SAND2015-0547C

Influence of grain size on hydrogen sorption properties in cryomilled Pd-10Rh

Joshua K. Yee[1], Lilia Kurmanaeva[1], Patrick J. Cappillino[2,3], Zhihui Zhang[1], Christopher San Marchi[2], Nancy Yang[2], and Enrique J. Lavernia[1]

[1]University of California, Davis, Davis, CA 95616

[2] Sandia National Laboratories, Livermore, CA 94550

[3] University of Massachusetts, Dartmouth, North Dartmouth, MA 02747

The authors gratefully acknowledge the support of Sandia National Laboratories under contract 826008.
Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of the Lockheed Martin Corporation, for the US Department of Energy's National Nuclear Security Administration under contract no. DE-AC04-94AL85000.

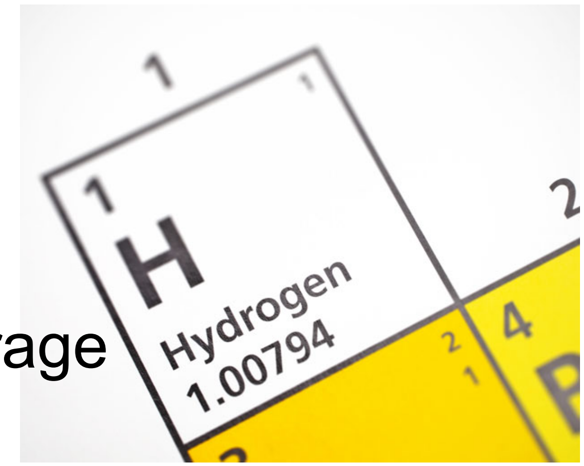
UCDAVIS COLLEGE of ENGINEERING

SAND #

Sandia National Laboratories

Background

- Depletion of fossil fuels drives search for alternative fuel; H has emerged as alternative, sustainable fuel [1]
- Solid state storage preferable [2]
  - Metal hydrides show promise as H storage materials
  - Influence of decreasing length scales on storage and absorption/desorption kinetics
- Pd and alloys are simple fcc metals which can absorb large amounts of H [3]
  - Model material for solid state H storage studies



[1] A. Léon, in:, A. Léon (Ed.), Hydrogen Technology, Springer Berlin Heidelberg, 2008, pp. 11–13.
[2] A. Léon, in:, A. Léon (Ed.), Hydrogen Technology, Springer Berlin Heidelberg, 2008, pp. 81–128.
[3] A. Pundt, R. Kirchheim, Annual Review of Materials Research 36 (2006) 555.

Motivation/Objective

- Optimize processing route for producing Pd used for H storage
  - Manufacturability/scalability
  - Uniformity of composition
- Understand and study the mechanisms behind H uptake/discharge in heavily worked and defected Pd

Approach

- Material selection
  - Pd-10%Rh has increased H storage capacity[1]
  - Solid solution alloy
- Inert gas atomization
  - Produce micron sized powder[2]
- Cryomilling
  - Decrease length scales (particle dimensions and grain size) in Pd for study[3]
- Characterization
  - OM, SEM, XRD, TEM, and H sorption properties (PC isotherms)

UC DAVIS COLLEGE of ENGINEERING

Sandia National Laboratories

[1]A.K.M. Fazle Kibria, Y. Sakamoto, Int. J of H Energy **25** (2000) 853–859.
[2]Yang et al., J of Mat. Sci. **32** (1997) 6589-6594.
[3]Yang et al., Acta Mat **82** (2015) 41-50.

