A Method to Control Palladium Crystallographic Texture and Surface Morphology

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Abstract

Statistical studies performed at SRI (1) and ENEA (2) have identified a potential threshold deuterium loading (D/Pd ~0.9), surface texture {100}<001>, and surface morphology that give the highest probability to observation of the Fleischman-Pons excess heat effect using palladium foils. The development of crystallographic texture, grain size distribution, and rate of recrystallization are controlled by many factors. The surface morphology that develops during strong acid etching is strongly influenced by the thickness of the type of oxide layer that forms during recrystallization and subsequent cooling. This paper will report on annealing, oxidation and etching procedures to produce foils with desired crystallographic texture, surface morphology, strong grain boundary grooving, and the apparent discount between metallurgical treatment treatments and hydrogen loading.

[1] McKubre, M.C.H. and F.L. Tanzella, "Using resistivity to measure H/Pd and D/Pd loading: method and significance", The 12th International Conference on Condensed Matter Nuclear Science. 2005. Yokohama, Japan.
[2] Violante, V., et al., "The Study of the Fleischman and Pons Effect through the Materials Science Development", J. Condensed Matter Nucl. Sci., 2012. 8.

Study to Produce Strong Cube Texture Pd Foils Production

D.L Knies, R. Cantwell, O. Dmitriyeva, G. Stanish, E. Goulet, S. Hamm and M. McConnell

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ICCF-19, Padua (Italy) 13-17 April 2015

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Motivation

After nearly three years, the production of over 300 cathodes, and 35,000+ hours of run time, Coolescence LLC has been unable to reproduce the excess heat effect. To improve our chances of seeing the effect, we decided to take a step back and try to gain control of a number of specific material properties of pure palladium foils thought to play a crucial role:

- ✓ **Texture (crystalline) - dominant <100> crystallographic orientation**
- ✓ **Pronounces peaks in the Power Spectral Density Function between 10^4 and 10^7 m^{-1}**
  “Labyrinthic Surface”
- ✓ **Mean grain size ~100 μm with well-defined grain boundary grooving**
- ✓ **Capable of exceeding D/Pd “Threshold”**
  (D concentration >0.9 atomic faction with low current density “Easy Loading”)
- ✓ **Capable of supporting high flux across the cathode/electrolyte boundary**

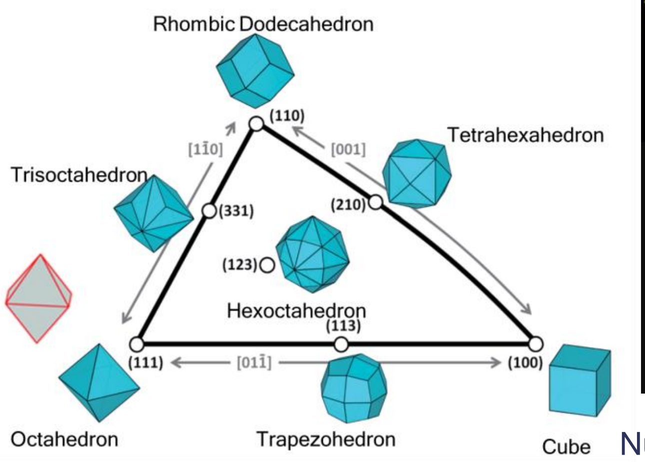
[1] Violante, V., et al. Proc. ICCF15 ENEA: Rome, Italy 5-9 Oct 2009, Vol 1. p.1
[2] M. McKubre, et al., in Frontier of Cold Fusion, Proc. ICCF3, H. Ikegami (Ed.), UAP, Tokyo, 1993, pp. 5-19.
[3] K. Kunimatsu, et al., in Frontiers of Cold Fusion, Proc. ICCF3, H. Ikegami (Ed.), UAP, Tokyo, 1993, pp. 31-45.

The number of atoms in the surface plane is one factor controlling the etching rate and subsequent development of surface morphology

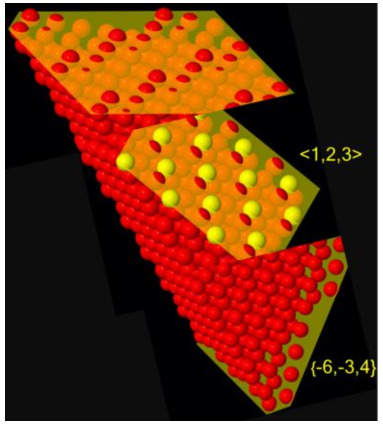
Electron Backscatter Diffraction (EBSD) gives us the

Orientation Map

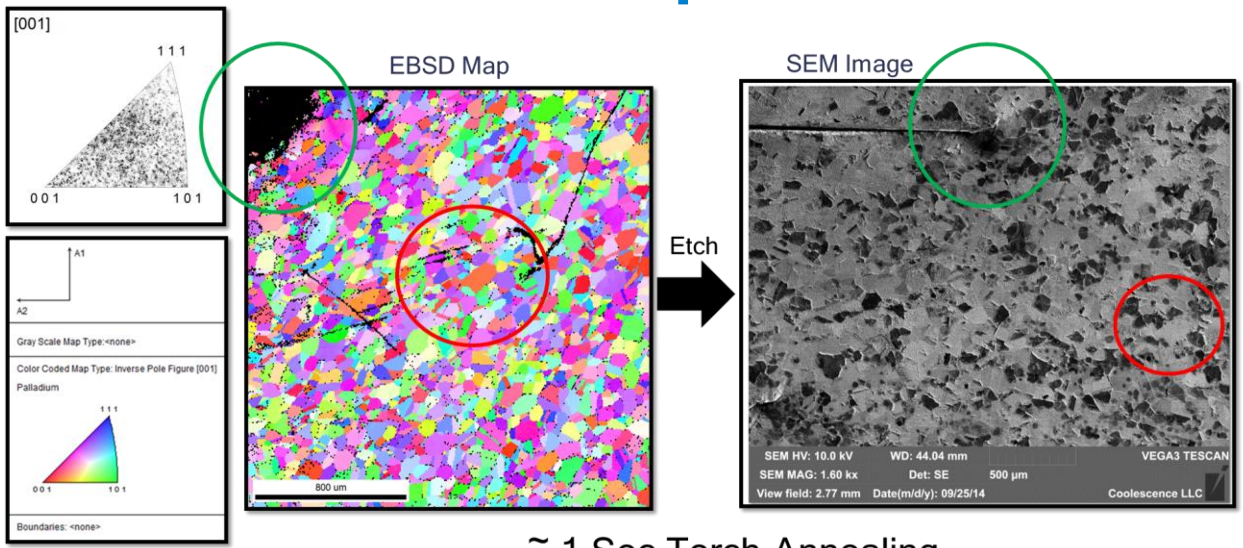
Pd Low-Index Single-Crystal Surfaces



Adapted from A.S. Barnard,Nanoscale, 2014, 6, 9983



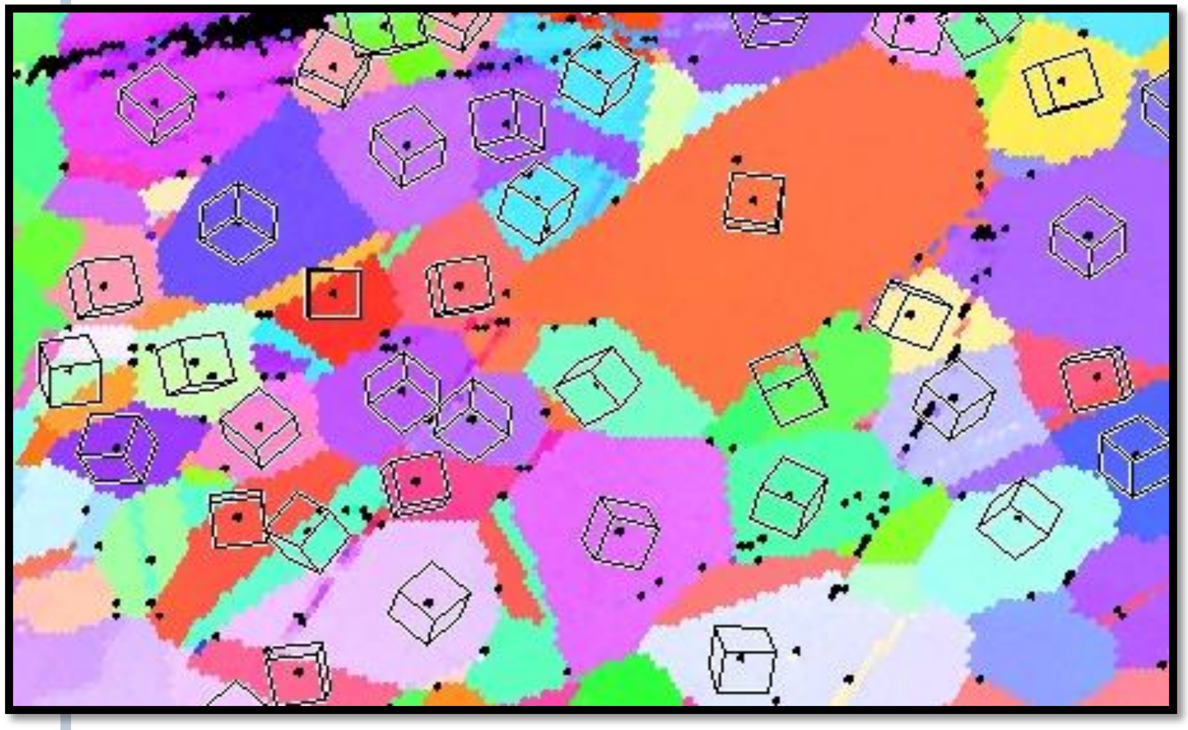
Number atoms on the surface depends on facet exposed

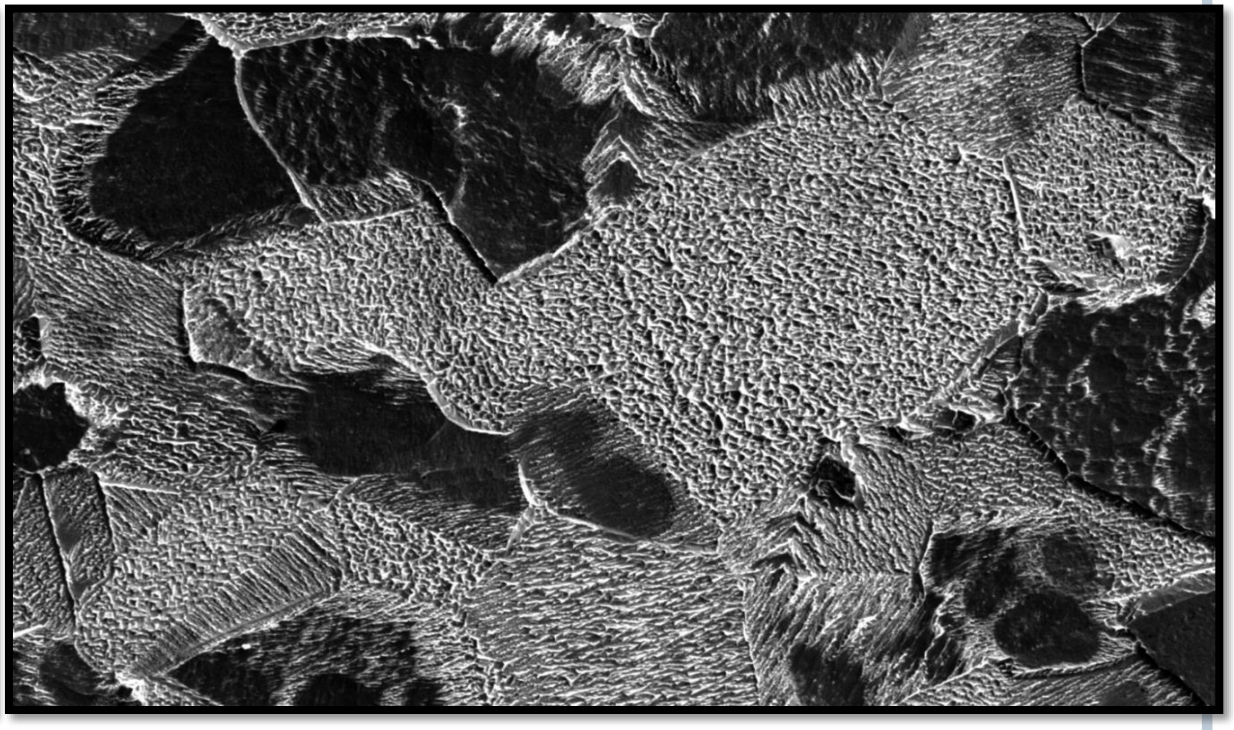


~ 1 Sec Torch Annealing

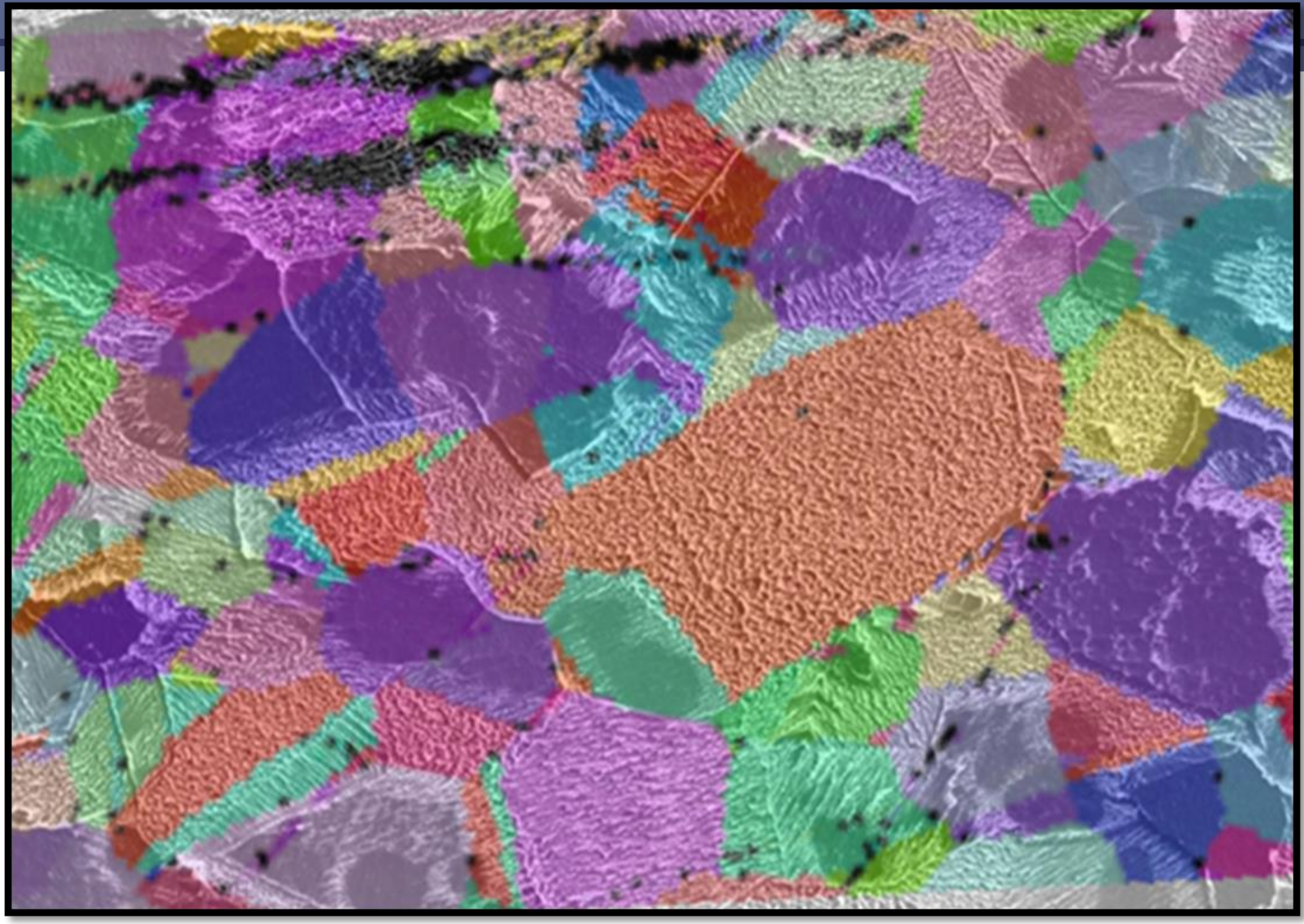
The EBSD map tells us which crystallographic planes meet the surface. This information provides insight into the evolution of the surface features revealed by etching and their relationship to the underlying texture.

