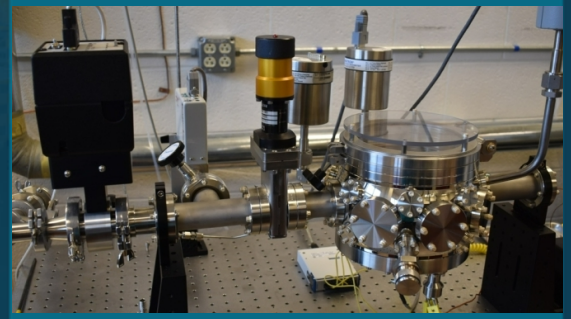
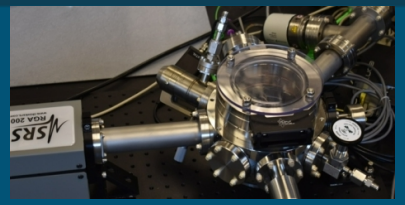
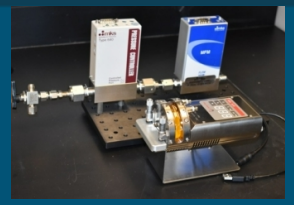
SAND2021-13970PE

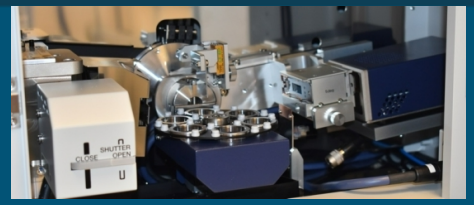
Sandia National Laboratories

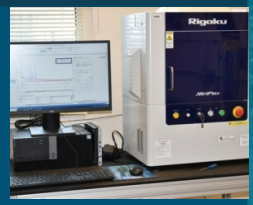
Exploring The Titanium Subhydride (TiH_x) Phase Space











By Chad Macziewski

Collins Aerospace Interview

22 November 2021

Acknowledgements: Daniel Bufford, Brynal Benally, Michael Dewey, Benjamin Juba, Jessica Kustas, Melody Teixeira, Michael Thomas, Rafael Spillers, Adam Pimentel, and Hua Wang

U.S. DEPARTMENT OF ENERGY NNSA

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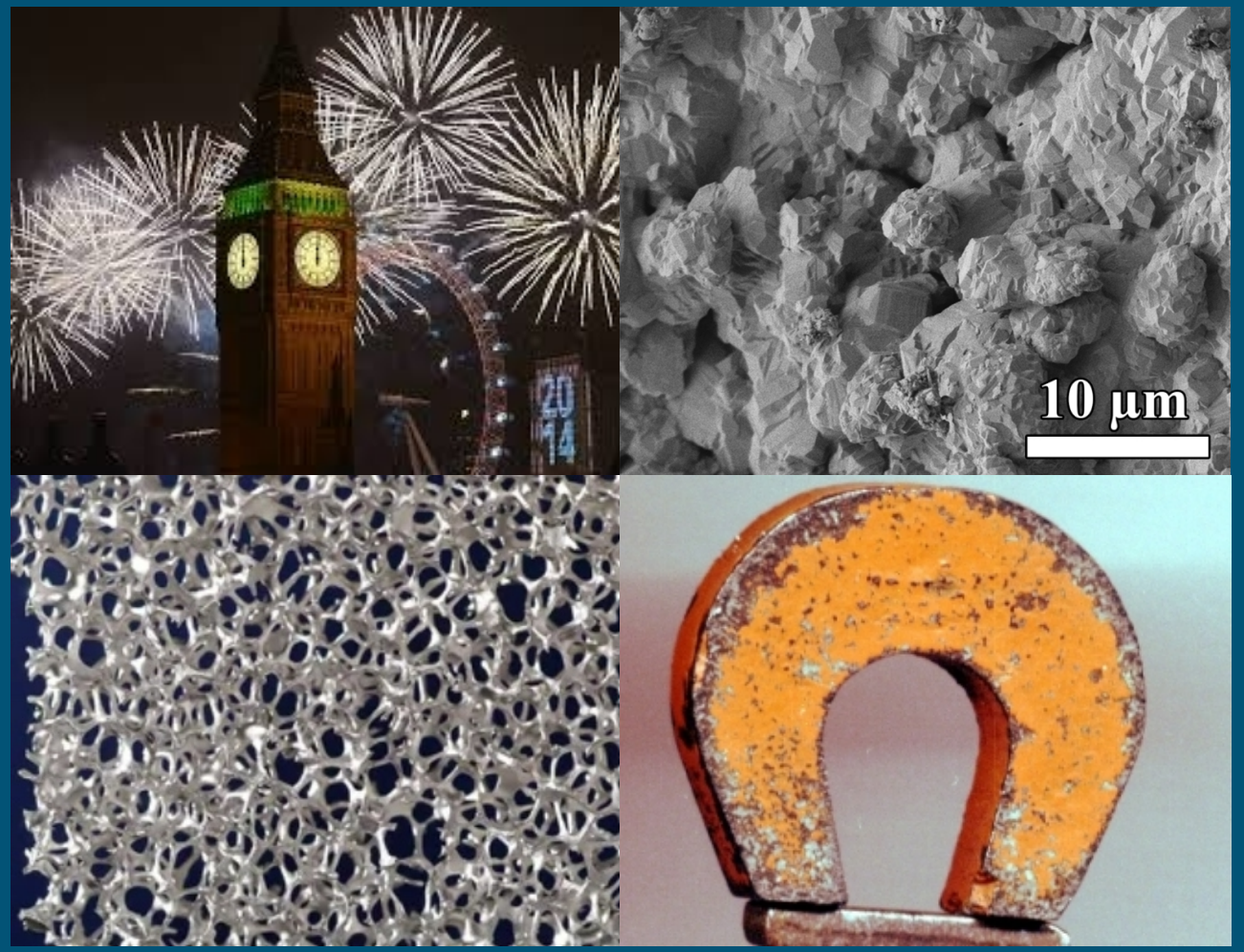
History - What Is Titanium Subhydride?