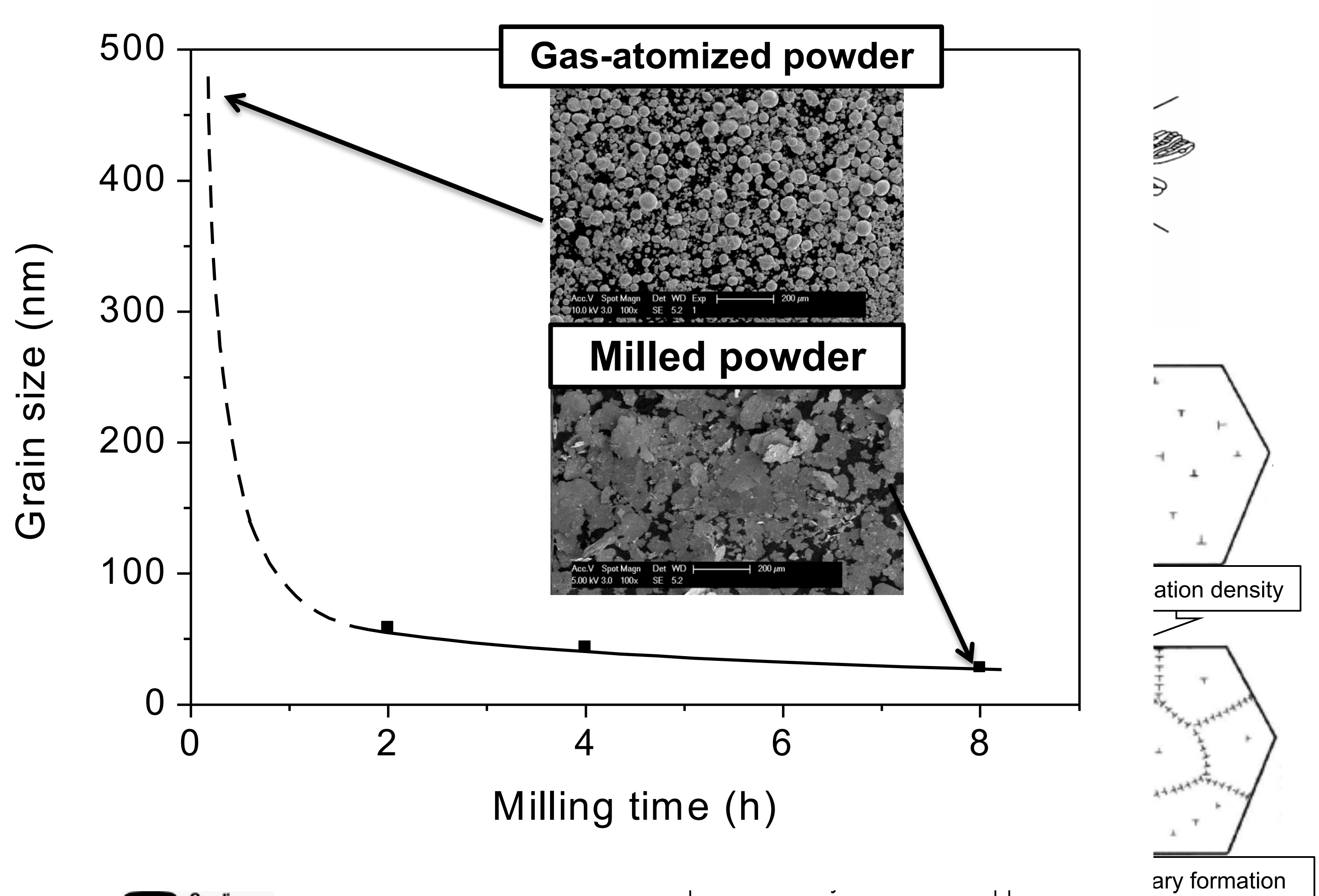
Synthesis: Cryomilling

Grain

Localiz
(Inc

Formatio

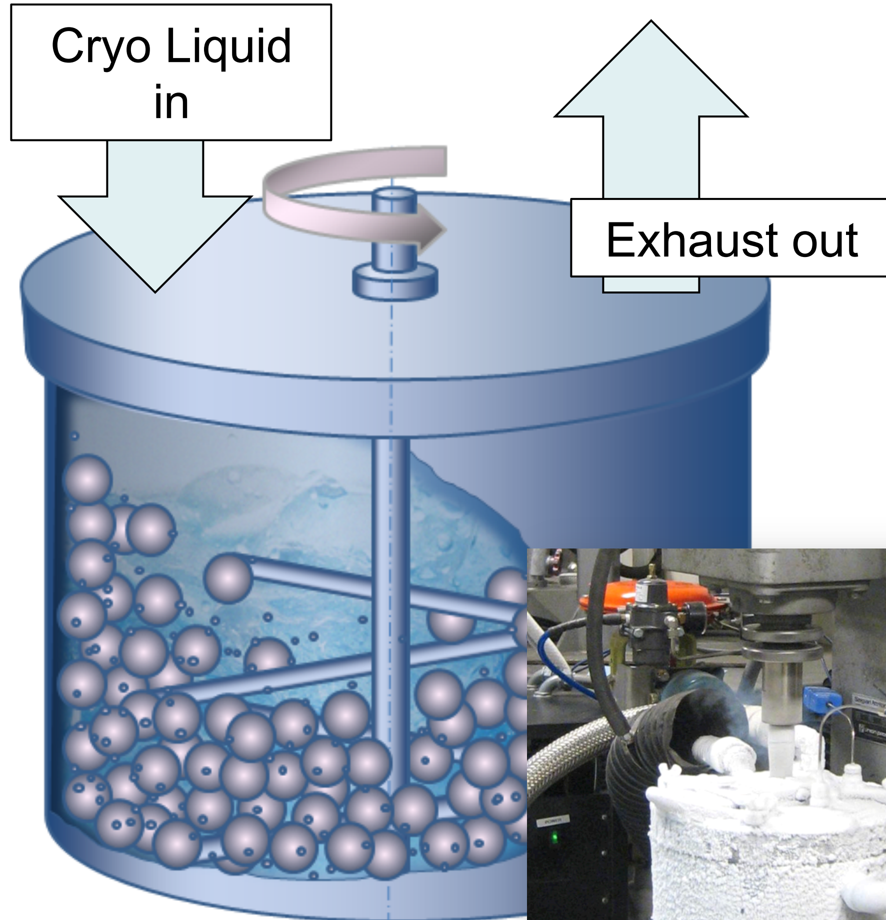
Low /
R



[1] Fecht et al. 1989, 1990, 1995
[2] Y. Xun, F. Mohamed, E. Lavernia, Metallurgical and Materials Transactions A 35 (2004) 573–581.

Synthesis: Cryomilling

- Pd powder milled via attrition ball milling in cryogenic slurry (cryomilling)
