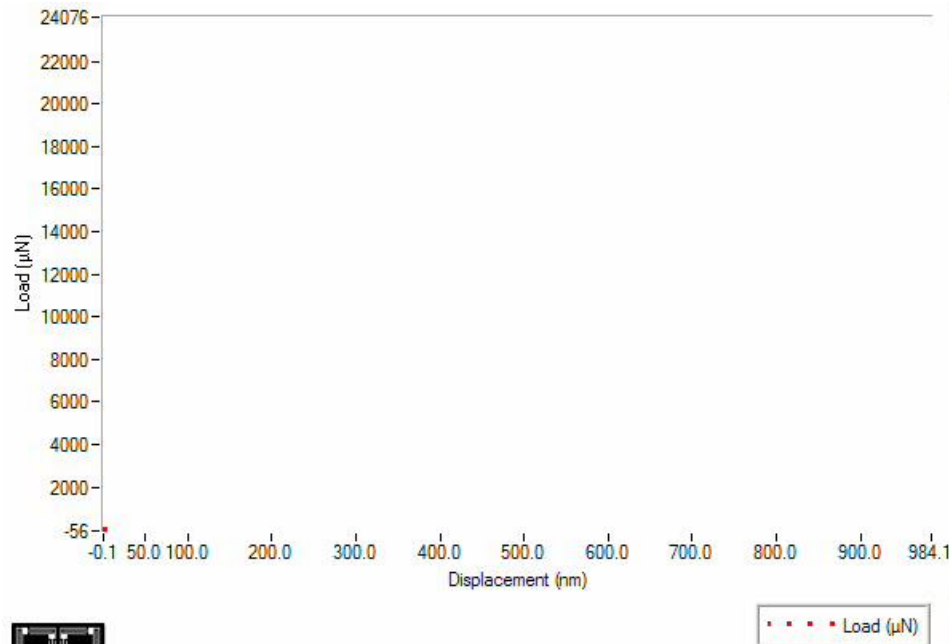
0.3µm Nearly Defect Free



10 nm Defect Free 10 nm with a GB 17

In Situ SEM micro-compression – 3.0 μm

Displacement control, Strain rate $\sim 0.003 \text{ s}^{-1}$

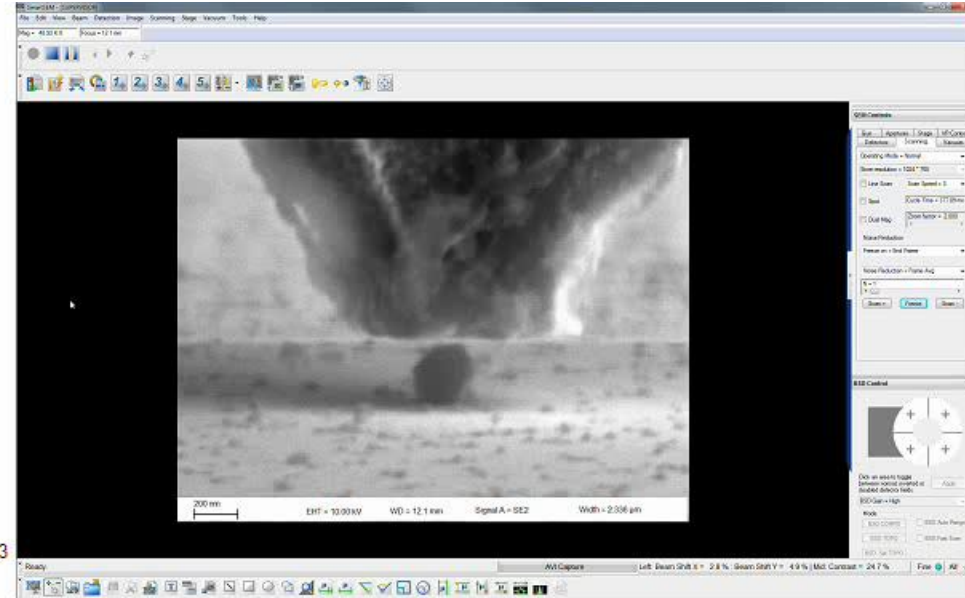
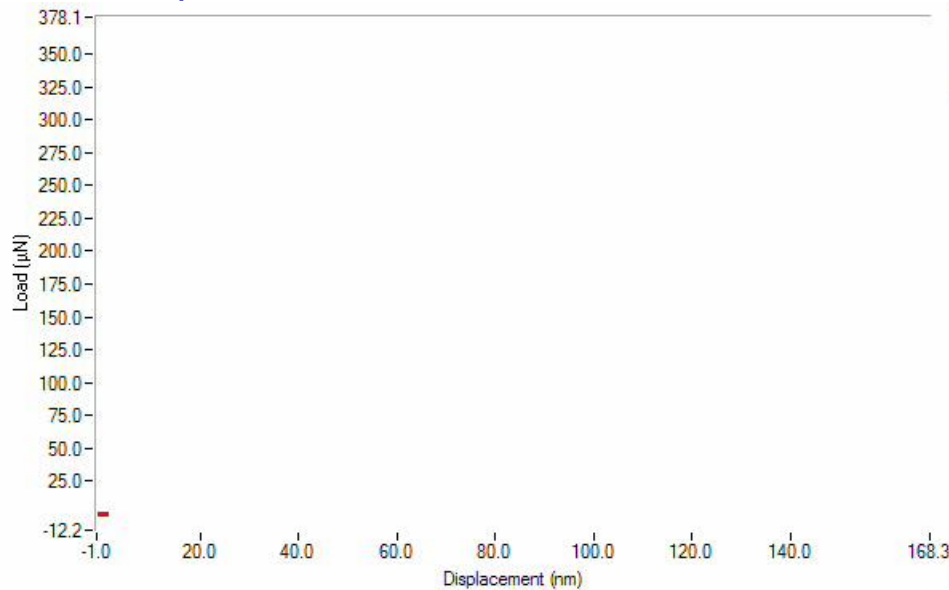