Used in a variety of ways

- Fuel for pyrotechnic blends (current industrial/SNL use)
- Sintering Agent
  - Alnico Magnets (current industrial use)
  - Titanium powder metallurgy/additive manufacturing (potentially)
- Metal Foaming (current industrial use)
- Hydrogen storage (current industrial use)

Properties vary with hydrogen content



www.medgadget.com/2010/09/titanium_foam_as_new_material_for_implants.html
en.wikipedia.org/wiki/Alnico#/media/File:MagnetEZ.jpg
www.medgadget.com/2010/09/titanium_foam_as_new_material_for_implants.html

History - Why Are We Interested?

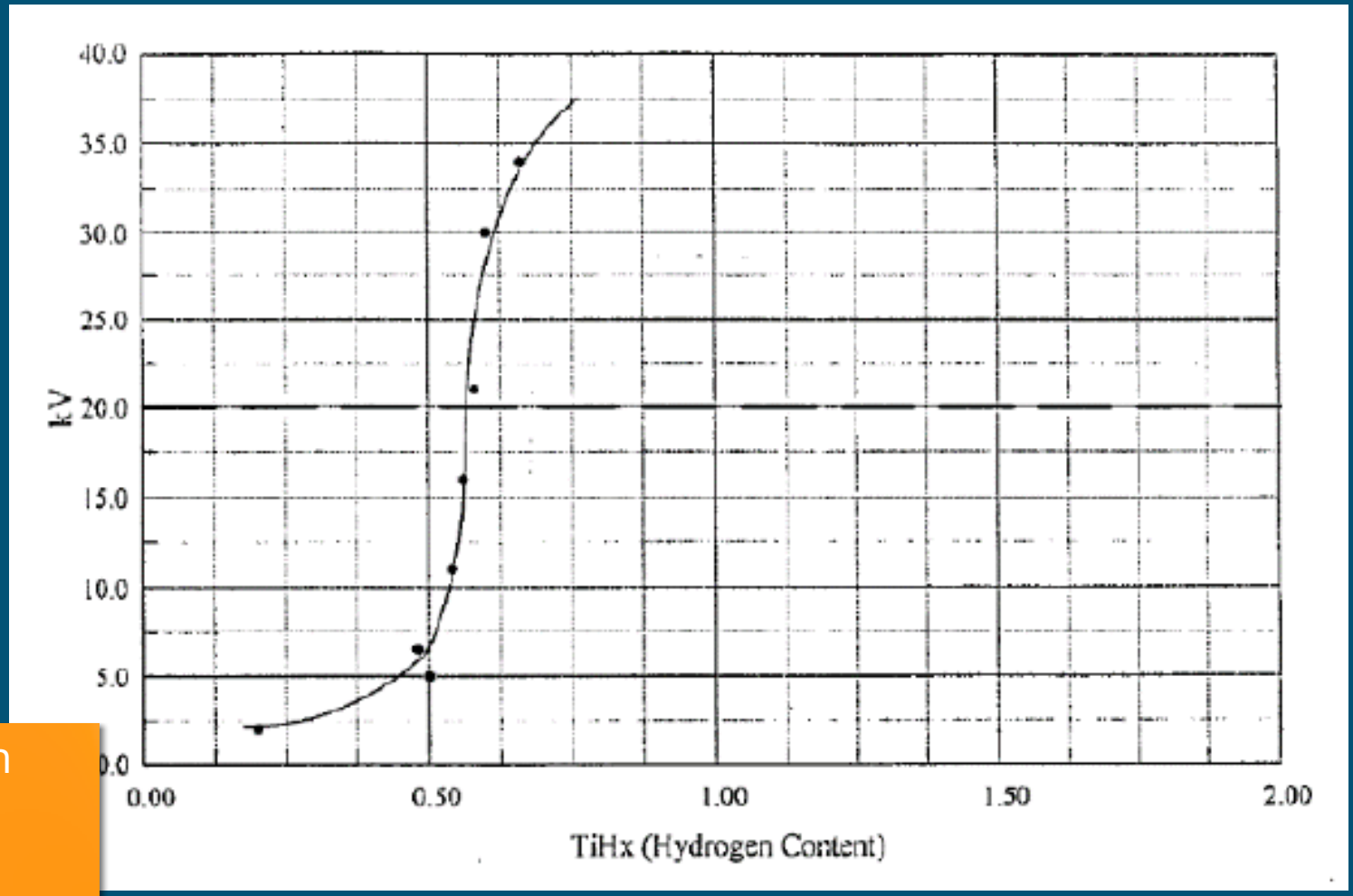
Tunable Sensitivity
- More hydrogen = Less Reactive
- Less Hydrogen = More Reactive

Reliable Response
- Chemically Stable
- Measured Output
- Controllable Ignition

Challenges
- Hydrogen Quantification
- Particle size control
- Reproducibility

Pyrotechnic performance depends on hydrogen content, chemistry, and morphology of the particles.