  - Liquid Ar and N_2 used as cryogenic medium
  - Milling time varied (1h*, 2h*, 8h, 16h)
  - Ball-to-powder ratio varied (32:1 vs. 64:1)



UCDAVIS COLLEGE of ENGINEERING

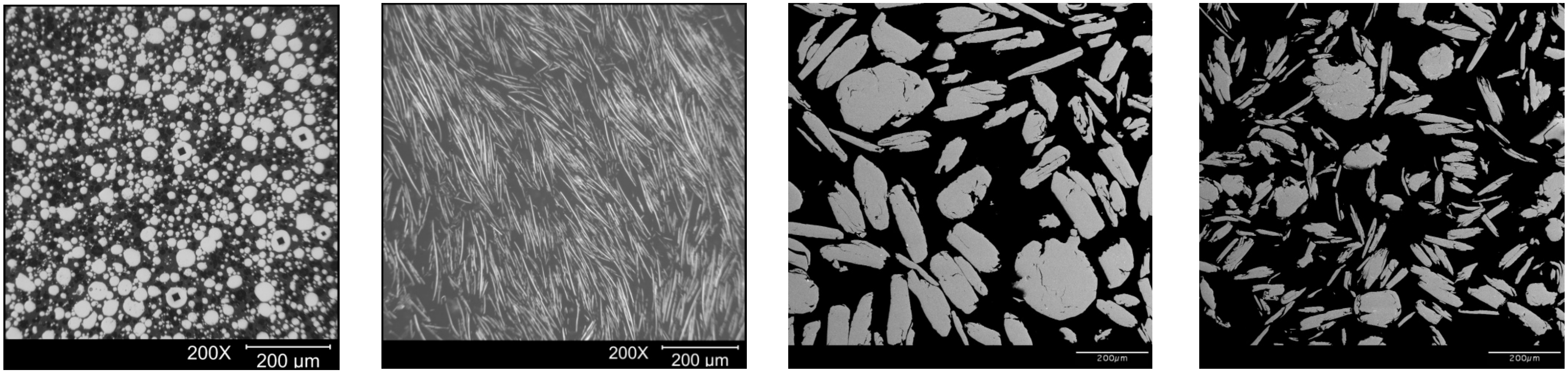
Sandia National Laboratories

*Can be found in **[1]**

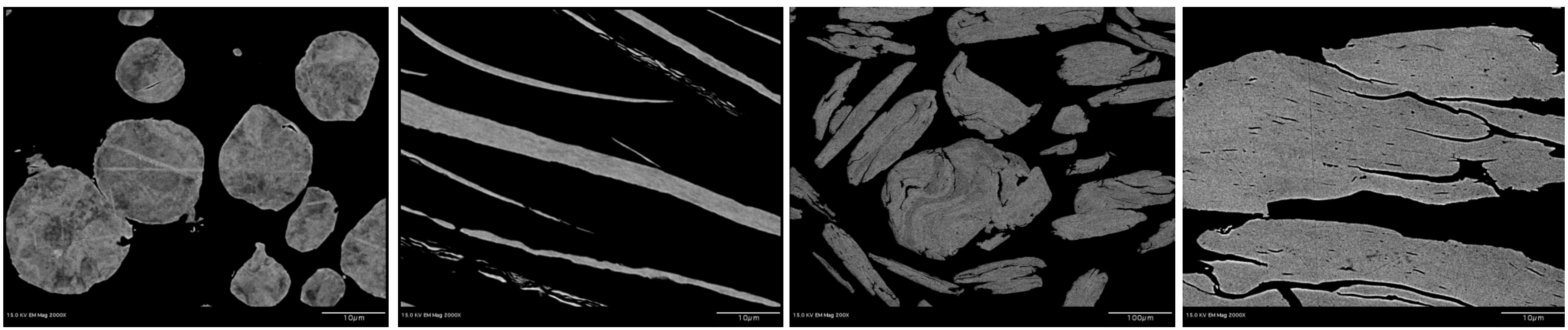
[1]Yang et al., Acta Mat **82** (2015) 41-50.
[2]Yee et al., Scripta Mat, in preparation

