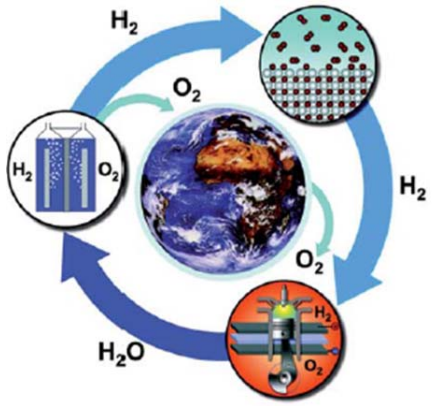
Centre for Advanced Hybrid Materials

Magnesium alloys for hydrogen storage



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ALMA Meeting, Tokyo, 10 November 2018

MONASH University

Collaborations with:

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- Efrain Carreño-Morelli

General Electric, USA:

- S. Jorgensen

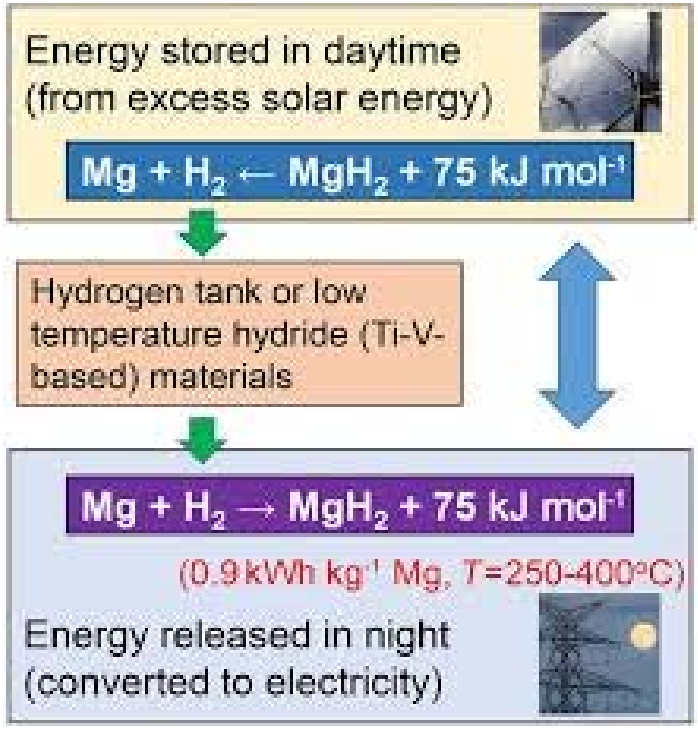
Why Mg?

- Advantages:
- Fourth most common element in the Earth crust
- Cheap
- Can reversibly store up to 7.6 wt% of hydrogen

Main drawback: slow absorption/desorption kinetics

- MgH2 hydride is relatively stable (desorption at 1 bar requires temp. of 300°C) - impractical for mobile applications.
- High reactivity toward oxidation. Formed oxide layer inhibits the dissociative adsorption of hydrogen.

Hydrogen storage in Mg alloys



Volume of 4 kg of hydrogen compacted in different ways, with size relative to the size of a car

Mg_2NiH_4 **$LaNi_3H_6$** **H_2 (liquid)** **H_2 (gas, 200 bar)**

Schlapbach & Züttel, Nature (2001)

Benefits of Solid State Storage

- Reversible metal hydrides operate at low pressure – advantage over compressed gas storage (700 to 2,100 bar)
- No need for storage at the cryogenic temperatures – advantage over liquid hydrogen storage.

Current mobile applications:
Toyota Mirai

https://str.llnl.gov/2018-01/wood

Solid hydrid storage (stationary)

McPhy, France

INGRID Project, 750 kg storage capacity

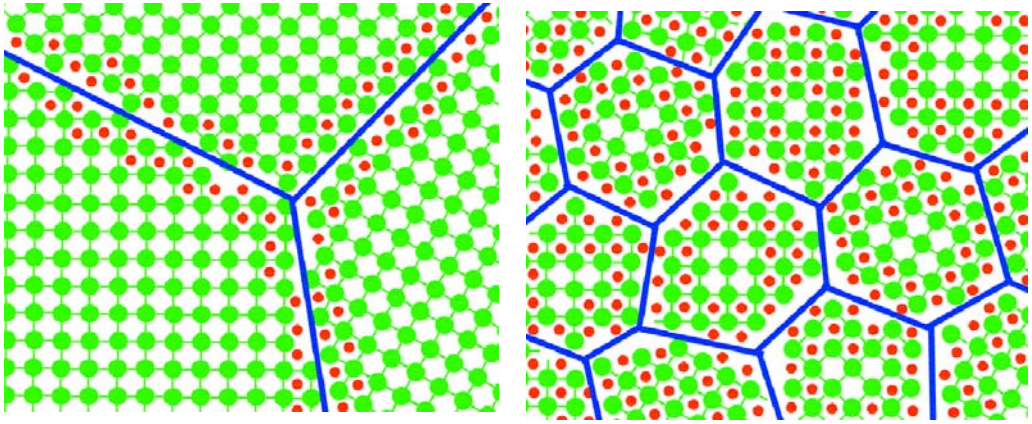
https://mcphy.com/en/our-products-and-solutions/storage-solutions/

How Can the Kinetics be Improved?

Control over particle size/surface area	**Addition of transition metals that act as catalysts**	**Introduction of lattice defects**
	↓	
Working with chips (thickness up to 50µm)	**Alloying with Ni**	**Severe plastic deformation (ECAP)**

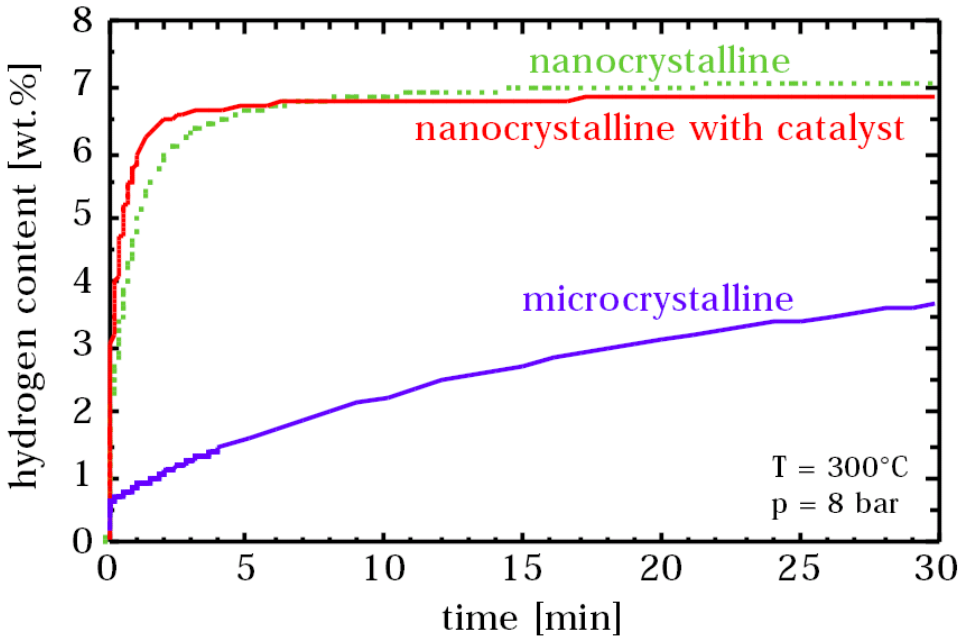
Strategies for enhancing H_2 storage kinetics

- Nanostructuring

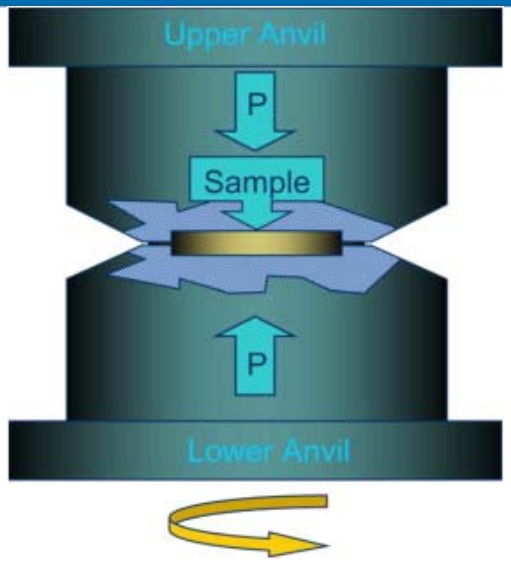


- Addition of catalysts

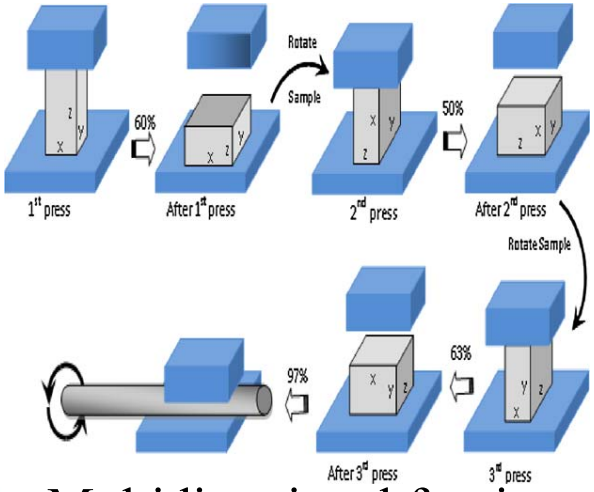
(Ni, Ti, Fe, Pd, V, Oxides)



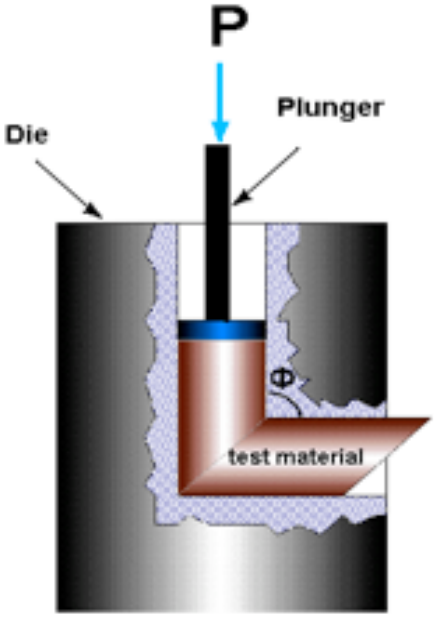
SPD techniques



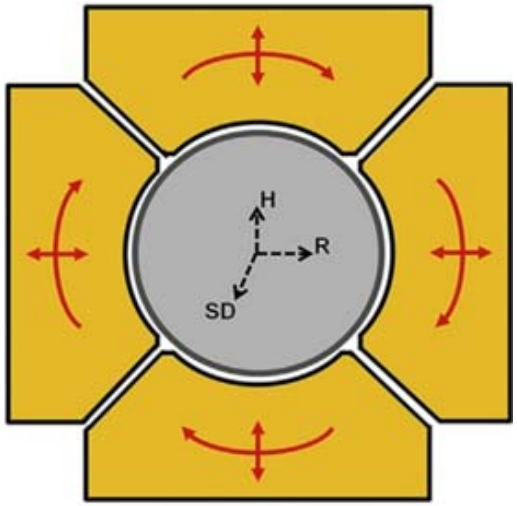
High pressure torsion



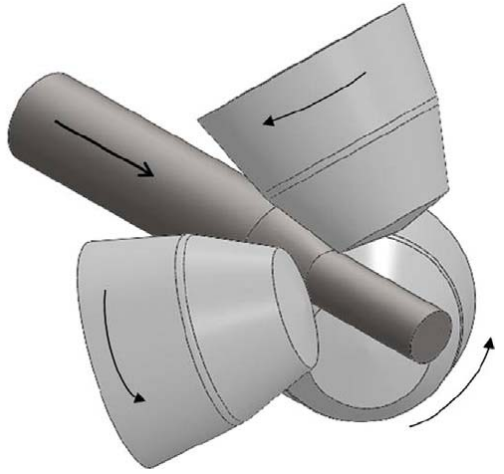
Multidirectional forging



Equal channel angular pressing



Rotation forging



Radial-shift rolling

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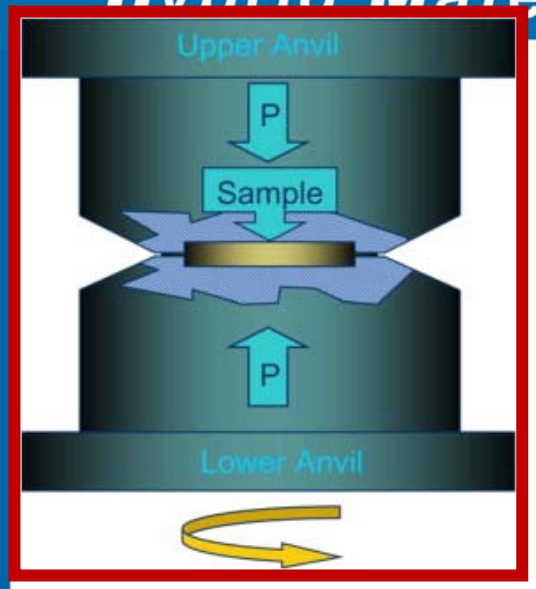
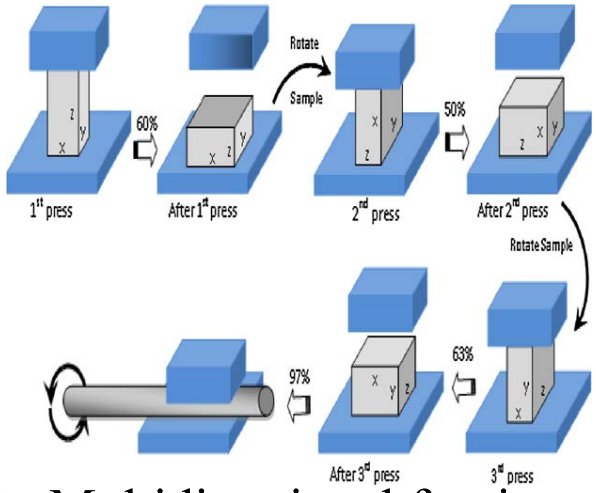
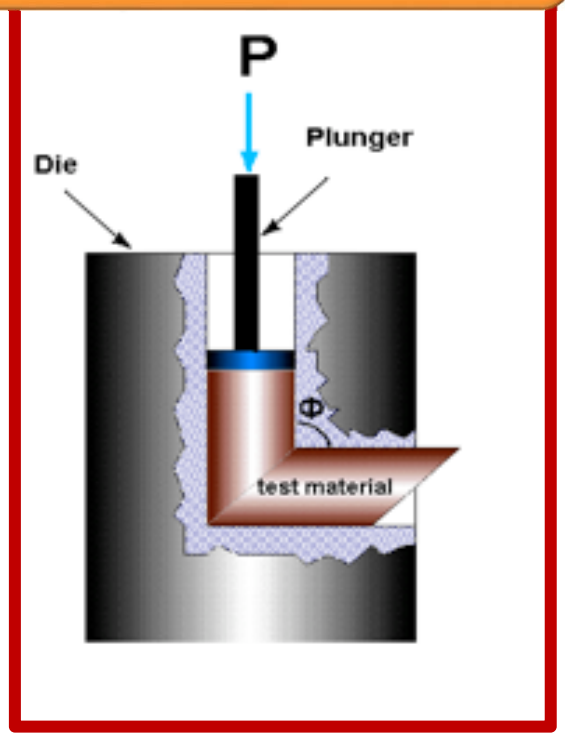
SPD techniques