Hydrogen Content VS Energy Necessary to Ignite

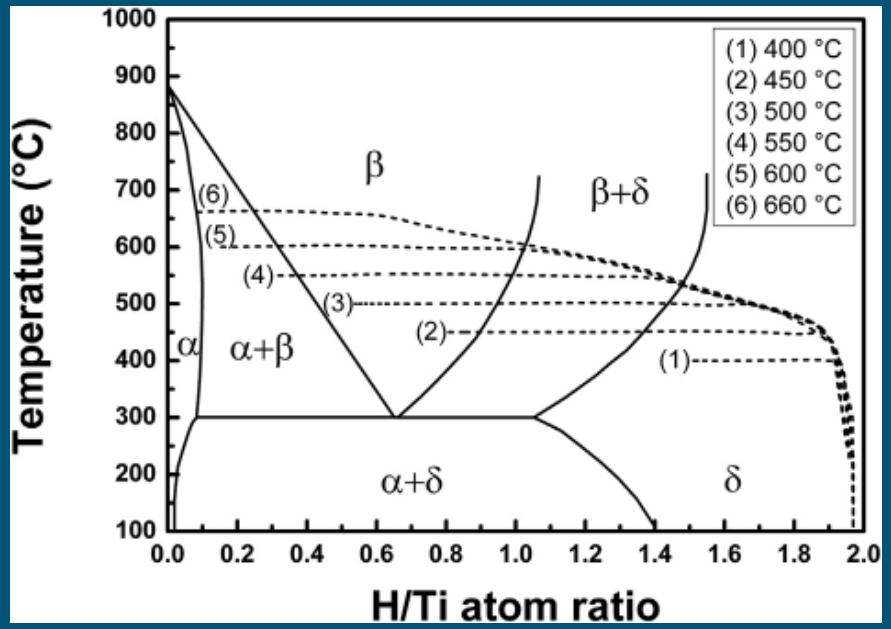


Massis SAND 1996

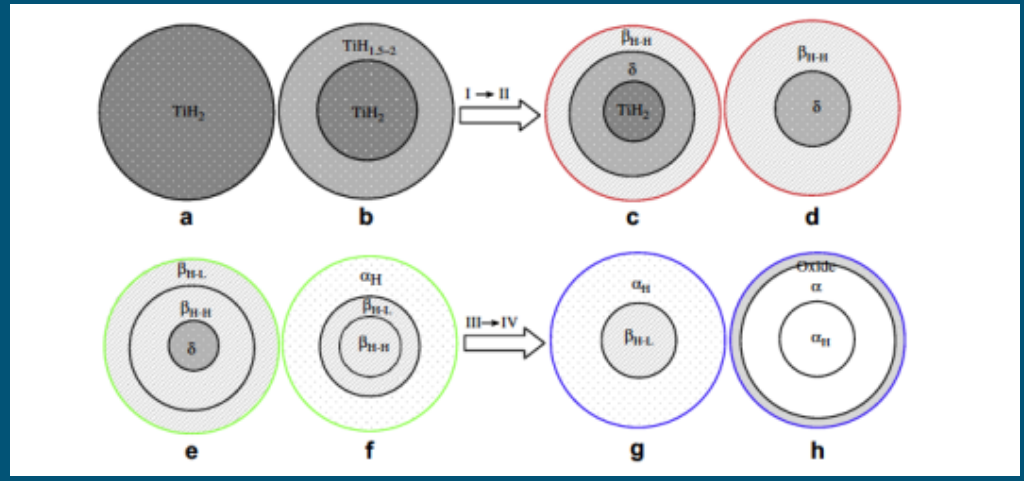
Process -Dehydriding process

- General processing approach
  - Initial vacuum was pulled
  - Samples were heated under vacuum or hydrogen-containing atmospheres to add/remove hydrogen
  - Sample was then cooled down and passivated
- Want to control
  - Surface area/particle size
  - Impurity content
  - Hydrogen content
- Historical documentation lacking on what really matters
- How do you control your process variables to reach those goals

Alter hydrogen content with teperature and pressure



Ma et al, Int J Hydrogen Energy 2017

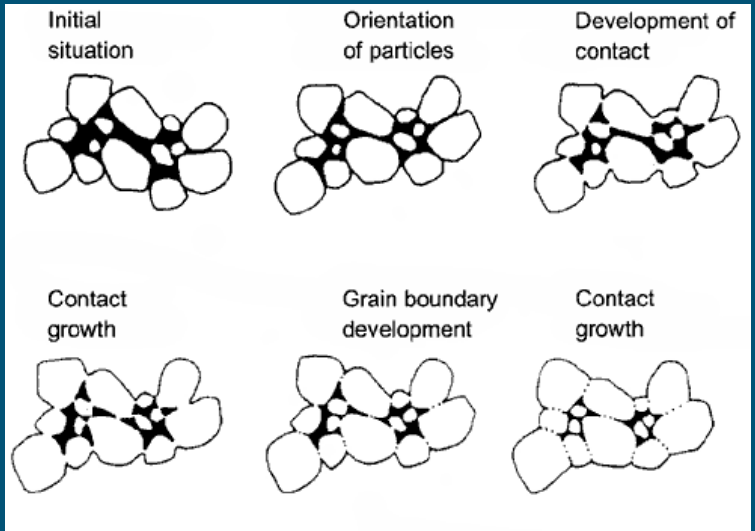


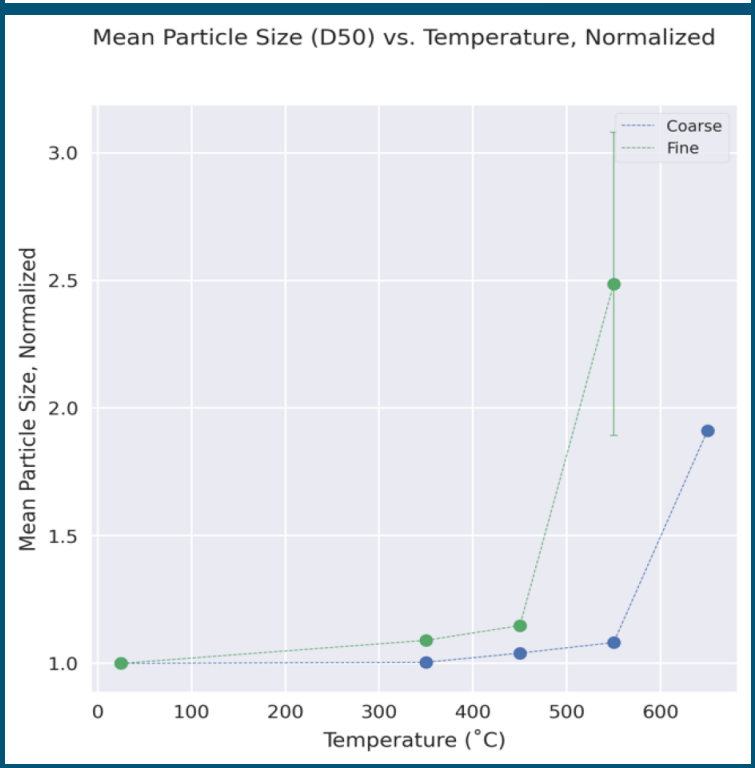
Wang et al, Int J Hydrogen Energy 2009.