Particle Morphology

Optical Microscopy (OM)- 200x



Scanning Electron Microscopy (SEM)- 2000x



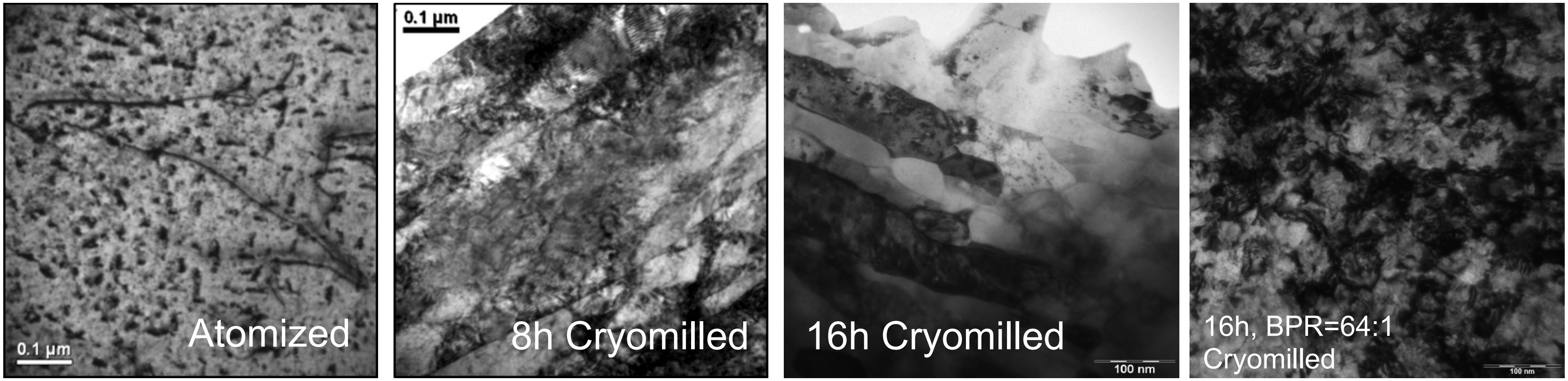
Atomized | 8 hour | 16 hour | 16 hour, BPR=64:1

UC DAVIS COLLEGE OF ENGINEERING

Sandia National Laboratories

[1]Yang et al., Acta Mat **82** (2015) 41-50.

Microstructural Characterization



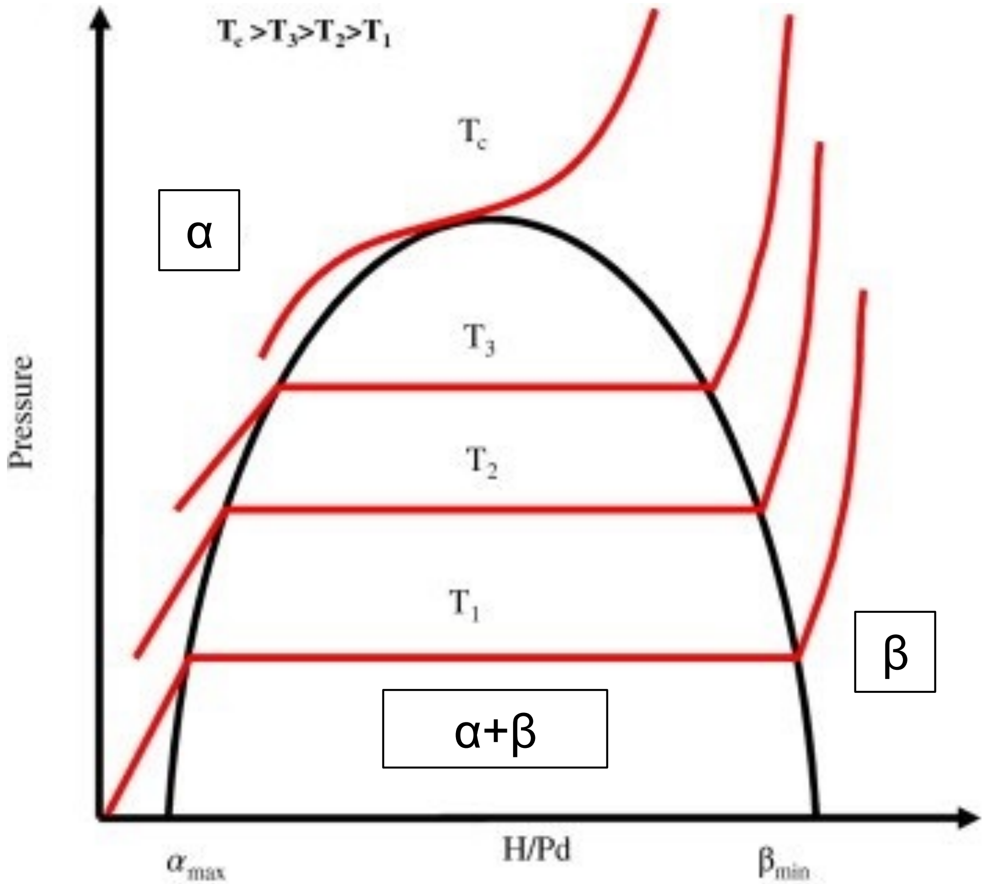
- Dense dislocation cell walls present in samples up to 8h of cryomilling
  - Hundreds of nm in diameter
- High angle grain boundaries present in 16h cryomilled sample
  - Dislocations still present
  - Elongated grains: Aspect ratio ~3
- 16h, BPR=64:1 material is highly deformed