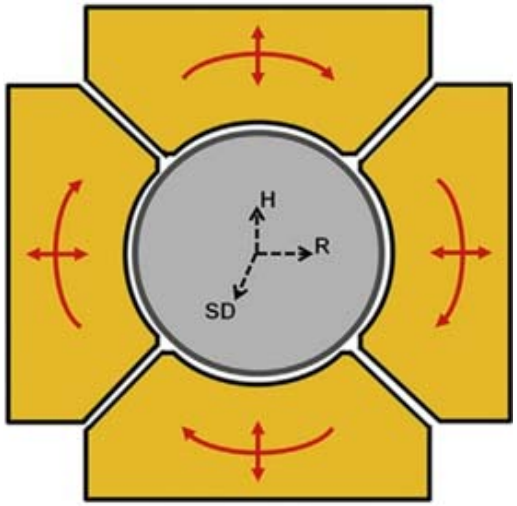
High pressure torsion



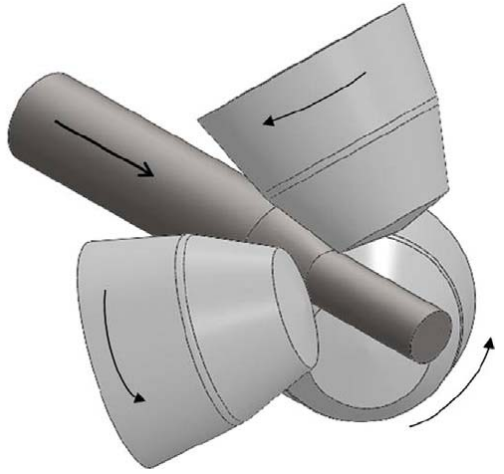
Multidirectional forging



Equal channel angular pressing



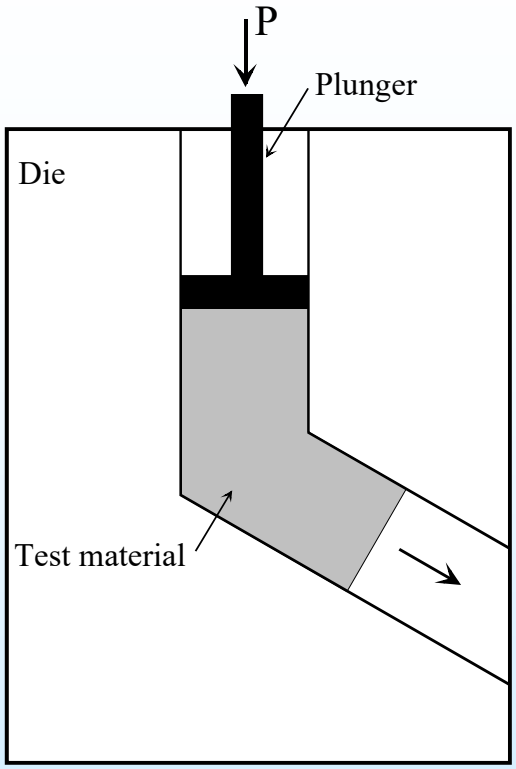
Rotation forging



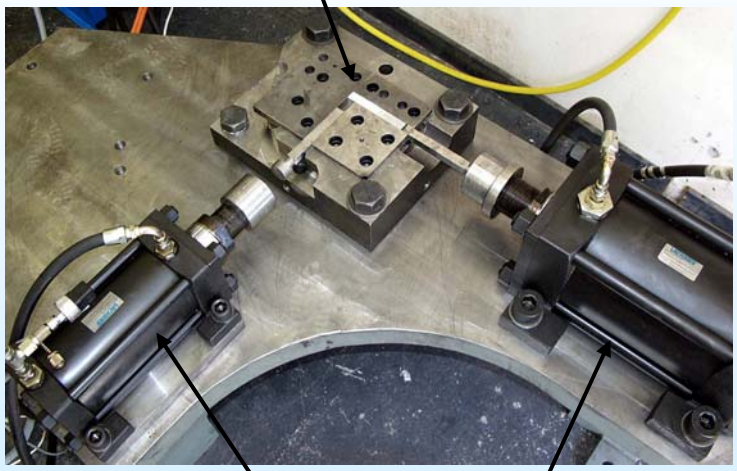
Radial-shift rolling

MONASH University

Equal channel angular pressing (ECAP) at Monash Uni



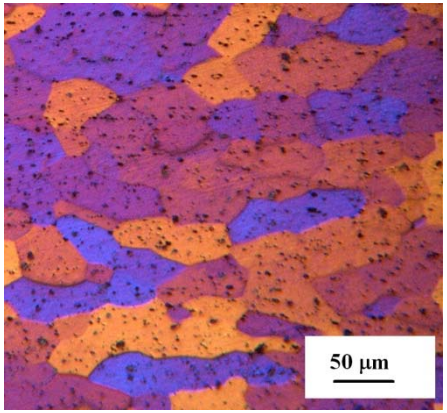
Highly defective, sub-μm grains are obtained

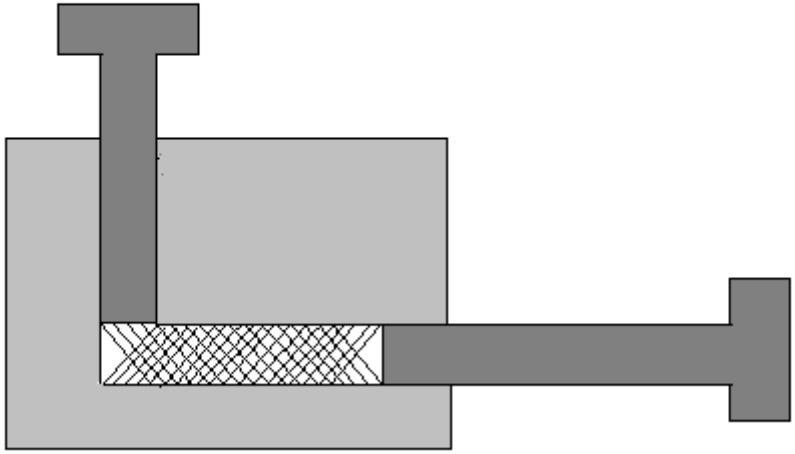


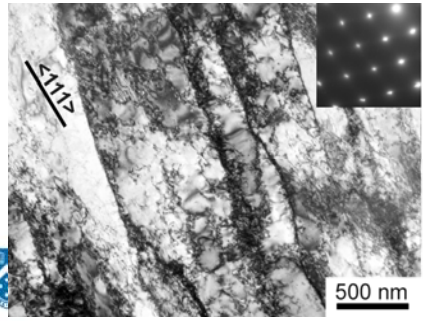
ECAP improves hydrogenation properties of Mg alloys:

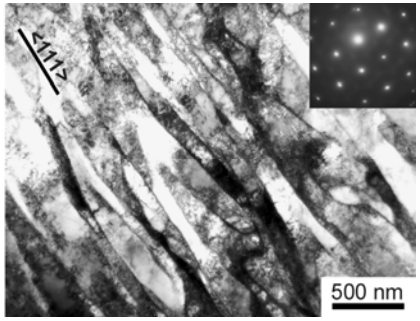
V. Skripnyuk, E. Rabkin, Y. Estrin, R. Lapovok
Improving hydrogen storage properties of magnesium based alloys by equal channel angular pressing
Int. J. of Hydrogen Energy 34 (2009) 6320-6324

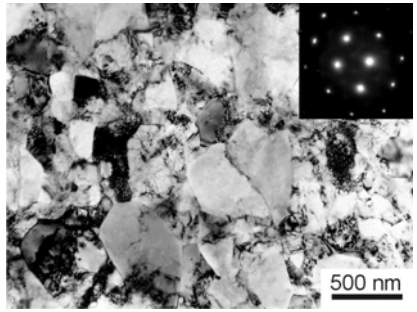
MOST POPULAR TECHNIQUE: EQUAL CHANNEL ANGULAR PRESSING (ECAP)



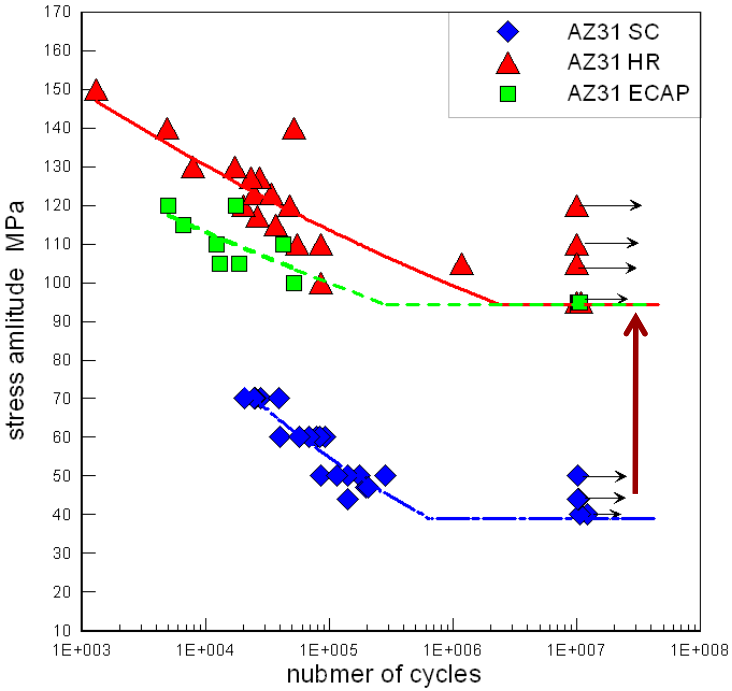




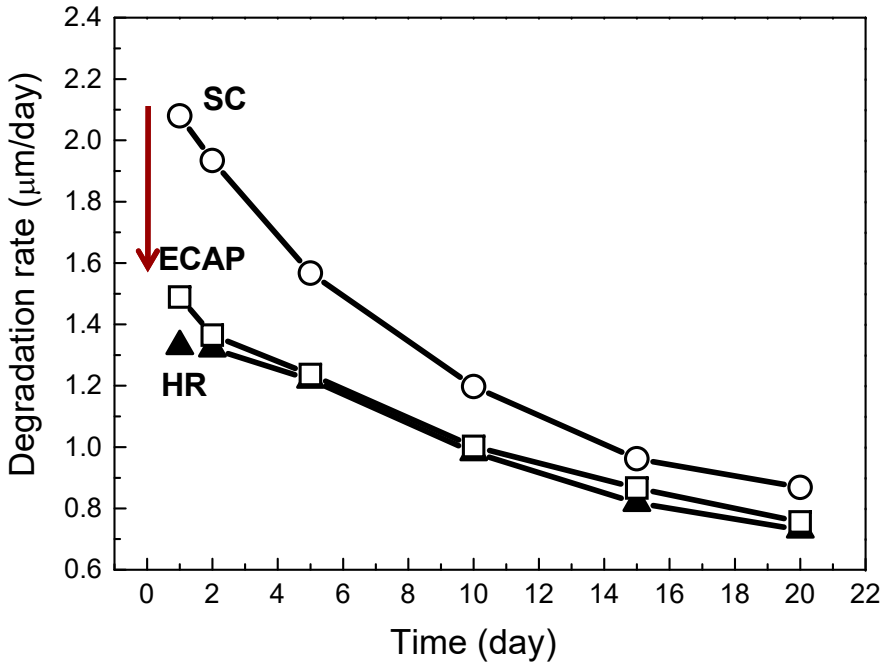




Effects of grain refinement, Alloy AZ31



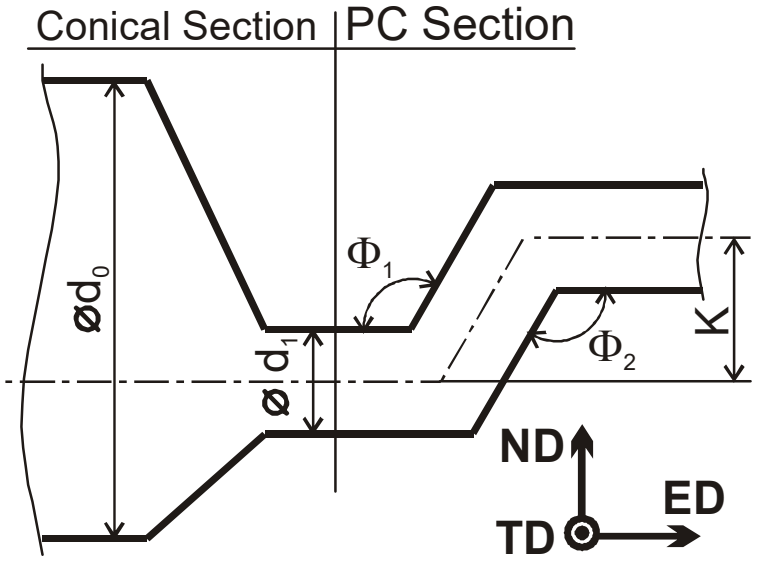
Fatigue strength

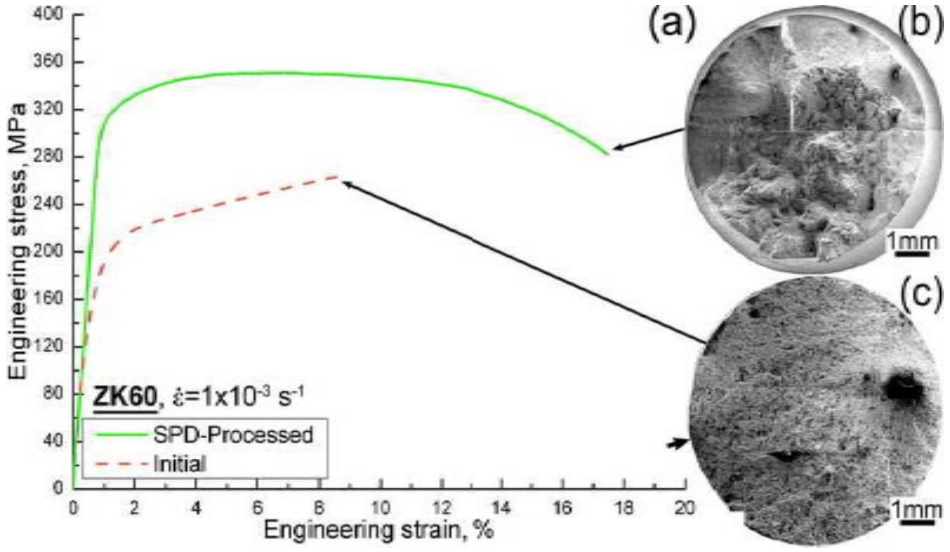


Corrosion in NaCl solution

Wang, Song, Estrin, Zuberova, Adv. Eng. Mater. 9 (11), 967-972 (2007)