Zoom to the Red Circle

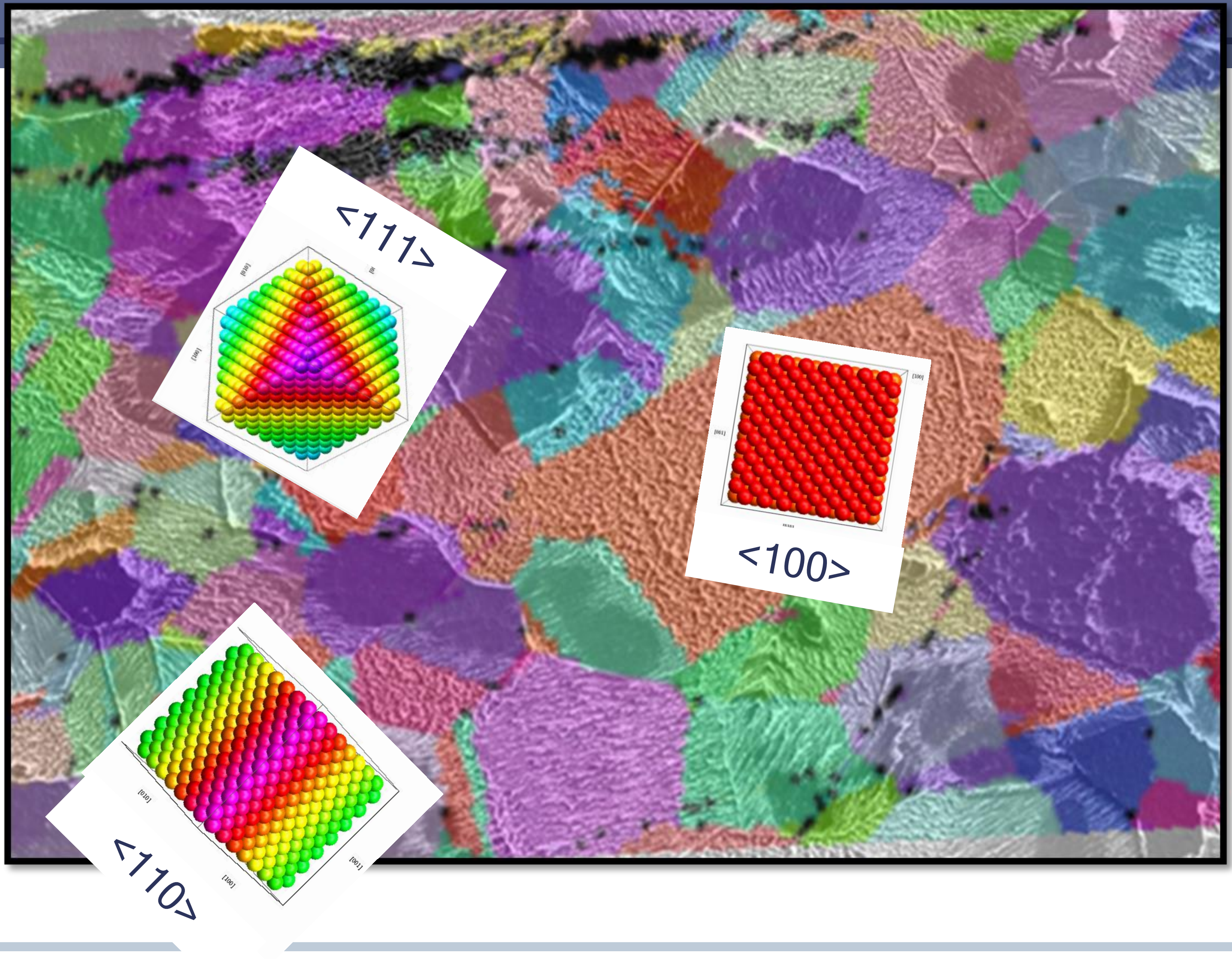




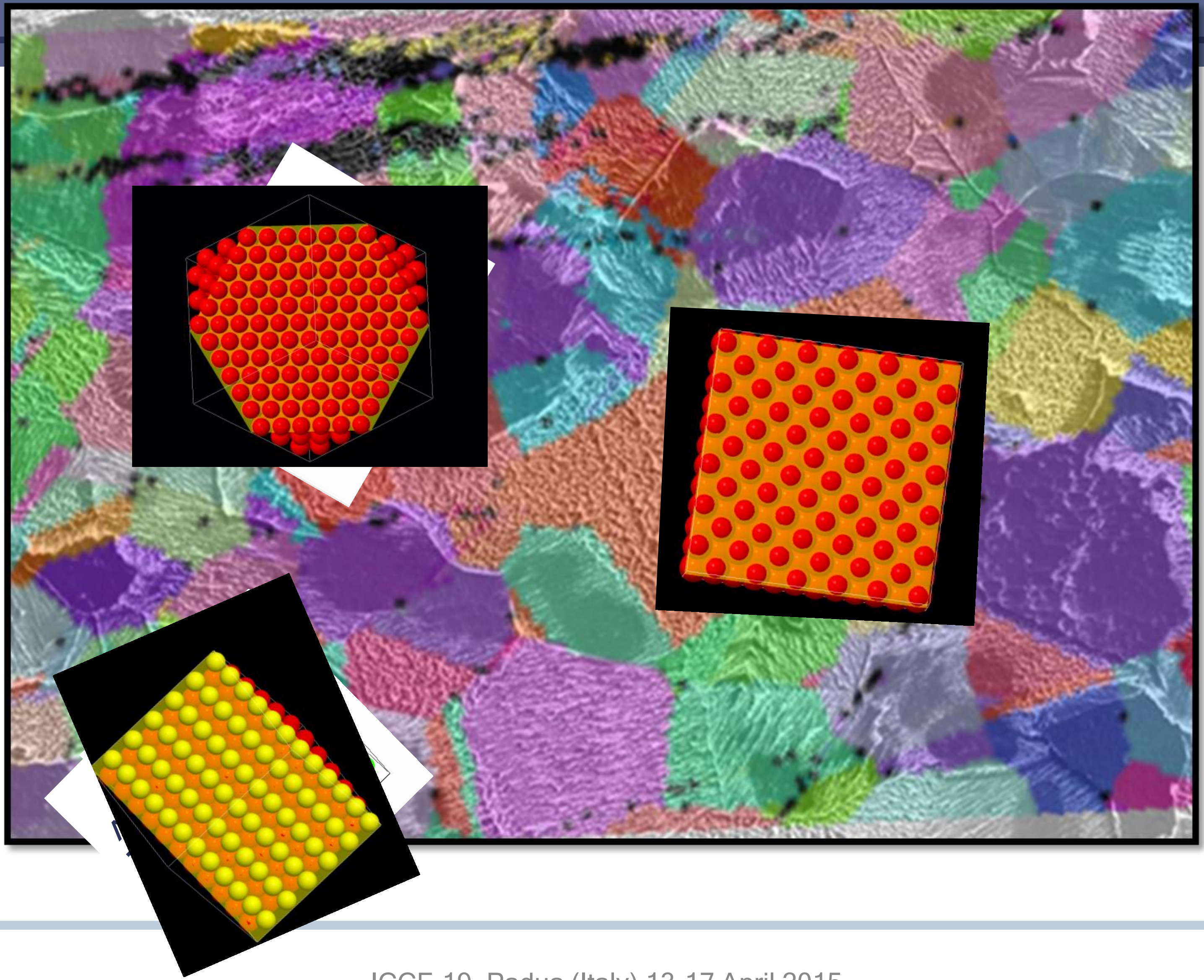
Overlay



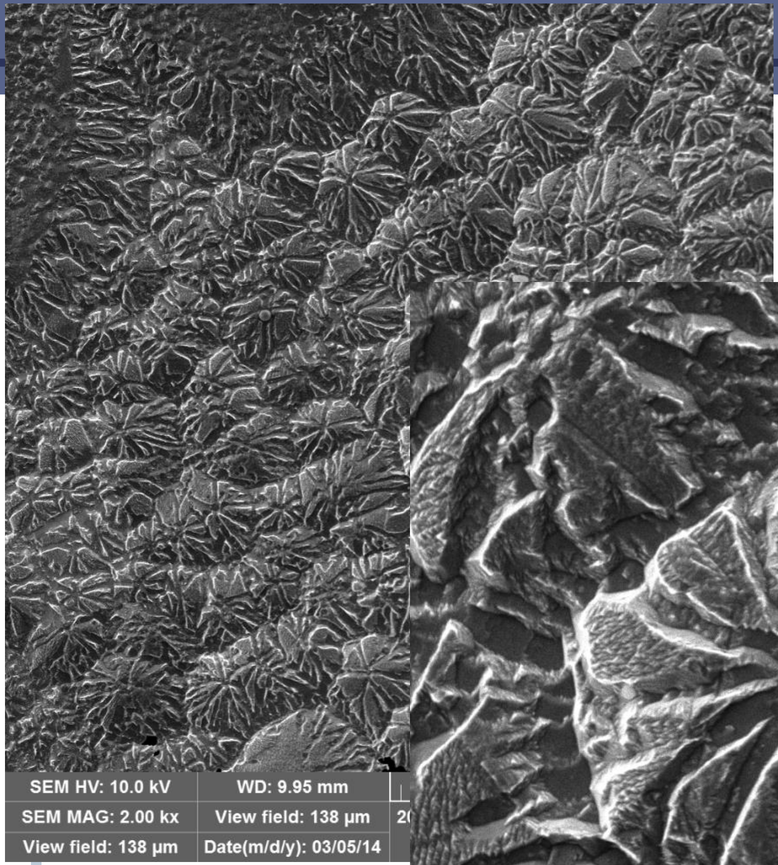
Overlay

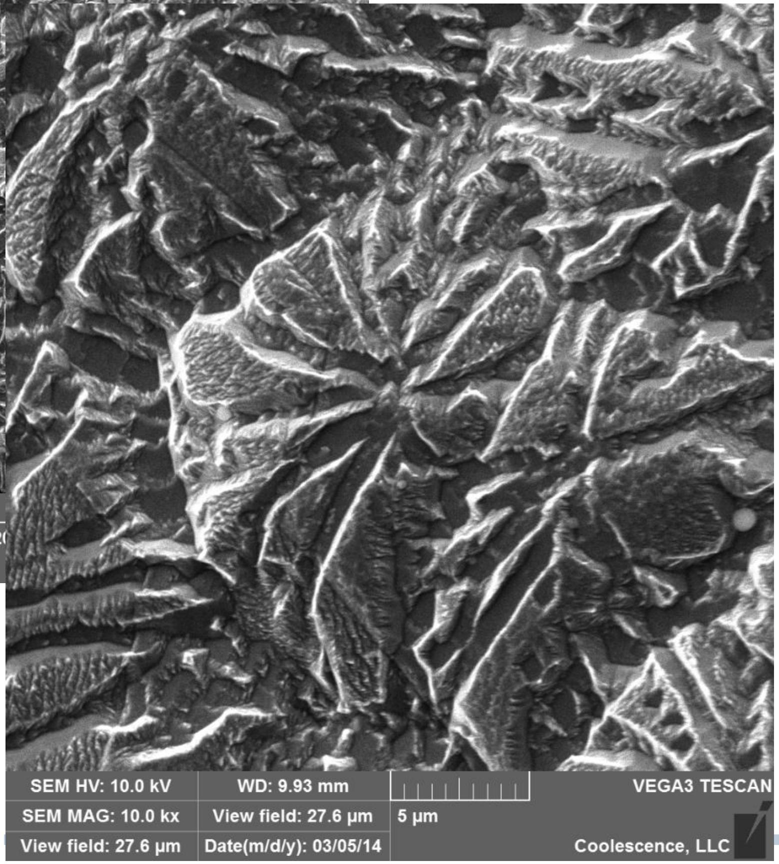


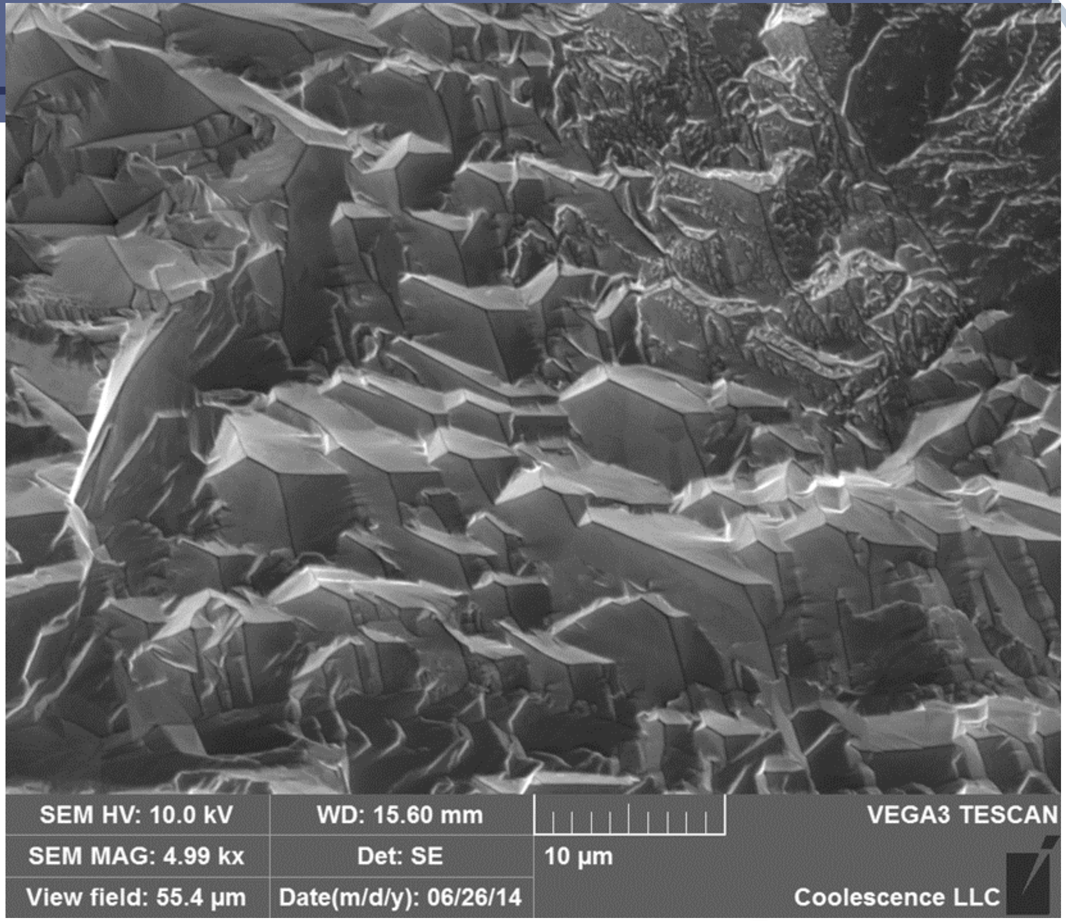
Overlay



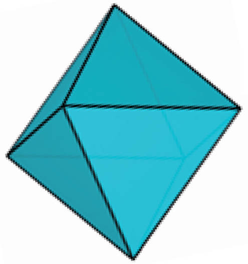
Palladium Facets Revealed by Etching





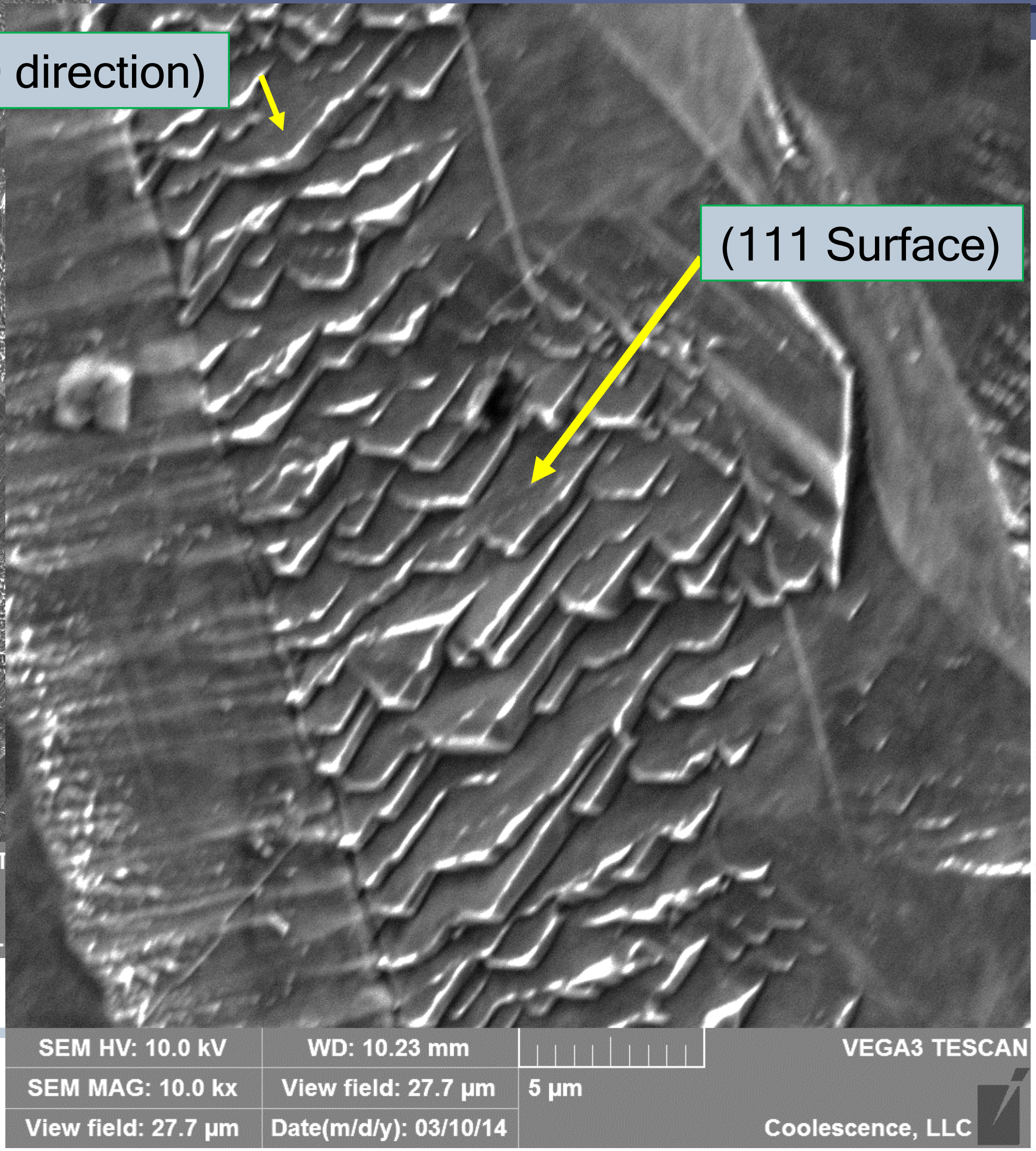


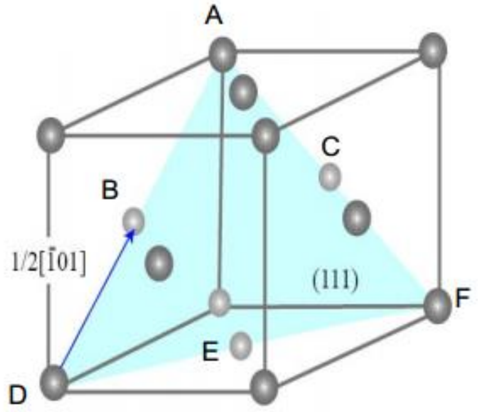
(123)



(111)

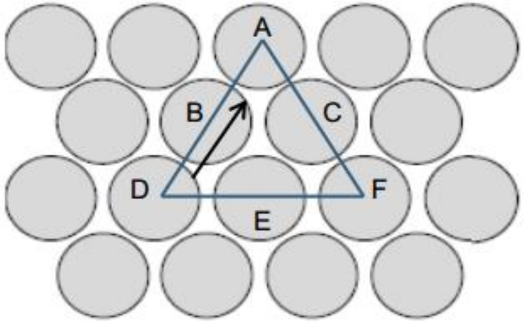
The FCC Slip System





Slip Plane: {111}

Figures by MIT OpenCourseWare.



Strong Cube Texture "Recipe"

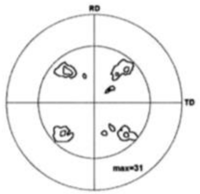
The as deformed texture components should be in the range:

S+C > 2B

S = {123}<63$\bar{4}$> Slip deformation texture

C = {112}<11$\bar{1}$> Copper texture

B = {110}<$\bar{1}$12> Brass texture



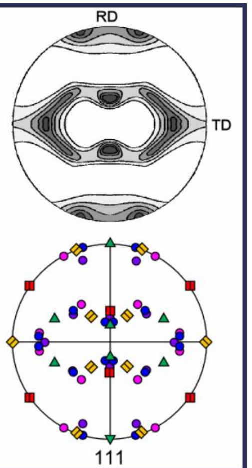
{111} pole figure for 99.987 pure palladium after Rolling (98.6%) and annealing at 850° for 1 h

If this case is met, strong cube text is reported after 850° C anneal for 1 hour with a grain size of 120 µm[1].

Pole Figure Key

Roll Texture/No Dominant Orientation

Name	Indices	Bunge (φ_1,Φ,φ_2)
copper	{112}<11$\bar{1}$>	90°, 35°, 45°
S1	{124}<21$\bar{1}$>	59°, 29°, 63°
S2	{123}<41$\bar{2}$>	47°, 37°, 63°
S3*	{123}<63$\bar{4}$>	59°, 37°, 63°
brass	{110}<$\bar{1}$12>	35°, 45°, 0°
Taylor	{4 4 11}<11 11 $\bar{8}$>	7°, 71°, 70°