Material	Grain Size (nm)	Dislocation Density (m^{-2})
Atomized	~5000	1.2×10^{14}
8h CM	77	2.4×10^{15}
16h CM	69	5.0×10^{16}
16h, BPR=64:1 CM	32	1.2×10^{17}

UC DAVIS COLLEGE OF ENGINEERING
Sandia National Laboratories

[1]Yang et al., Acta Mat **82** (2015) 41-50.
[2]Yee et al., Scripta Mat, in preparation

Pd-H PC Isotherm Characteristics

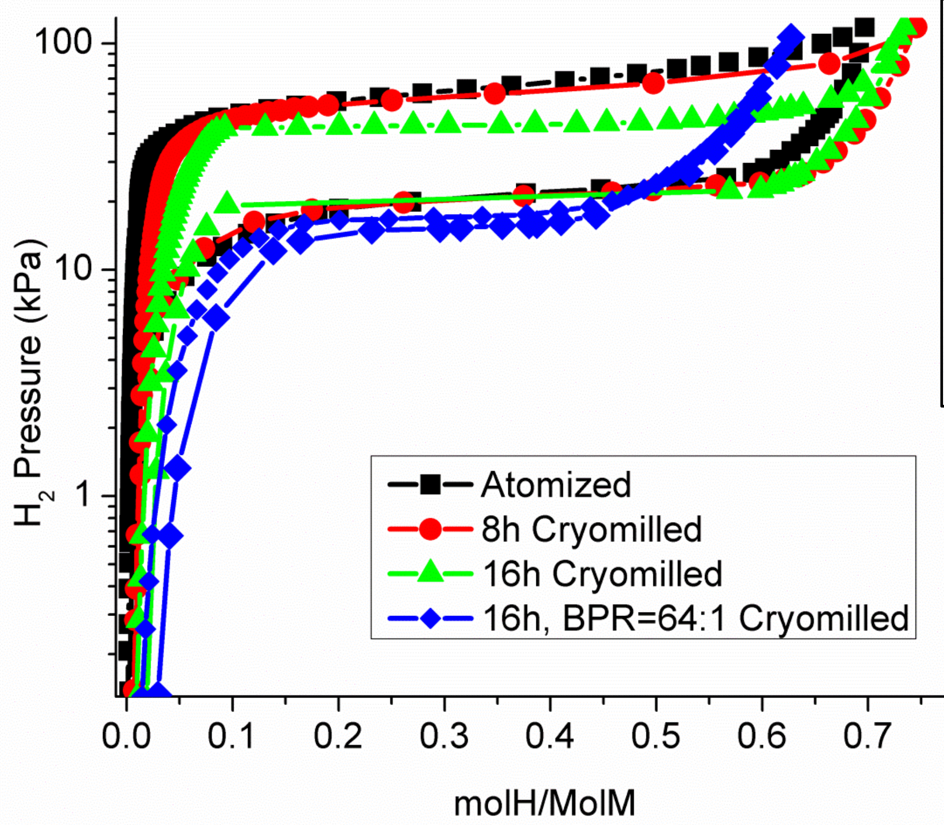


- 2-phase miscibility gap (α+β)
- 3 parameters measured in present investigation
  - α_{max}- maximum α-phase solubility
  - C_H- H concentration when P_{H2}=760 torr/ 101 kPa. Measure of β-phase
- All PC isotherms measured at RT in this study

UCDAVIS COLLEGE OF ENGINEERING Sandia National Laboratories

[1] B.D. Adams, A. Chen, Materials Today 14 (2011) 282.