Concerns – Side Effects of Dehydriding

- Particle growth and surface area loss are concerns
  - Can change the sensitivity/reactivity
  - Full sintering above ≈ 850 ˚C
  - Onset at lower temperatures
  - Changes may occur at processing conditions
    - #1 Temperature
    - #2 Time at temperature
    - #3 Wildcard: passivation (exothermic reaction)
- How do we address it?
  - Lower dehydriding temperature
  - Shorten time at dehydriding temperature
  - Slowly passivate at low oxygen pressures
- Might be reversible if the sintering is incomplete
  - Powder is caked but breakable
  - Sieving greatly decreases agglomeration

Onset of sintering may overlap with processing temperatures.
Relatively little information in literature for this temperature range.

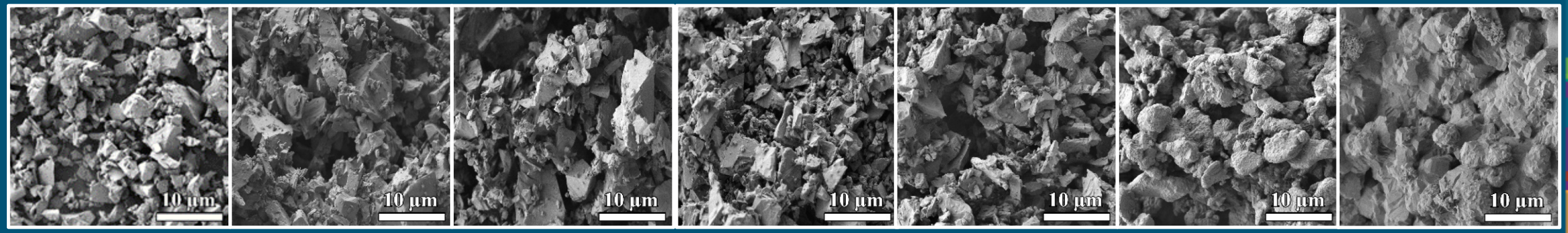




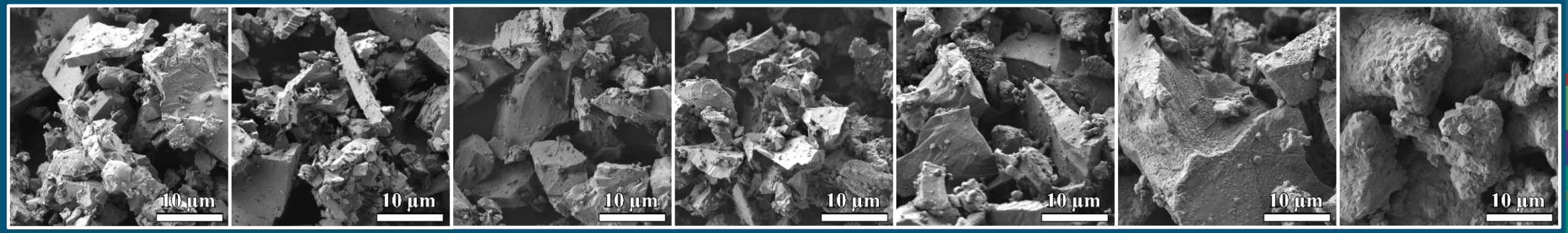
Brevier Tecnische Keramik

Concerns – Side Effects of Dehydriding

≈ 2 µm initial average particle size



≈ 40 µm initial average particle size



AR | 350 ˚C | 450 ˚C | 550 ˚C | 650 ˚C | 750 ˚C | 850 ˚C

Particle size and surface area changes can occur at otherwise viable processing temperatures.

Subhydride – Chemical Analysis

- Consistent fractions of Fe, Cr, Ni, and Zr
  - Likely associated with stainless steel vessels used in synthesis
- Decrease in Mg, Na, Ca
  - Likely associated with Ti synthesis processes
- Increase in O
  - Independent of processing condition
- Hydrogen fractions as expected