Goss	{110}<001>	0°, 45°, 0°

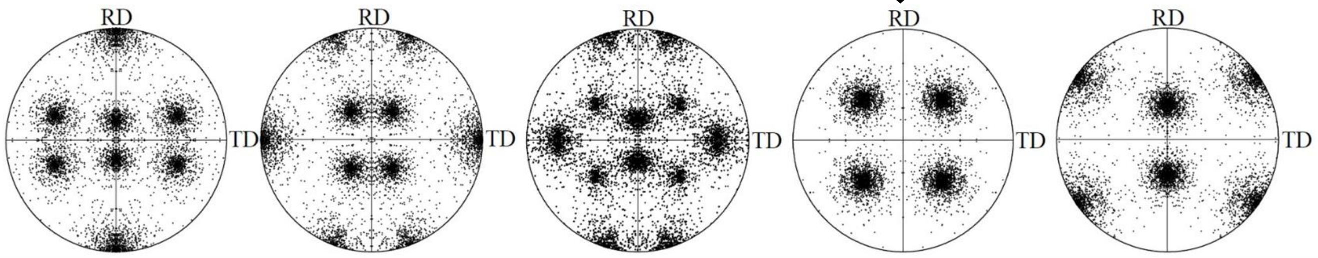


Typical Textures: Thermomechanical Processing (TMP) of Metals, 27-750, Spring 2006
Advanced Characterization and Microstructural Analysis, A.D. Rollett, P. Kalu, D. Waryoba

Strong Cube Texture

{100}<001>

Computationally Generated {111} Pole figures



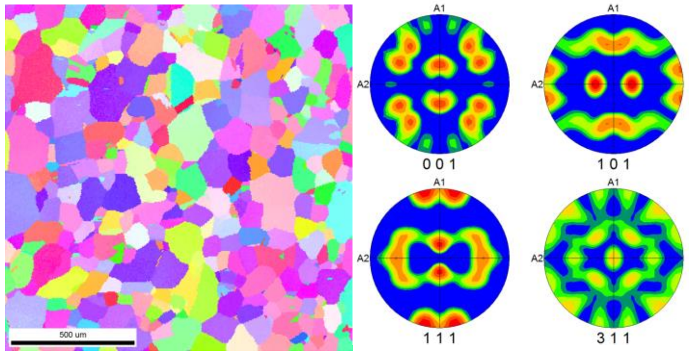
Copper Texture | Brass Texture | S Texture | Cube Texture | Gross Texture

Yoshida, K., Ishizaka, T., Kuroda, M., Ikawa, S., 2007. The effects of texture on formability of aluminum alloy sheets, Acta Materialia, 55 (13), 4499-4506.

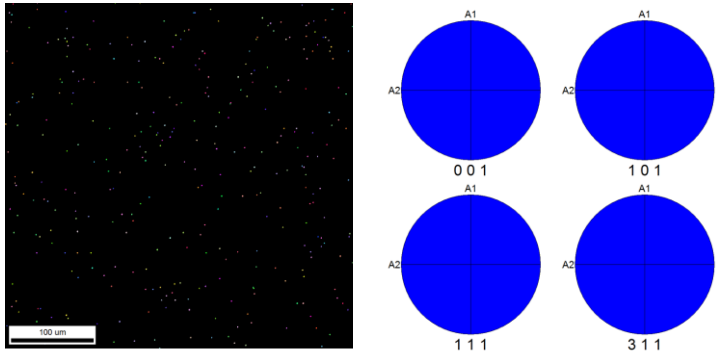
[1] Cube Texture Formation in Ni-Pd and Ni-Pd-W Alloys for HTS Tapes, I.V. Gervasyeva et al, Applications of Texture Analysis: Ceramic Transaction A. D. Rollett, John Wiley & Sons, Dec 5, 2008 - Technology & Engineering

Strong cube textured methodology
(best practices)

Starting Texture (Random)

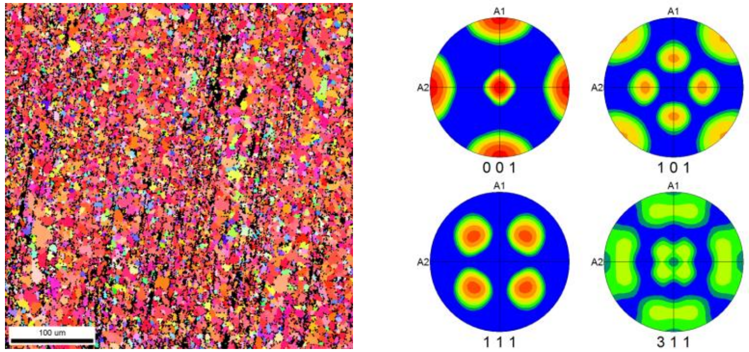


Critical Damage (~99% Reduction)



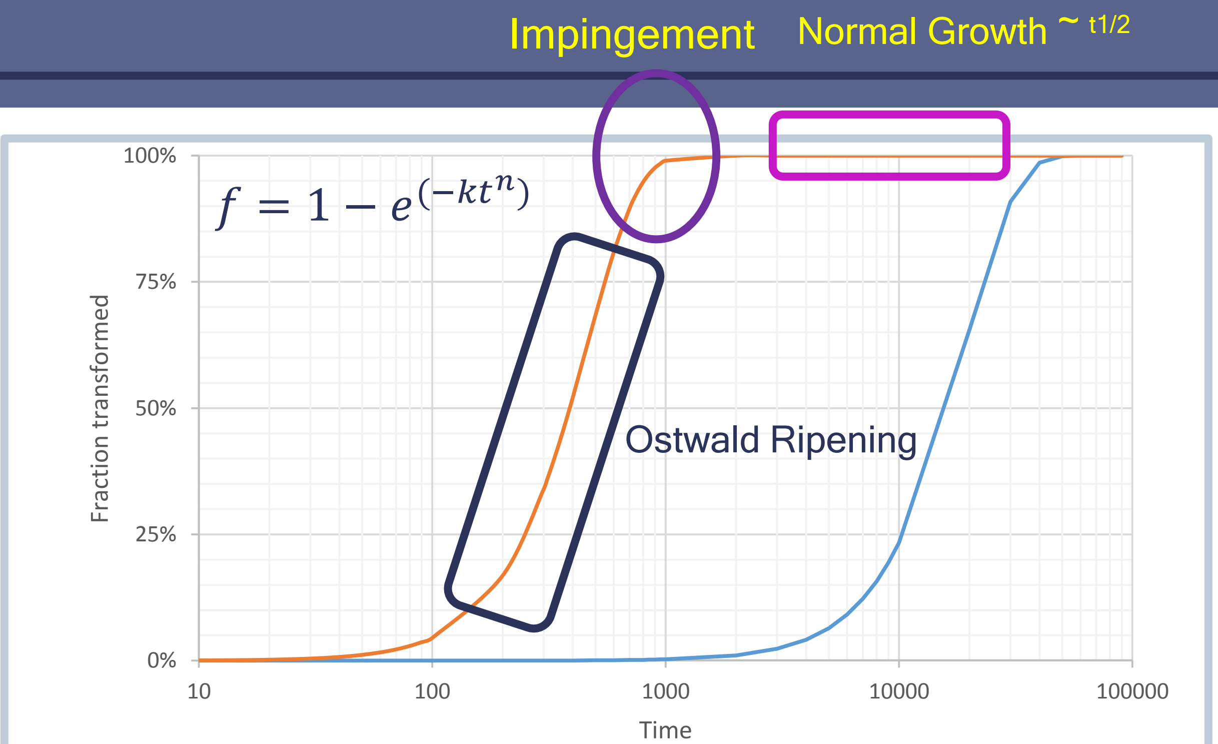
Large Δh, Slow Rolling Rate

Recrystallize to Strong Cube Texture

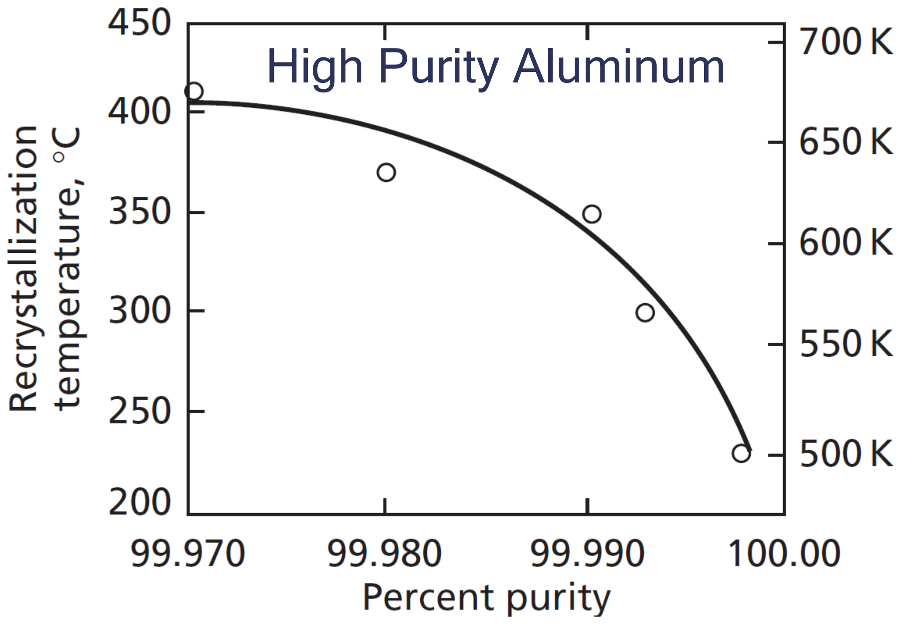


Sub Critical Temperature Anneal

Recrystallization/Grain Growth



Johnson–Mehl–Avrami–Kolmogorov (JMAK) equation



Effect of impurities on recrystallization temperature of aluminum, Perryman, E.C.W., ASM Seminar, Creep and Recovery, 1957, p. 111

