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Customer Success Is Our Mission

New Perspectives on Tin Whiskers based on Atomistic Modeling

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15 September 2011

1-Raytheon Missile Systems

Agenda

- Effect of Oxygen on whisker surface
- Need for Compressive stress
- Inter-granular transport of Sn
- Inhibition mechanism of Pb
- Promotion mechanism by Zn, Cu and Mn
- Summary and conclusions

Engineering use of models

	INPUT	MACHINERY	OUTPUT
Structural and electromagnetic modeling Material properties	Finite element mesh Mechanical and electromagnetic properties External mechanical strain and EM fields	Classical mechanics and electrodynamics	Prediction of mechanical and electromagnetic response
Database			
Fluid modeling Material properties	Finite element mesh Fluid properties Flow conditions	Navier-Stokes equations	Prediction of flow behavior
Atomistic modeling Fundamental physical constants	Chemical elements and initial atom positions Temperature, stress, electromagnetic field	Schrödinger's equation and statistical thermodynamics	Prediction of materials properties

Atomistic modeling provides inputs for FEA ad CFD

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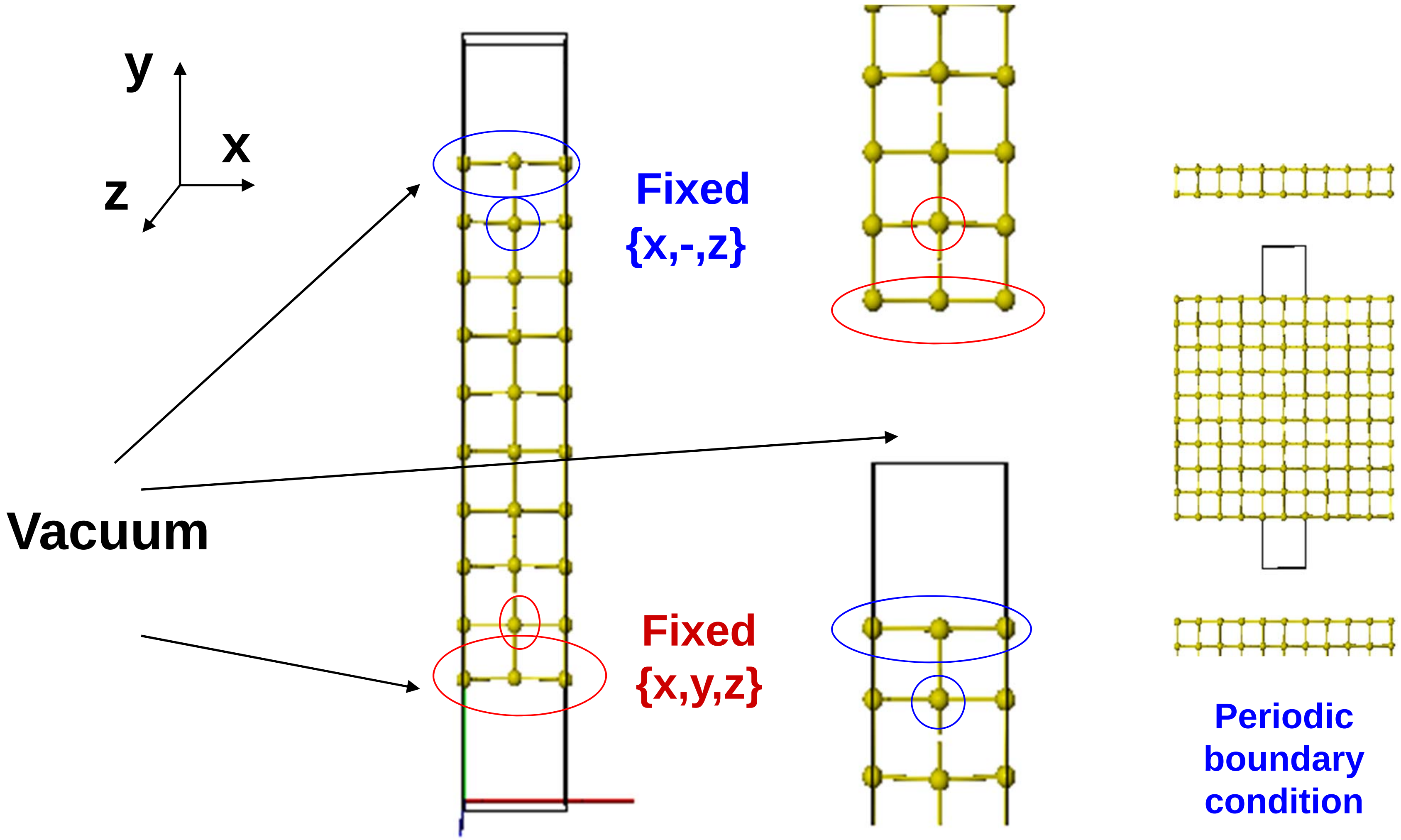
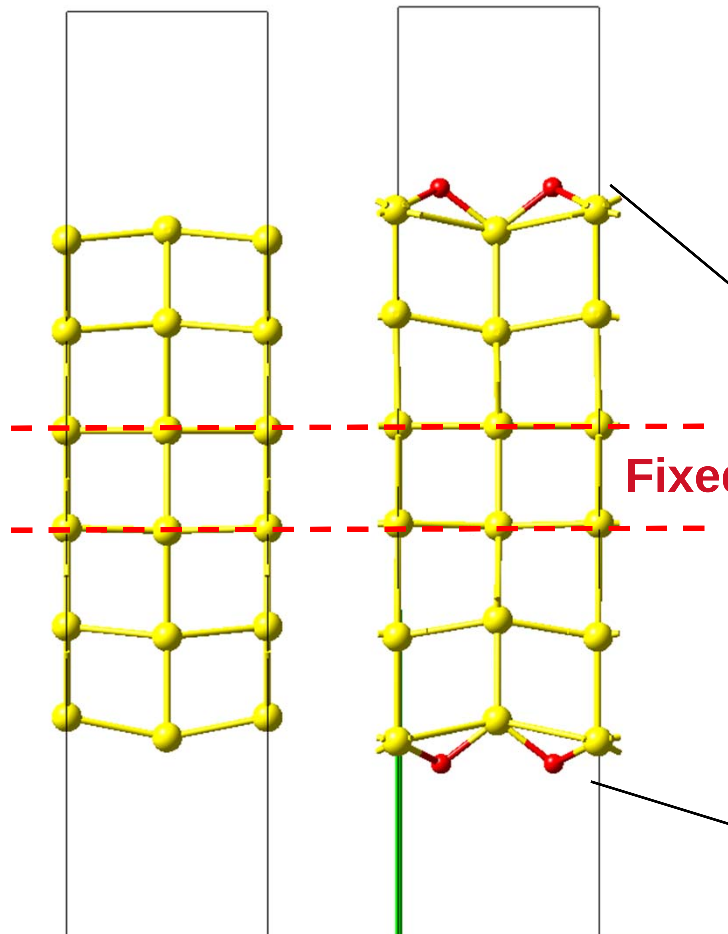
The (1 0 0) model

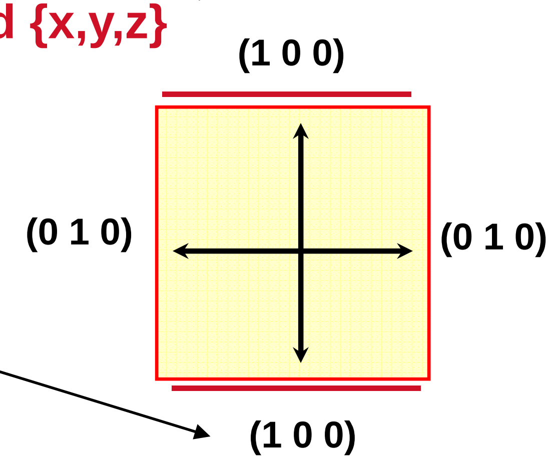


Surface oxygen puts whisker in tension

β-Sn (1 0 0)
$\sigma_a = \sigma_b = -0.16$ (GPa)
$I_1 = 0.11$ (GPa)
$\varepsilon_V = 0.0025$
ε_v = volume strain

β-Sn (1 0 0) + 2 O_2
$\sigma_a = \sigma_b = -2$ (GPa)
$I_1 = -2.51$ (GPa)
$\varepsilon_V = -0.057$





Choi reported compressive stress at whisker base *relative to Whisker*

Choi et al, Structure and kinetics of Sn Whisker growth on Pb Solder finish, (2002) IEEE, 628-633

Oxide induces ~ 5% volume strain
Can't stop the driving force! Must control Sn flow to whisker base

I_1,The first invariant

```
Pressure:    839.000 MPa
           =   8.390 kbar

  Stress:    -1.570    -0.004    -0.941    -0.016    -0.003    -0.003 GPa
           = -15.700   -0.040    -9.410    -0.160    -0.030    -0.030 kbar
The pressure and stress include only electronic terms, i.e. the vibrational,
temperature and other terms are not included here.
```

Sn_{12} O_4 (1 0 0)

$$\varepsilon_V = \frac{I_1}{K}$$

$$\begin{bmatrix} -1.570 & 0 & 0 \\ 0 & -0.004 & 0 \\ 0 & 0 & -0.941 \end{bmatrix}$$

	K	*E*	*G*	
	Bulk (GPa)	Young's (GPa)	Shear (GPa)	
MedeA	14	20	25	(1 0 0)
MedeA	50	55	21	β Sn
Literature	**53**	**53**	**19**	β Sn

$$I_1 = a_{11} + a_{22} + a_{33}$$

$$I_1 = -1.570 + -0.004 + -0.941 = -2.515$$

System	I_1 (GPa)
Sn_{12} (1 0 0)	-0.11
Sn_{12} O_4 (1 0 0)	-2.52

The first invariant, I_1,of the stress tensor describes expansion & contraction under hydrostatic loads