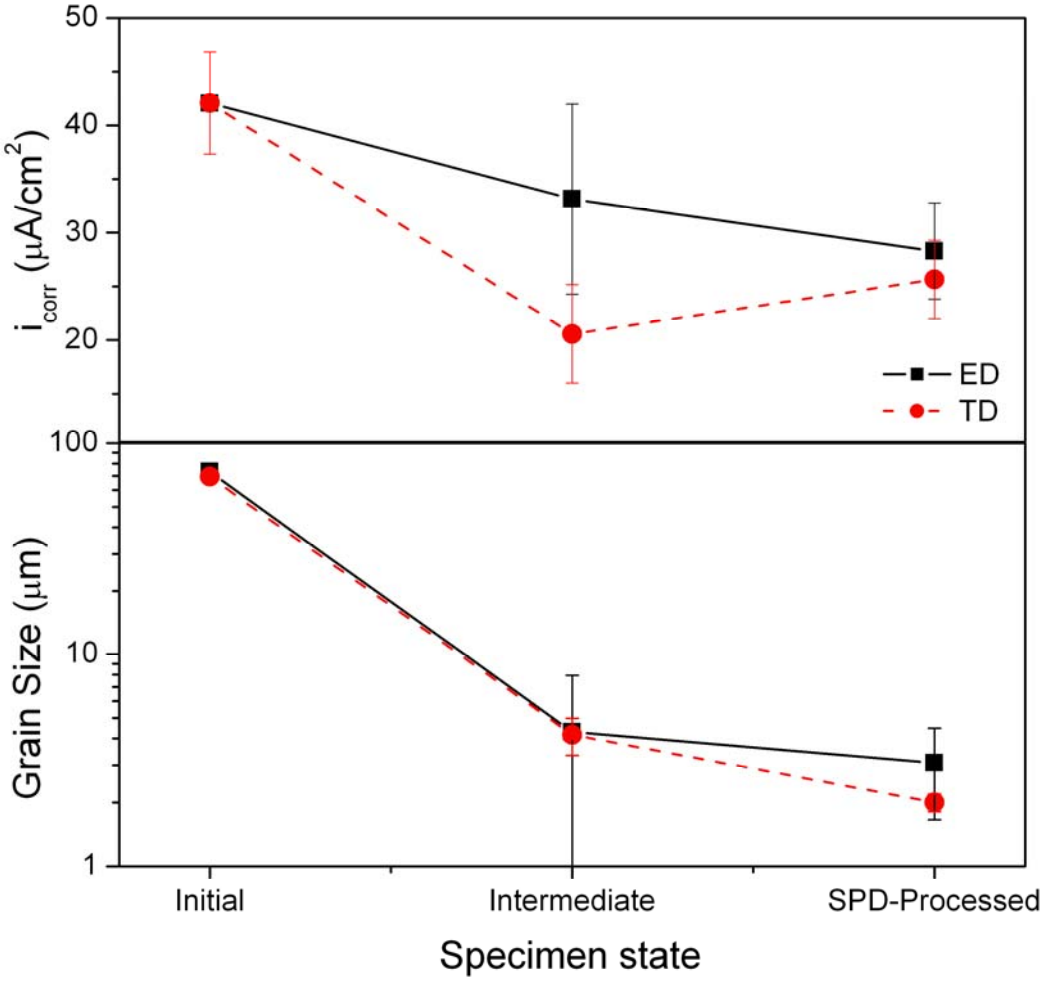
Multi-step ECAP, Alloy ZK60



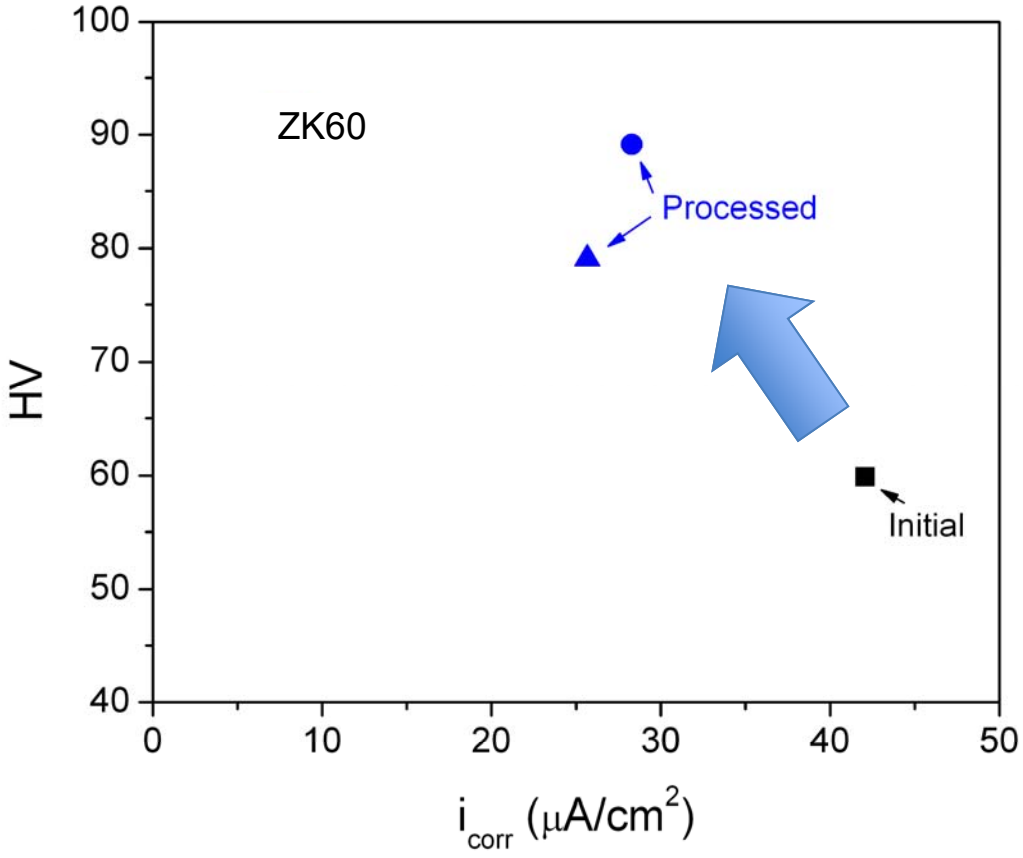


Orlov et al., Acta Mater. 2011

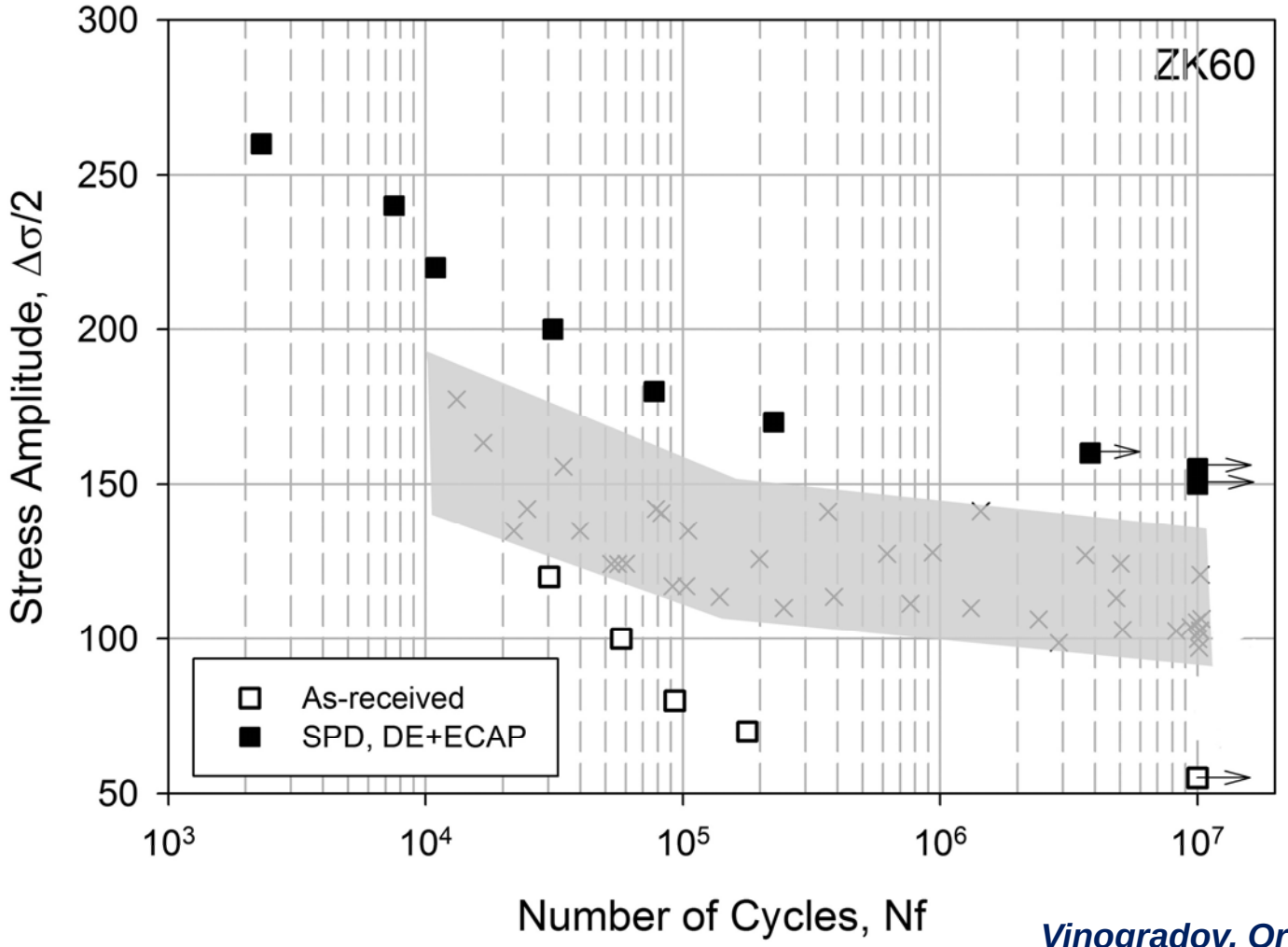
Variation of the corrosion current density



Corrosion-strength property space

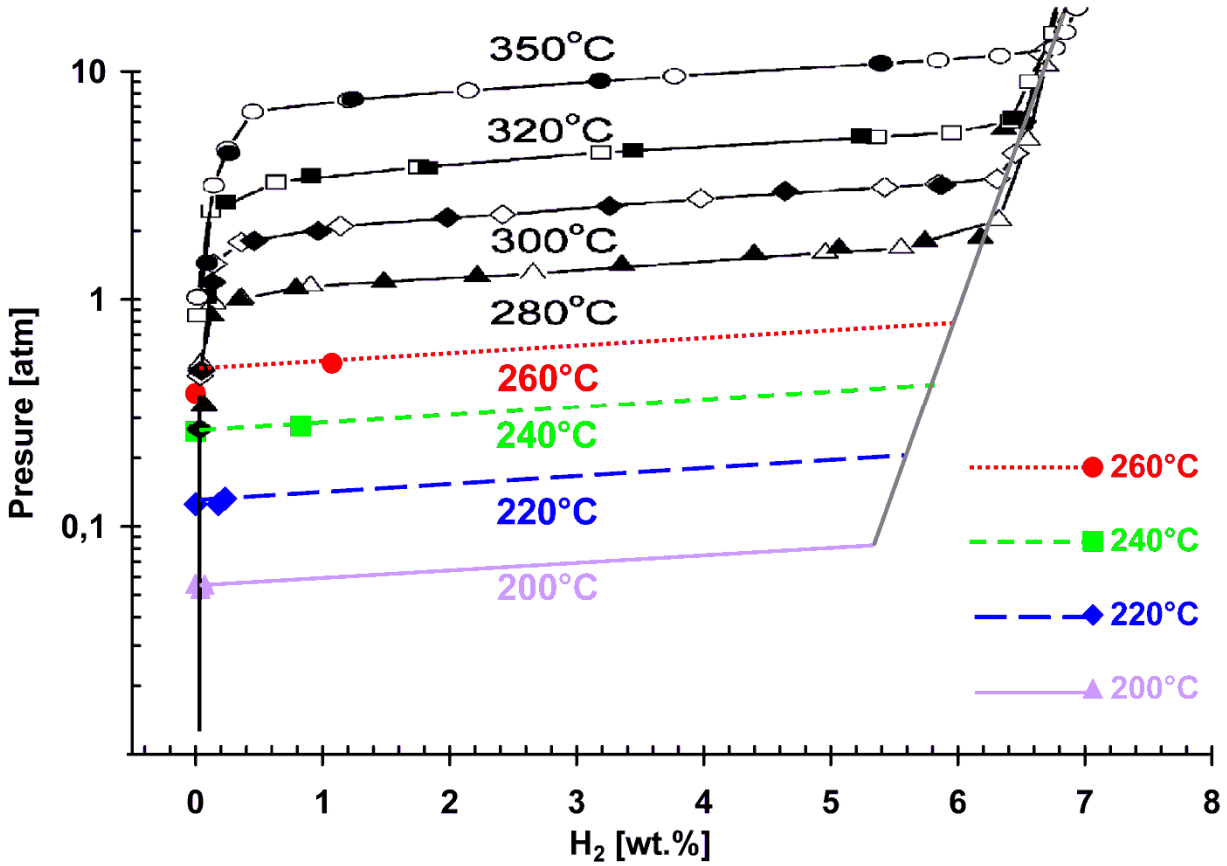


Enhanced Fatigue Strength



Vinogradov, Orlov, Estrin, 2011

PCT diagram of ECAP processed ZK60



Black Lines: V.M.Skripnyuk et al., Acta Mater. 52, 405 (2004)

Coloured Lines: M. Krystian, M. Zehetbauer, G. Krexner, H. Kropik, B. Mingler, J.Alloys Comp. (2011)

Sievert-type Apparatus

Before the beginning of the absorption:

$$P_b V = n_b RT,$$

After full absorption:

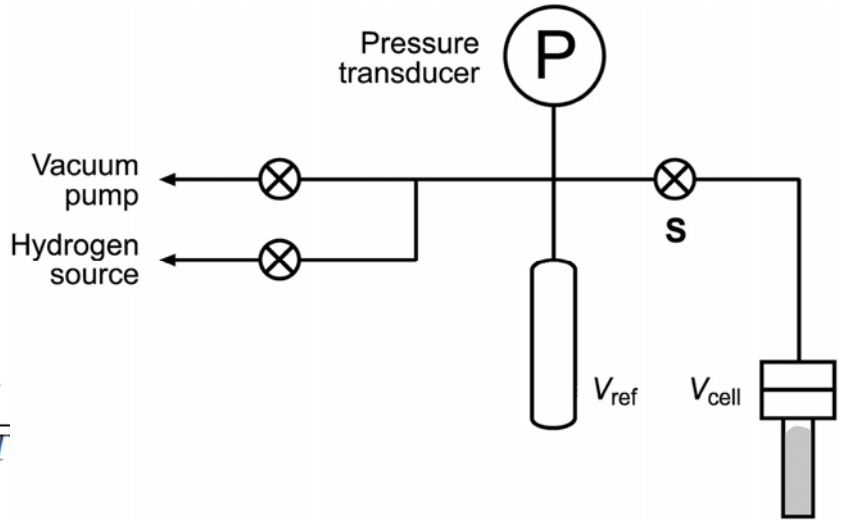
$$P_a V = n_a RT,$$

Difference= moles of absorbed hydrogen:

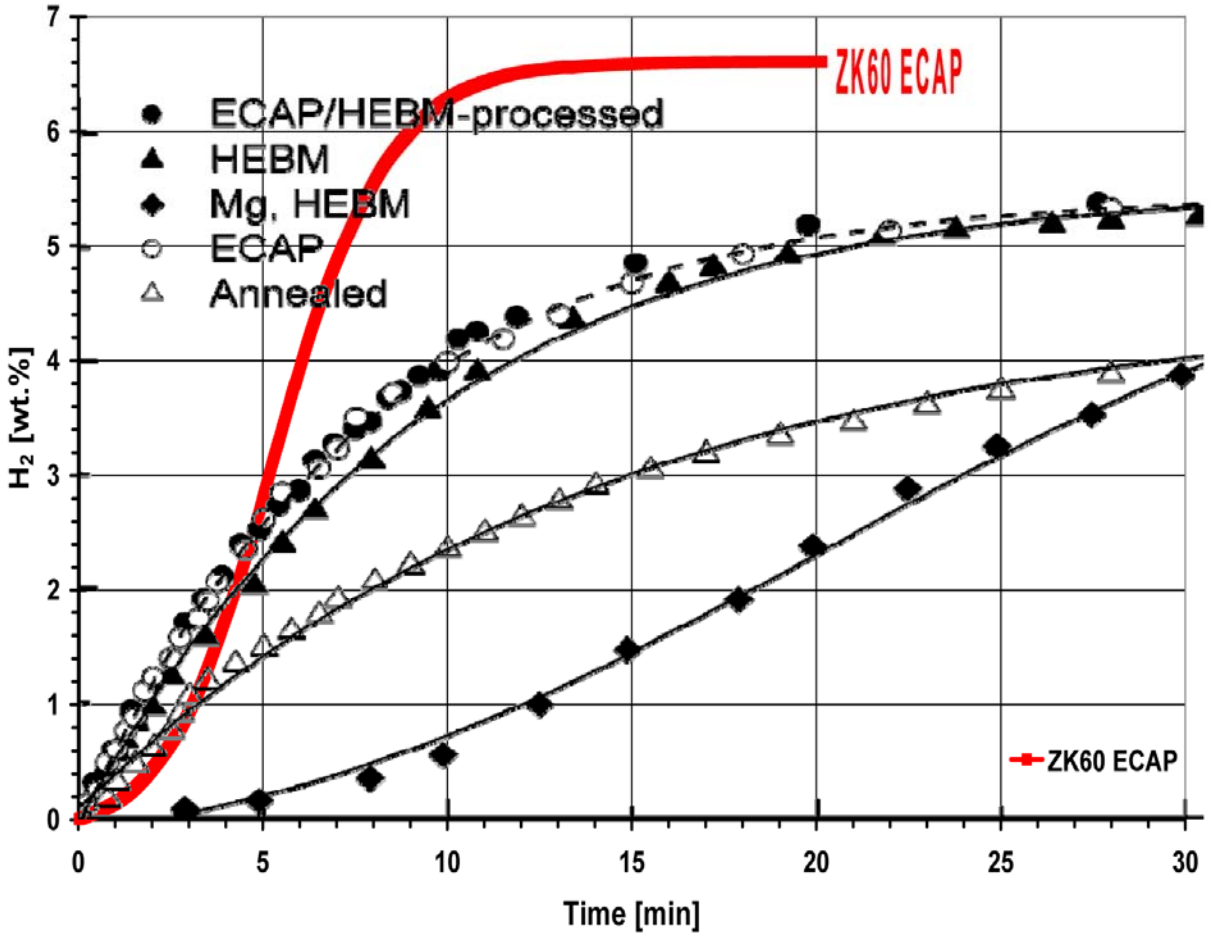
$$\Delta n = n_b - n_a = \Delta P \frac{V}{RT}$$

Mass of absorbed hydrogen:

$$m_H = 2.016 \Delta P \frac{V}{RT}$$



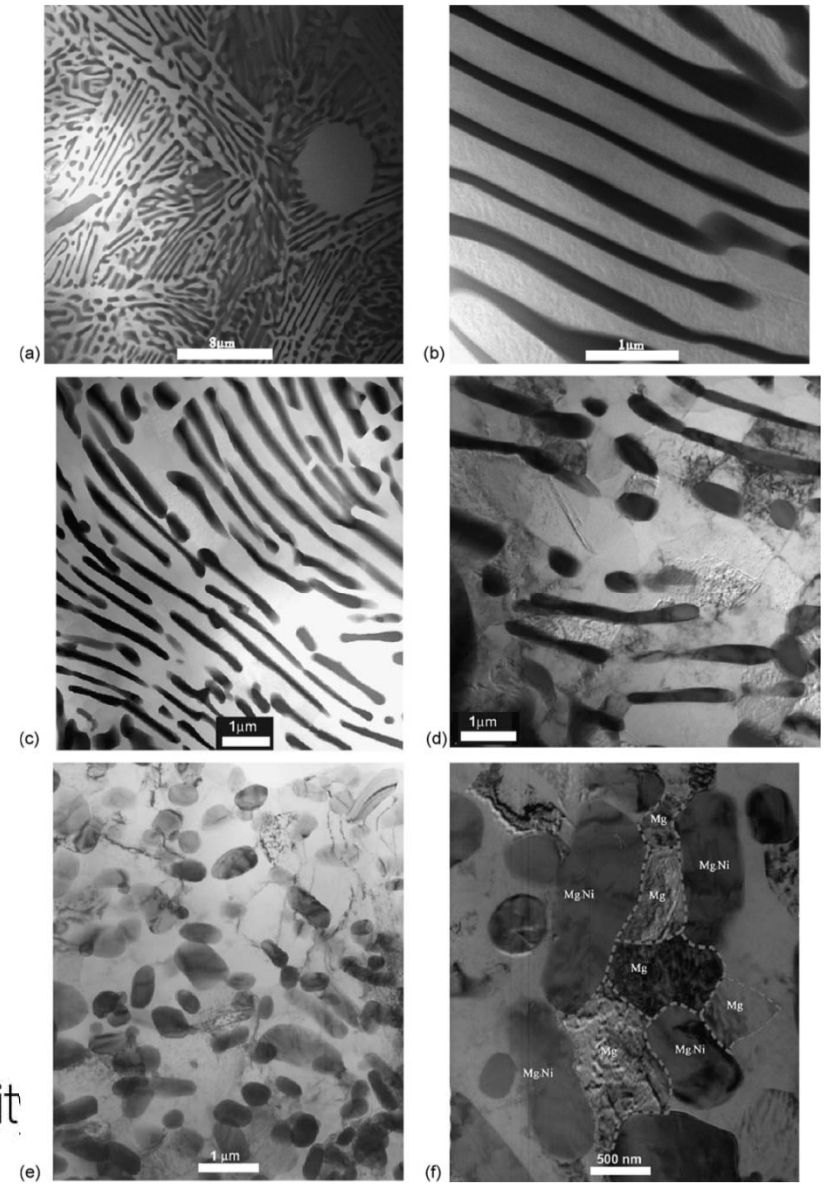
Accelerating absorption/desorption of hydrogen, and replacíng expensive and hazardous ball milling