Hydrogen Sorption Characteristics- PC Isotherms



- Sloping plateau pressure possibly due to inhomogeneous composition in Pd-10%Rh[1]
- Decrease in plateau pressure due to decrease in grain size[2]
- Decreased pressure hysteresis

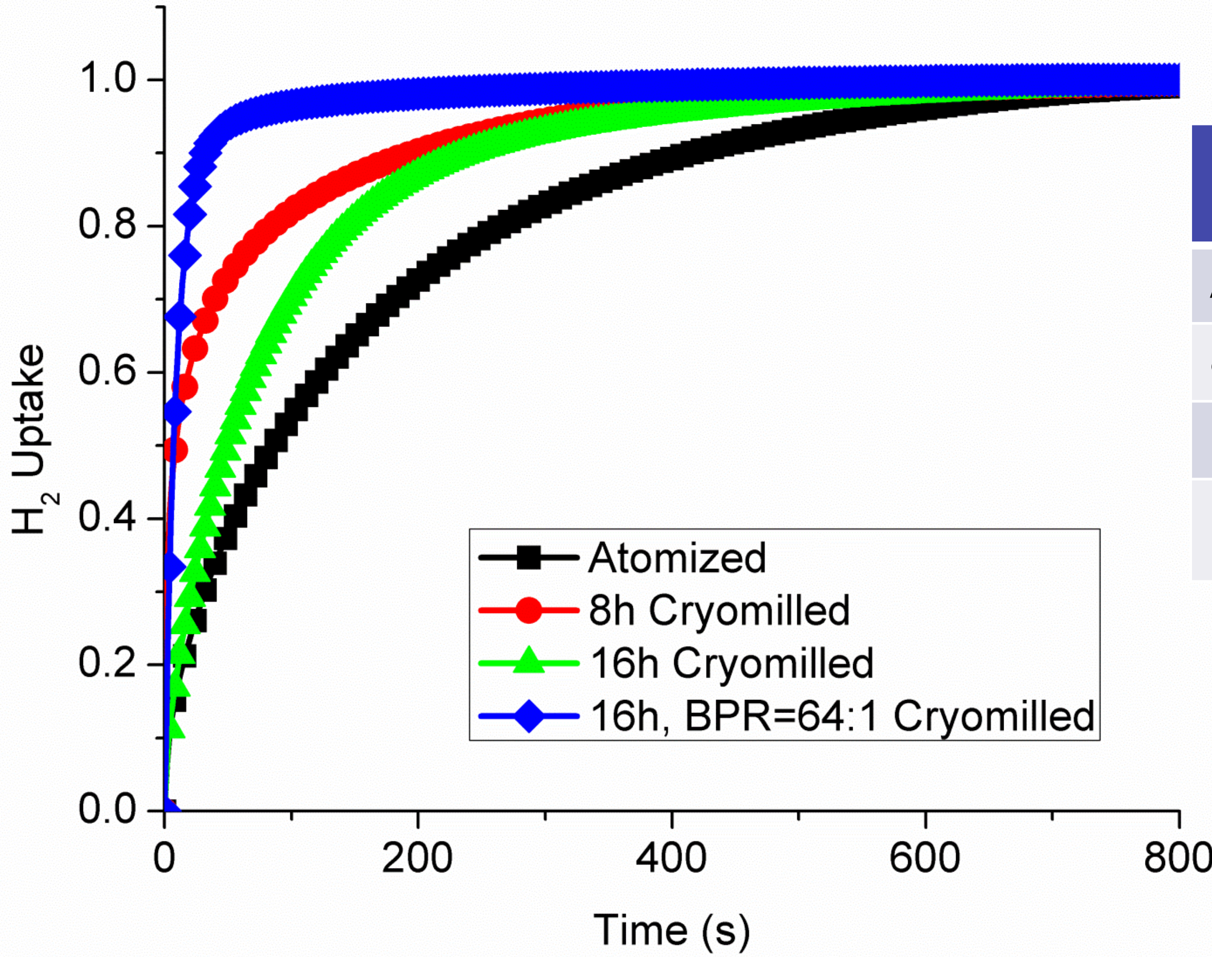
Material	α_{max} (H/M)	C_H (101 kPa) (H/M)	$P_{plateau}$ (kPa)
Atomized	0.046	0.66	64.5
8h CM	0.070	0.72	64.2
16h CM	0.092	0.72	43.3
16h, BPR=64:1	0.17	0.62	17.3