Driving force for grain growth ΔG

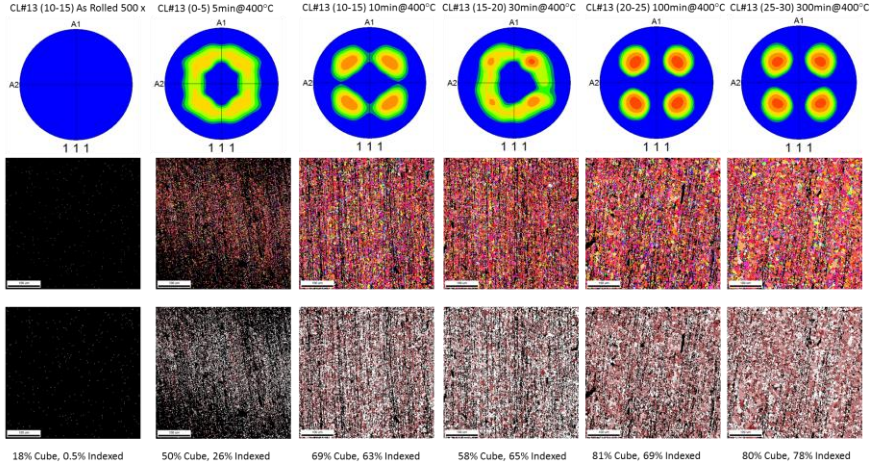
$\Delta G = E_{grain\ boundaries} + E_{stacking\ faults} + E_{dislocation} + E_{surface\ energy} + E_{elastic\ strain} + \ldots + E_{zener\ pinning}$

Microstructural evolution is in part controlled by the compilation of different sources of stored energy in the as-rolled material. ΔG acts to modify the activation energy in either direction.

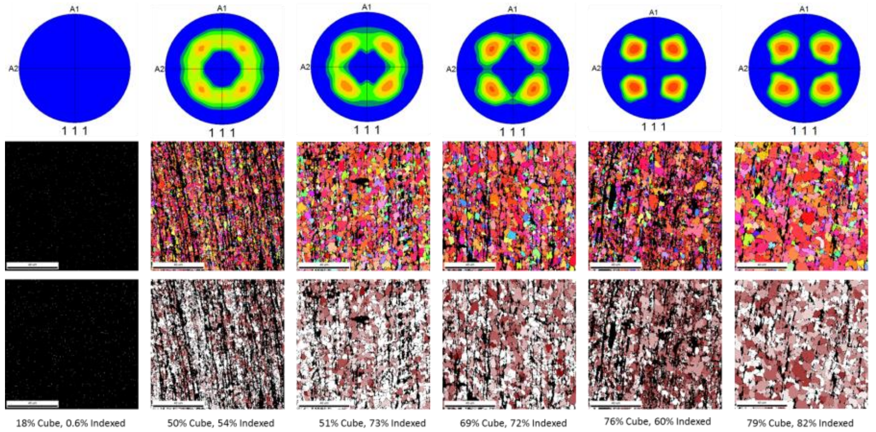
Two main theories have been proposed for the formation of recrystallization textures. One of these suggests that the recrystallization texture is determined by the orientations of the nuclei formed, and the other, by the orientation-dependence of the rate of growth of the nuclei.

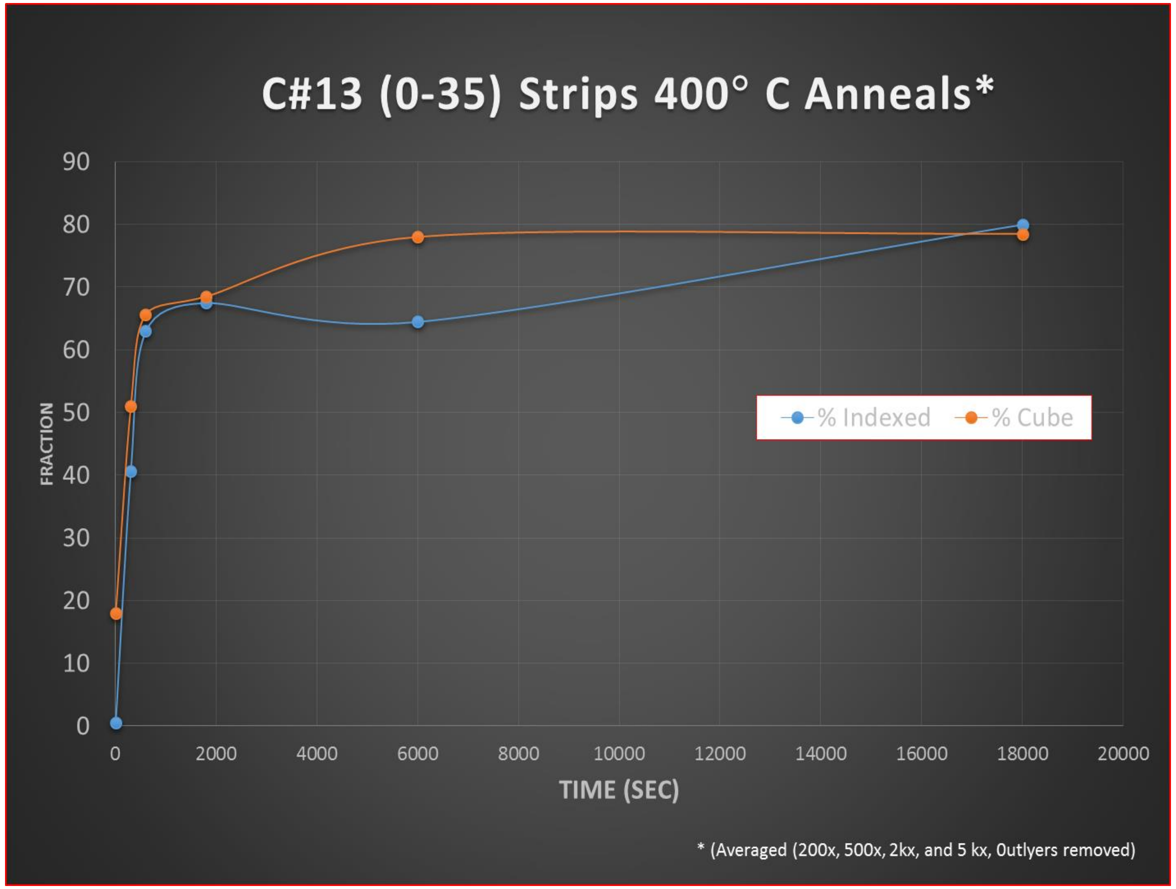
Seed Strong Cube Texture

500 x (0 to 300 min@ 400° C)



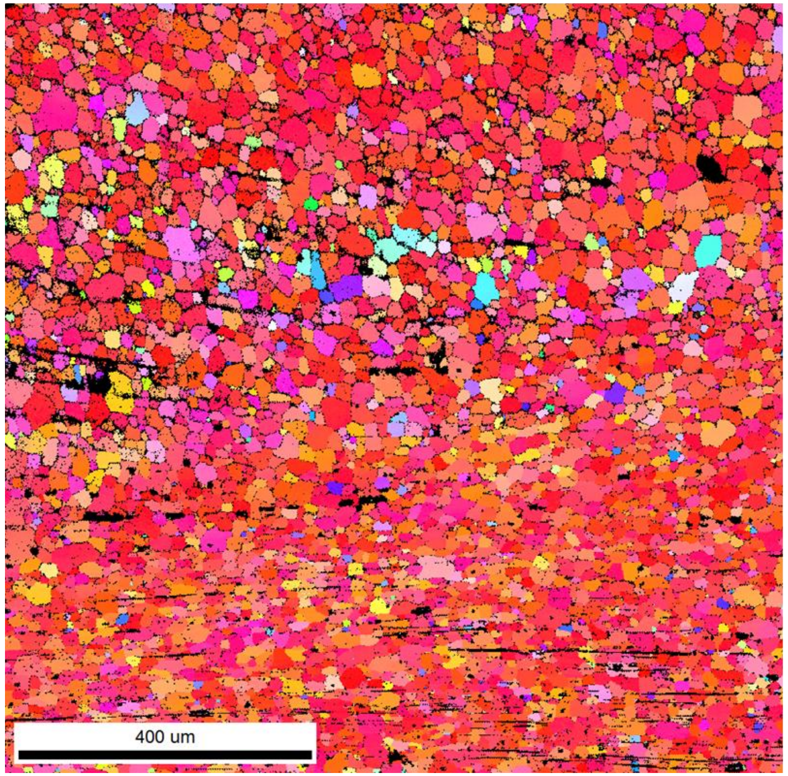
2 kx (0 to 300 min@ 400° C)

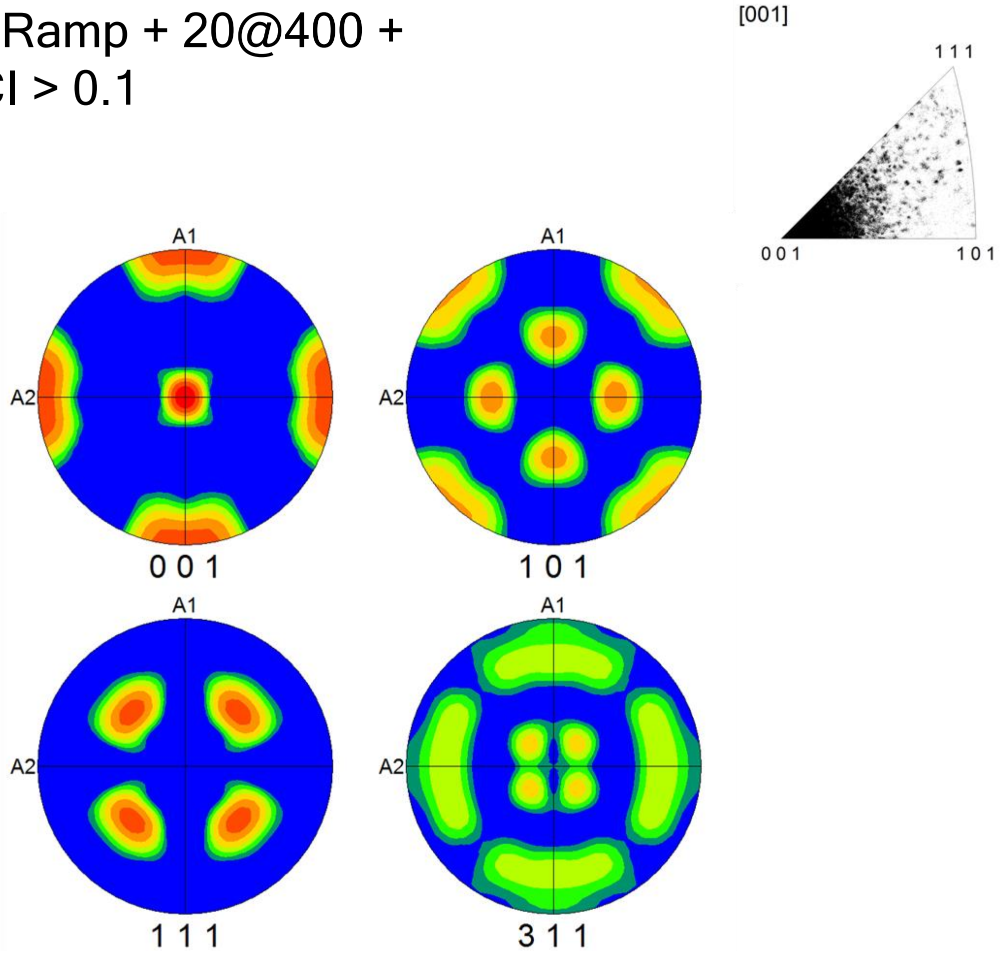




Requires Develop Lot Dependent Annealing Protocol

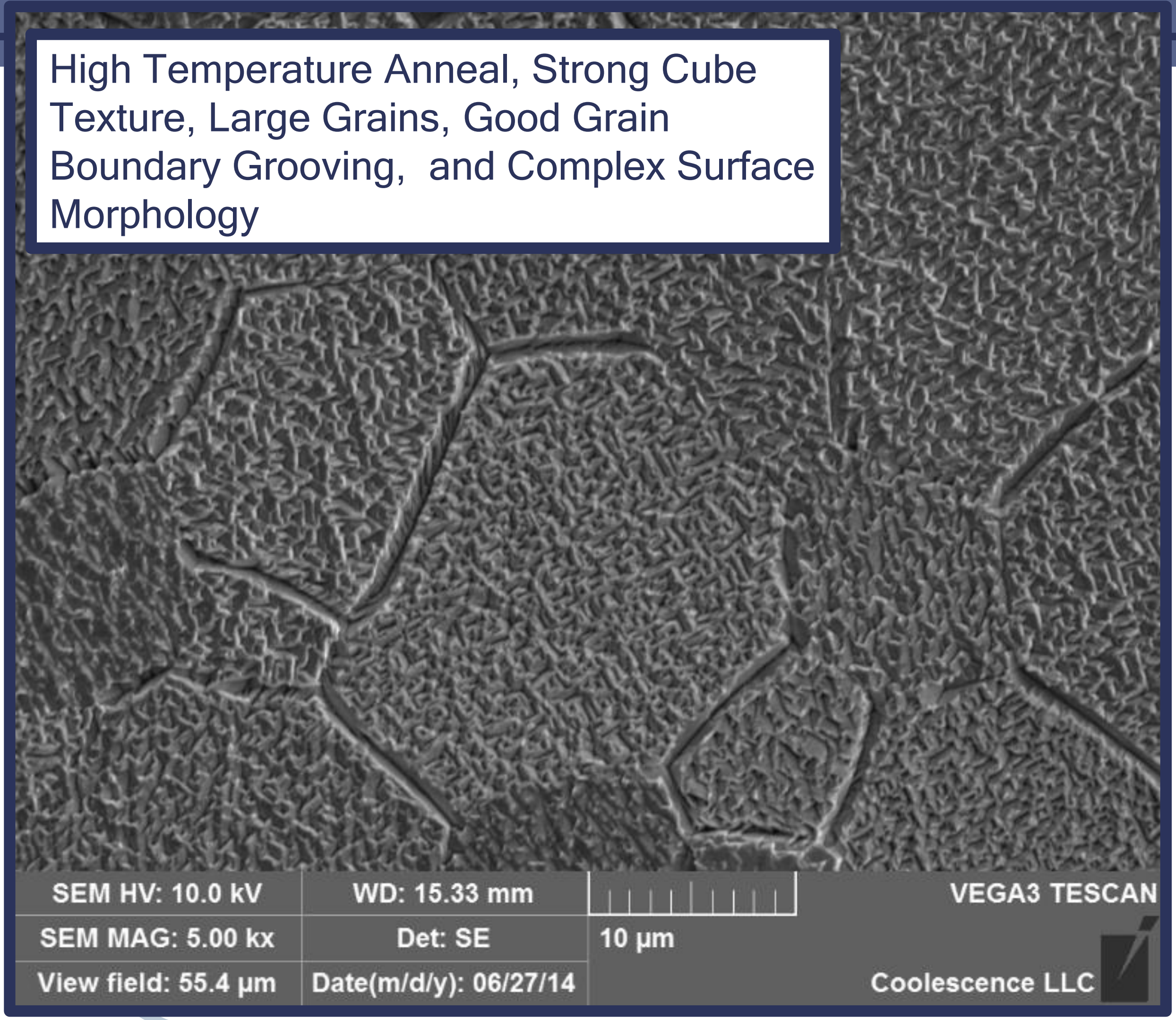
CL#13 (188-228) (0-40)b RA 20@300 + Ramp + 20@400 + 12hr@675 200 x rotated PCI > 0.1