From: **M.Skripnyuk, E.Rabkin, Y.Estrin, R.Lapovok, Acta mater. (2004)**
M.Krystian, M.Zehetbauer, **G.Krexner,** B. Mingler, J.Alloys Comp. (2011)

Eutectic Mg-Ni alloy
$Mg_{89}Ni_{11}$

Eutectic Mg-Ni alloy



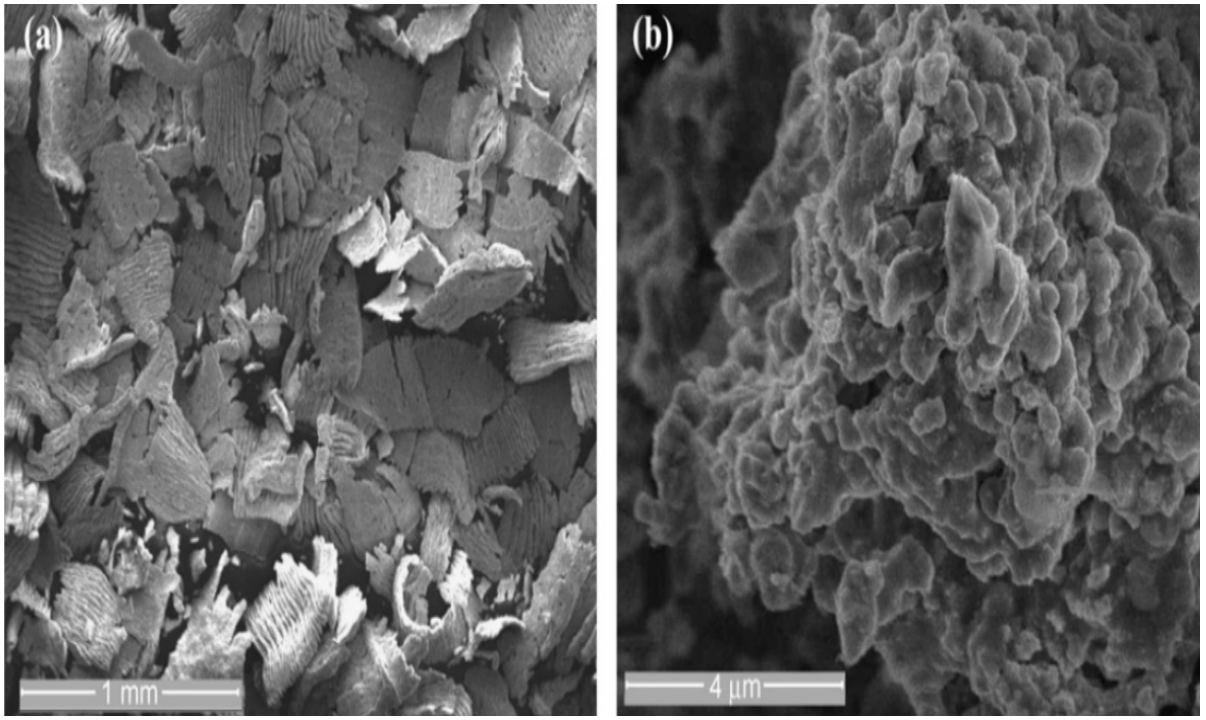
As-cast

1 ECAP pass

10 ECAP passes

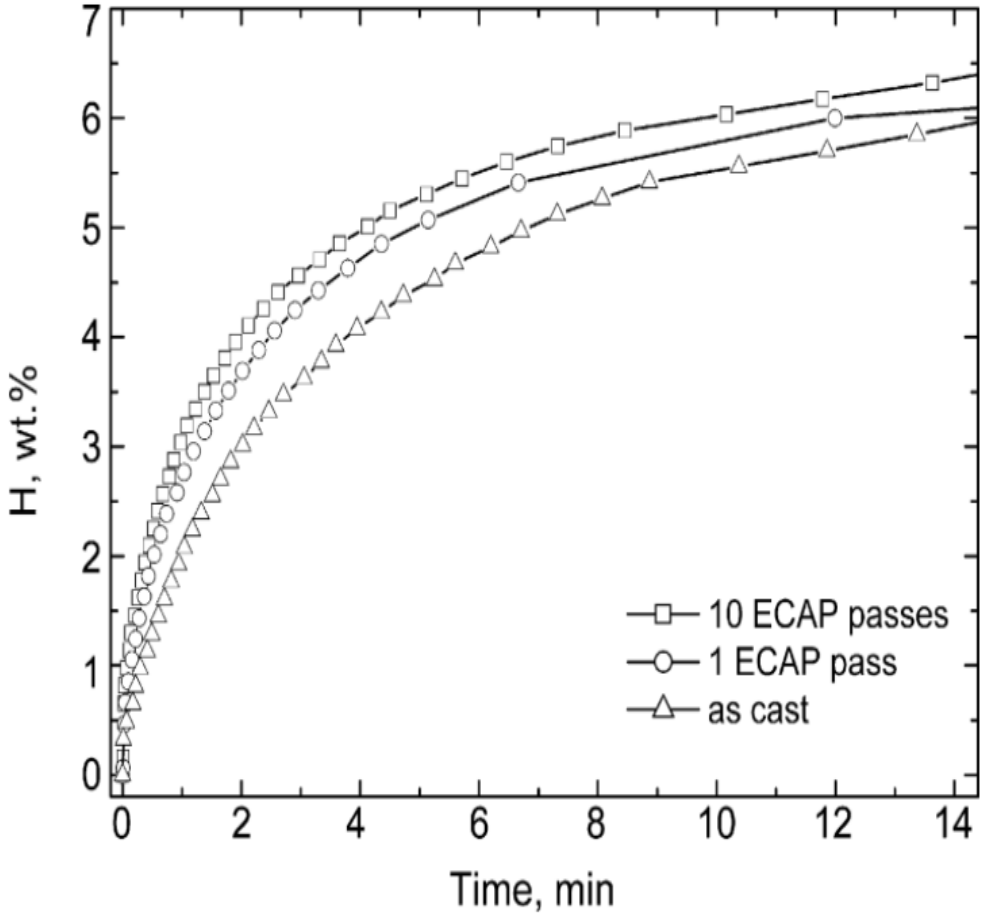
V. Skripnyuk et al. J Alloys Comp. 2007

SEM micrographs taken after 10 passes

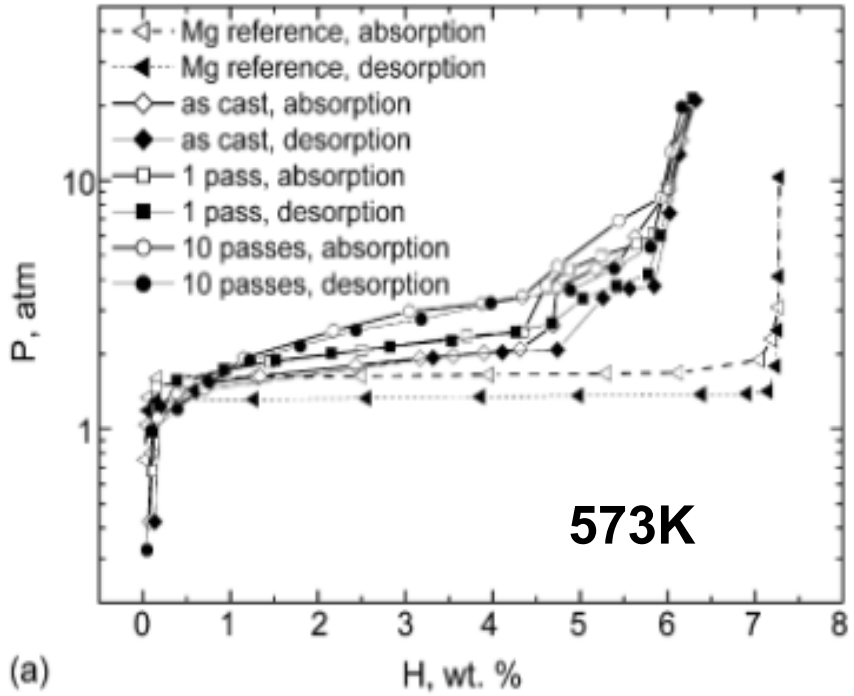


After ECAP

Hydrogen desorption



Pressure-composition isotherms

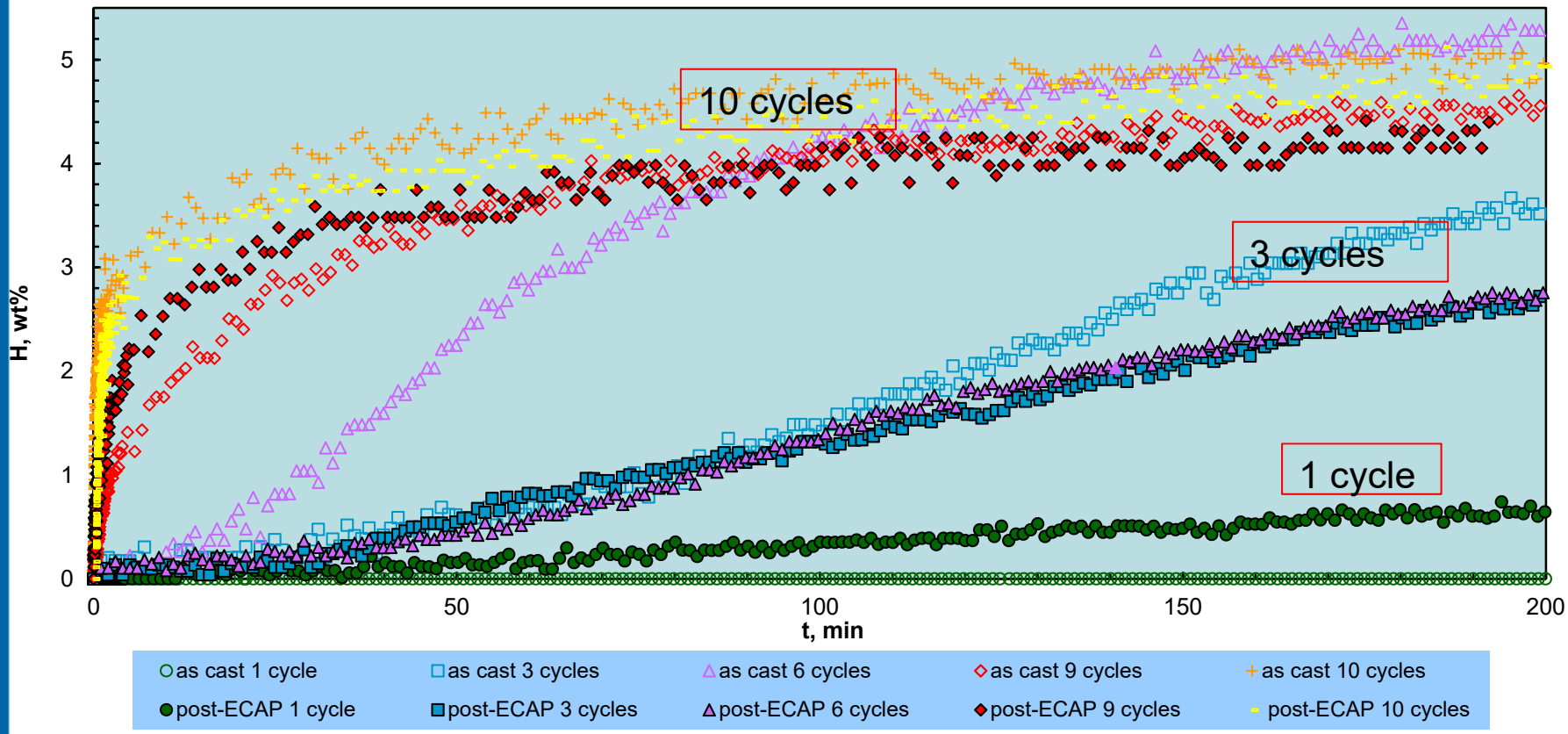


Effects:

- ***Accelerated kinetics***
- ***Increase in pressure by 50%***

Hypo-eutectic Mg-10 wt% Ni alloy

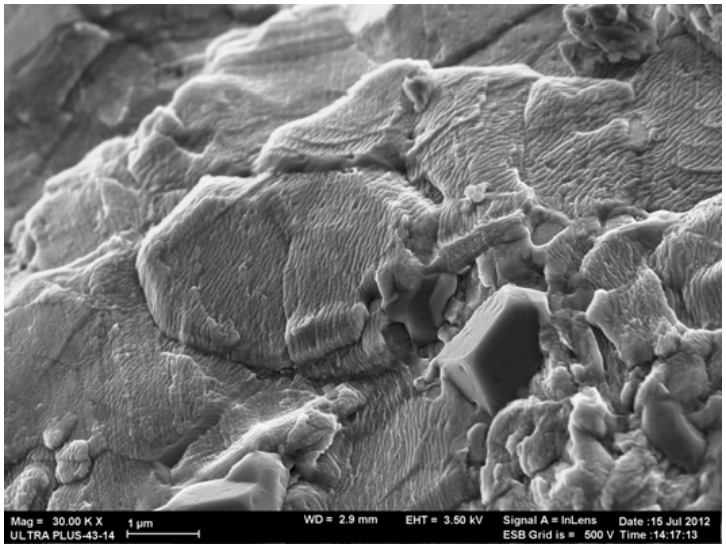
Dependence of Absorption Kinetics on the Number of Cycles

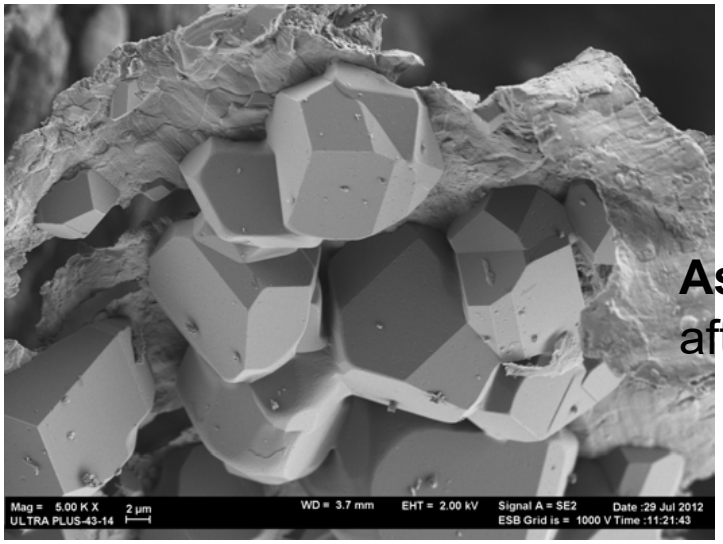


Faster kinetics are expected for the ECAP-ed alloy.

What is the reason for the reversal of kinetics?