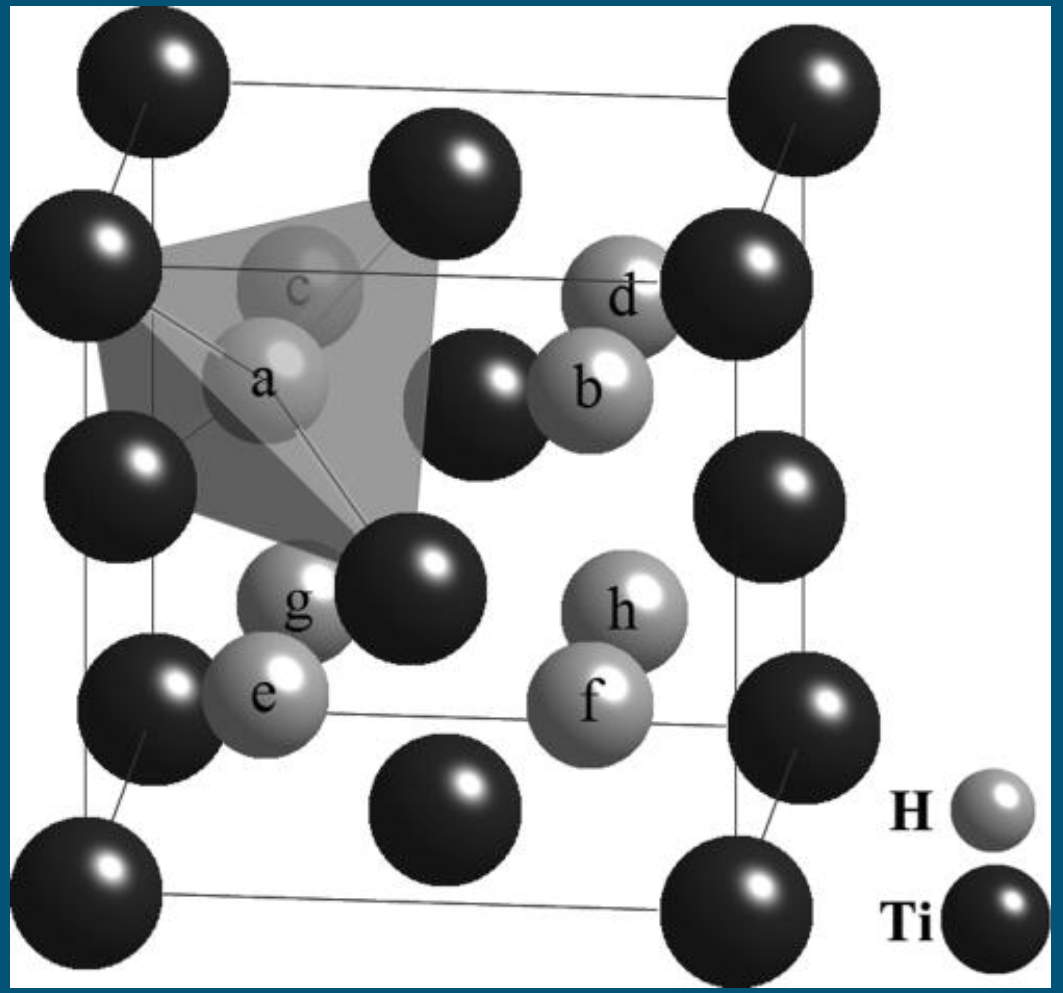
	TiH2		TiH1.75		TiH1.65		TiH1.55	
	PPM	StDev	PPM	StDev	PPM	StDev	PPM	StDev
Fe	184.34	3.29	180.19	1.95	177.97	3.91	180.19	2.27
Cr	129.93	1.54	128.1	2.55	127.36	3.05	128.16	2.35
Ni	168.85	0.59	166.97	2.82	163.55	4.91	166.88	2.77
Ca	15.75	3.98	8.64	2.91	6.65	0.28	10.14	2.17
Na	85.48	18.77	53.53	17.97	37.39	3.25	57.89	10.45
Mg	102.79	2.36	96.7	2.42	74.31	1.23	72.96	3.12
Zn	0.63	0.3	0.66	0.5	0.66	0.51	0.57	0.14
Zr	104.56	1.25	103.5	2.18	107.65	2.93	109.3	1.76
	792.33	32.08	738.29	33.3	695.54	20.07	726.09	25.03

	TiH2		TiH1.75		TiH1.65		TiH1.55	
	Wt. %	StDev	Wt. %	StDev	Wt. %	StDev	Wt. %	StDev
O	1.38	0.10	1.82	0.26	1.80	0.16	1.88	0.07
H	4.01	0.15	3.52	0.02	3.09	0.03	2.16	0.06

Oxygen increases, trace metals remain consistent or decrease.

Hurdles – Hydrogen Concentration

- Measurement Approaches
  - Heating + desorbed gas analysis
    - Analysis of released gas by optical spectra and thermal conductivity (LECO), pressure, or quantitative mass spec (MS)
    - Requires calibration by reference material
  - Heating + gravimetric analysis
    - Thermogravimetric analysis (TGA), quartz crystal microbalance
    - Sensitive to oxygen even under vacuum or carrier gas
  - Combined TGA-MS
    - Improved accuracy by comparing simultaneous data
    - Increased instrument complexity
  - XRD
    - Nondestructive
    - Depends on single phase region
    - Requires calibration by reference material



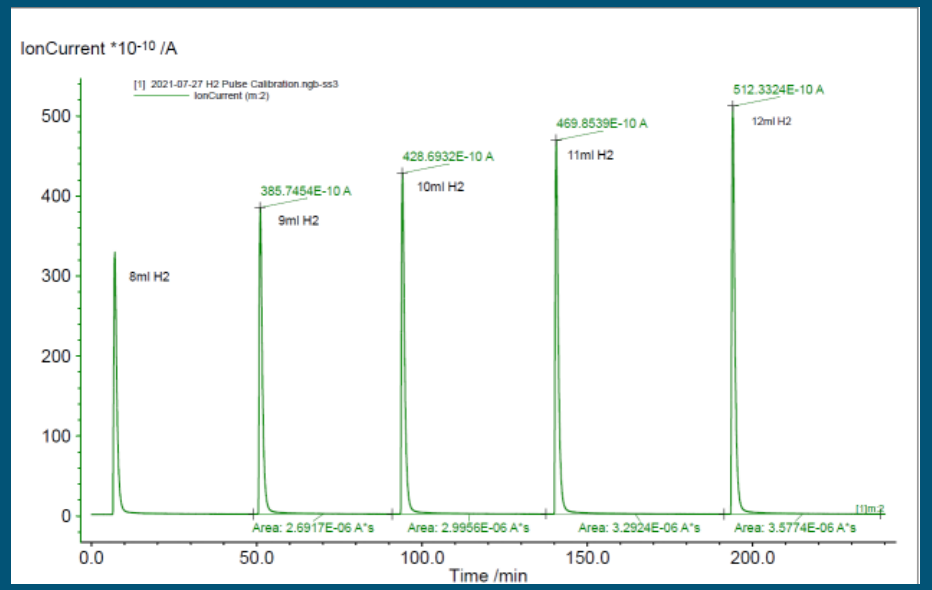
Liang, C. P. & Gong, Haoran. (2013).