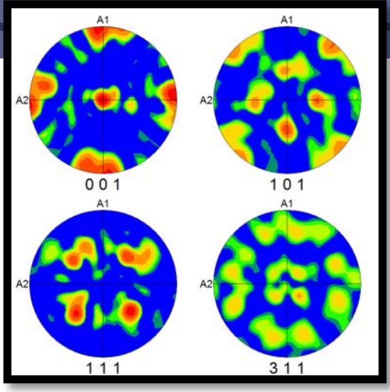


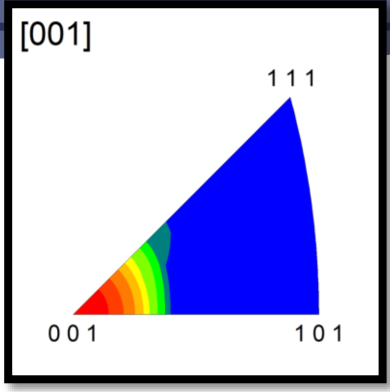


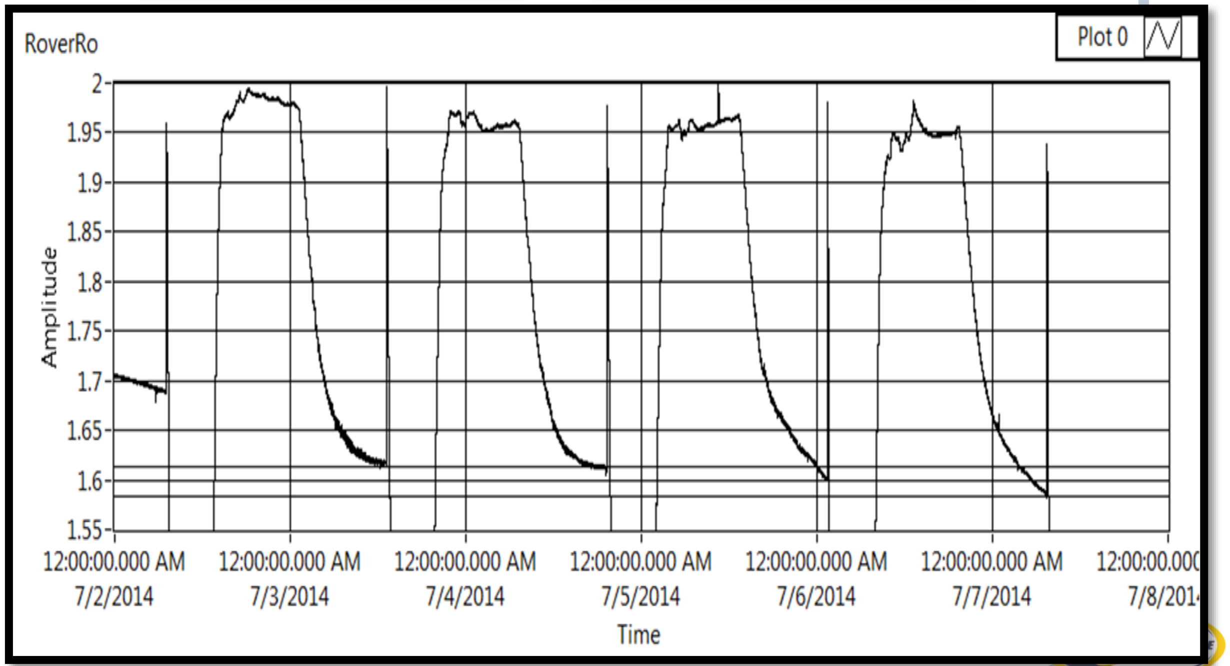
Heavy Rolling Brake Down Rollers Δh ~ 1 mm + Cross Rolled Until Flat

The Perfect Foil: C#255 RAE is from Pd Ingot#3 Part#1





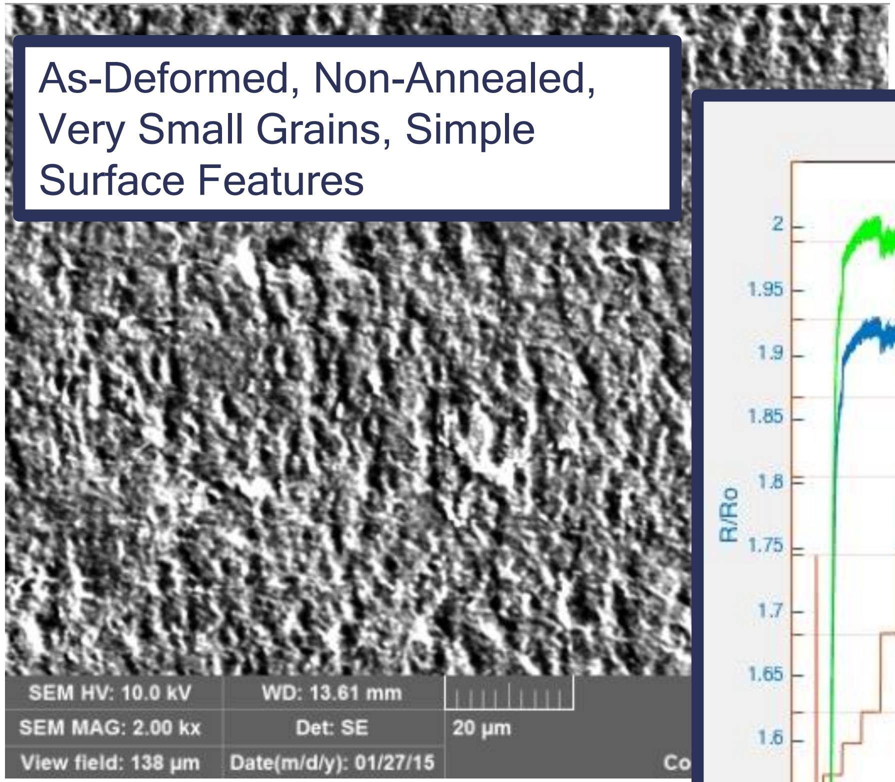




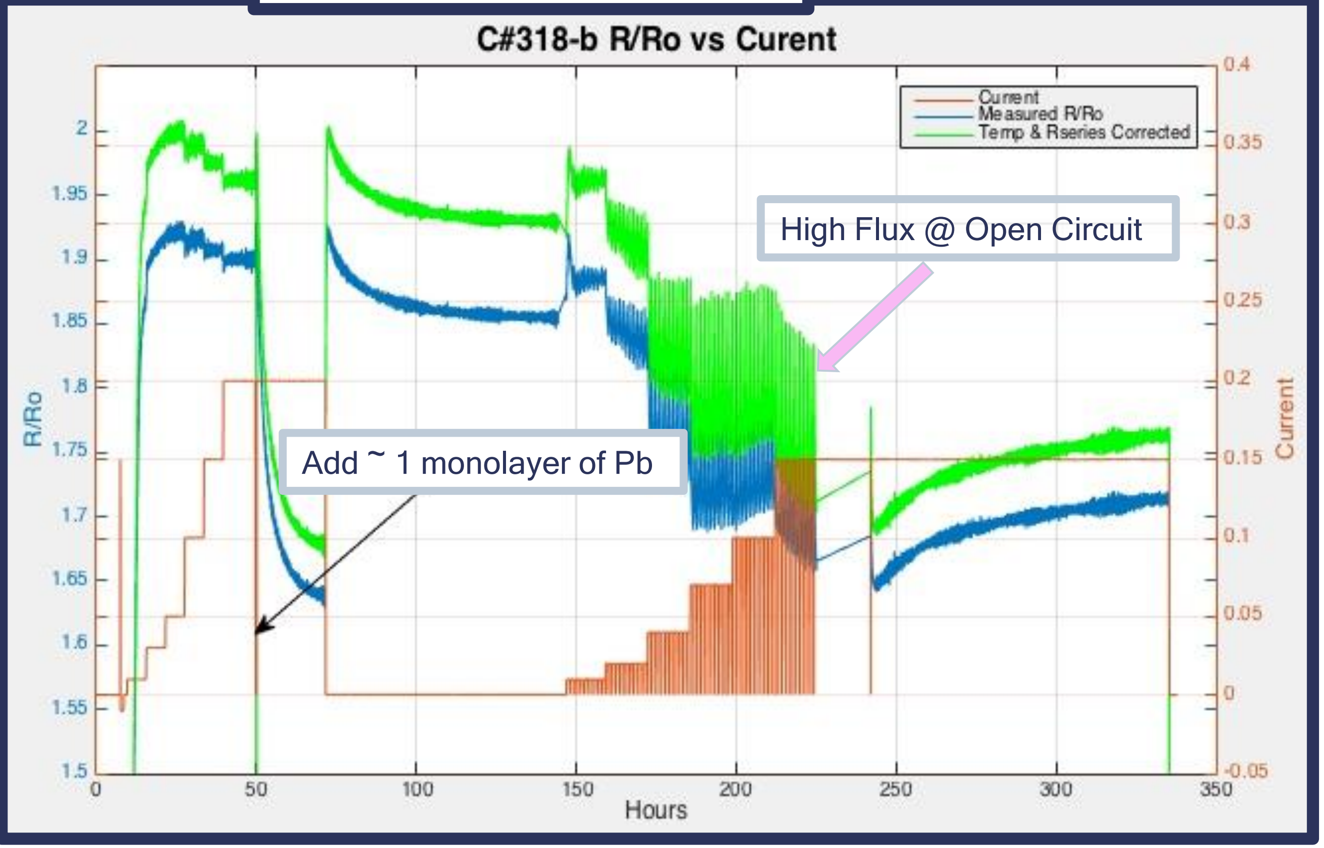
Best R/R_o =1.62, 1.61, 1.60, and 1.58 ~ D/Pd=0.95.

The Anti-foil C#318

As-Deformed, Non-Annealed, Very Small Grains, Simple Surface Features



Excellent loading and fast breathing after Pb addition



Electrochemical Performance

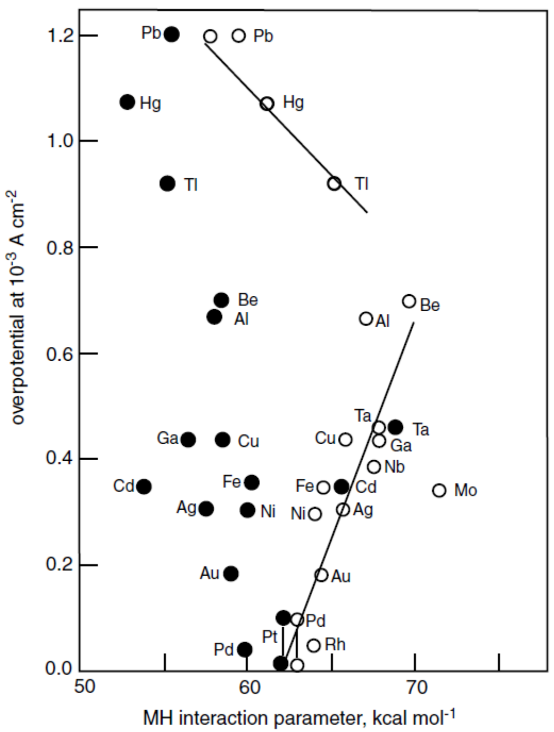
I. Disconnect between high loading and metallurgical treatment

II. As-deformed (non-annealed) foils are just as likely meet or exceed the loading threshold as highly textured foils.

III. The primary predictor of high loading was determined to be the presence of non-uniform thin coatings (< 10 nm) of various surface promoters (Cu, Pb, In, Bi, and etc.)