Microstructures after hydrogenation: after the first cycle

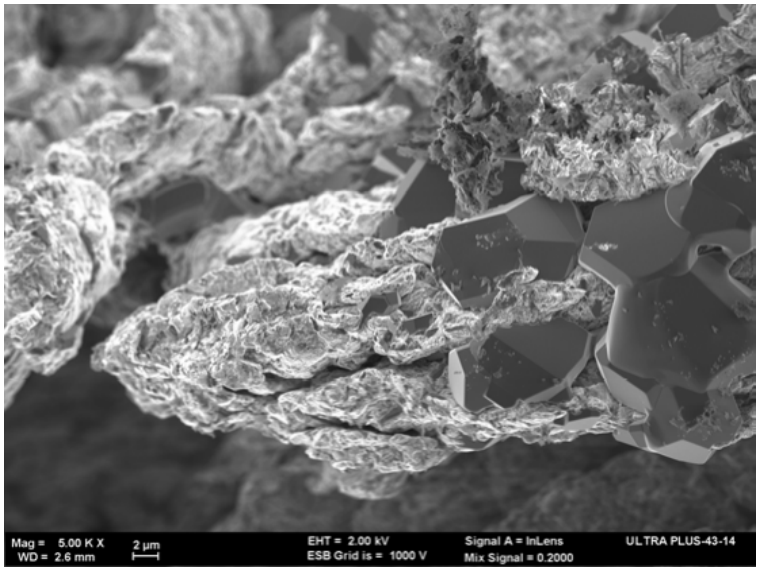


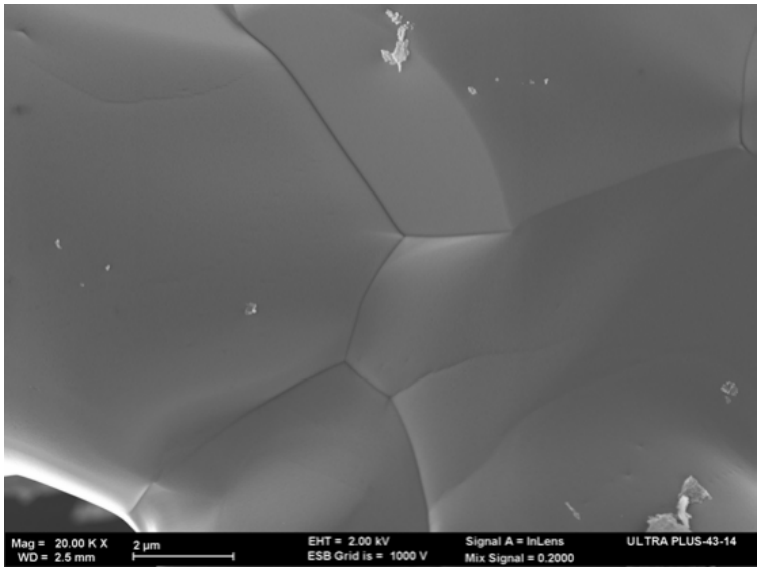


As-cast, after first cycle

Large faceted Mg crystals grew in the as-cast sample after the 1st full hydrogen absorption/desorption cycle.

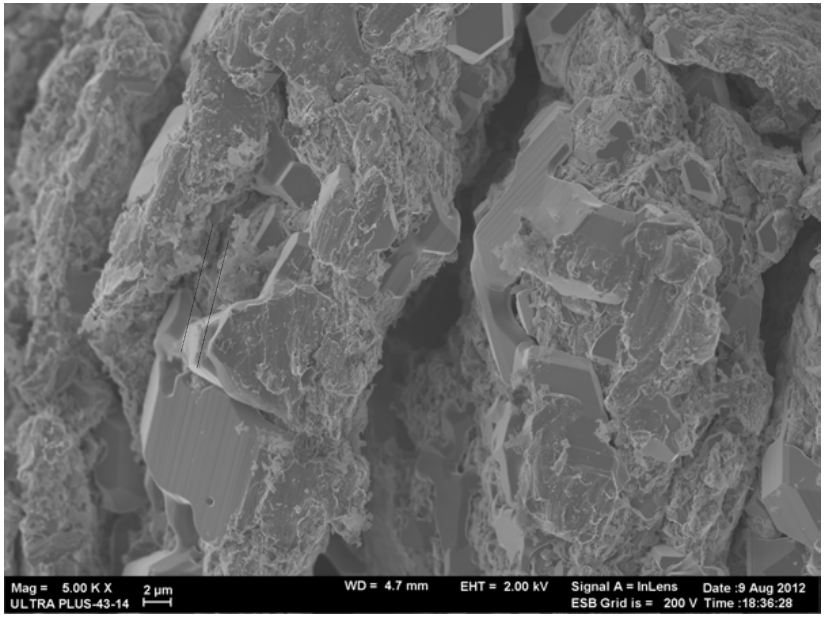
As cast Mg-Ni after 4 cycles

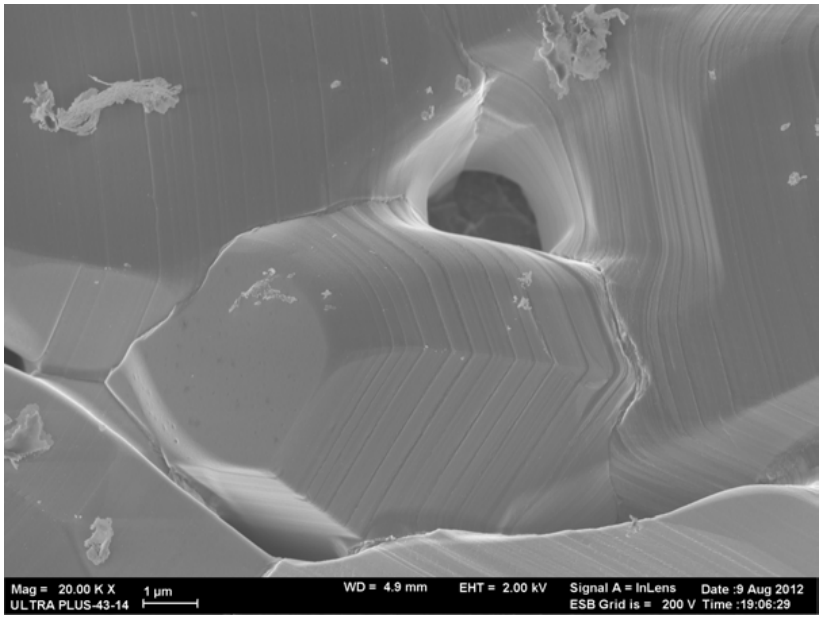




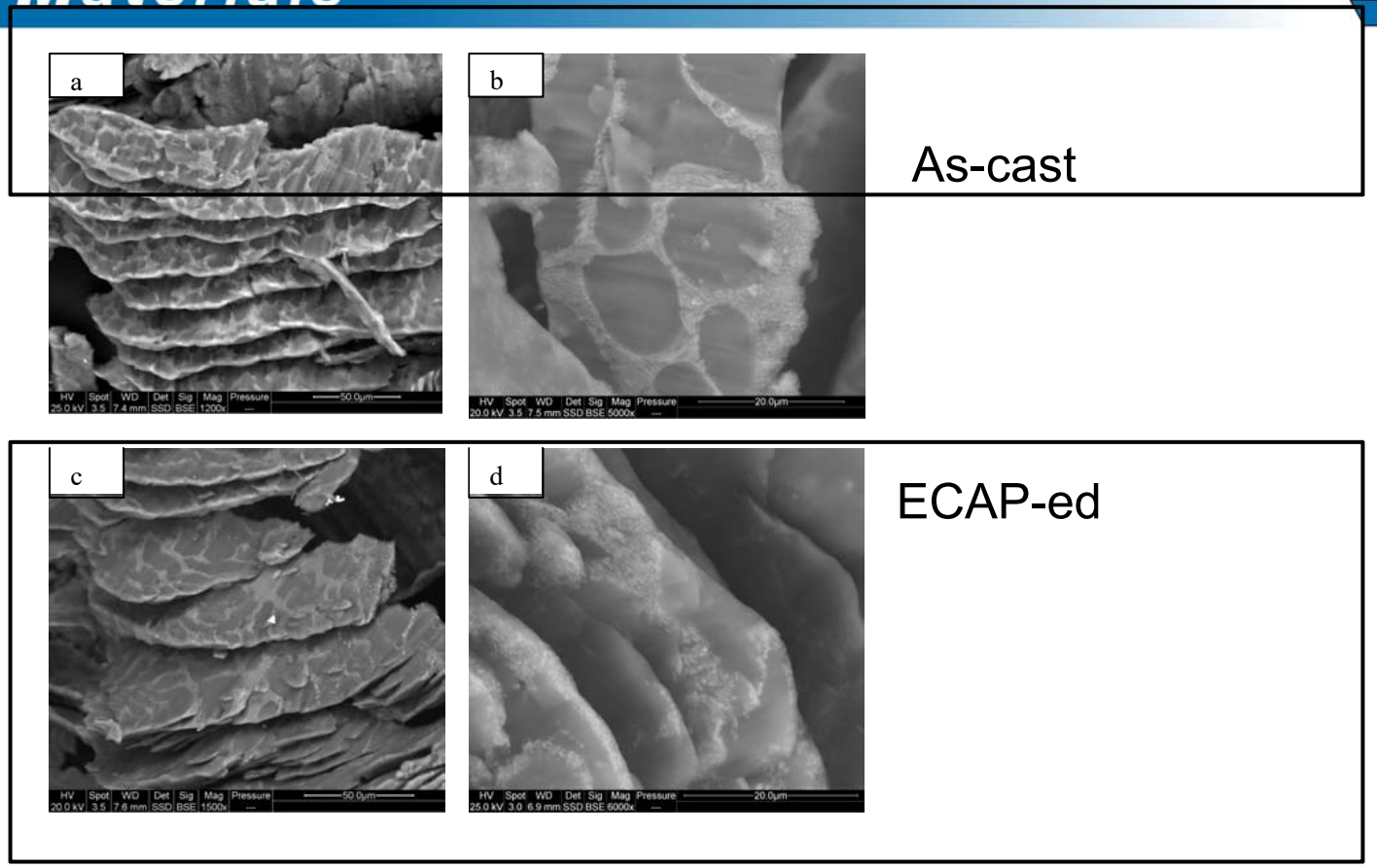
Facets of the grown grains are smooth. Smallest grains are a few microns in size.

ECAP processed Mg-Ni after 4 cycles





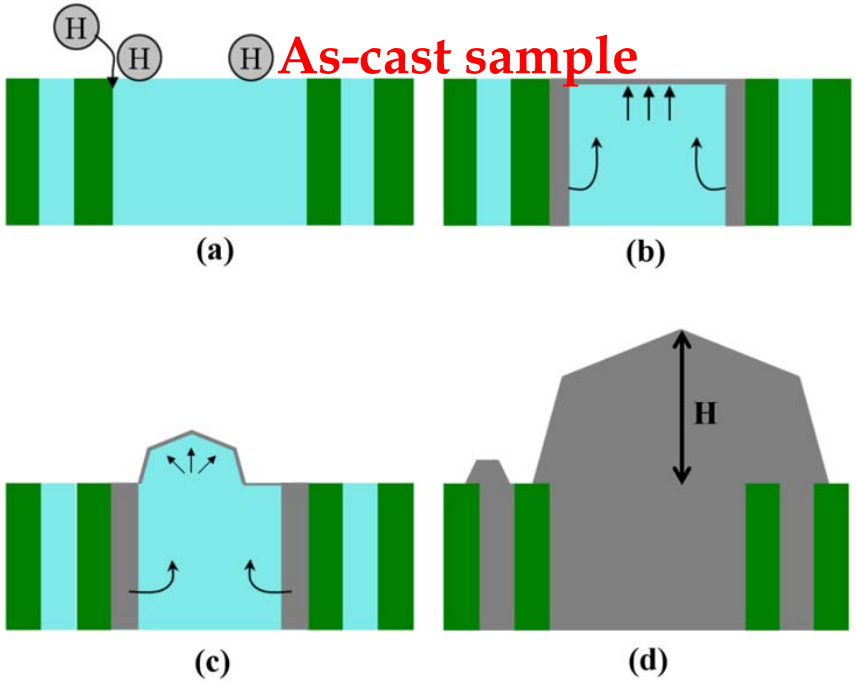
A porous structure is covered with faceted grains.
Slip lines (as dash lines indicate) cover the facets of all of the grains.
Sub-micron grains were observed.



Chips of two alloys prepared by filing. Primary Mg grains are separated by Mg-Mg2Ni eutectics. ECAP has broken and refined Mg2Ni lamellae, otherwise not much difference between the two samples.

Mechanism of Formation of Large Faceted Mg Crystals

Mg_2Ni
Mg
MgH_2

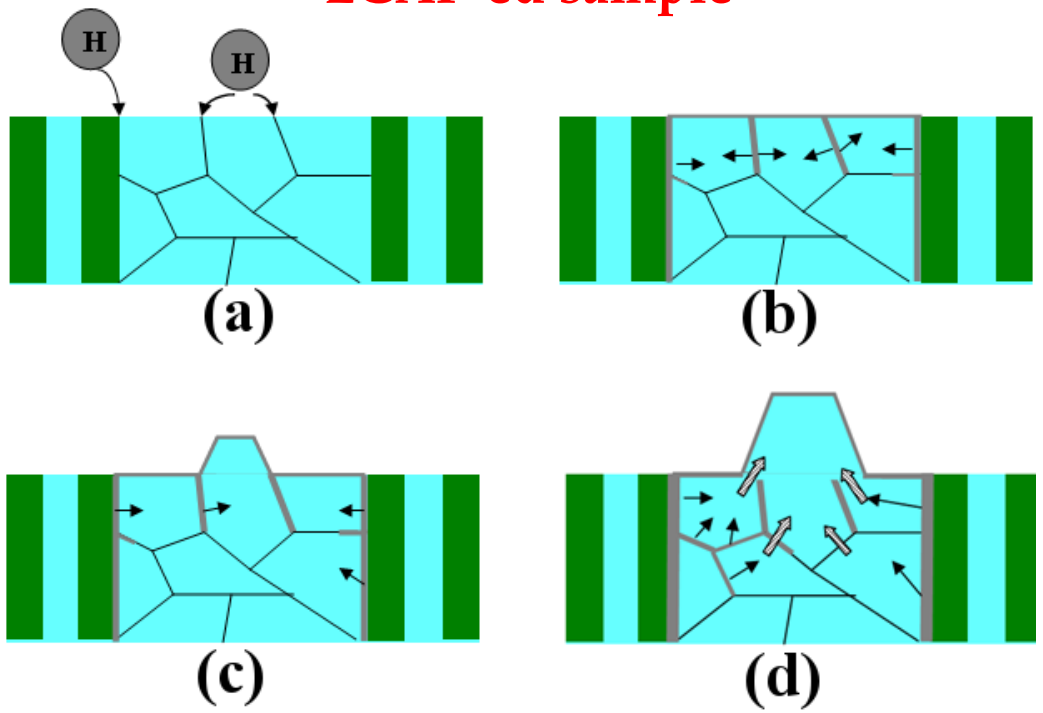


•Doyama *et al* (1982): formation of MgH_2 and Mg_2NiH_4 is accomplished by volumetric expansion up to approximately 30% of molar volume relatively to the Mg and Mg_2Ni phase.
•Compressive stresses during hydrogenation are the driving force for the crystals growth.
•Mg particle growth has a direct influence on the kinetics, since catalyst phase is left behind.

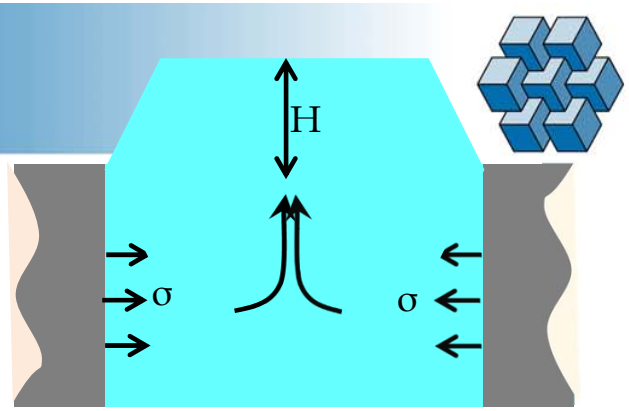
Mechanism of Formation of Large Faceted Mg Crystals

ECAP-ed sample

Mg_2Ni
Mg
MgH_2



The Model



$\sigma \approx \sigma_y \approx 229$ MPa (for the as - cast alloy)

Gradient of chemical potential of Mg :

$$\nabla\mu \approx \frac{\sigma_y \Omega}{H} \quad (1)$$

Volumetric flux that leads to the formation of extruded Mg crystal:

$$J \approx \frac{H}{\Omega \cdot t} \quad (2)$$

t is the time of hydrogen absorption process

On the other hand :

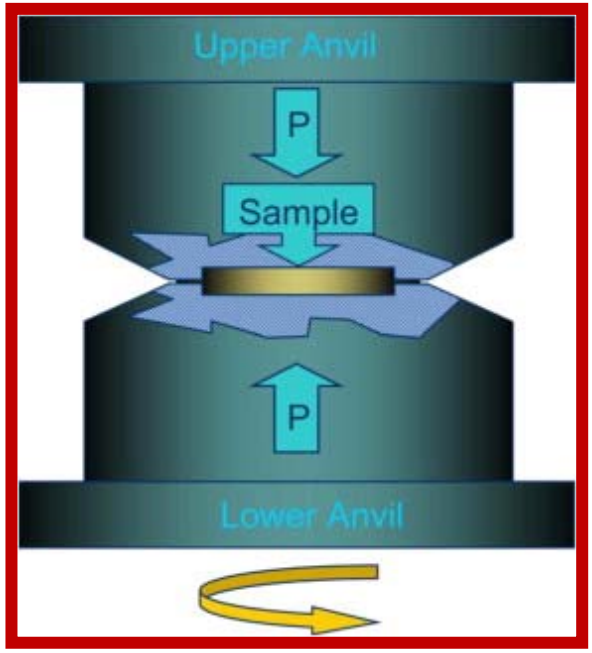
$$J \approx \frac{D}{\Omega \cdot k_B T} \cdot \nabla\mu \quad (3)$$

$$H \approx \sqrt{\frac{D\sigma_y \Omega t}{k_B T}}$$

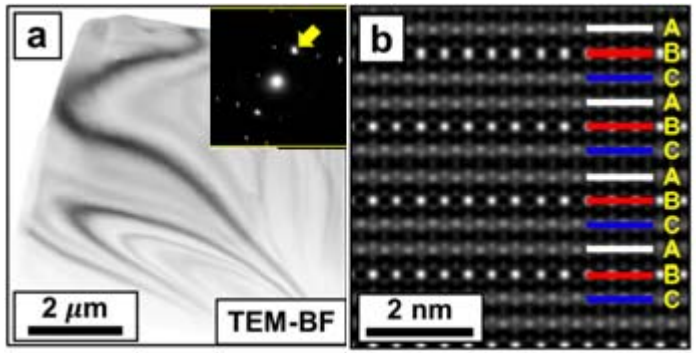
Comments

- Hydrogenation encourages growth of large faceted Mg single crystals. In ECAP-ed samples these crystals are nucleated earlier than in as-cast sample, and they are larger. Tendency for nucleation and growth depends on stored internal energy and defect density inside the chip.
- Current phenomenon is observed in chips (that are relatively large compared to BM powder) and not in ball milled powder. This indicates that faceted grain nucleation and growth are related to the size and geometric constrains during growth of hydride phase.
- The size of faceted Mg single crystals decreases with every hydrogenation cycle, but their amount increases. This mechanism of increasing surface probably accelerates hydrogenation kinetics. On the other hand, growth of crystals leads to areas that are rich in Mg2Ni particles, that serve as catalysts, while faceted grains are poor in catalyst.
- ECAP process doesn't refine the microstructure significantly, yet influences absorption behavior. As-received microstructures are very similar, but intermittent hydrogenation behavior is very different.
- Although there is significant morphological difference between as cast and post-ECAP powders during first cycles, after 9 cycles topography is similar and so is the hydrogenation kinetics.