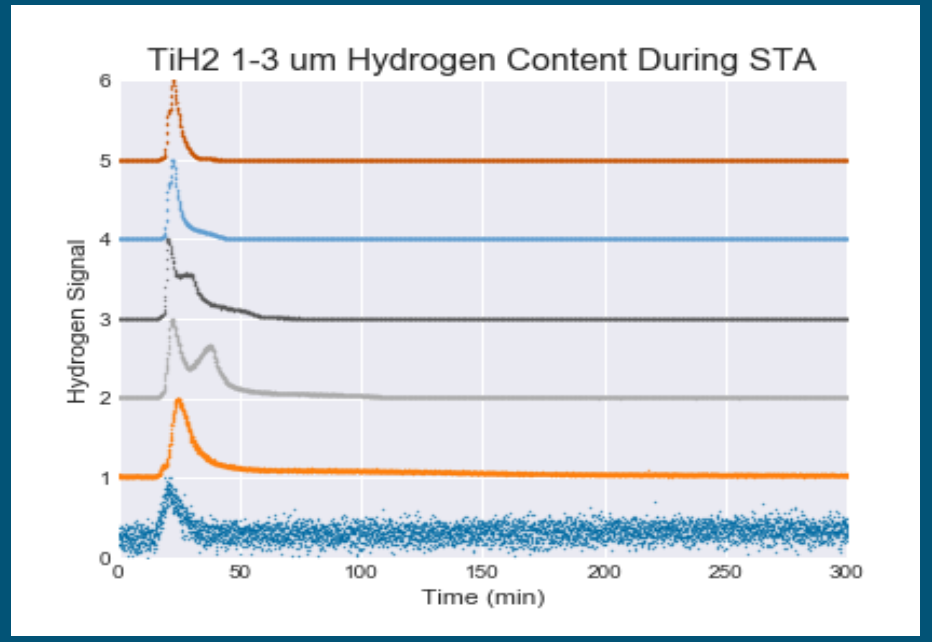
Multiple methods currently under evaluation. In house diffractometer takes 15 minutes to scan one sample!

Subhydride – Pulse TA Results

- Known volumes of gas injected to establish a calibration curve for MS signal
- Once calibrated, can measure the amount of hydrogen being released from samples
- Establishes an analytical technique that can quantitate hydrogen (or other gases) over time despite irregular peaks and simultaneous release of multiple species.

Pulse TA: new method for hydrogen quantification.

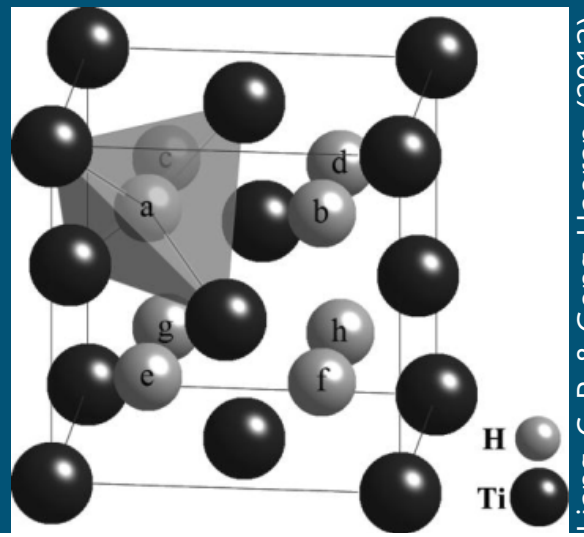




Subhydride – XRD

- The lattice parameter is dependent on the atoms sitting in the lattice
- The FCC structure of TiH_2 has 8 tetrahedral sites occupied with hydrogen
- TiH_x only has a fraction of the sites occupied
  - This leads to a contraction of the lattice
  - A smaller lattice shifts peaks to the right
- The FCC structure is stable down to x = 1.54
  - Below this concentration the material has a second phase
  - A second phase shows up as different peaks
  - If the original phase disappears so do the peaks
- The shift is only on the order of a degree
  - Still enough to determine peak position accurately