Whisker growth is marginal for stress relaxation compared to *plastic creep*

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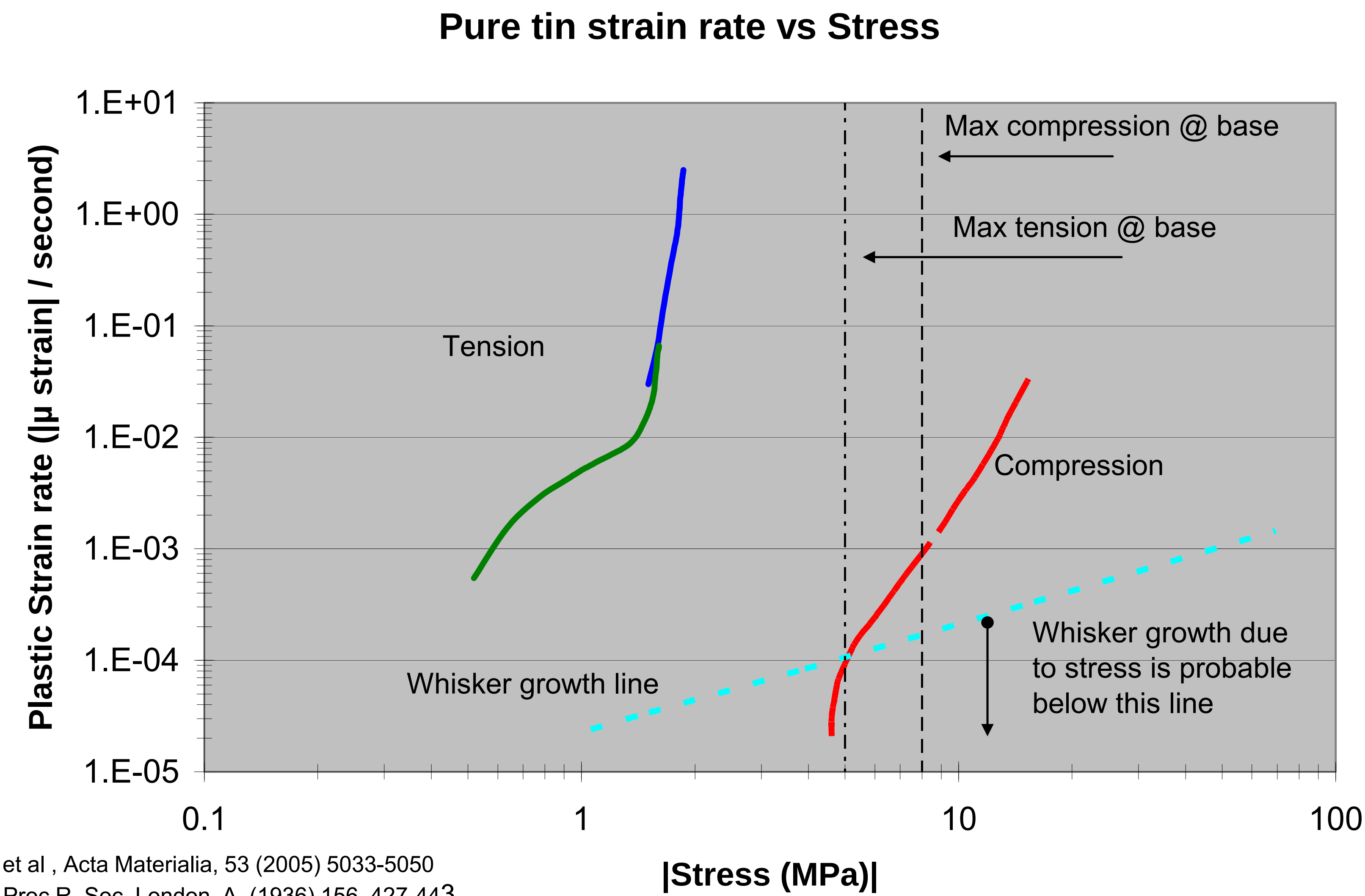

Boettinger et al , Acta Materialia, 53 (2005) 5033-5050
Chalmers, Proc R. Soc. London, A, (1936) 156, 427-443

Plastic creep often occurs faster than whisker growth

The compressive stress paradox

- Local topographic features at whisker base generally do not change as the whisker grows
  – Suggests local compressive stress are not relieved by transferring local material into whisker.
- Hillocks form quickly, sufficient to reduce compressive stress
  – Boettinger, et al 2005
- Material in whiskers comes from the entire volume of tin
  – isotope studies by Woodrow 2006, 2009
- Creep rate of pure Tin is rapid with respect to whisker growth
  – Boettinger, et al 2005, Chalmers 1936, 1937
- Micro beam x-ray data showing compressive stress is relative to stress state of whisker.
  – Choi et al 2002
- Manganese alloys grow whiskers while in tension & continue to grow with out intergranular contact
  – Chen et al 2005

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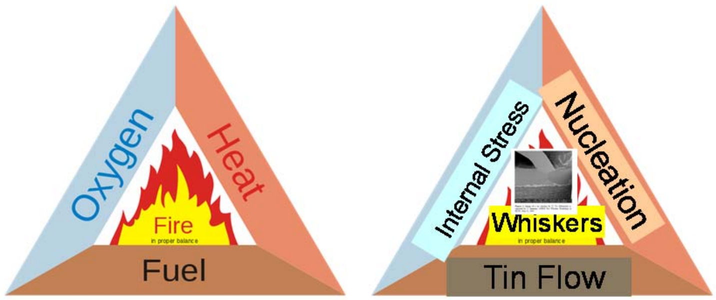
Diffusion

- Woodrow showed us:
  - Tin transport between grains is fast
  - Whisker contains tin from a very large volume of basal tin
  - 2% (m/m) Pb does not seem to inhibit diffusion
- To get insight into Pb inhibition mechanism
  - Model diffusion of Sn on Sn and Pb surfaces
  - Model stability of Sn at & near Pb surface
  - Model stability of Pb at & near Sn surface
  - Model lone Sn atom at boundary between Pb & Sn surfaces

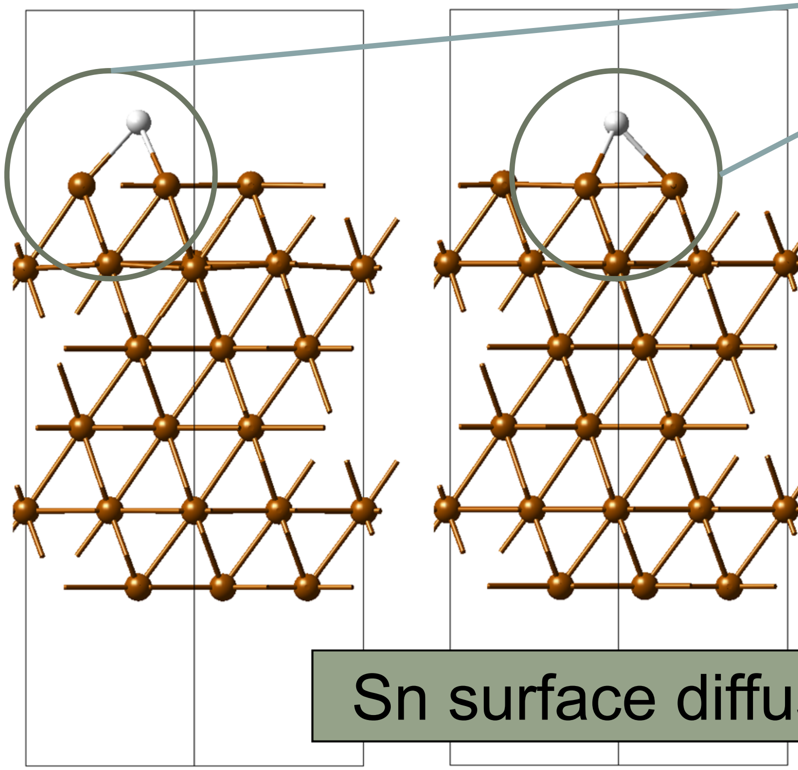
- These results lead to other models…… be patient….

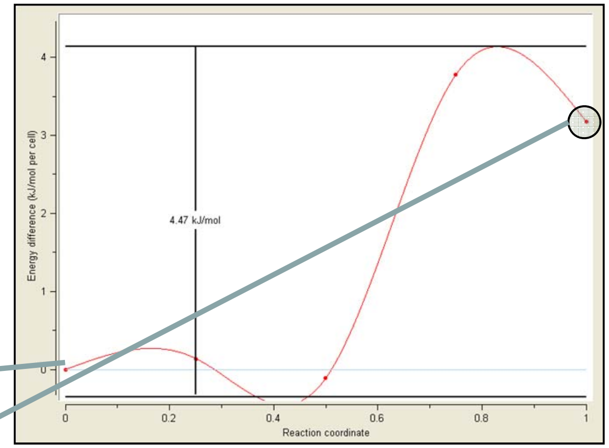


Sn diffusion on Pb (111)

The diffusion profile not symmetrical because each minimum has a different coordination beneath the surface

ABC ABA





Sn diffusion on surfaces

- Sn on Sn (1 0 0) || to c-axis = 5 ($kJmole^{-1}$)
- Sn on Sn (1 0 0) $\perp$ to c-axis = 29 ($kJmole^{-1}$)
- Sn on Pb (1 0 0) = 4.5 ($kJmole^{-1}$)
- Pb on Pb (1 1 1) = 4.5 ($kJmole^{-1}$)
- 2 Sn on Sn (100) =141 ($kJmole^{-1}$) Concerted motion

Sn surface diffusion Similar on Pb and Sn

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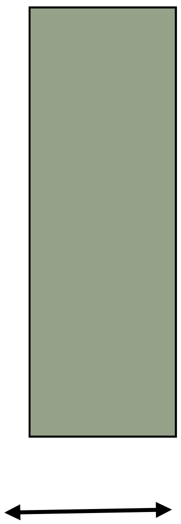
A really interesting result

Sn is more mobile along the whisker than across it



|| C-axis
E_a = 5 (kJ mol^{-1})

⊥ C-axis
E_a = 29 (kJ mol^{-1})

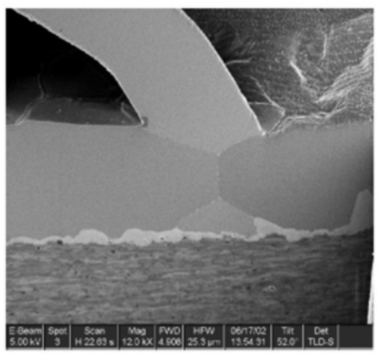
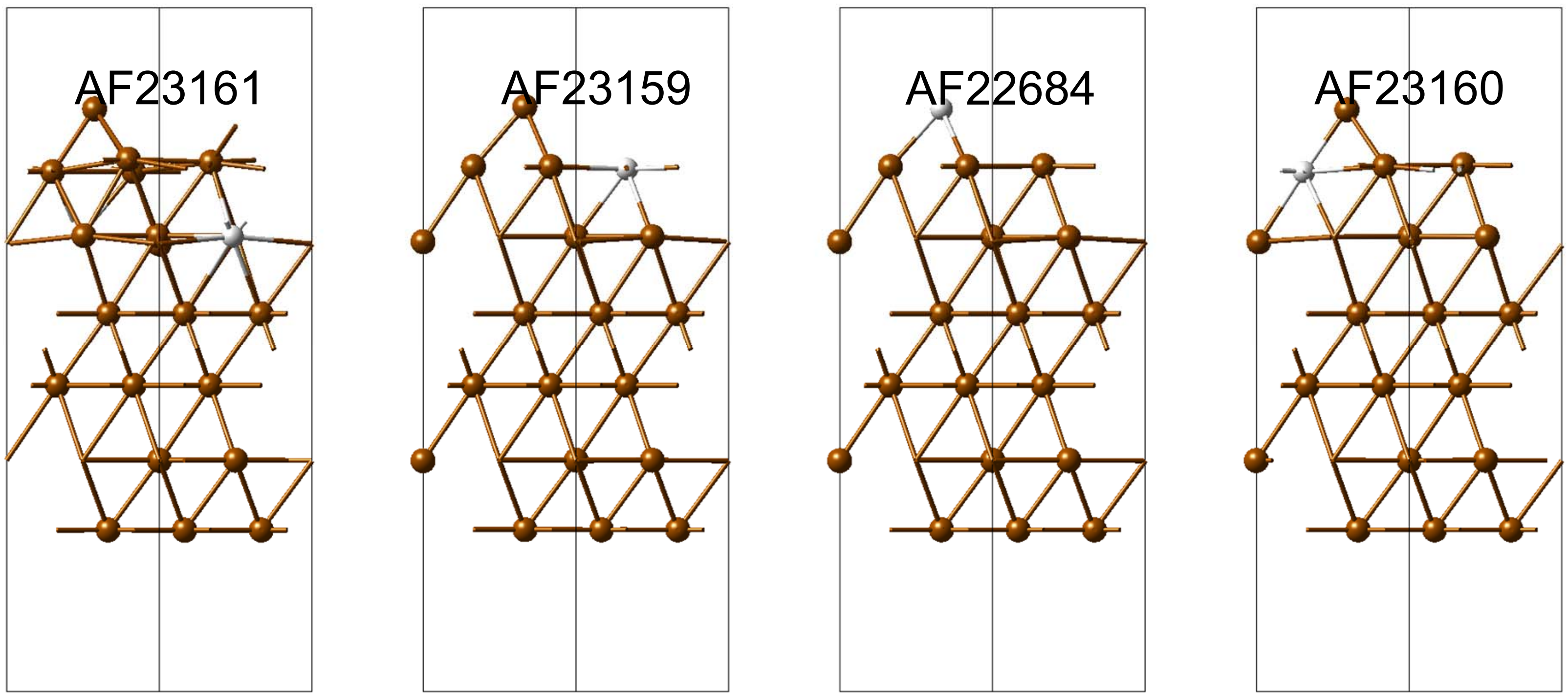