- Compressed 4 particles
- No observable shape change prior to fracture and fragmentation
- Displacement excursion corresponded to a fast fracture event
 - Strain Energy Density before Fracture $\sim 203 \text{ MJ/m}^3$
 - Strain at fracture $\sim 7\%$

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

In Situ SEM micro-compression – 0.3 μm

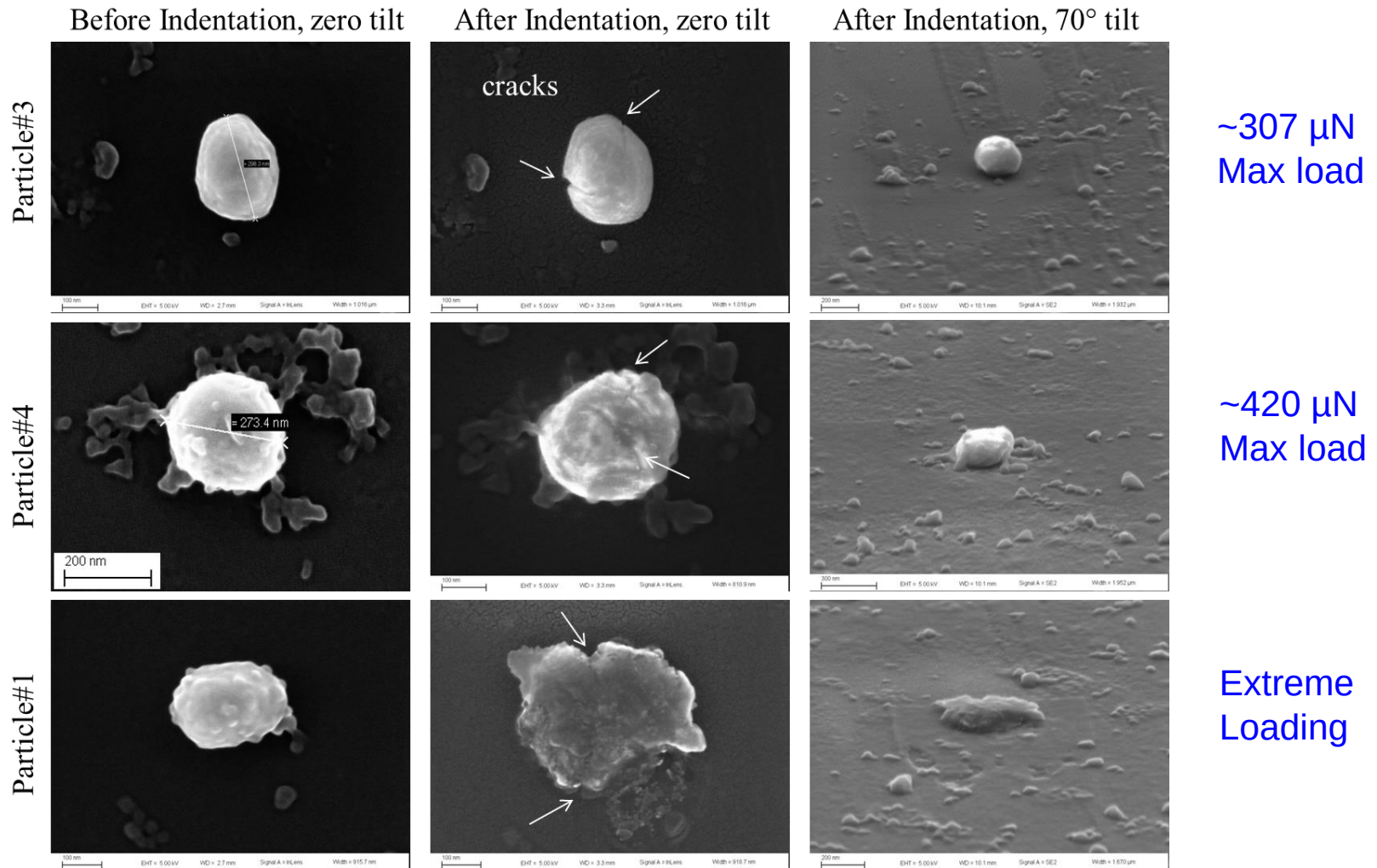
Displacement control, Strain rate $\sim 0.05 \text{ s}^{-1}$