UC DAVIS COLLEGE OF ENGINEERING

Sandia National Laboratories

[1]S. Luo, C.-N. Park, T.B. Flanagan, Journal of Alloys and Compounds 384 (2004) 208.
[2]Kuji et al., J. Alloys and Cmpds, **293-295** (1999) 19-22.
[3]Yang et al., Acta Mat **82** (2015) 41-50.
[4]Yee et al., Scripta Mat, in preparation

Hydrogen Sorption Characteristics- Rate of Absorption



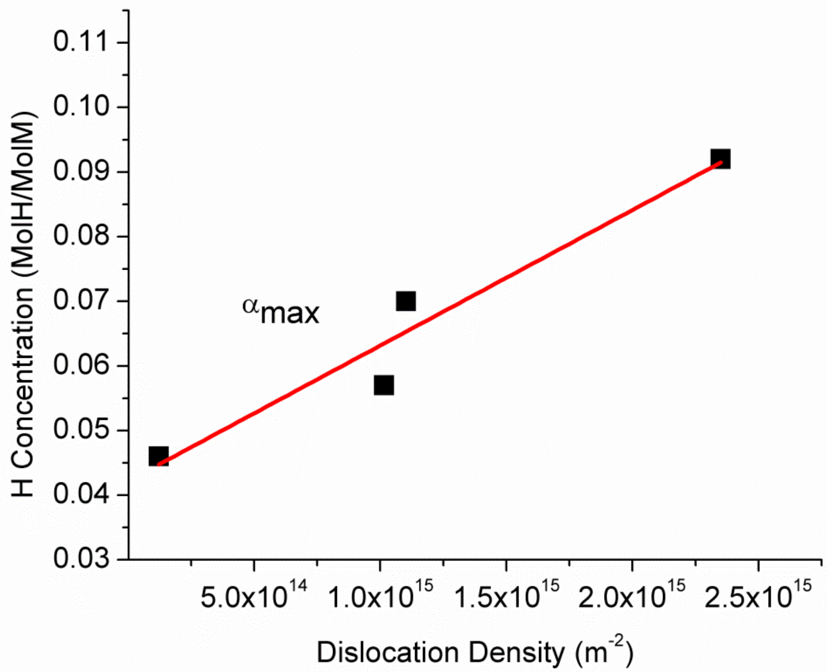
Material	Half-life (s)	Surface Area (m^2/g)
Atomized	88	0.037
8h CM	8	0.44
16h CM	64	0.034
16h, BPR=64:1	6	0.044

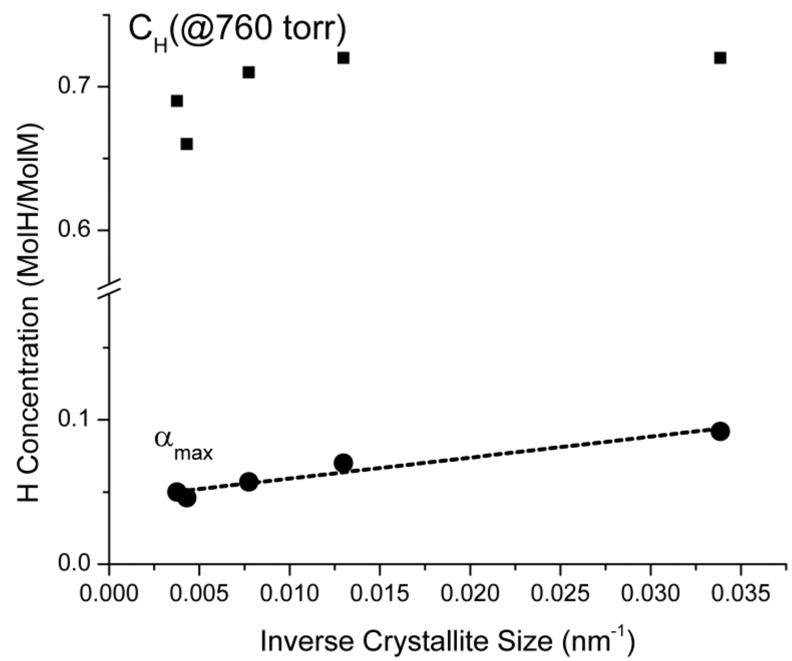
- Fast rates of absorption correlate with either high surface area or large grain boundary volume

UC DAVIS COLLEGE OF ENGINEERING
Sandia National Laboratories

[1]Yang et al., Acta Mat **82** (2015) 41-50.
[2]Yee et al., Scripta Mat, in preparation