Figure 4. Image of a tin whisker by N. Vo (Motorola) as reported by J. Smetana, iNEMI Tin Whisker Workshop at ECTC, May 31, 2005

Sn diffusion on *surfaces*
- Sn on Sn (1 0 0) || to c-axis = 5 (kJmole^{-1})
- Sn on Sn (1 0 0) ⊥ to c-axis = 29 (kJmole^{-1})
- Sn on Pb (1 0 0) = 4.5 (kJmole^{-1})
- Pb on Pb (1 1 1) = 4.5 (kJmole^{-1})
- 2 Sn on Sn (100) =141 (kJmole^{-1}) Concerted motion

At 25 (°C):
159 Sn atoms out of every 160 Sn atoms move along the axis of the whisker.

Sn stability on Pb



ΔE 5 kJ/mol

ΔE -3 kJ/mol

ΔE 0 kJ/mol

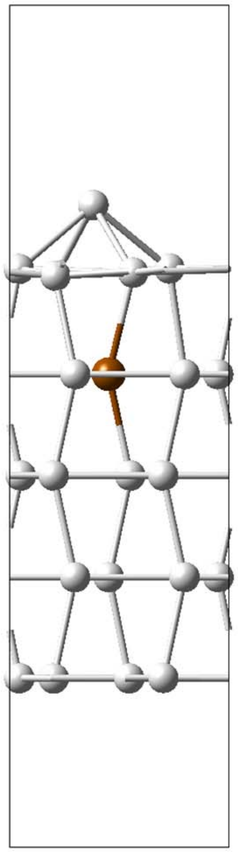
ΔE -10 kJ/mol

Sn is stable at Pb surface and in Pb

Pb stability on Sn

Freeman, Materials Design

AF23175



ΔE 25 kJ/mol

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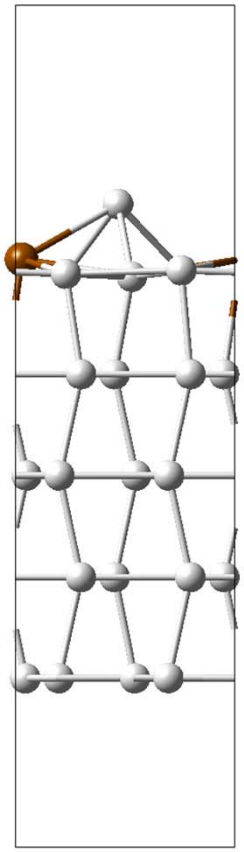

ΔE 2 kJ/mol

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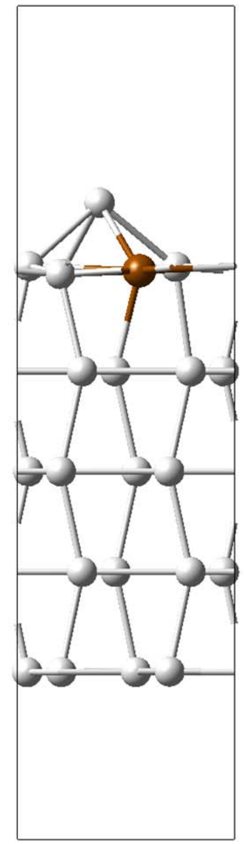

ΔE 25 kJ/mol

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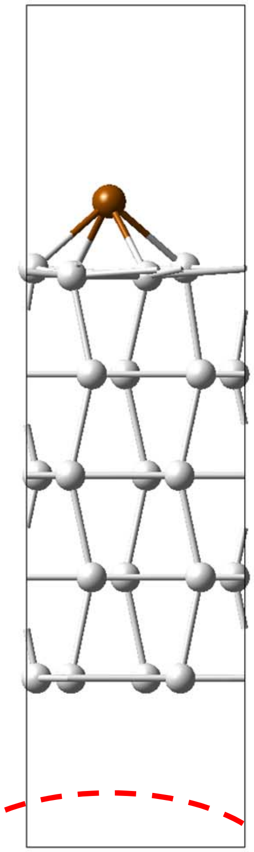
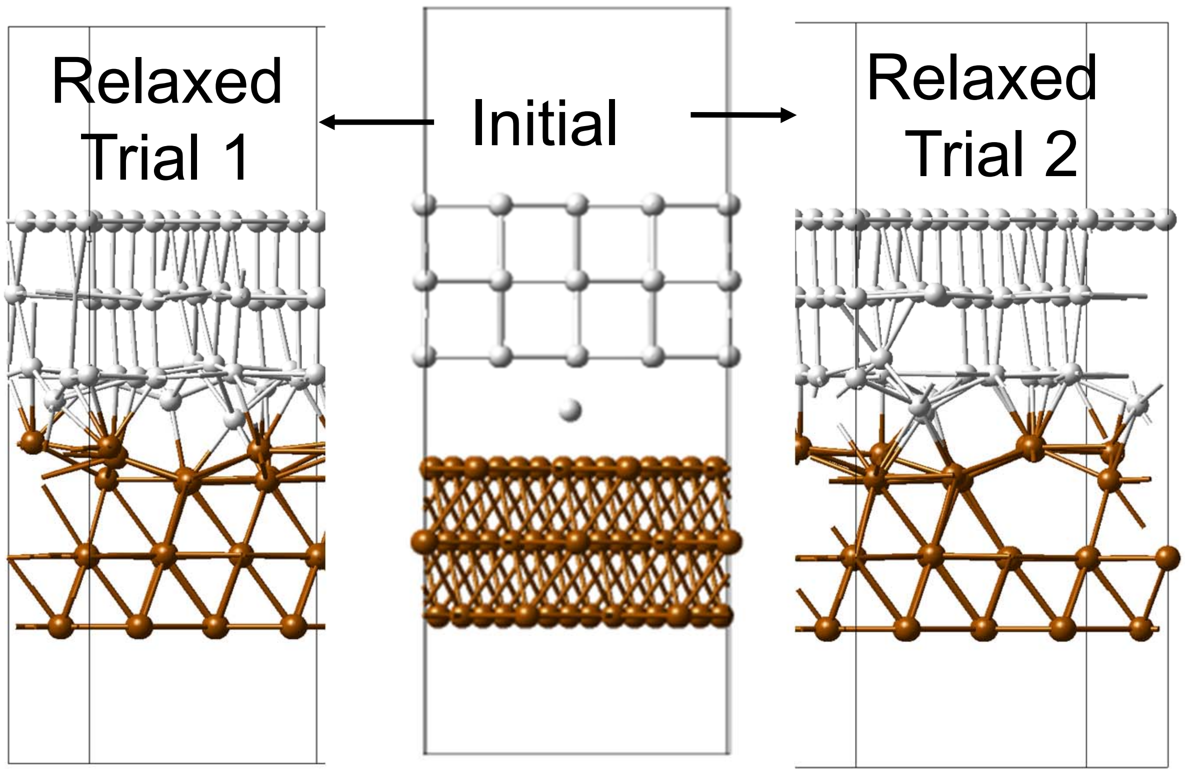


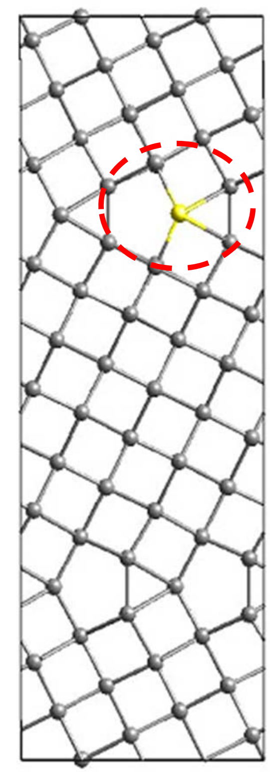
ΔE 0 kJ/mol

Pb is stable at Sn surface but not in Sn

Initial Grain Boundary Model Calculations



Sn in Sn-Pb (1 0 0)

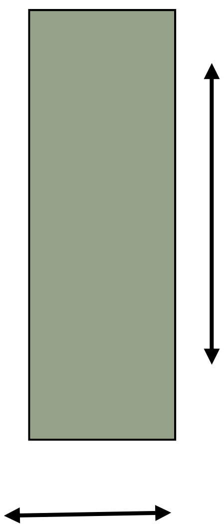


Pb in Sn-Sn (2 1 0)

Sn-Pb grain boundary collapses
Glues surfaces & Traps Sn

Do we really know the driving force?

- At 25 (°C):
- **13%** of Sn atoms, have energy to move **along** Whisker length
- **0.0008%** of Sn atoms have energy to move **across** whisker base
- Motion ∥ c-axis is 160 times more probable than motion ⊥ c-axis



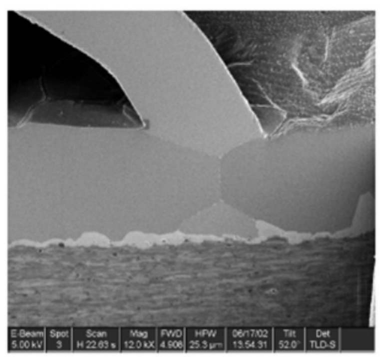


Figure 4. Image of a tin whisker by N. Vo (Motorola) as reported by J. Smetana, iNEMI Tin Whisker Workshop at ECTC, May 31, 2005

- Most theories invoke compressive stress near base as driving force
  - Choi measured compressive stress
    - *relative to whisker as neutral*
    - *Initial results showed no compressive* stress at whisker base using published cell constants
    - Publishes stress map shows compressive stress > 400 (psi) at base of whisker
  - Chalmers reports compressive relaxation of single crystal tin (1935)
    - Yield limit near 100 to 200 (psi)
    - Creep is irreversible
    - Occurs in hours
    - *Uses Hg diffusion along grain boundaries to separate crystals within minutes*
- RMS work shows Oxygen on (100), (010) and (001) surfaces puts Sn in tension, with ~ 5% volume strain!