XRD: Fastest and most reliable method



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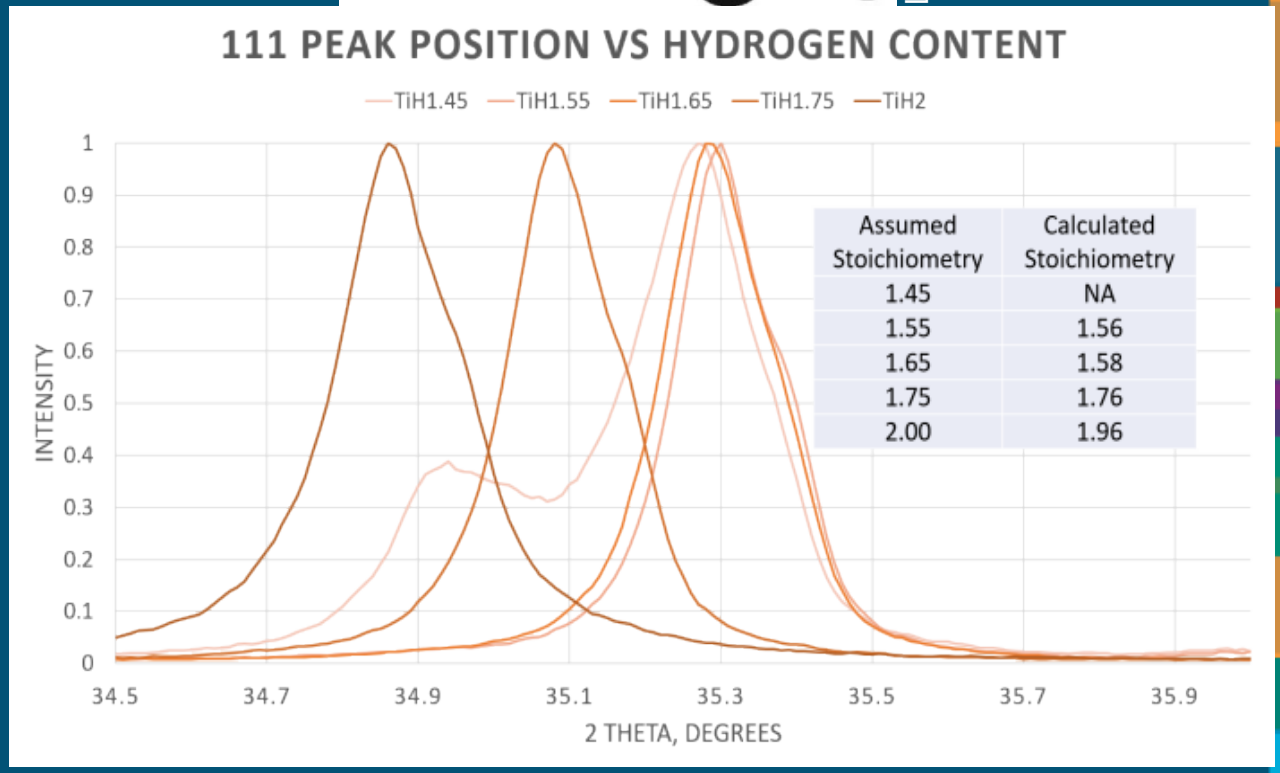
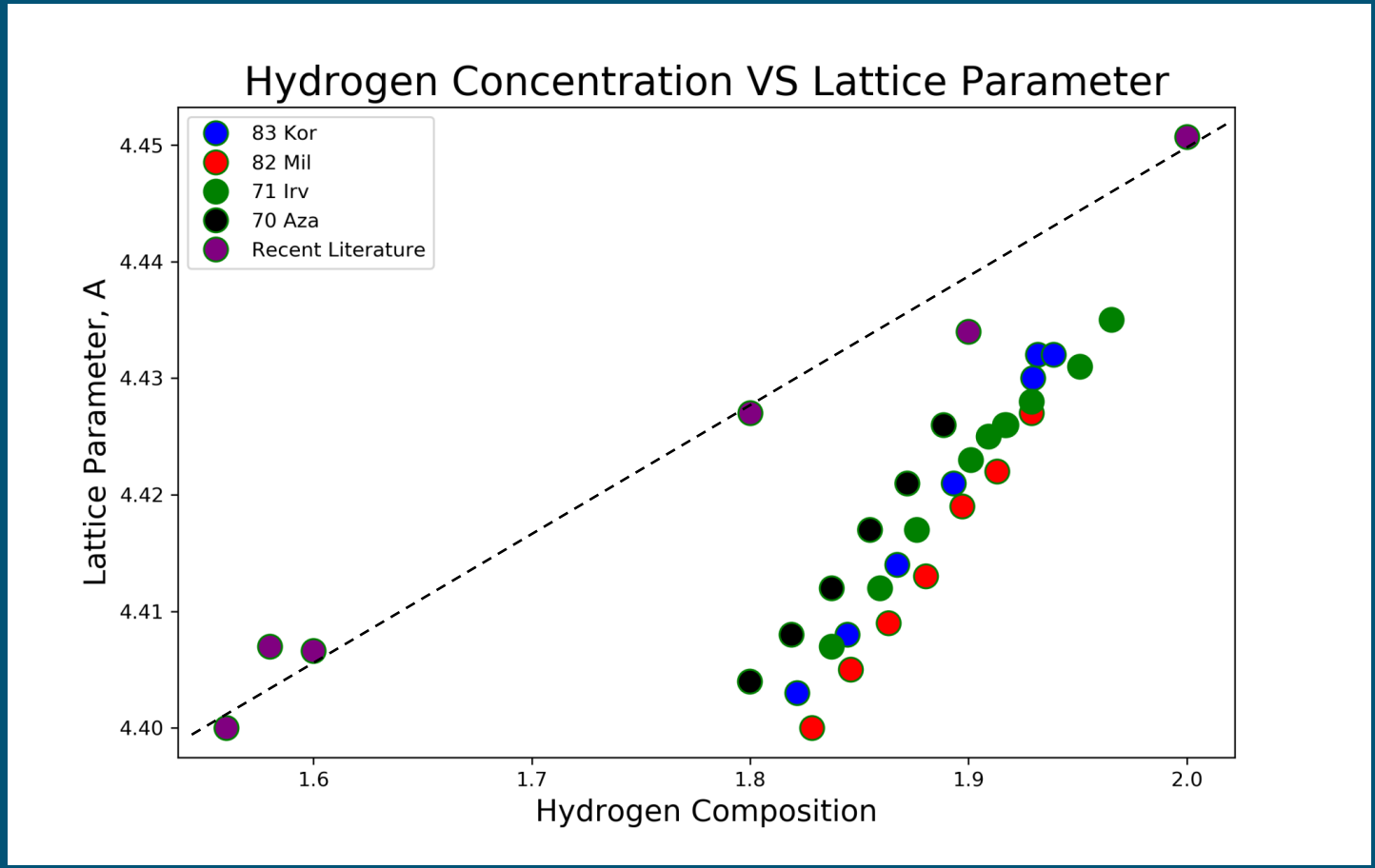


Subhydride – XRD Matching to Literature

- XRD studies of TiH_x go back decades
  - However, some samples are of questionable purity
  - Shows a definite linear relationship
  - Can be overcome by establishing a few standard hydrogen compositions and creating a calibrated database.

- Concerns
  - Repeatability of the dehydriding process
  - Other factors causing a peak shift
    - Presence of impurities
    - Z-Height
    - Optic misalignment
    - Thermal Expansion

XRD: Fastest and most reliable method



Future Works – Hydriding & Scale Up

Why not start from Ti?

- Exothermic Reaction to Hydride
  - Potential for runaway
  - Increased chance of sintering
- Harder to obtain material
  - Starting material can be pyrophoric
  - “It burns in air!” –contract manufacturer