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

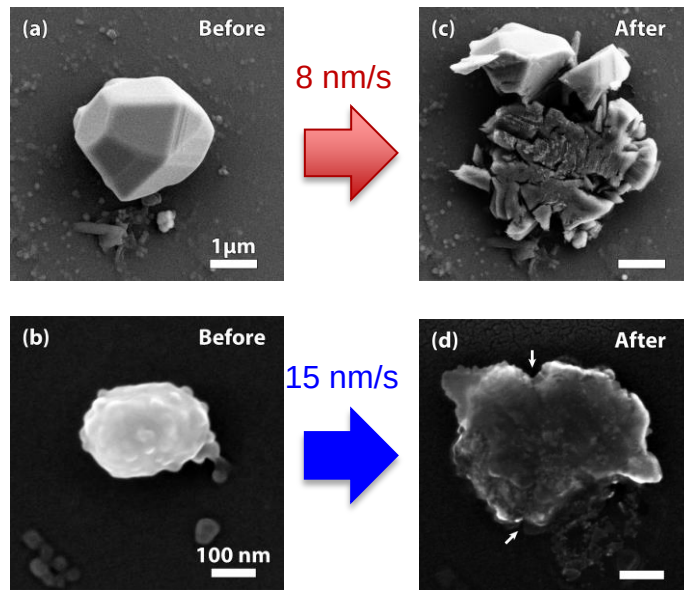
Tip could not keep up with large displacement gained during fracture.

Ex Situ SEM observation – 0.3 μm



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.

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

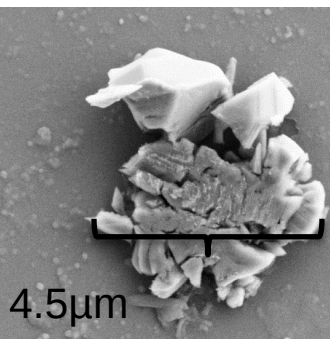
	Micron	Sub-micron
# Pre-existing Defects	High	Moderate
Energy Density Input	Low	Moderate
Governing Mechanism(s)	Fracture	Plasticity + Fracture
Response to Compression	Crack initiation & Propagation	Dislocation nucleation, slip, crack initiation & propagation

- 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.

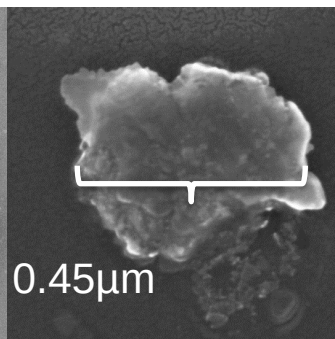
Ceramic Particle RT Deformation - Alumina

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

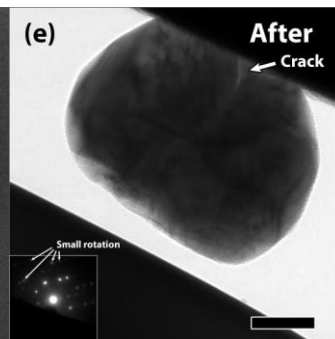
Verified		Micron	Sub-micron	Single Crystal Nano	Bicrystal Nano
	# Pre-existing Defects	High	Moderate	None	Grain Boundary
	Energy Density Input	Low	Moderate	High	Low
	Governing Mechanism(s)	Fracture	Plasticity + Fracture	Plasticity	Fracture
	Response to Compression	Crack initiation & Propagation	Dislocation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



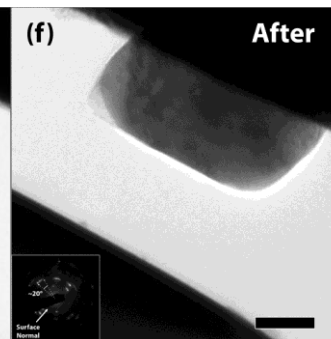
3.0μm - Fracture and Fragmentation



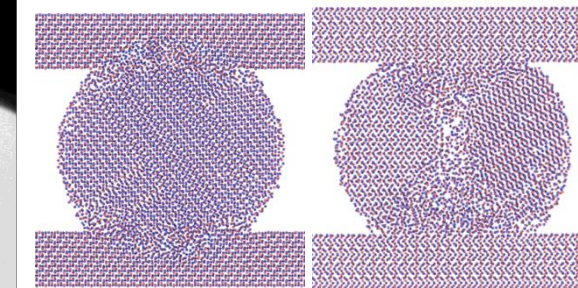
0.3μm – plastic deformation, shape change, cracking



0.3μm - Dislocation Plasticity & through particle fracture



0.3μm - Coordinated Shear Deformation - Polycrystalline



10 nm - Coordinated Shear Deformation
10 nm - Fracture

MD Simulation Results

10 nm diameter, contain a GB, 'Janus' α -alumina,
20 m/s, left side randomly oriented and right side compression axis $\perp$ (0001) $\rightarrow$ Fracture