Anisotropic self diffusion promotes whiskers

Ready?
The next step is a BIG one!

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And now for something completely different….

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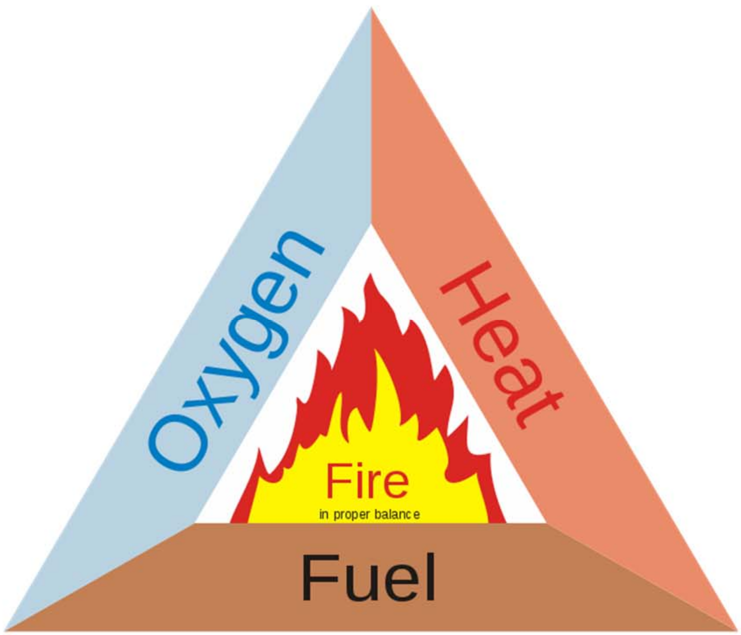
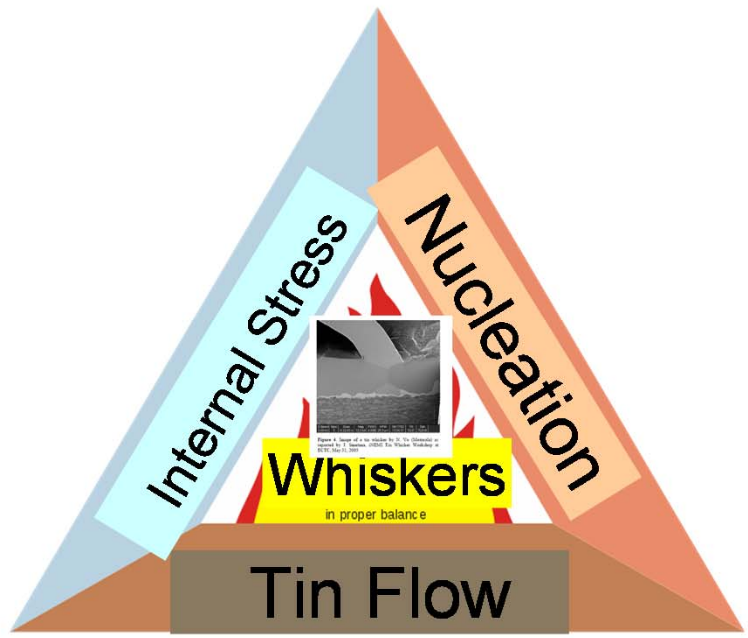
- Sn Diffusion between adjacent Pb and Sn grains must be slower than between adjacent Sn grains
  – QUESTION: How much Pb is needed to ‘stop’ transport?

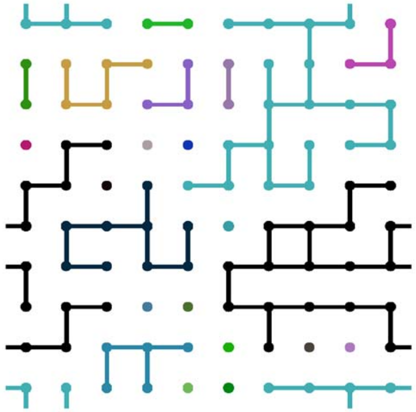




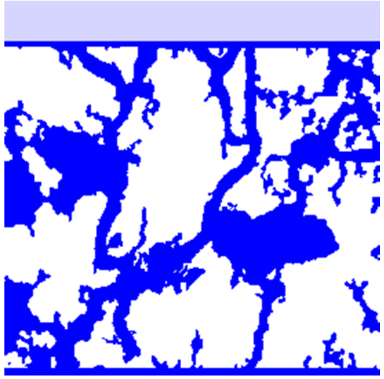
Percolation

It's not just for coffee anymore!

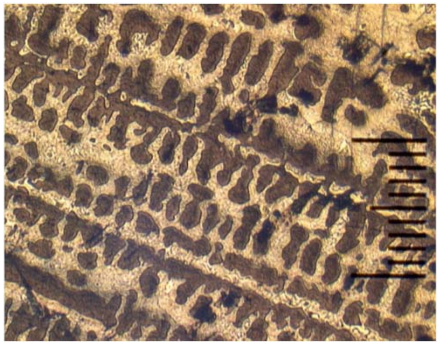
- Percolation describes connectivity between adjacent sites
  - Describes:
    - Electrical conductivity of particles (e.g. filled polymers)
    - Modulus & strength of polymers
    - ***Diffusion*** & permeation
  - P_C: the critical point for properties
    - Electrical continuity
    - Gel point for polymers
    - ***Diffusion allowed / inhibited***
  - ***P_C***
    - ***~ 0.5 for 2D square array***
    - ***~ 0.25 for 3D cubic array***
    - ***But, Pb inhibits at 5% < Pb < 10% (m/m)…….. Hmm….***



Adjacent sites may, or may not be connected



An *infinite network* spans the sample at $P = P_C$



A Sn Pb (dark) alloy

Sn diffuses between Sn grains. . .
Does Pb create a percolation network?

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Why does 3% (m/m) Pb not inhibit whiskers?

Inverse Swiss Cheese Model
P_C~ 3.5% (v/v)
creates infinite network

3%(m/m) Pb is ~ 1% (v/v)
Only delays whiskers
& makes them smaller

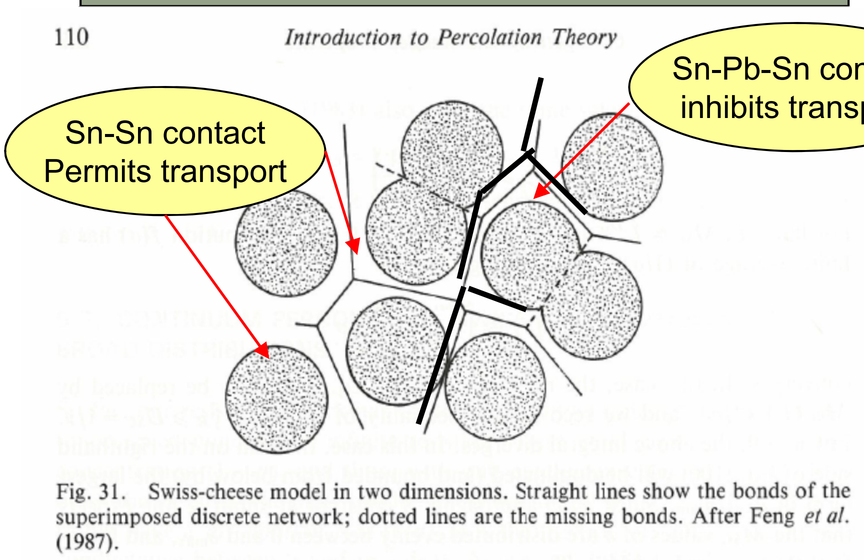
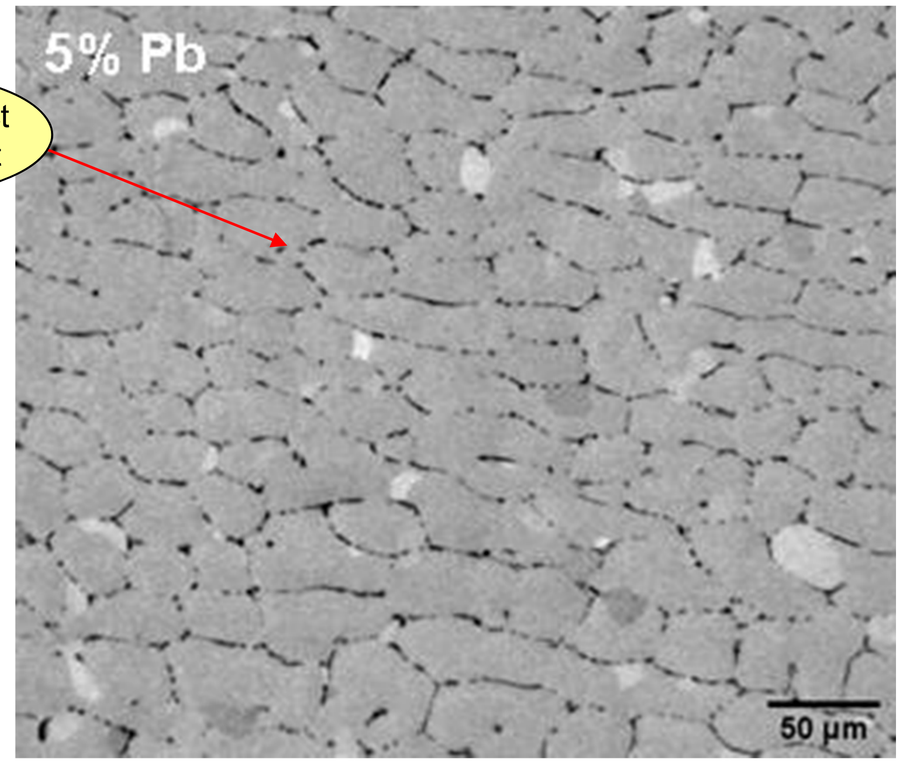

110 *Introduction to Percolation Theory*

Fig. 31. Swiss-cheese model in two dimensions. Straight lines show the bonds of the superimposed discrete network; dotted lines are the missing bonds. After Feng *et al.* (1987).



3.5 %(v/v) Pb is about 6.5%(m/m) Pb, including solubility

Percolation theory
Scaling & experimental validation

- Scaling of percolation controlled observable
  - Electrical conductivity
  - Modulus
  - Isotope transport
  - Inverse Swiss cheese model
    - Electrical conductance scales as **$(P-P_c)^{1.3}$** and **$(P-P_c)^{1.9}$** in 2D and 3D.
    - Modulus & mass transport scales as **$(P-P_c)^{1.3}$** and **$(P-P_c)^{1.4}$** in 2D and 3D.
- Experimental
  - Look for change in whisker induction stress
  - Isotope study of Sn transport using SIMS (Woodrow, Boeing)

TABLE I. Estimates of the differences between the transport percolation exponents in the continuum models ($\tilde{t}$, $\tilde{f}$, and $\tilde{e}$) and the corresponding exponents on a discrete lattice. Nonzero entries in the table correspond to the upper bounds in Eq. (5), and therefore are slight overestimates of the actual values. (a) The Swiss-cheese model; (b) the inverted Swiss-cheese or potential model.