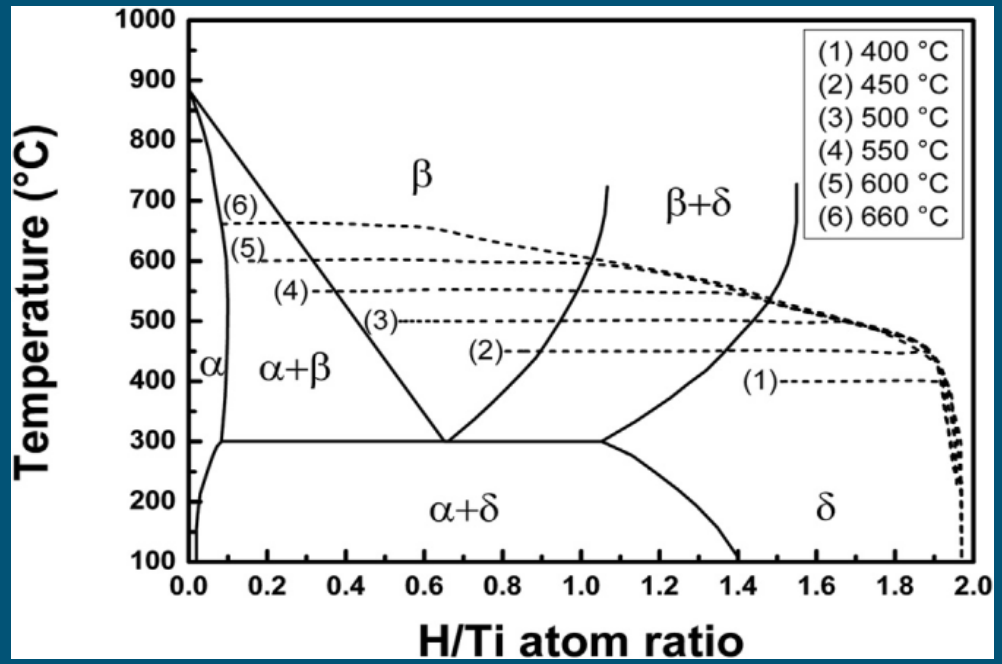
Scale Up

- Current work focuses on <10g batches
  - Enough for testing but not ideal
  - Need a larger reaction vessel for larger batches
- How about a tube furnace
  - Larger capacity
  - Stable temperature
  - Rotating capability to mix powder
- Concerns
  - Heating too quickly = Large volume of gas produced
  - Increased vacuum bandwidth necessary
  - Ease of cleaning reaction vessel

Is dehydriding the only method? Can we go bigger?

Questions?

- Reinvented a unique process
- Used equilibrium conditions
- Controlled temperature and pressure
- Monitored chemical and physical changes
- Quantified hydrogen content
- Created a roadmap to new compositions



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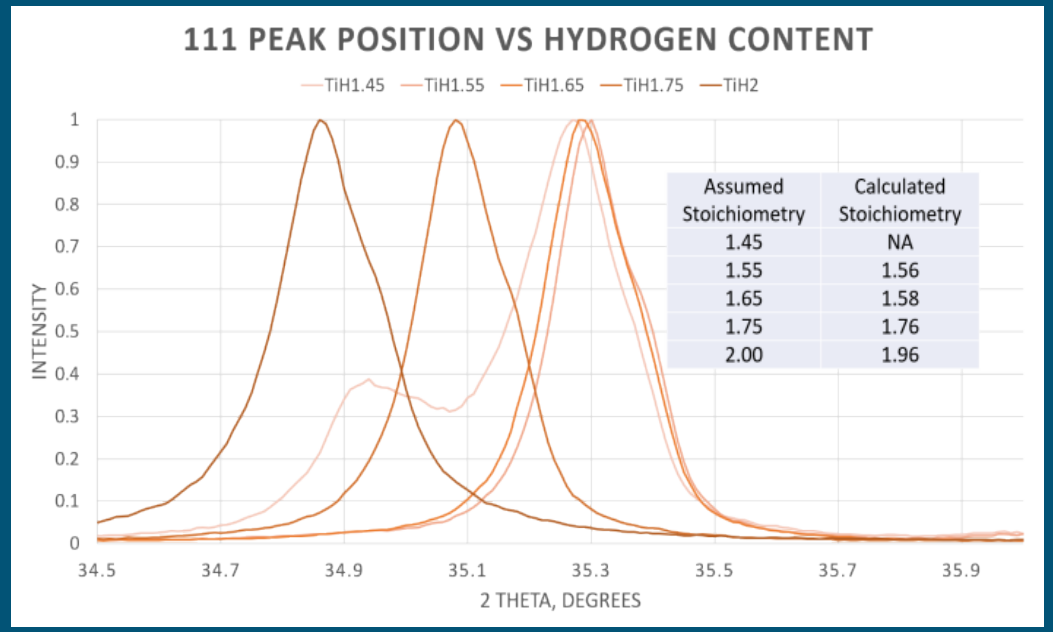

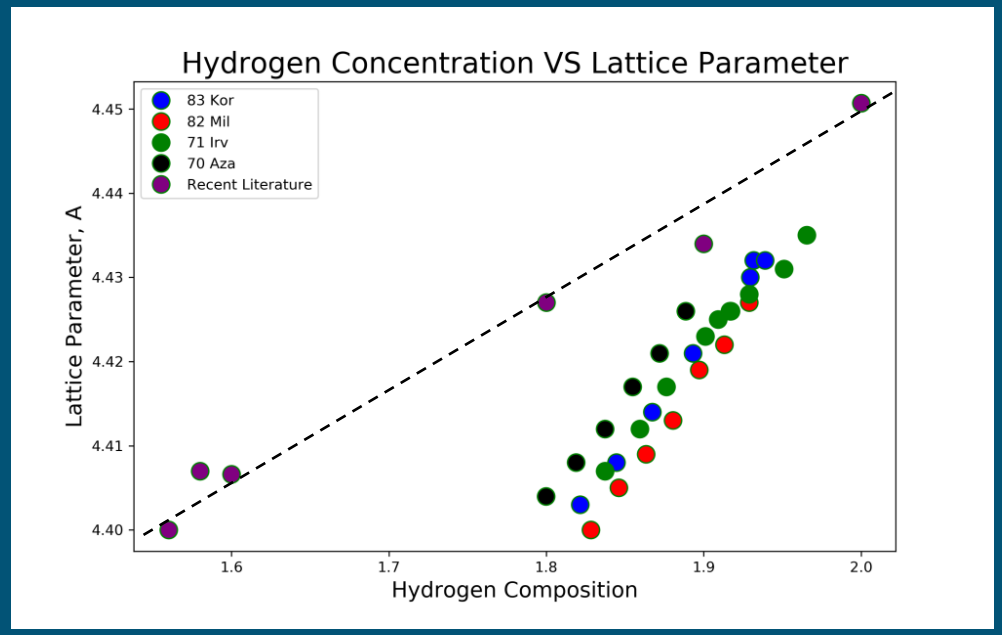

Subhydride – STA Results

Appears to be a link between when hydrogen comes out and oxygen/nitrogen diffusion begins.