Islands of Promoter Impurities Enhance Loading

Overpotential Equivalent HER



Plot of hydrogen overpotential at 10^{-3} A cm^{-2} as function of metal-H interaction energy parameter[1]

Exchange current density [A cm^{-2}]

Overpotential [V]

$$J_{Tot} = \sum_{i}^{n} J_{oi}\left(C_R e^{\beta f \eta} - C_O e^{-(1-\beta) f \eta}\right)$$

J_{Tot} = Total current density [A cm^{-2}]
J_{oi} = Exchange current density [A cm^{-2}]
C_i = Concentration(t)/Concentration(t=0)
β = Symmetry coefficient
f = F/RT [V^{-1}] @25 C ~ 38.9 V^{-1}
η = Overpotential [V] from Equilibrium Potential

Electric Circuit Analogy

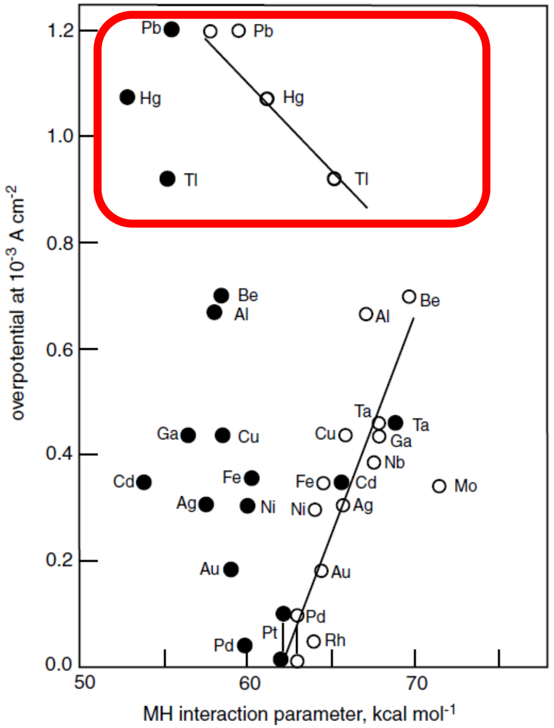
Under galvanostat control as surface coatings form, the overpotential must be increased to maintain constant current

[1] Catalysis in Electrochemistry: From Fundamentals to Strategies for Fuel Cell Development, First Edition. Edited by Elizabeth Santos and Wolfgang Schmickler. © 2011 John Wiley & Sons, Inc. Published 2011 by John Wiley & Sons, Inc

Islands of Promoter Impurities Enhance Loading

Overpotential Equivalent HER	Red (High) - Pb, Hg, Ti (Basic Metals)

J_{oi} ~ 5 x 10^{-9} A/cm^2 for Pb



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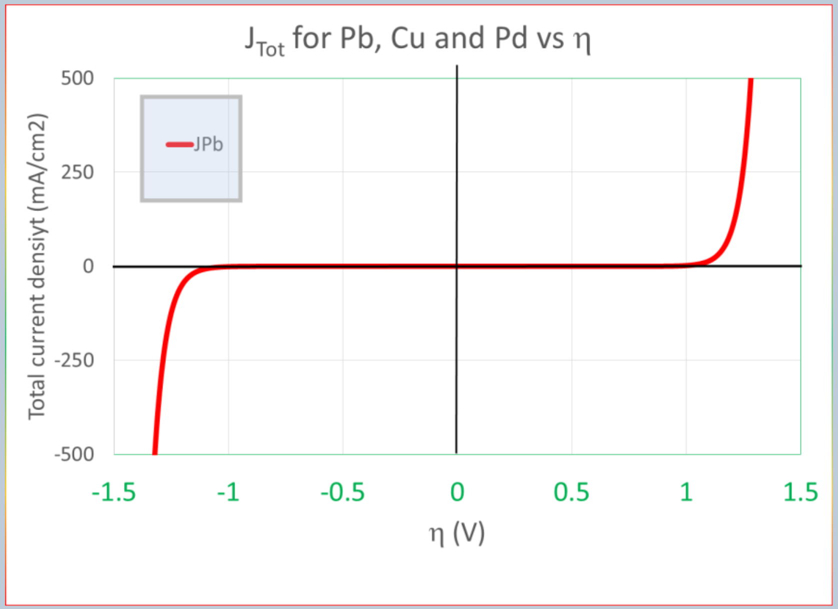

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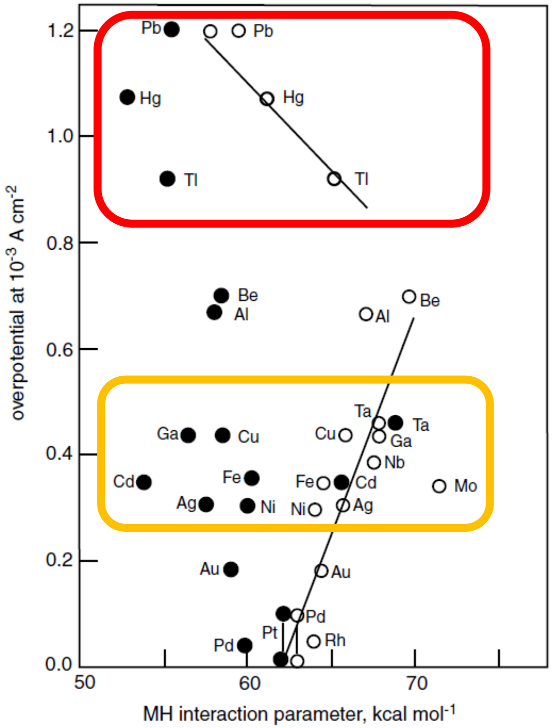
Islands of Promoter Impurities Enhance Loading

Overpotential Equivalent HER	Red (High) - Pb, Hg, Ti (Basic Metals) Yellow(Medium) - Cu, Fe, Ni (Light Transition Metals)

J_{oi} ~ 5 x 10^{-9} A/cm^2 for Pb
J_{oi} ~ 1 x 10^{-6} A/cm^2 for Cu

Electric Circuit Analogy



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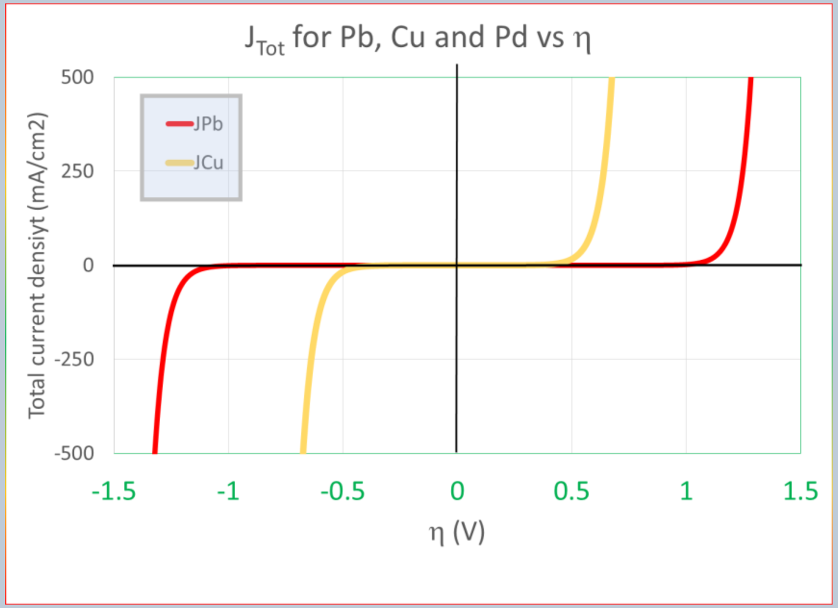

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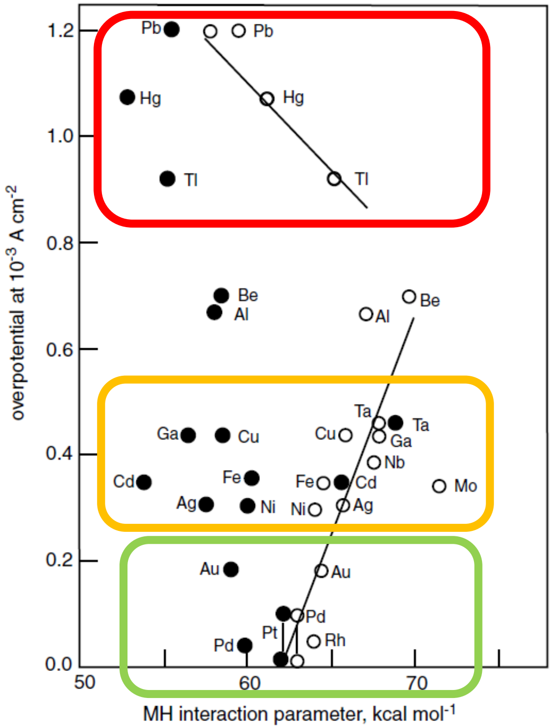
J_{oi} ~ 5×10^{-9} A/cm^2 for Pb
J_{oi} ~ 1×10^{-6} A/cm^2 for Cu
J_{oi} ~ 1×10^{-3} A/cm^2 for Pd

Electric Circuit Analogy



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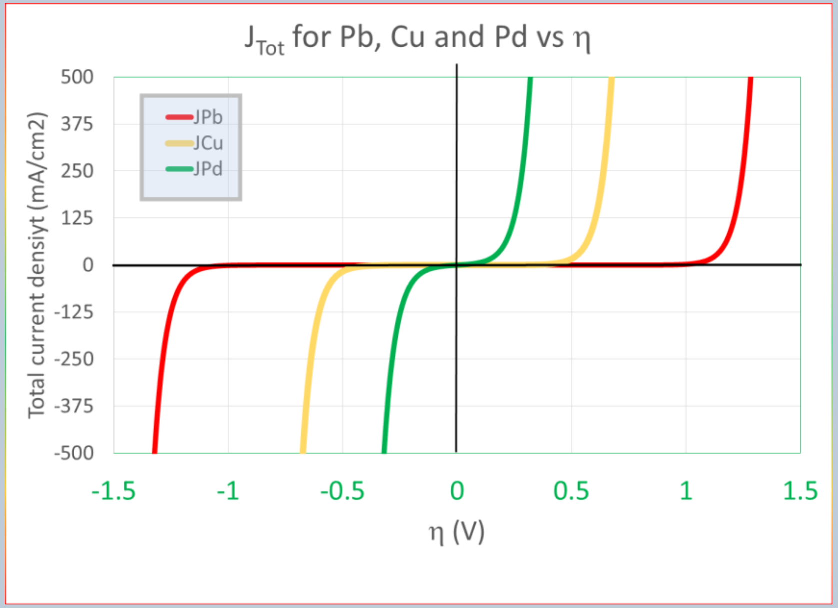

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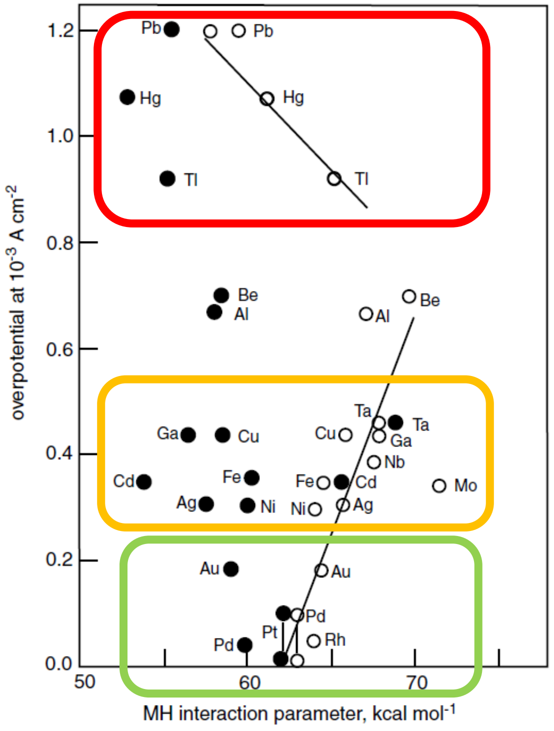
J_{oi} ~ 1 x 10^{-6} A/cm^2 for Cu
J_{oi} ~ 1 x 10^{-3} A/cm^2 for Pd

Electric Circuit Analogy



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C_i = Concentration(t)/Concentration(t=0)
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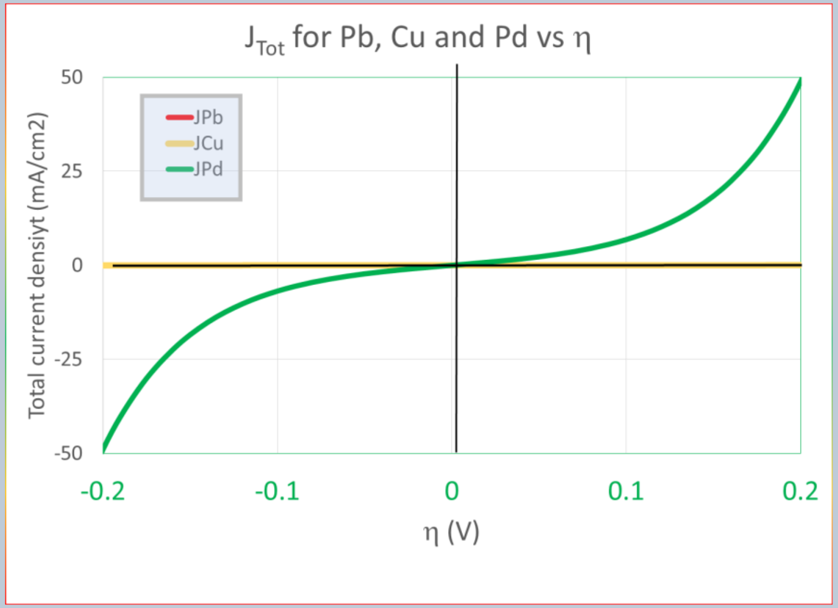
f = F/RT [V^{-1}] @25 C ~ 38.9 V^{-1}
η = Overpotential [V] from Equilibrium Potential



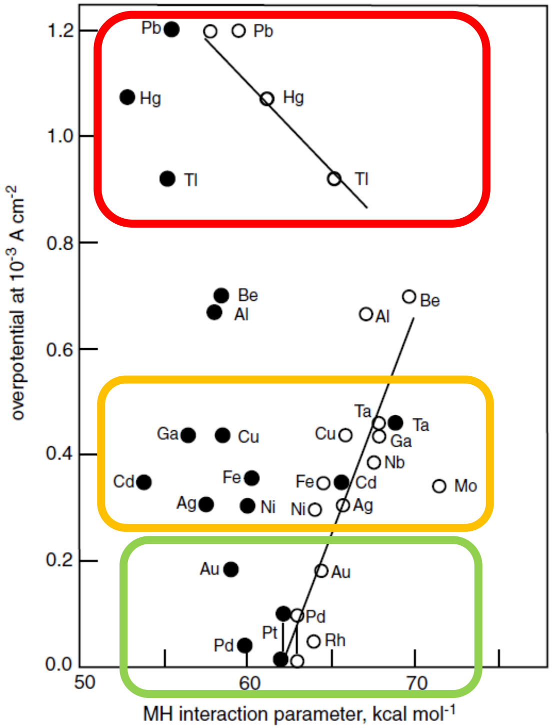
Under galvanostat control as surface coatings form, the overpotential must be increased to maintain constant current

[1] Catalysis in Electrochemistry: From Fundamentals to Strategies for Fuel Cell Development, First Edition. Edited by Elizabeth Santos and Wolfgang Schmickler. © 2011 John Wiley & Sons, Inc. Published 2011 by John Wiley & Sons, Inc

Islands of Promoter Impurities Enhance Loading

Overpotential Equivalent HER	Red (High) - Pb, Hg, Ti (Basic Metals) Yellow(Medium) - Cu, Fe, Ni (Light Transition Metals) Green(Low) - Pd, Pt, Rh (Platinum Group Metals)

J_{oi} ~ 5 x 10^{-9} A/cm² for Pb
J_{oi} ~ 1 x 10^{-6} A/cm² for Cu
J_{oi} ~ 1 x 10^{-3} A/cm² for Pd



Plot of hydrogen overpotential at 10^{-3} A cm^{-2} as function of metal-H interaction energy parameter[1]

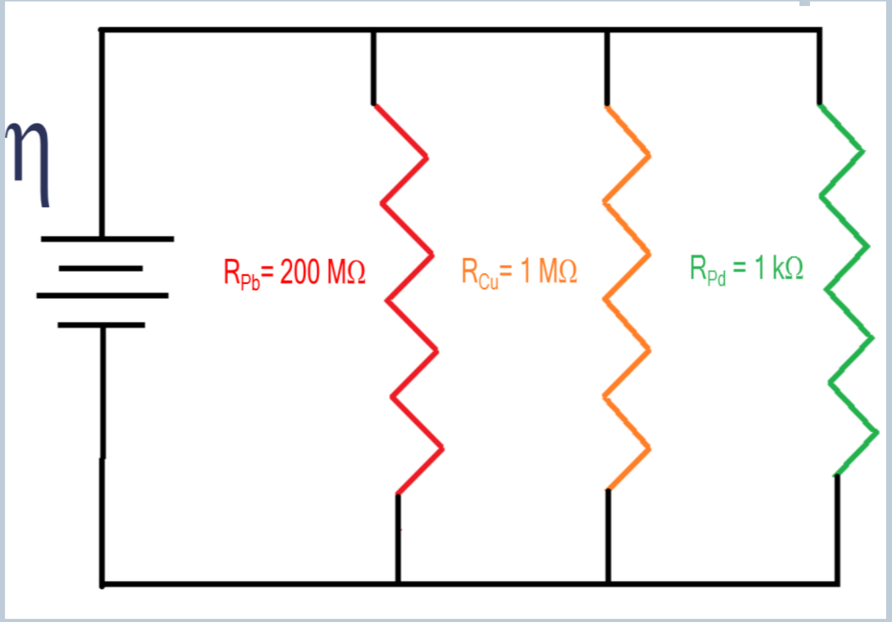
Exchange current density [A cm^{-2}]