	Conductivity ($\tilde{t}-t$)	Elasticity ($\tilde{f}-f$)	Permeability ($\tilde{e}-t$)
		(a)	
$d=2$	0	$\frac{3}{2}$	$\frac{3}{2}$
$d=3$	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{5}{2}$
		(b)	
$d=2$	0	0	0
$d=3$	0	$\frac{1}{2}$	$\frac{1}{2}$

PHYSICAL REVIEW B VOLUME 35, NUMBER 1 1 JANUARY 1987

Transport properties of continuum systems near the percolation threshold

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(Received 27 May 1986)

Relationship between diffusion and percolation networks established.

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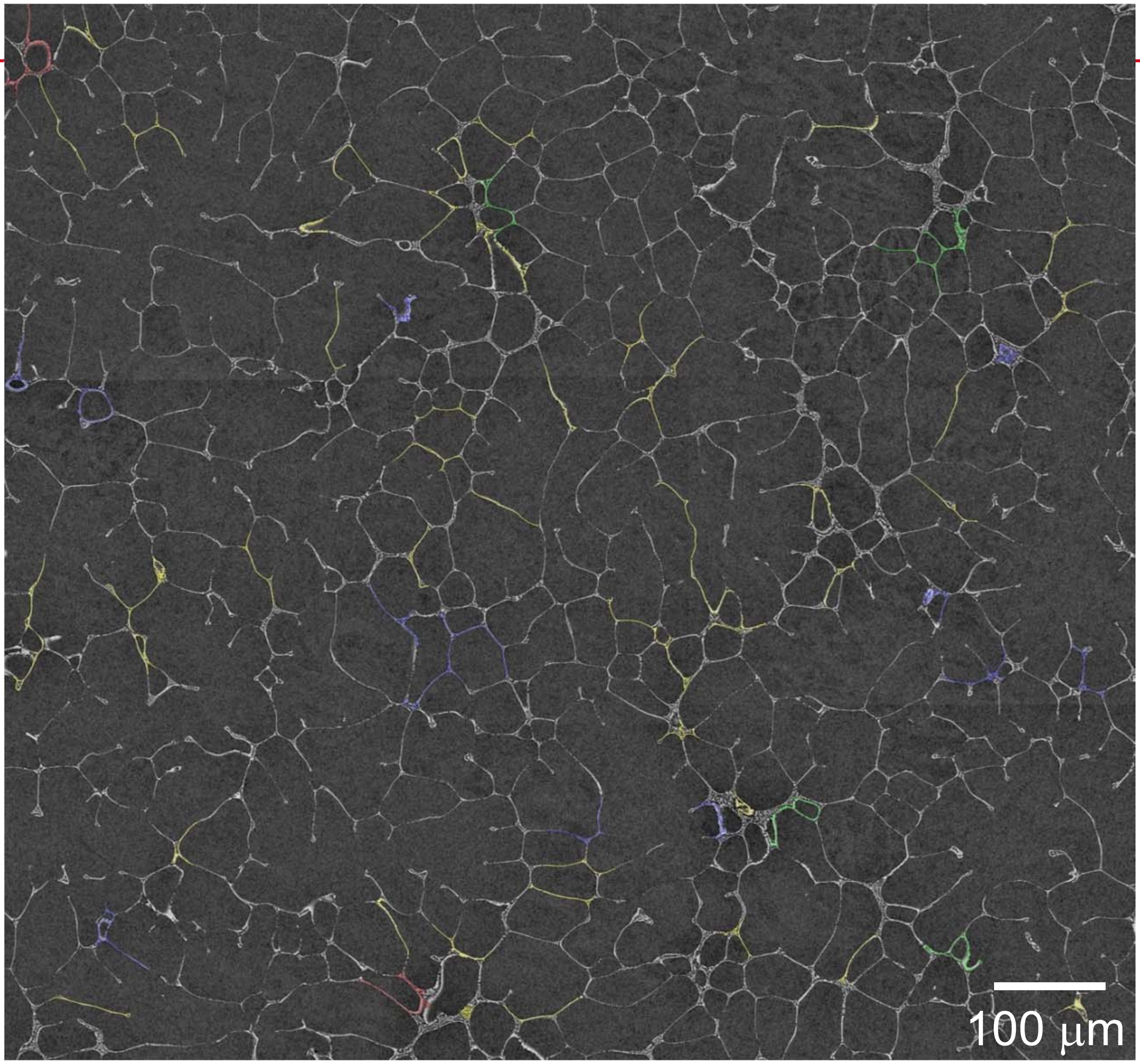
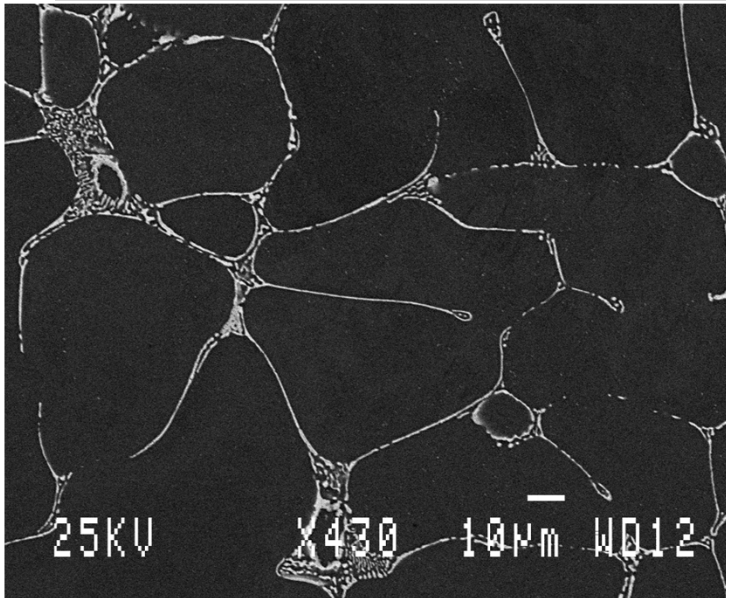
ASU: 5 wt% Pb Anode

Chawla & Williams, ASU



Exsolved Pb Volume Fraction
Phase Diagram: 2.7%
Image Analysis: 3.5%

Pb Cluster Sizes (μm^2)
Mean: 2.5
Yellow: 20 - 30 (50 clusters)
Blue: 30 - 40 (13 clusters)
Green: 40 - 50 (5 clusters)
Red: > 50 (2 clusters)
Largest: 67



Inverse Swiss cheese
Percolation network exists

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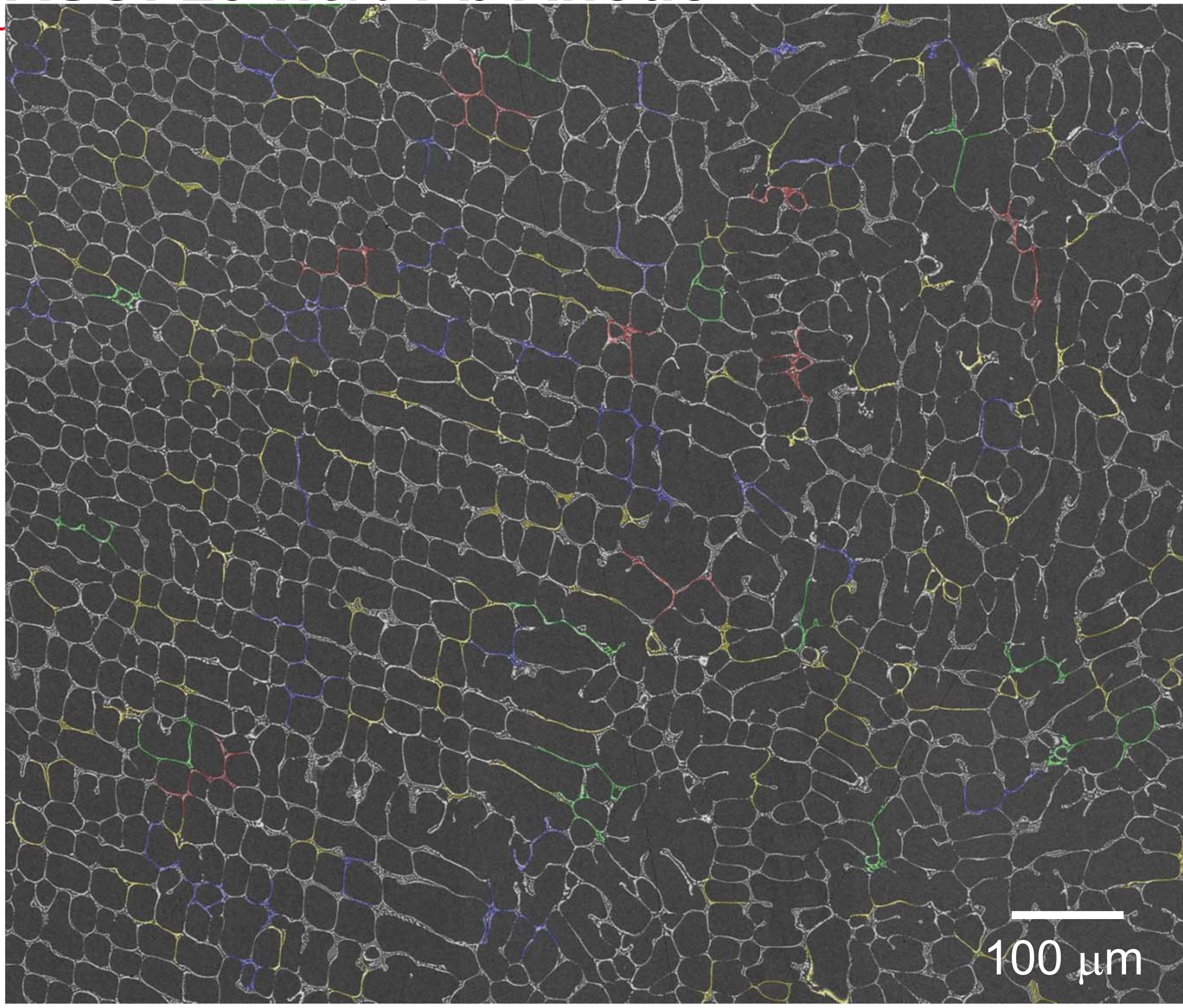
ASU: 10 wt% Pb Anode

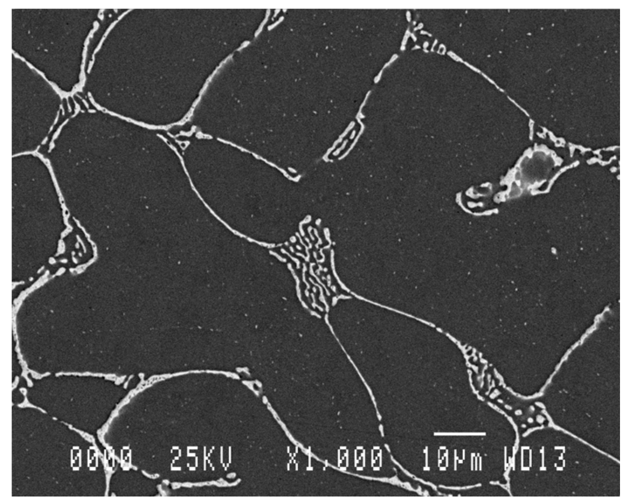
Chawla & Williams, ASU



Exsolved Pb Volume Fraction
Phase Diagram: 6.2%
Image Analysis: 6.7%

Pb Cluster Sizes (μm^2)
Mean: 2.9
Yellow: 20 – 30(101 clusters)
Blue: 30 – 40 (33 clusters)
Green: 40 – 50 (9 clusters)
Red: > 50 (8 clusters)
Largest: 81