Microstructural Influences on H sorption





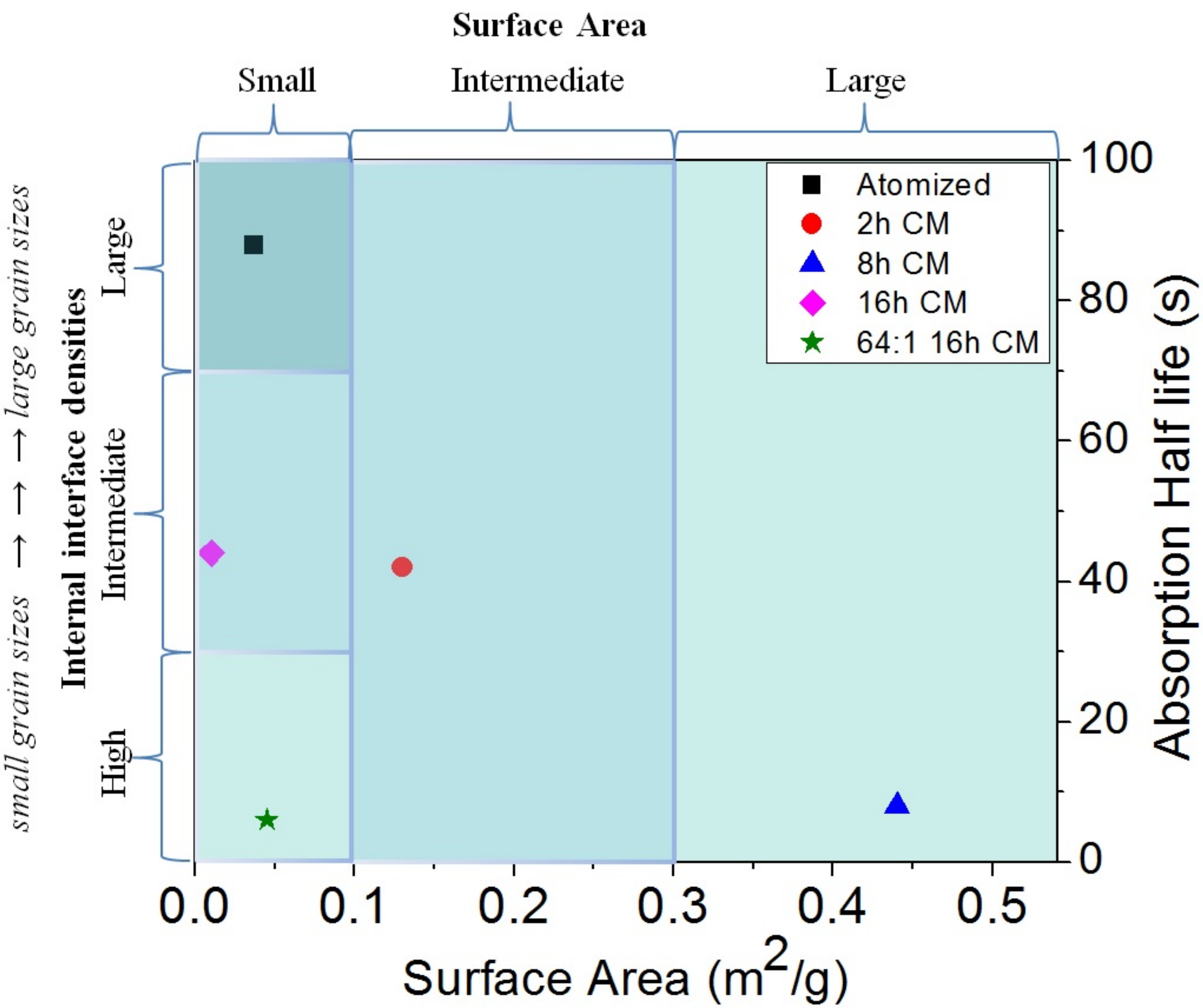
- α_{max} trend with increases in dislocation density and decreasing grain size
- C_H cannot be explained by a relationship with grain size
- Deformation induced by cryomilling introduces microstructural changes, which influence H sorption behavior

UCDAVIS COLLEGE OF ENGINEERING

Sandia National Laboratories

[1]Yang et al., Acta Mat **82** (2015) 41-50.

Microstructural Influences on H sorption



- 16h, BPR= 64:1 cryomilled material has fast rate of absorption, but low surface area
- Grain boundaries vs. surface area
- Adsorption rate-limiting
- Grain boundaries speed up adsorption and/or absorption?

Summary

- Cryomilling is an effective post-atomization processing method for producing nanostructured Pd-10%Rh
- Cryomilled Pd-10%Rh exhibited:
  - Increased surface area with milling time
  - Refined grain size
  - Increased dislocation density
- Hydrogen sorption parameters influenced by microstructural changes induced by cryomilling
  - Increased α-phase solubility and onset of β-hydride phase ($C_H(760)$)
  - Decreased hysteresis
  - Faster rates of absorption

THANK YOU FOR YOUR TIME!
QUESTIONS?