Overpotential [V]

$$J_{Tot} = \sum_{i}^{n} J_{oi}\left(C_R e^{\beta f \eta} - C_O e^{-(1-\beta) f \eta}\right)$$

J_{Tot} = Total current density [A cm^{-2}]
J_{oi} = Exchange current density [A cm^{-2}]
C_i = Concentration(t)/Concentration(t=0)
β = Symmetry coefficient
f = F/RT [V^{-1}] @25 C ~ 38.9 V^{-1}
η = Overpotential [V] from Equilibrium Potential

Electric Circuit Analogy



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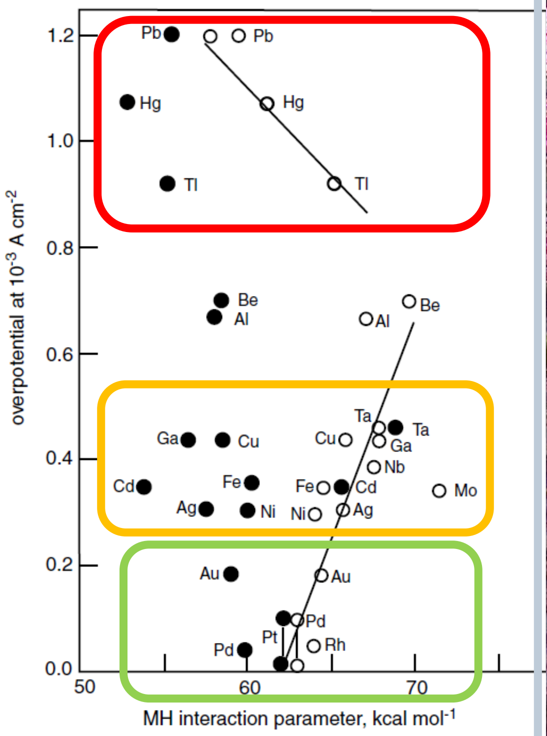
Islands of Promoter Impurities Enhance Loading

Overpotential Equivalent HER	Red (High) - P Yellow(Mediu Green(Low) - P



Plot of hydrogen overpotential at 10
as function of metal-H interaction energy

J_{oi} ~ 5 x 10^{-9} A/cm^2 for Pb
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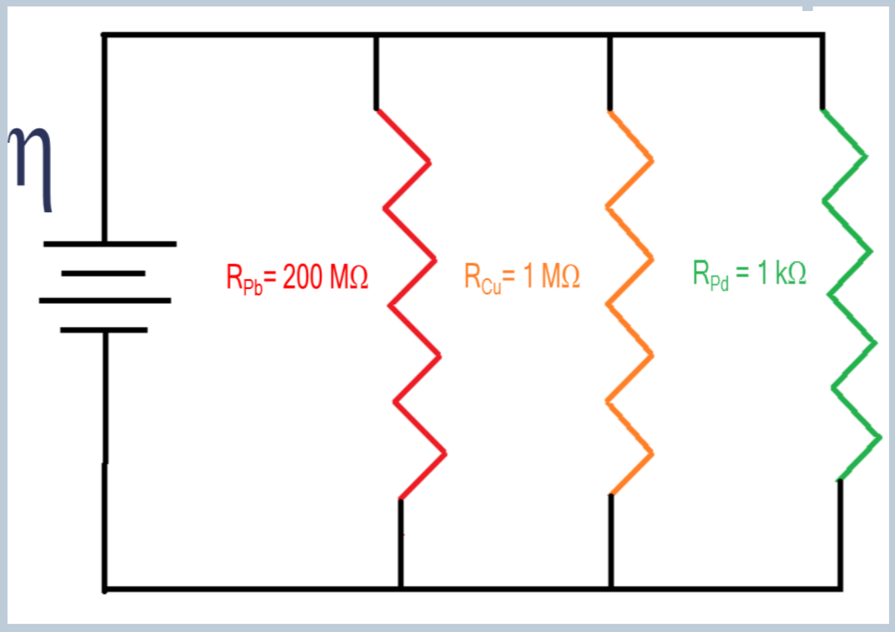
Electric Circuit Analogy



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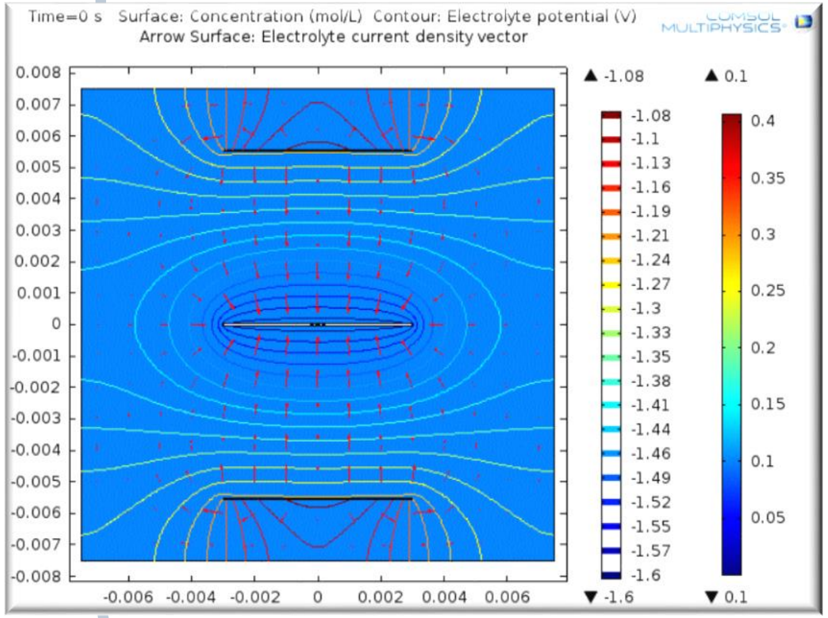
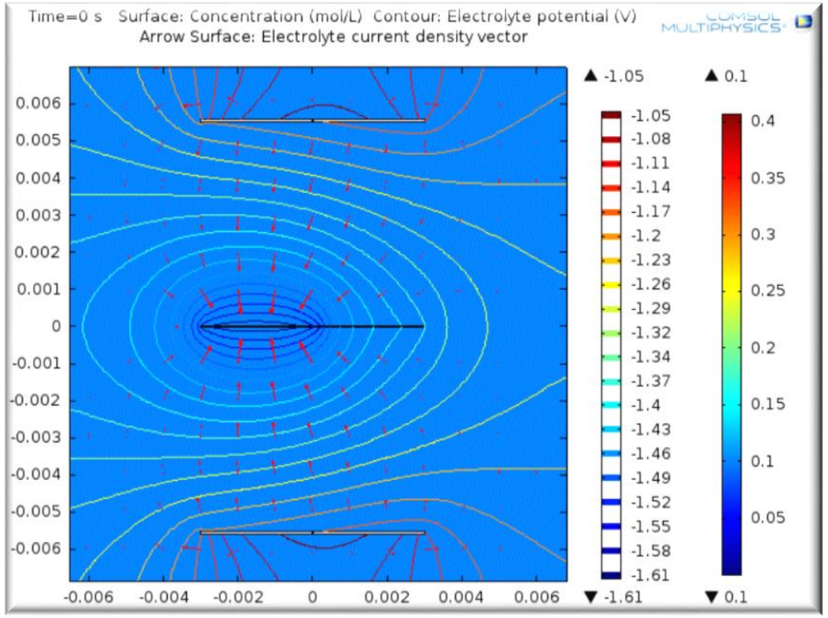
Electrofocusing increasing the local OD^- concentration

ii. What we are calling surface promoters would normally be thought of as poisons; however, in our voltaic cells the limiting current occurs when the local concentration of OD^- at the anode goes to zero. Therefore, it is possible to focus nearly all of the charge transfer/current on exposed palladium islands.

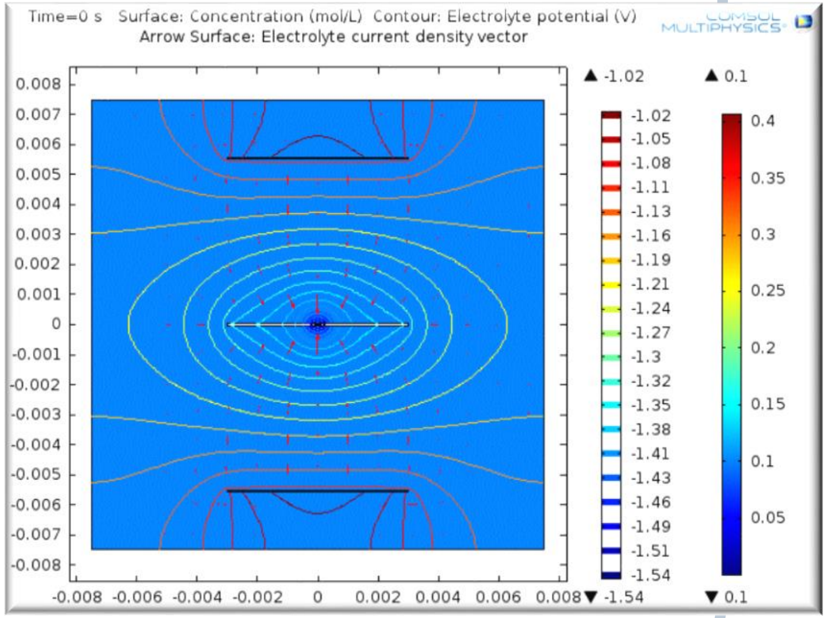
All Pd Cathode



Half Pd/Half Cu Cathode



Five 50μm patches of Pd on Cu Cathode



The red arrows show both the magnitude and direction for the current distribution. The electrolyte potential is shown by the contour lines (-1.6 to -1.08 V). The OH^- concentration is given by the fill color (dark blue is zero and red represents 400 mM).

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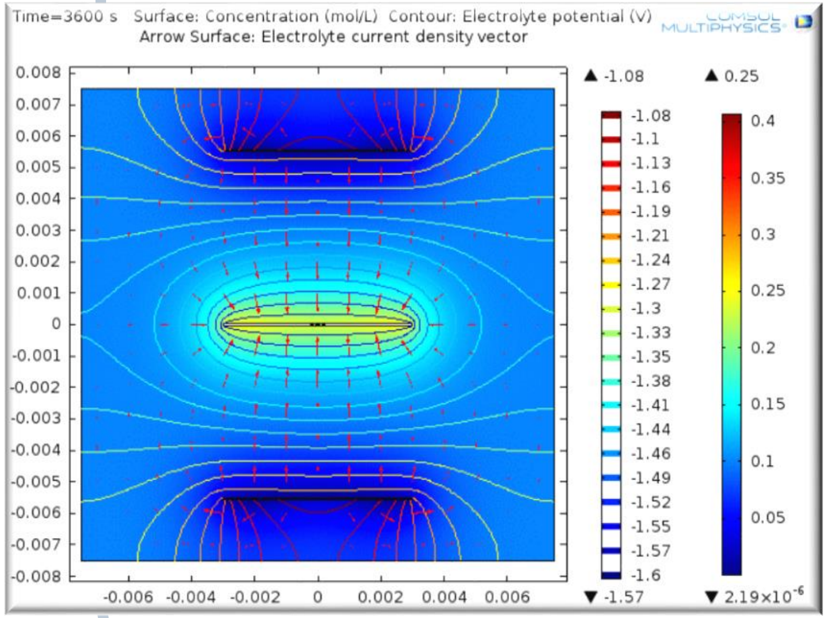
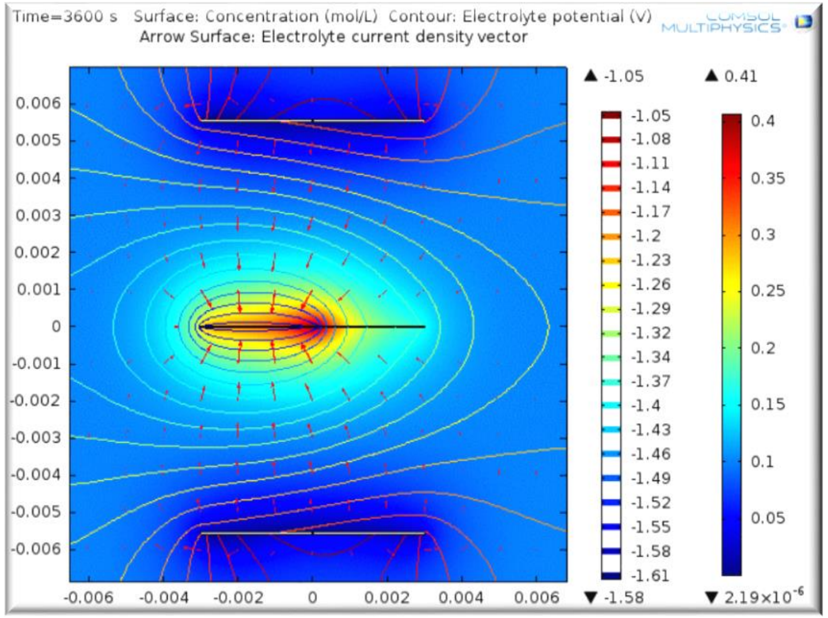
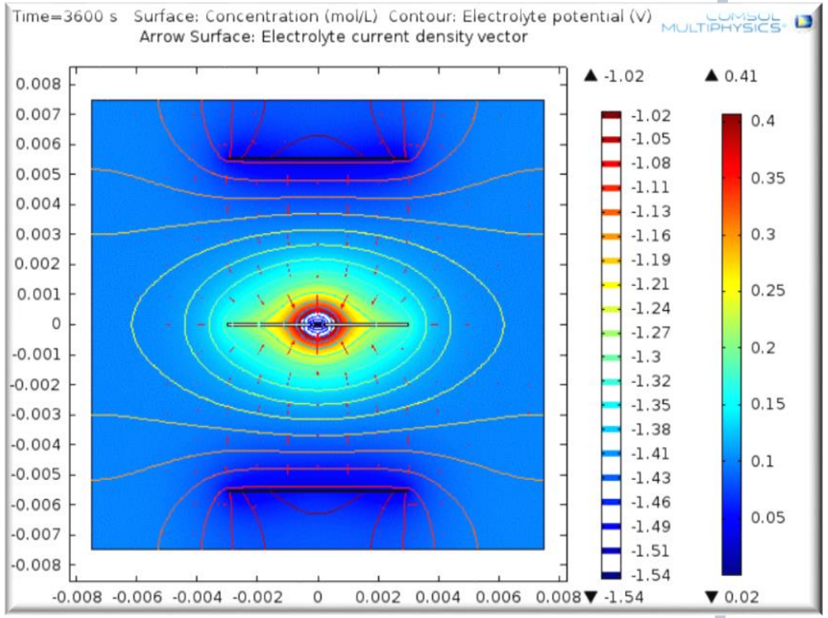