Additional Pb improves percolation network



Serial Sectioning Process Flow Chart (ASU)

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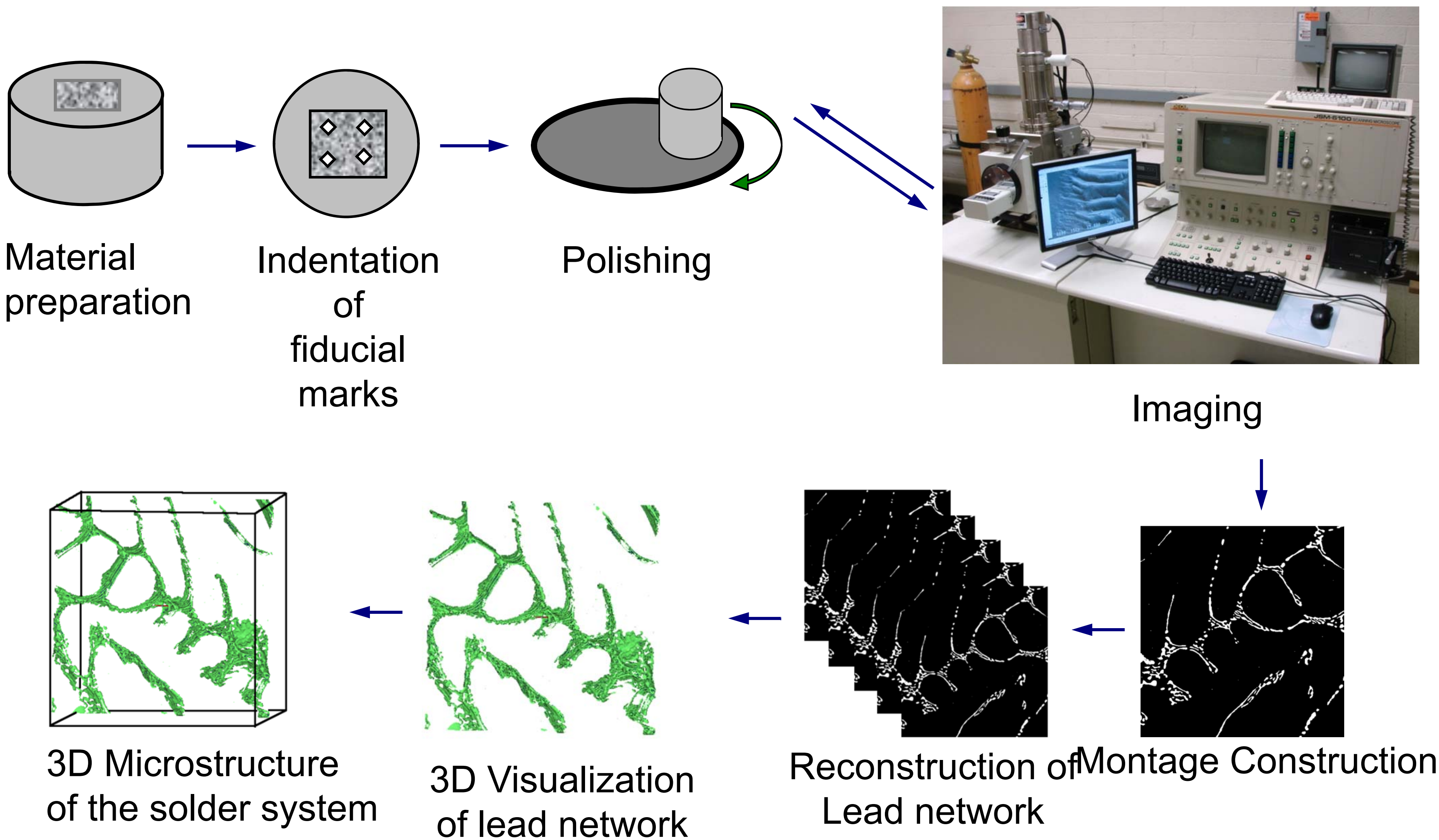
Chawla & Williams, ASU



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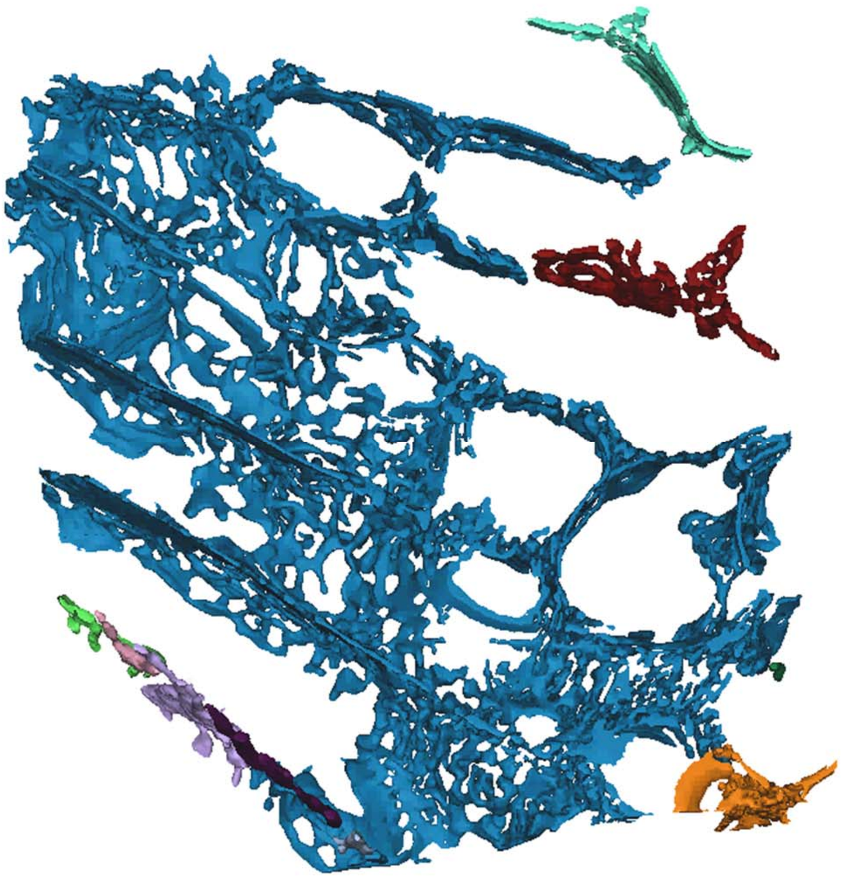
3D images of 10% (m/m0 Pb in Sn (ASU)

Chawla & Williams, ASU



…. percolation network? You bet!

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Method

- Create a model grain boundary
  - Permit motion perpendicular to boundary
  - Pin all motion along boundary
  - Insert other metals, as a second phase, into boundary
    - Find the minimum energy configuration (relax)
  - Insert a lone tin atom into the second phase
    - Find the minimum energy configuration

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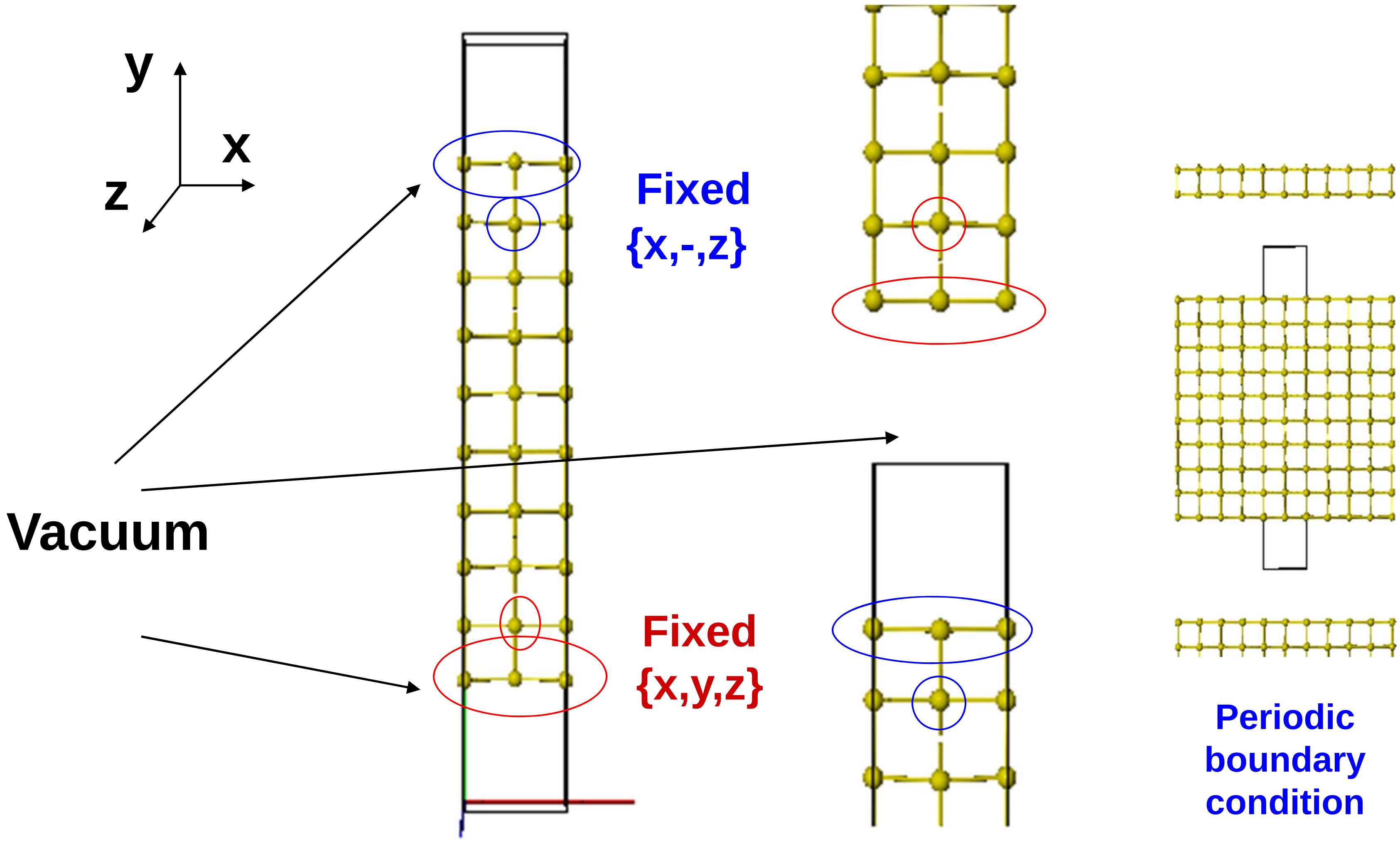
The (1 0 0) model