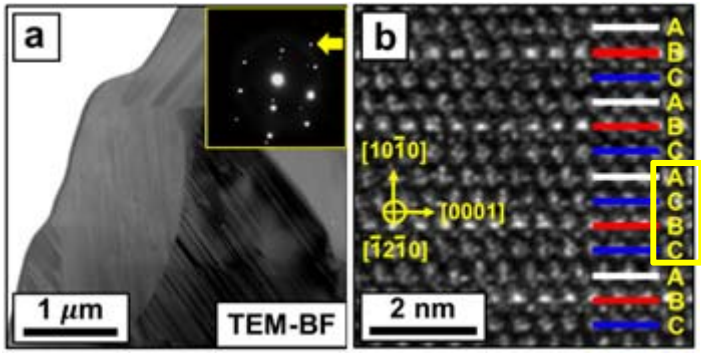
HPT Work at Kyushu University (Prof. Zenji Horita, Dr. Kaveh Edalati)

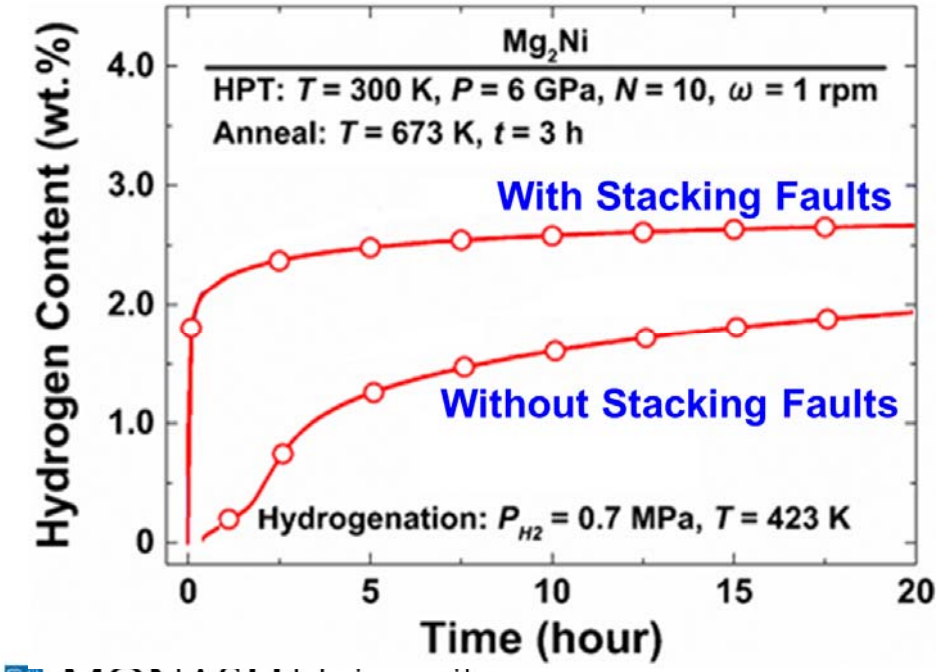


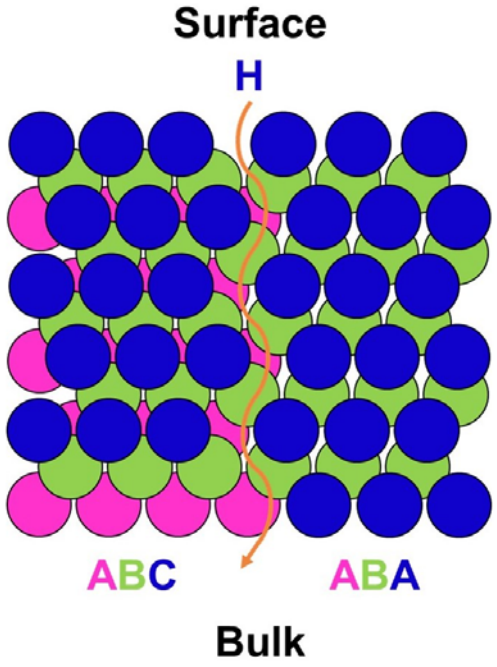
Coarse Grains



Coarse Grains with Stacking Faults





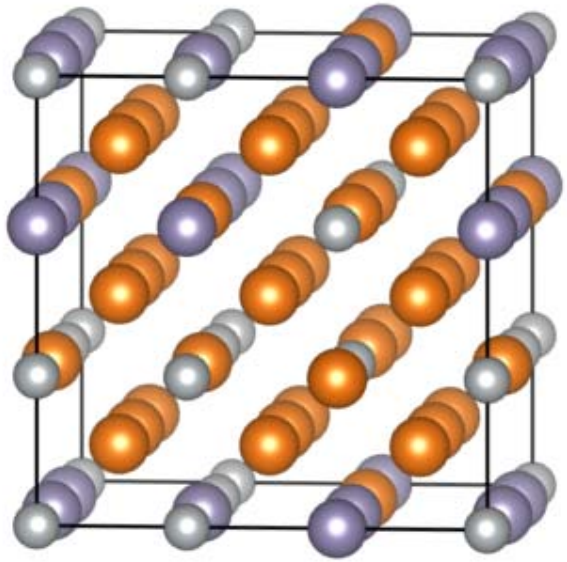


MONASH University

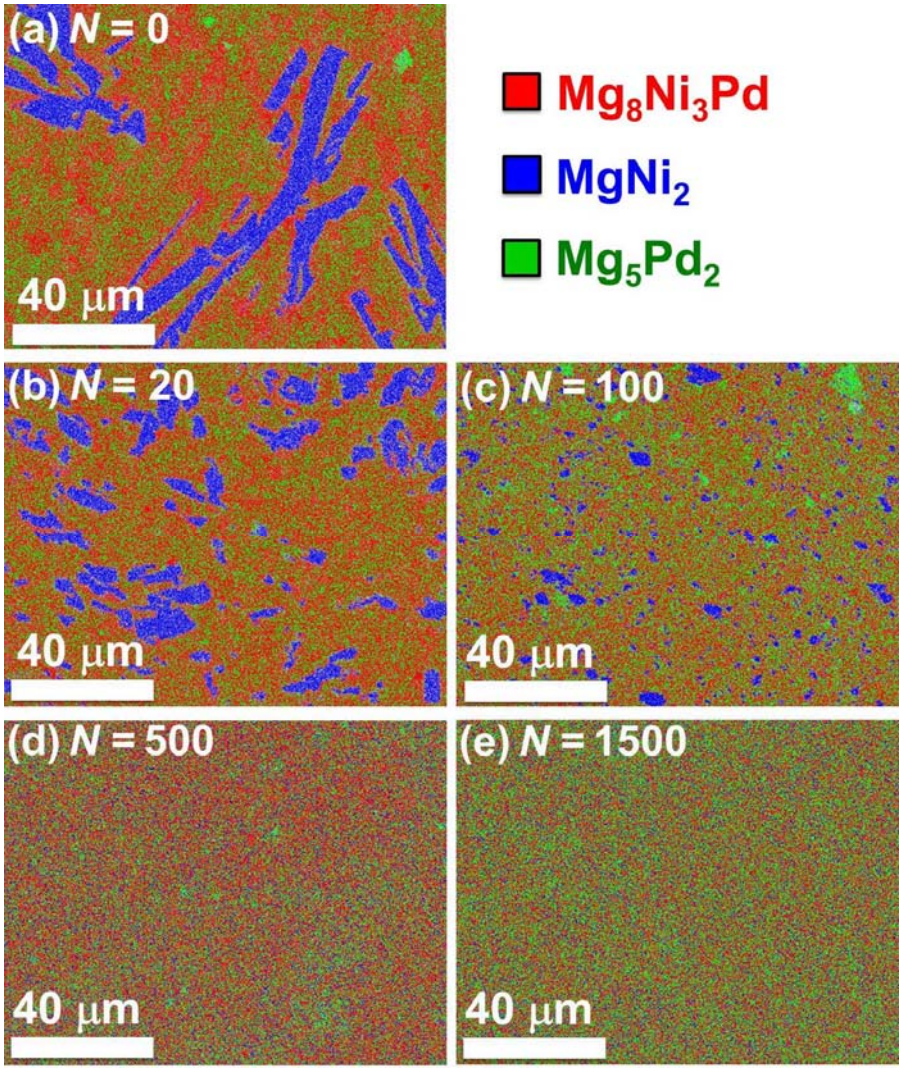
Hongo, Edalati, Arita, Matsuda, Akiba, Horita, Acta Mater. 92 (2015) 46-54.

Mg_4NiPd for Room-Temperature Hydrogen Storage

Calculations suggested if a homogenous Mg_4NiPd alloy is synthesized, it should have a B2 structure with low hydrogen binding energy.



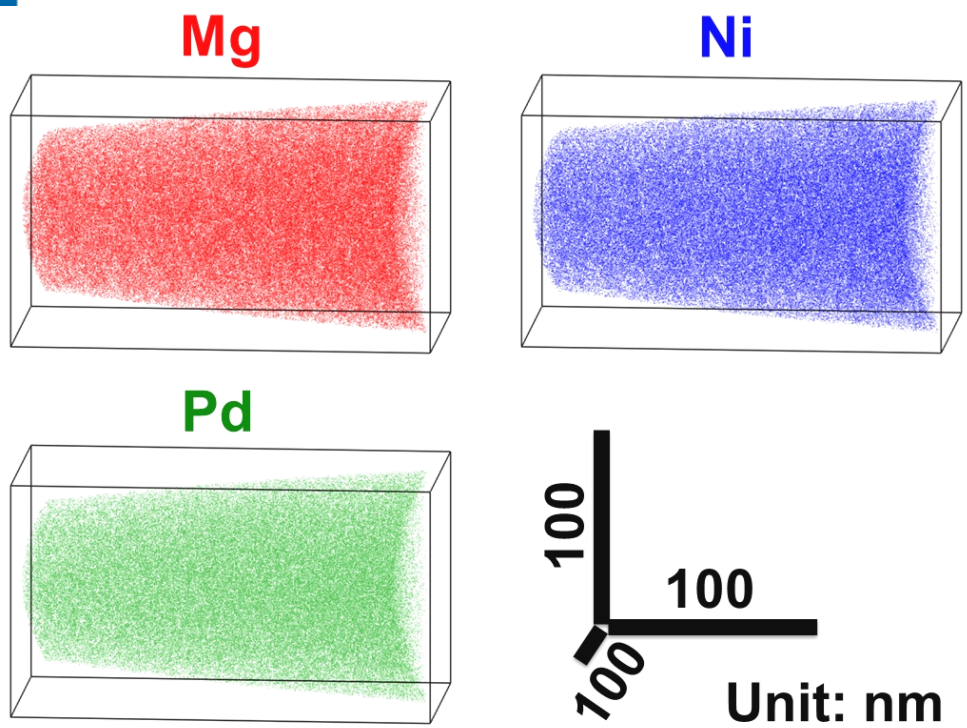
Mg
Ni
Pd

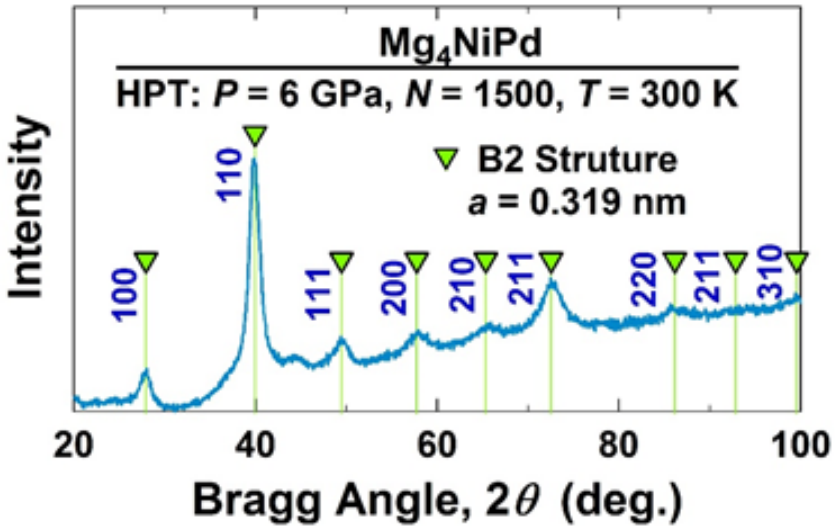


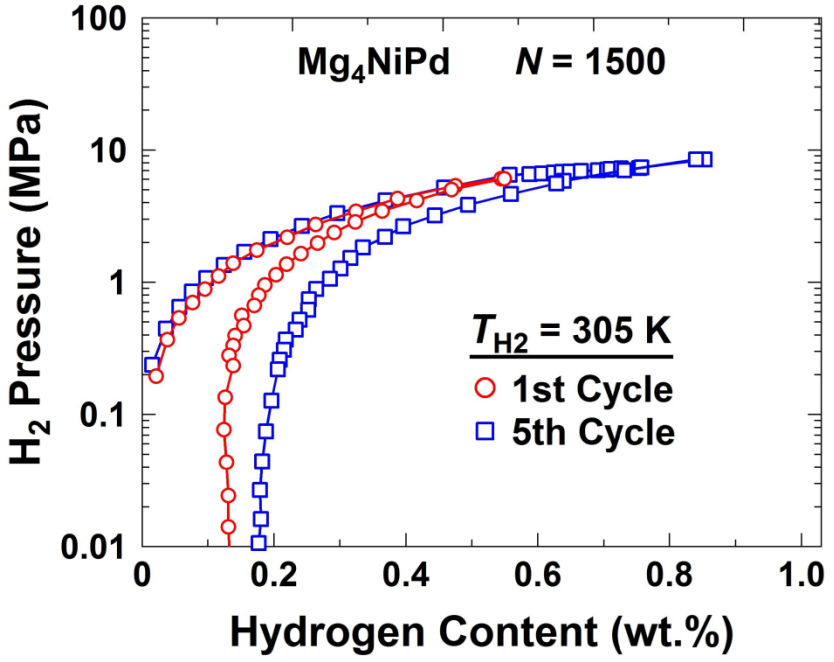
N: Number of HPT Turns

Edalati, Uehiro, Ikeda, Li, Emami, Filinchuk, Arita, Sauvage, Tanaka, Akiba, Horita, Acta Mater.149 (2018) 88.

Centre for Advanced Hybrid Materials







Edalati, Uehiro, Ikeda, Li, Emami, Filinchuk, Arita, Sauvage, Tanaka, Akiba, Horita, Acta mater. 149 (2018) 88.