Half Pd/Half Cu Cathode



Five 50μm patches of Pd on Cu Cathode



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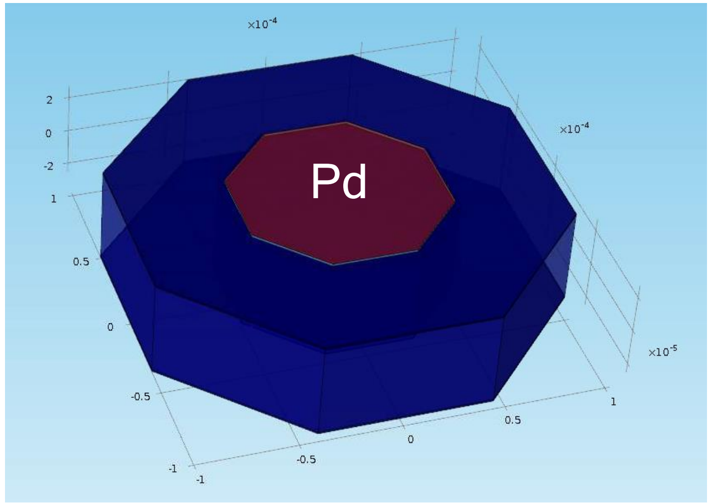
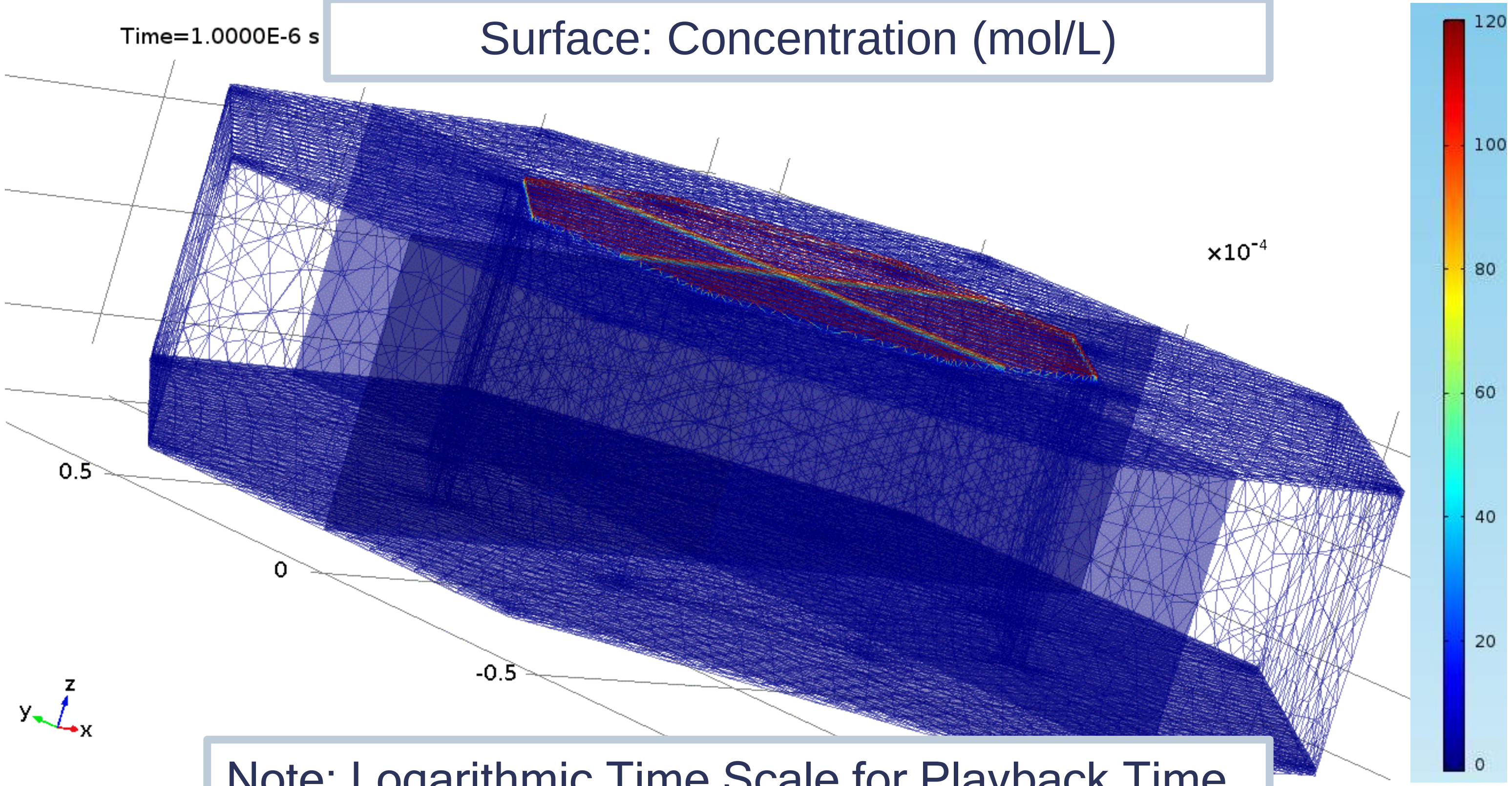
Deuterium enters bulk through Pd Islands

III. The diffusion coefficient for palladium is large enough that only a small fraction of the cathode need be open to achieve high bulk loading.

IV. Select promoter impurities can function as both spillover and reverse spillover catalysts. We believe this explains the extraordinary flux seen with Cu islands and reduced flux on Pb doped cathodes. (S. Hamm and O. Dmitriyeva posters)



200 μm Grain with 50 μm Pd island
with the D concentration set to 100 mol/L



Note: Logarithmic Time Scale for Playback Time

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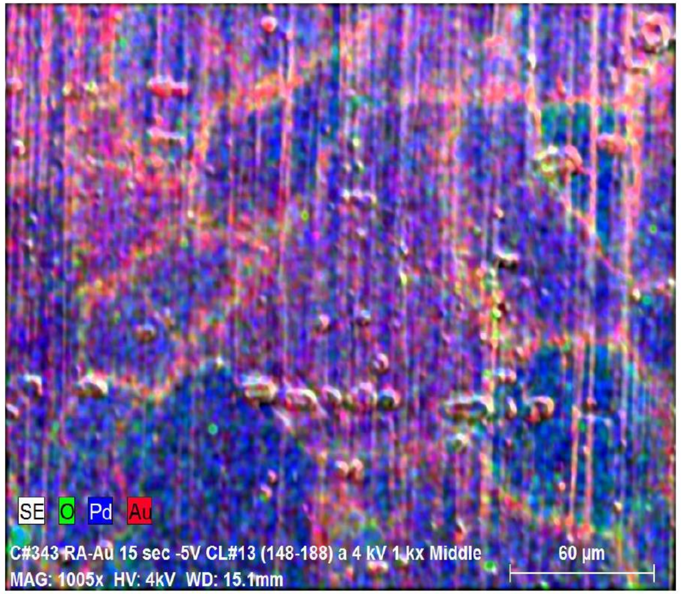
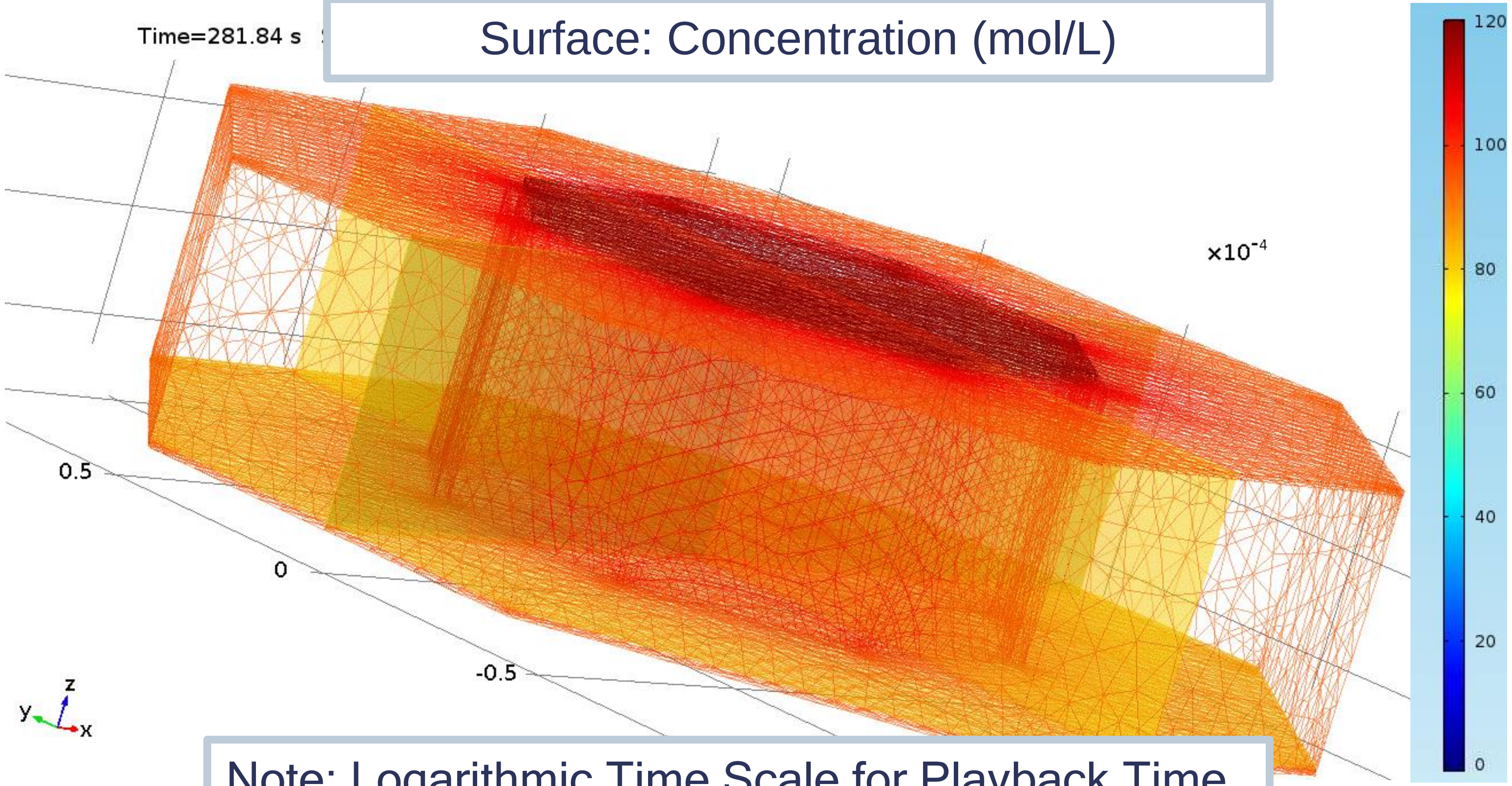


60 μm Au Islands on Pd foil. (Pink regions are Au rich and blue region are Pd rich)

Surface: Concentration (mol/L)



Note: Logarithmic Time Scale for Playback Time

Summary

I. A methodology to control the crystallographic texture and grain size of palladium foils was demonstrated

II. Select surface promoters[1] near a monolayer in thickness are first order factors controlling loading

∴Nanomolar intentional or accidental additions must be controlled!

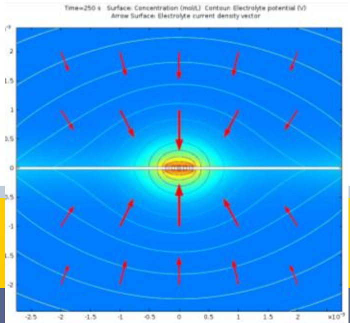
III. Loading appears to be nearly independent of metallurgical treatment
   a) Grain size, grain boundary grooving, annealing time and temperature, cracks formed along the {111} slip planes in the 〈011〉 slip directions, loading protocols (constant current, voltage control, and rate of change of either) are all second order effects at best
   b) As-rolled (non-annealed) foils perform similarly to annealed foils from a loading standpoint.

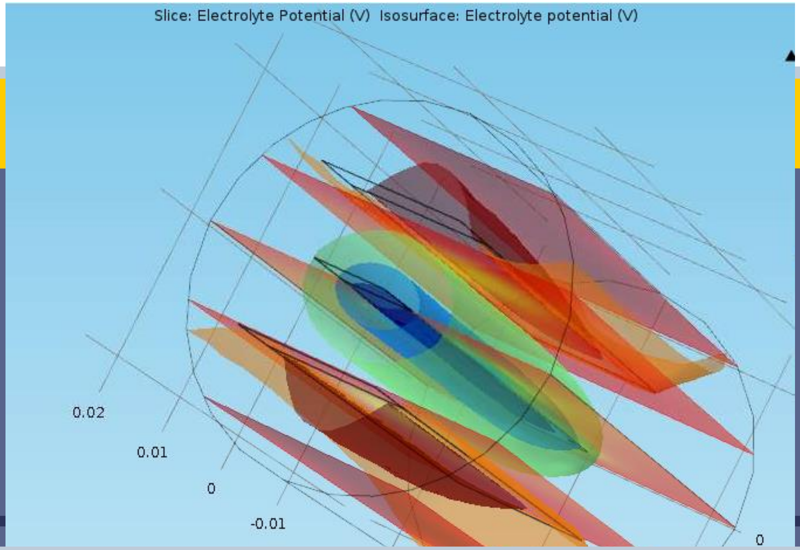
(See S. Hamm and O. Dmitriyeva presentations for more details on this topic)

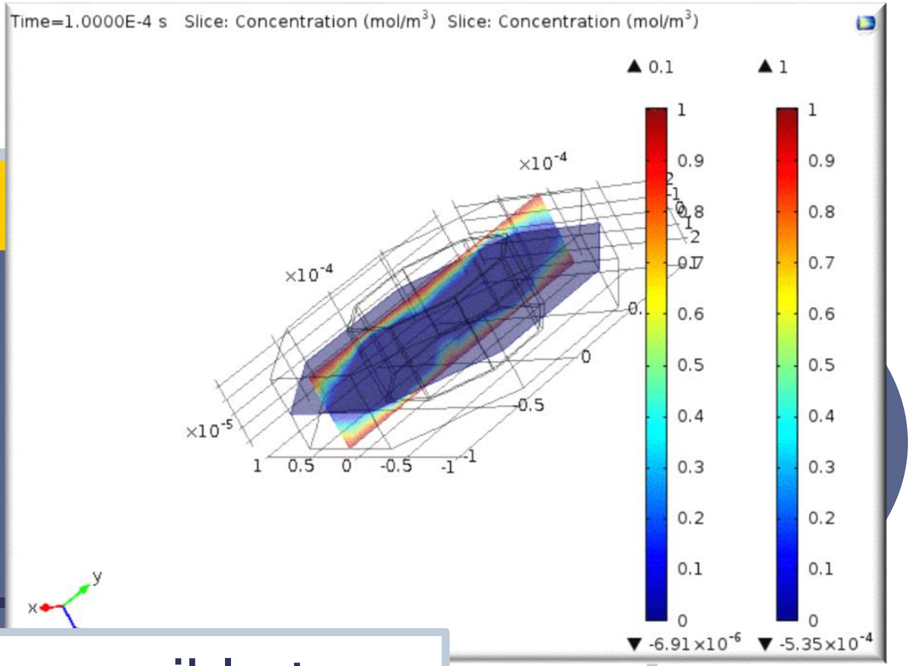
IV. This finding does not rule out the potential importance of grain size, crystallographic texture, and grain boundary type to the production of excess heat from the deuterium-palladium system.

[1] McKubre, M.C.H., et al. *New Hydrogen Energy Research at SRI*. in *ICCF6, Progress in New Hydrogen Energy*. 1996. Lake Toya, Hokkaido, Japan: New Energy and Industrial Technology Development Organization, Tokyo Institute of Technology, Tokyo, Japan.

Questions







The real question at hand is whether it is even possible to load pure Pd in pure 100 mM LiOD electrolyte beyond the equilibrium pressure value of ~ 0.75 D/Pd?