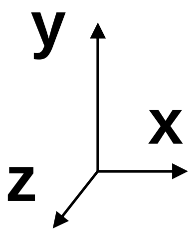


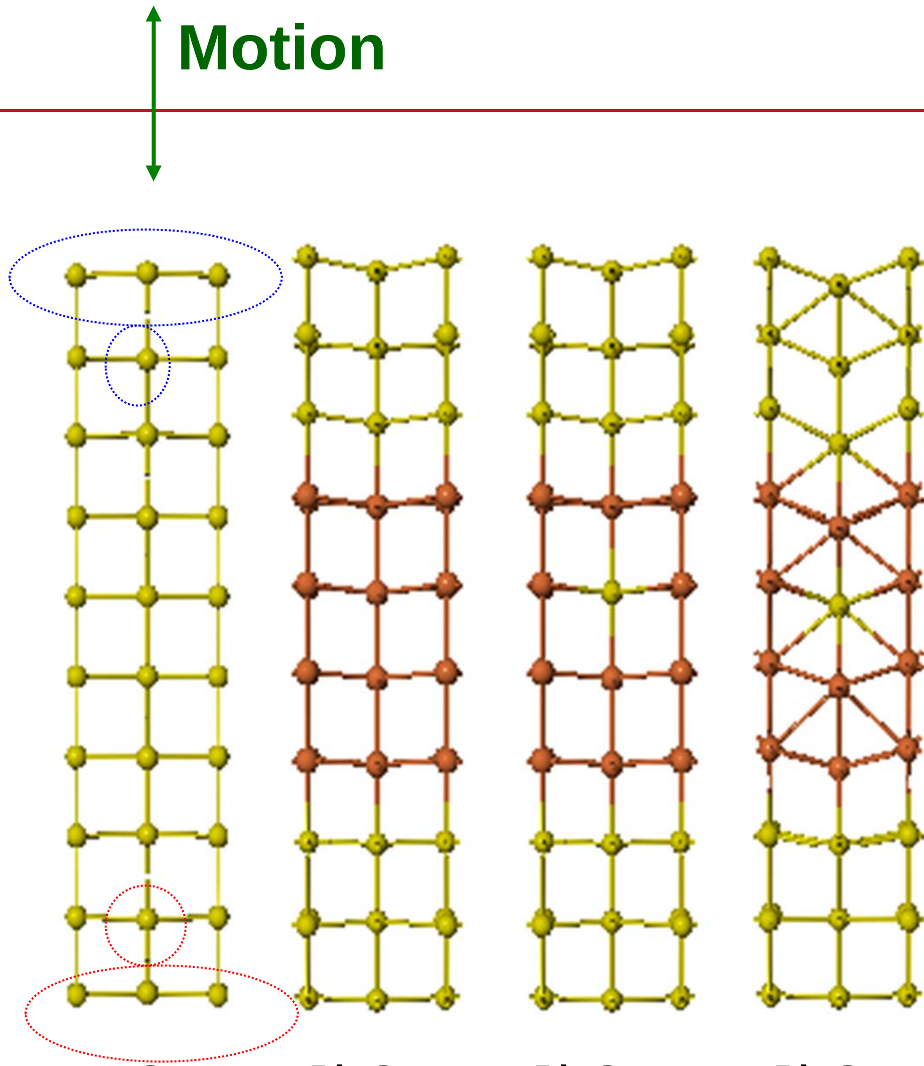
Pb

Motion

Fixed
{x,-,z}

Job # 2041





Sn | Pb_8Sn_{12} | Pb_7Sn_{13} | Pb_7Sn_{13}

Fixed
{x,y,z}

- Start with Sn (1 0 0)
- Fix atoms
  - Bottom {x,y,z}
  - Top {x-z}
- Relax atoms
- Change center atoms
- Relax atoms
- Change 1 atom to Sn
- Relax atoms

Pb is known whisker inhibitor

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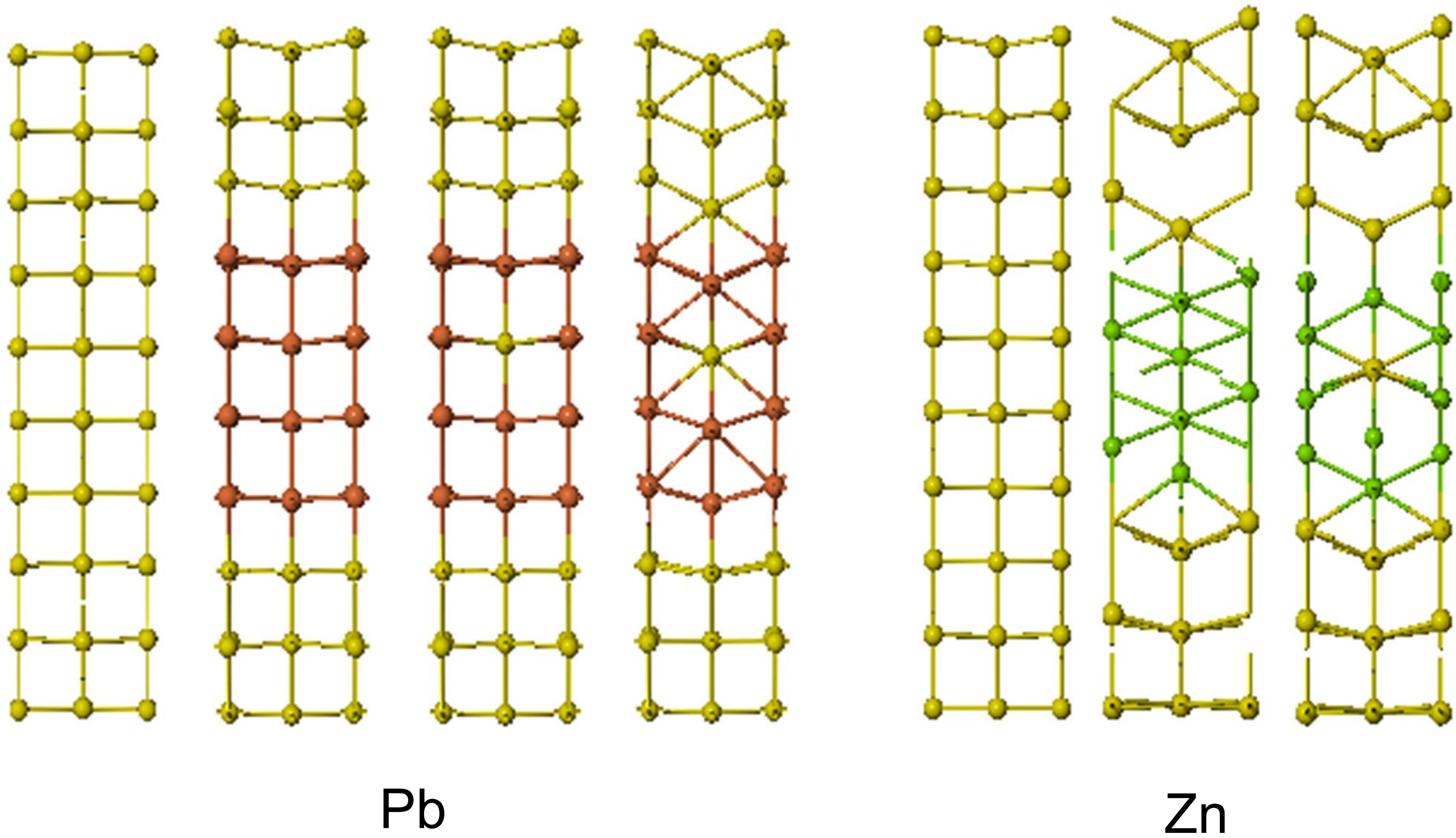
What does Zn do?