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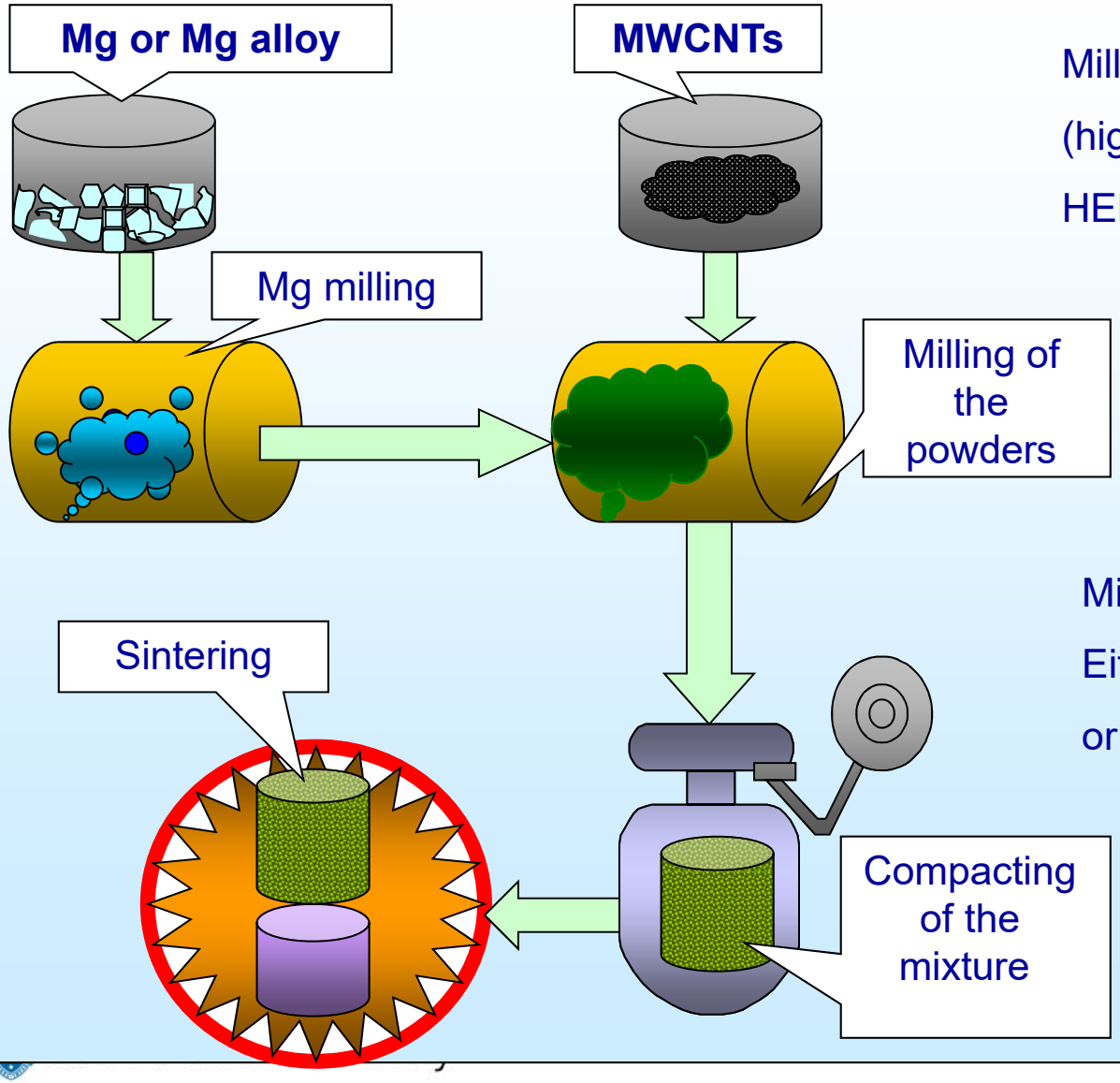
Magnesium with Carbon Nanotubes

Preparation of PMH+MWCNTs composites



Milling of Mg: 8 h at 960 rpm (high energy ball milling, HEBM)

Milling of Mg+MWCNTs: Either at 800 rpm (HEBM) or at 100 rpm (LEBM)

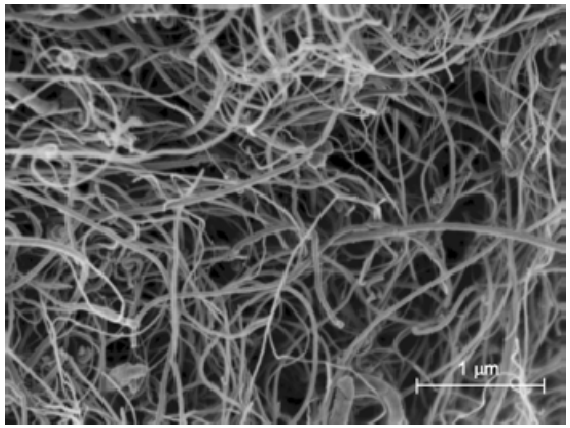
Processing of Mg-2 wt.% MWCNT composite

-MWCNT: catalytic decomposition of acetylene @ 720°C over Co-Fe/$CaCO_3$;

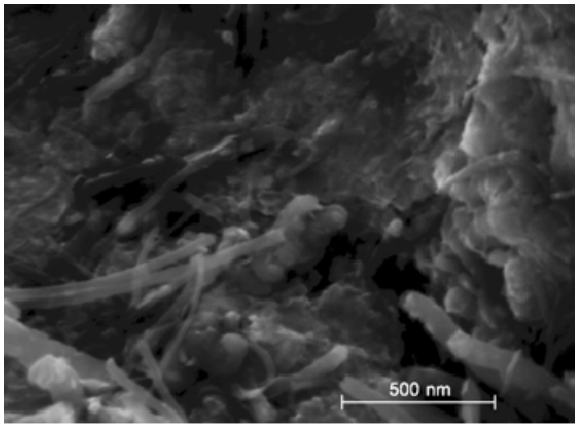
-Dry blending with 99.8 wt.%Mg (particle size of 38 μm) for 4 h;

-Hot pressing @ 600°C in vacuum, 50 MPa for 30 min;

-HIP @ 600°C in argon, 1800 bar for 60 min.



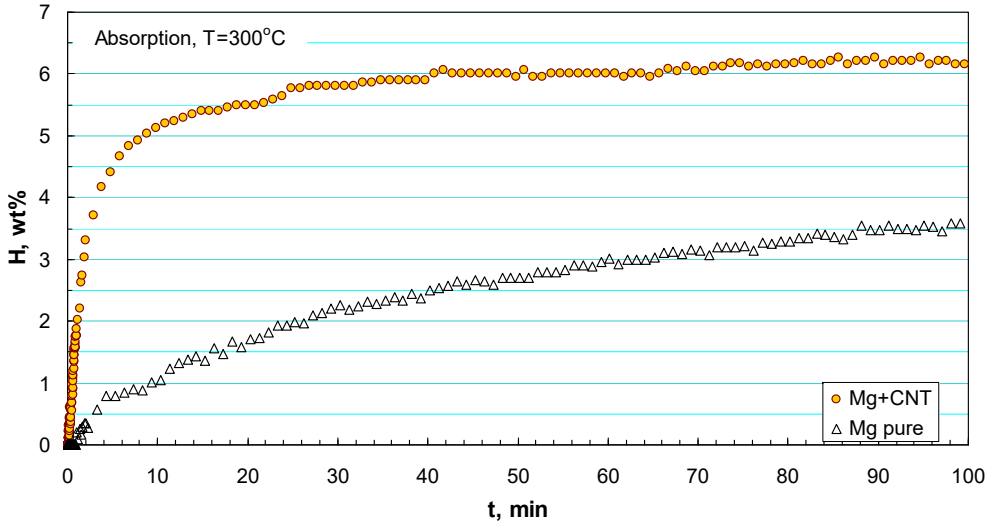
MWCNTs



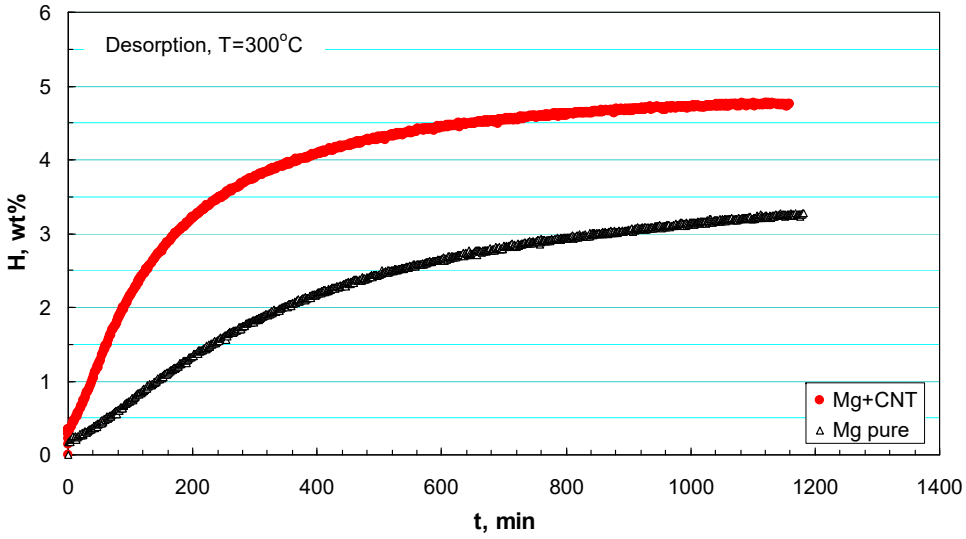
Fracture surface of the composite showing MWCNT pull-outs

V.M. Skripnyuk, E. Rabkin, L.A. Bendersky, A. Magrez, E. Carreño-Morelli, Y. Estrin
Hydrogen storage properties of as-synthesized and severely deformed magnesium – multiwall carbon nanotubes composite
Int. J. of Hydrogen Energy **35** (2010) 5471-5478

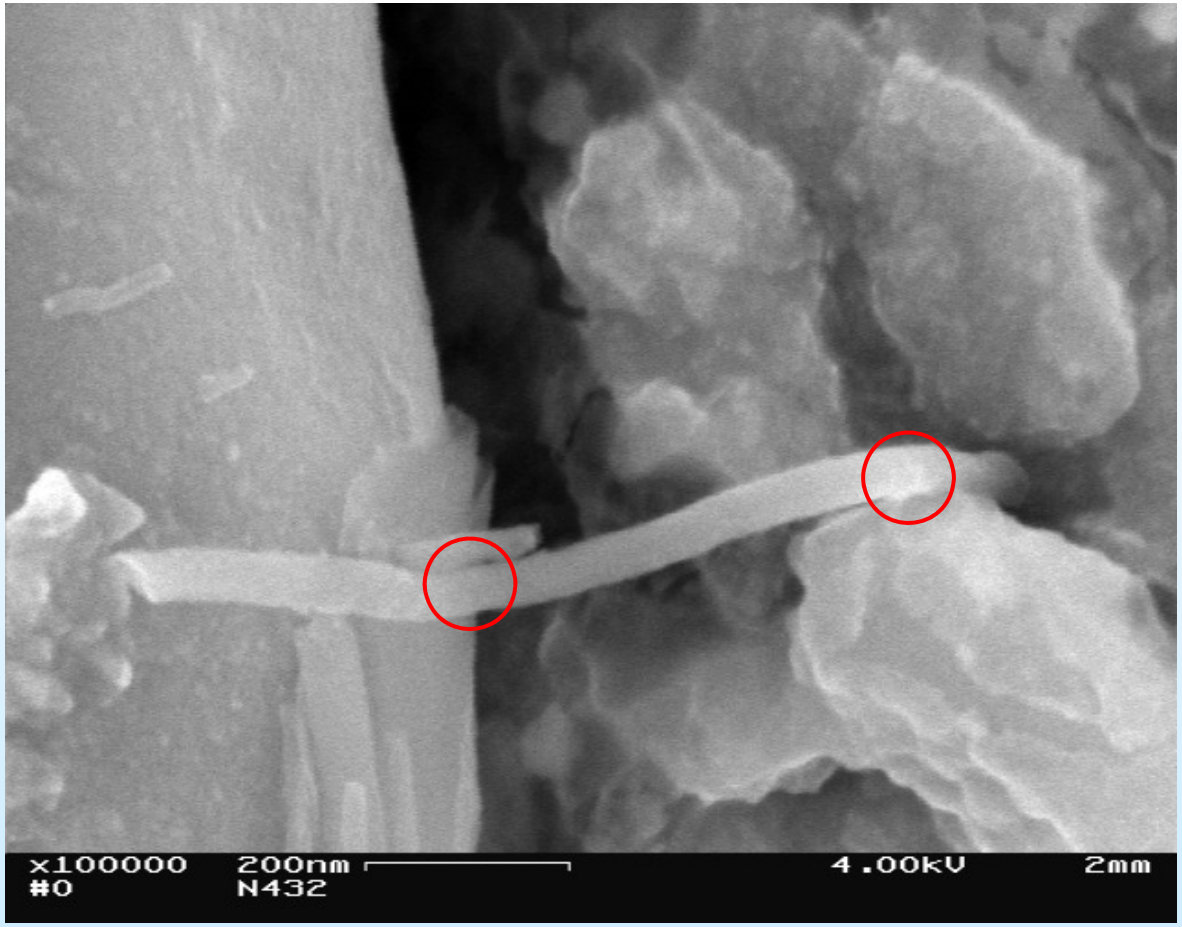
Kinetics of hydrogen *absorption* by the composite



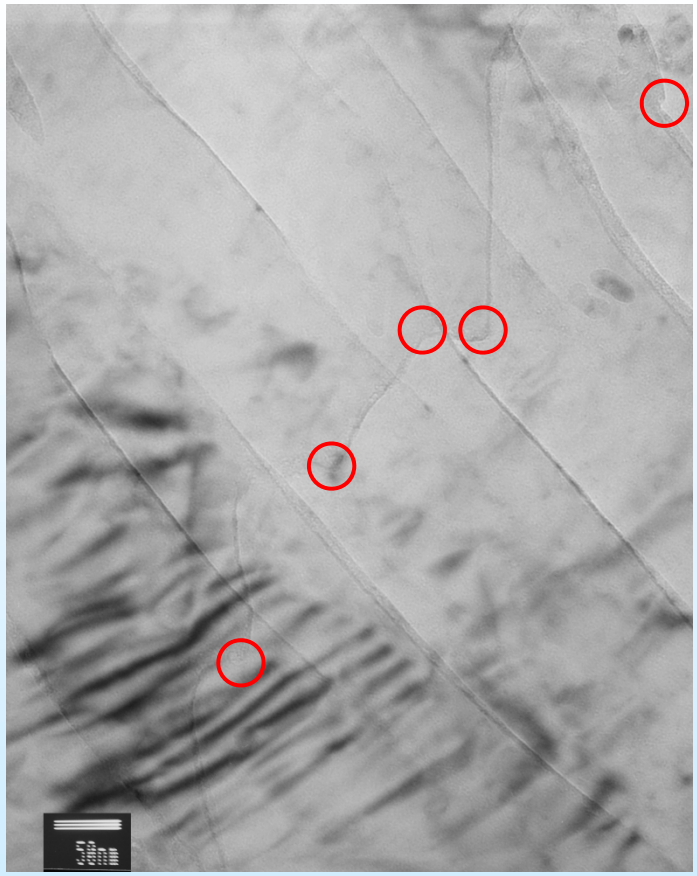
Kinetics of hydrogen *desorption* by the composite

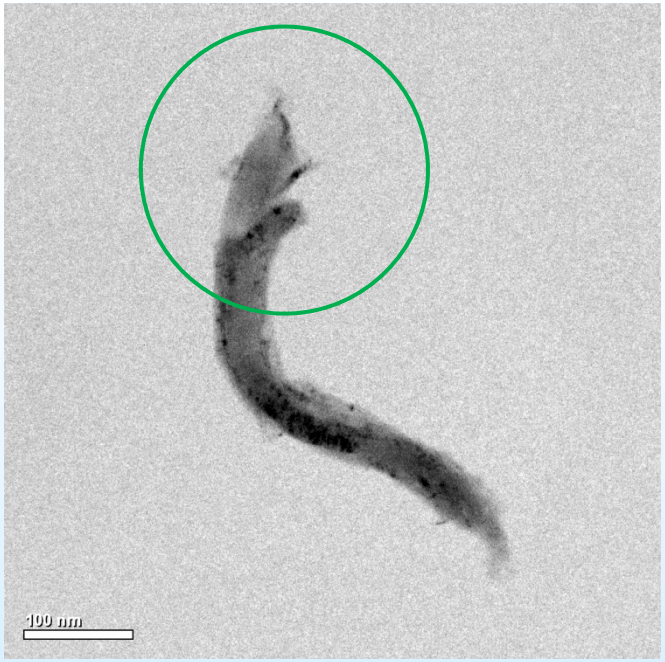


HRSEM of ECAP-ed Mg-MWCNT after hydrogenation cycle



TEM of ECAP-ed Mg-MWCNT after hydrogenation cycle

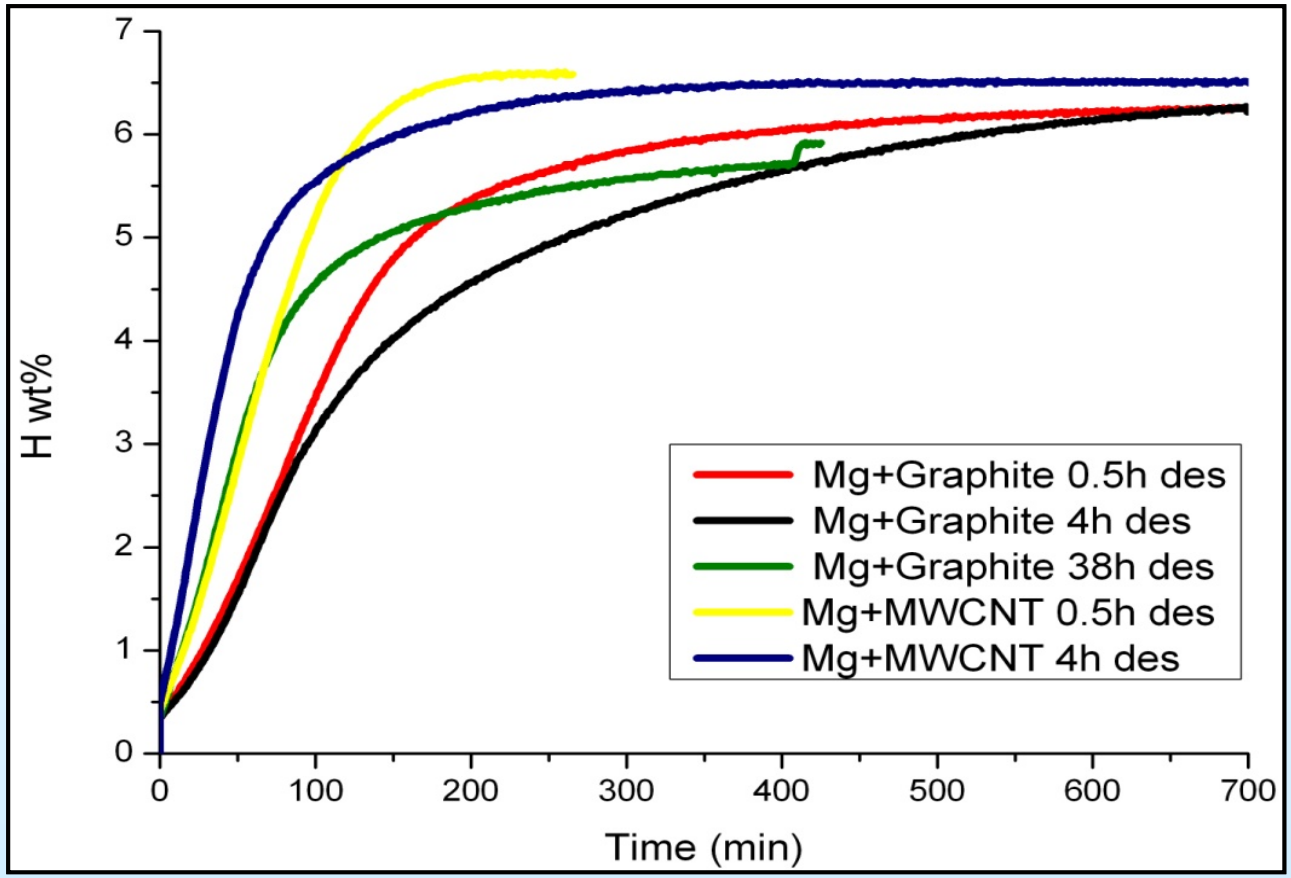




○ -bending sites

○ -sword-sheath failure

MWCNTs vs. Graphite



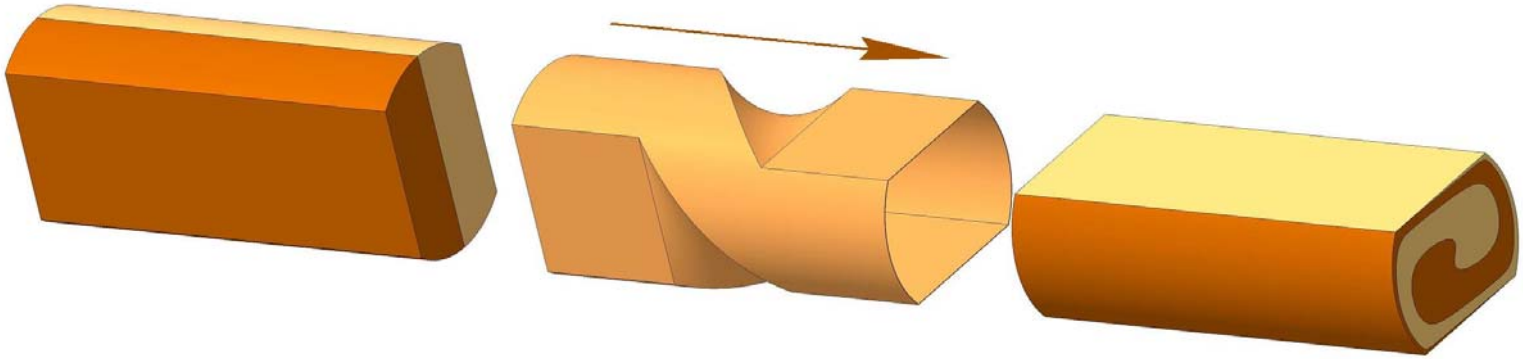
Conclusions

1. 4 h of high energy ball milling destroy MWCNTs;

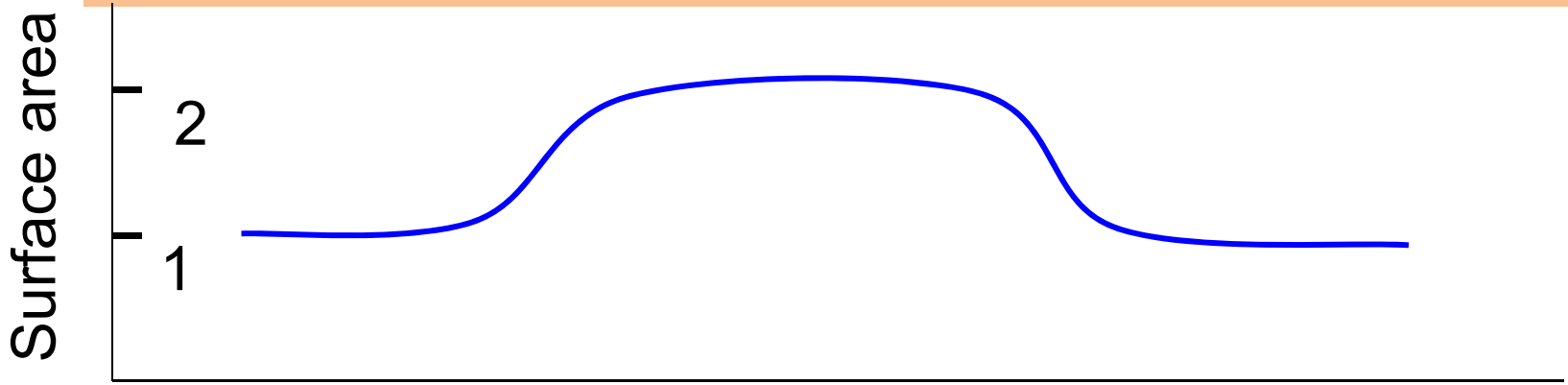
2. The hydrogen desorption kinetics and mechanical integrity of Mg-2wt.% MWCNT composites improve once the MWCNTs are destroyed;

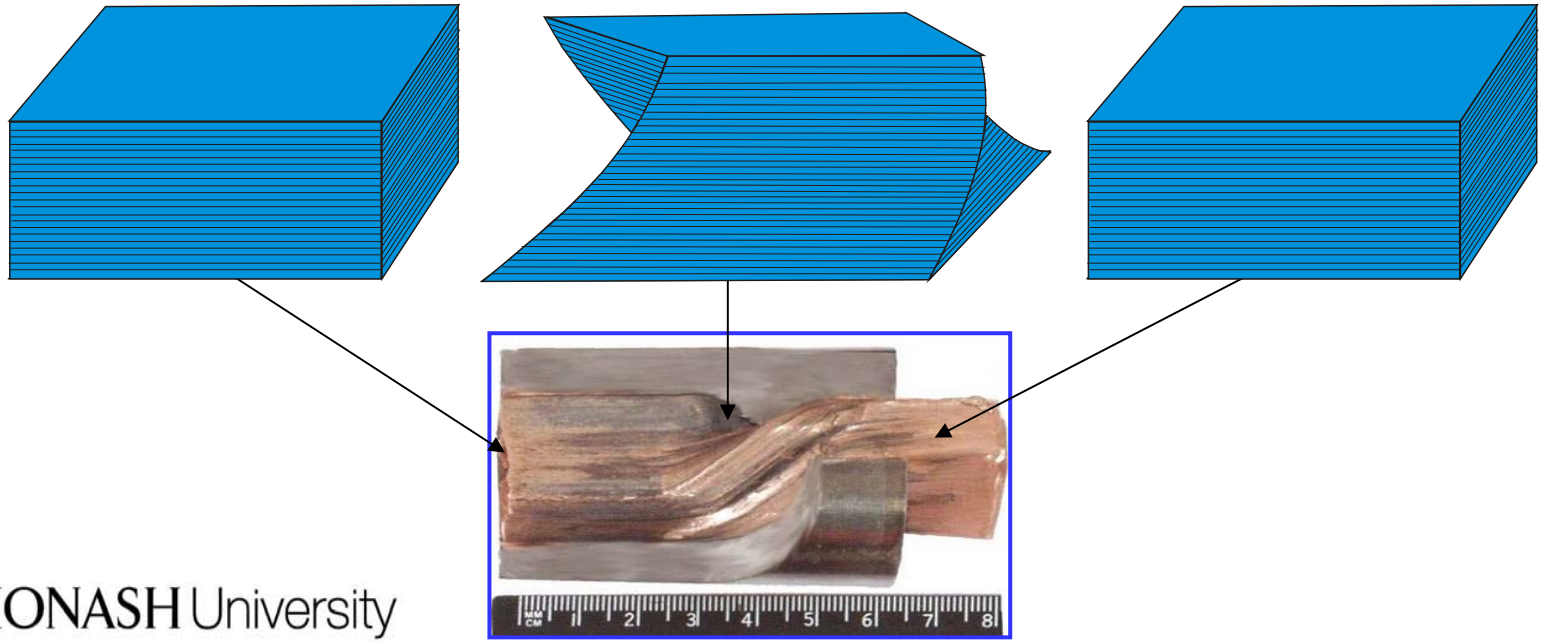
3. The addition of MWCNTs is more beneficial than that of Graphite;

Twist Extrusion: Worth trying?

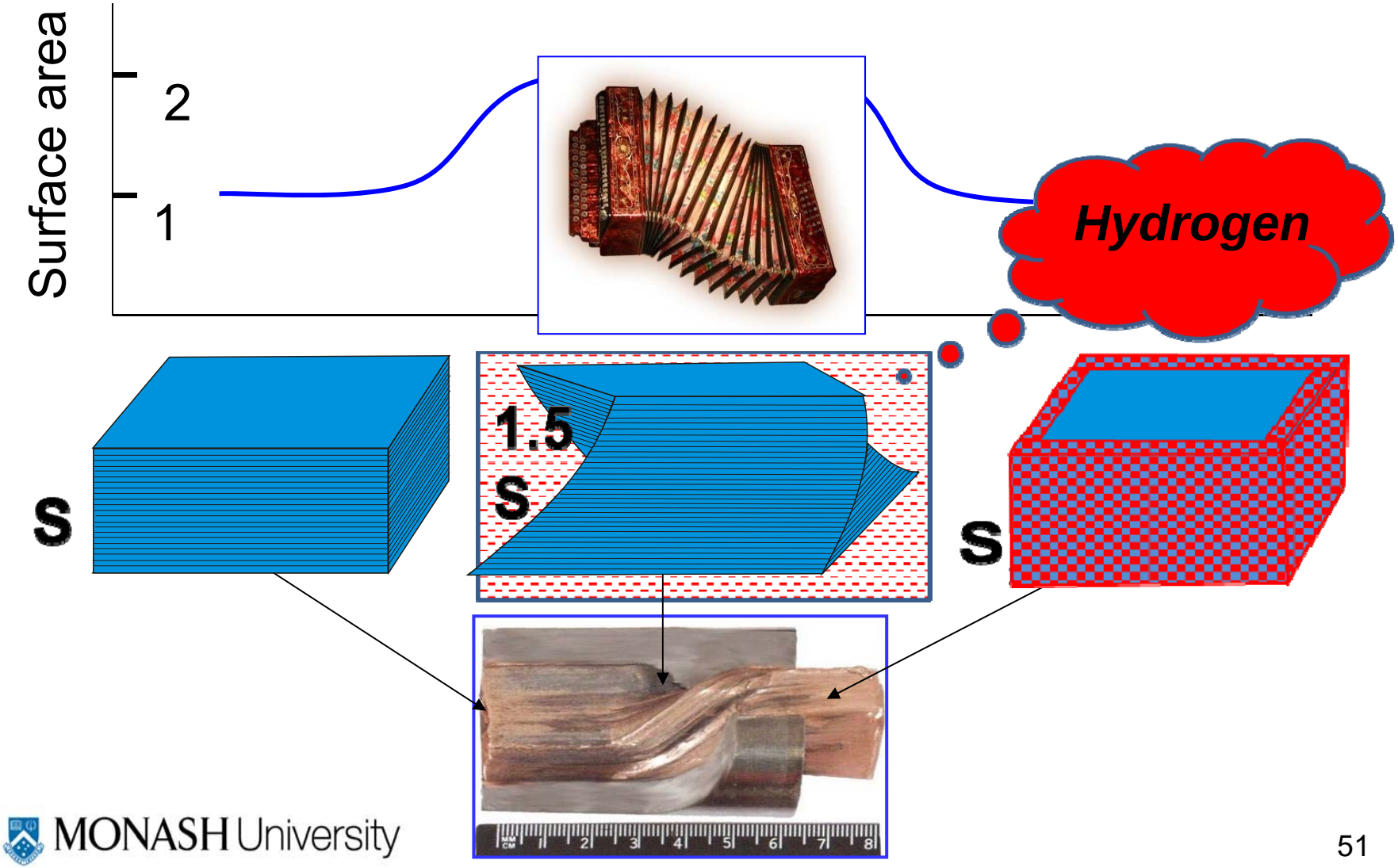


Variation of surface area during twist extrusion

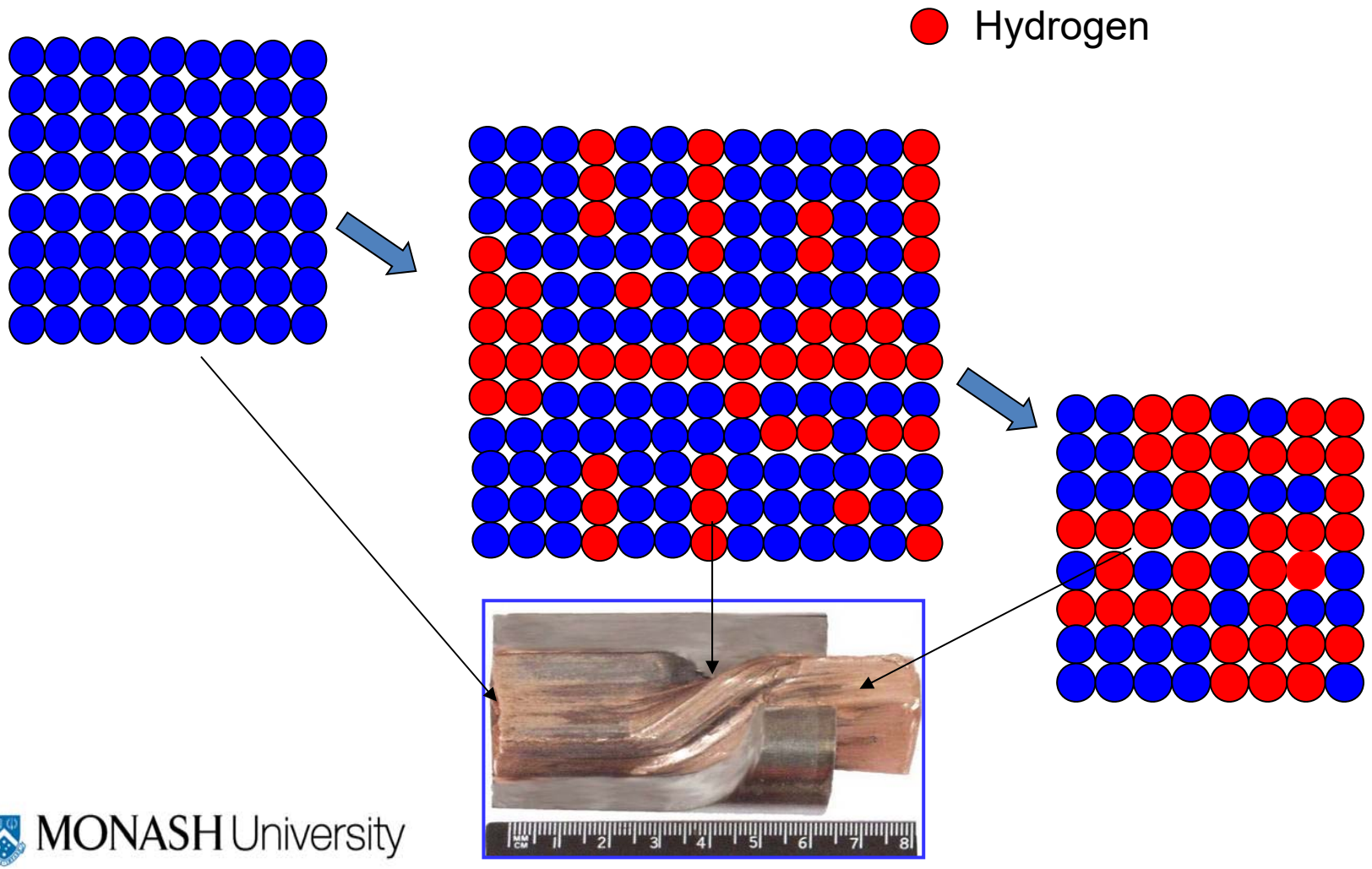




Variation of surface area during TE



Mechanochemical Process



Conclusion:

- *Severe plastic deformation techniques offer a wealth of interesting opportunities for acceleration of hydrogen sorption/desorption.*
- *Research in this area should be encouraged.*

Thank you for your attention!

yuri.estrin@monash.edu