Zn contacts at grain boundary and may open a channel for Sn diffusion

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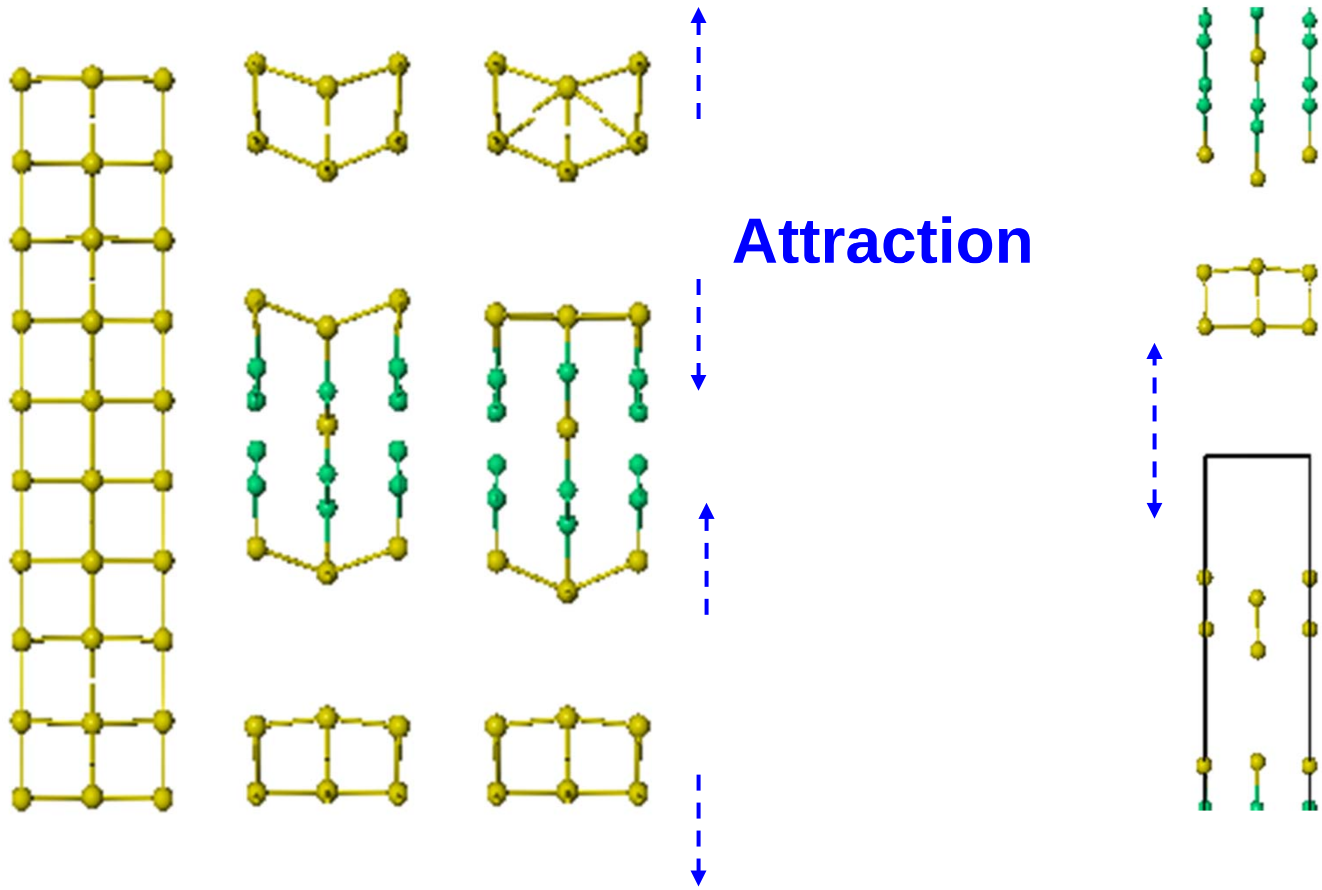
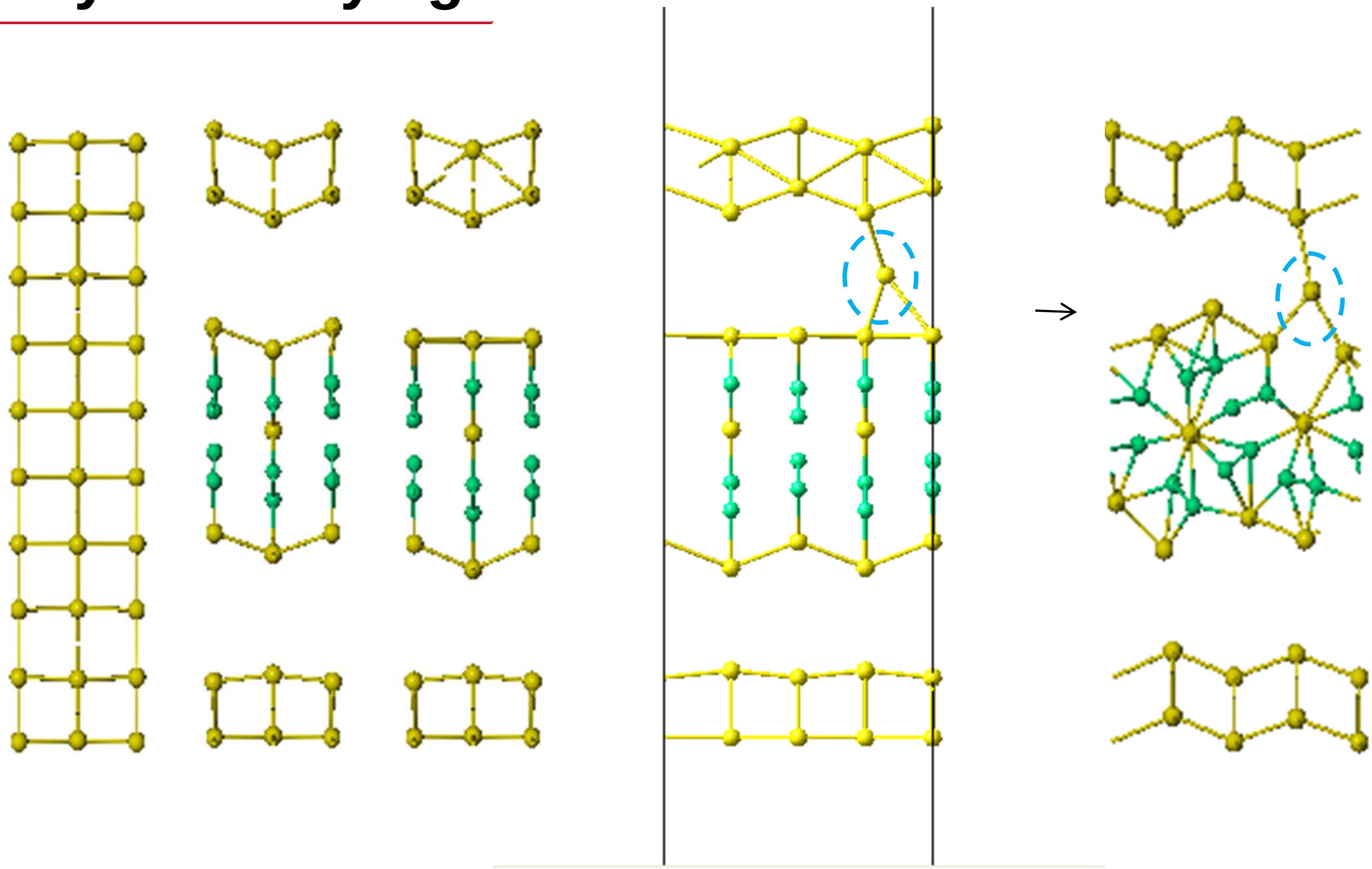
Mn

Job # 2042



Mn is known whisker Promoter
Will grow whiskers after gaps develop between Sn grains

Why Mn alloys grow whiskers in tension



Mn is known whisker Promoter

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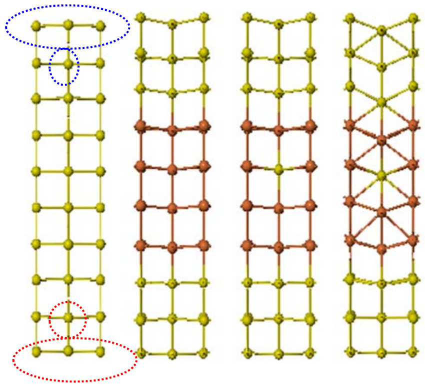
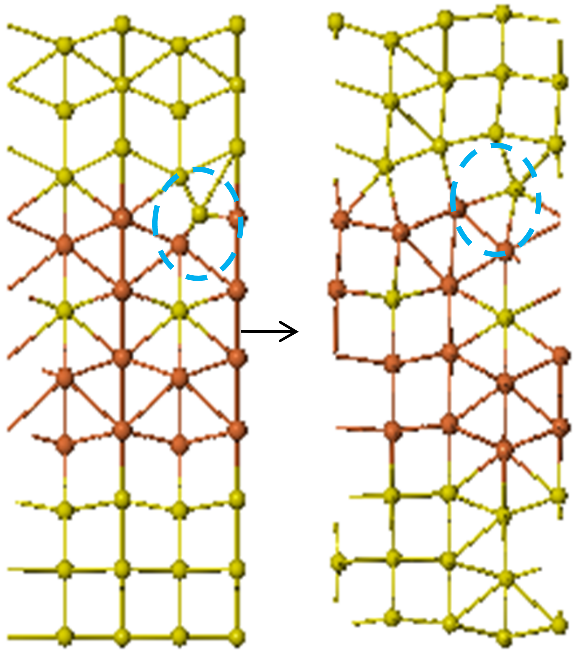
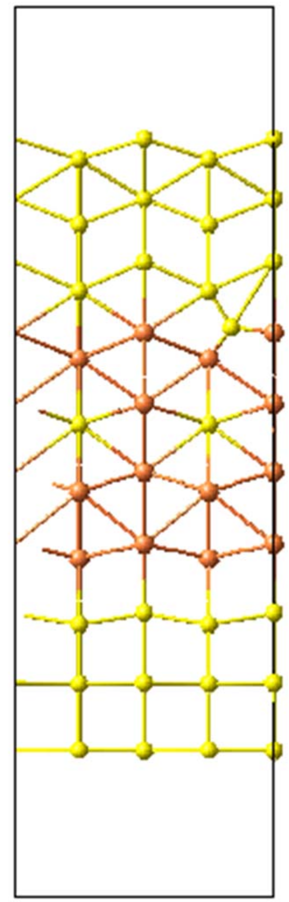
Why Pb inhibits whiskers…….







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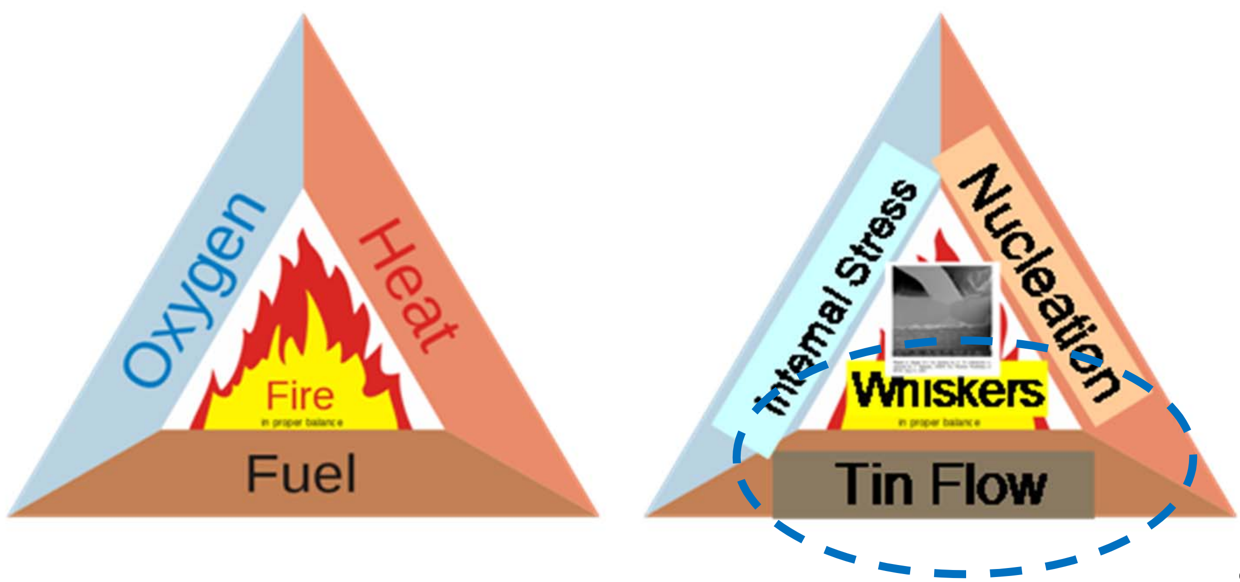
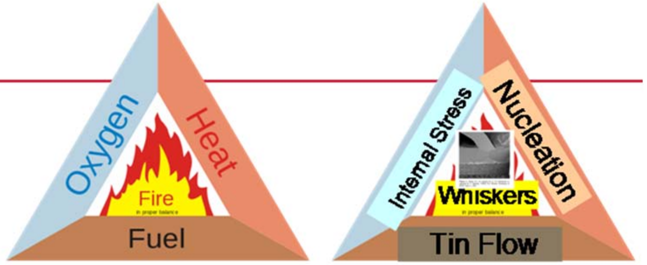
Agenda

- Effect of Oxygen on whisker surface
- Need for Compressive stress
- Inter-granular transport of Sn
- Inhibition mechanism of Pb
- Promotion mechanism by Zn, Cu and Mn
- Summary and conclusions



Summary



- Surface oxides put tin whisker in Tension
  – Whisker 'sucks' tin from base
- Pure tin relaxes by plastic creep within hours
- Diffusion of Tin along whisker is 160 times faster than diffusion across whisker base
- Inverse Swiss cheese model of percolation explains
  – > 3.5% (v/v) of second phase is needed to establish infinite network
  – This is 6.5% (m/m) Pb, including RT solubility
- Pb appears to 'trap' Sn
- Mn, & Zn appear to open channels
- Atomistic modeling is a useful tool for persistent problems

Acknowledgements

- Clive Freeman Materials Design, Inc
- Erich Wimmer Materials Design, Inc.
- Nikhilesh Chawla Arizona State University
- Jason Williams Arizona State University
- Bill Rollins Raytheon Missile Systems
- Dave Pinsky Raytheon Integrated Defense Systems.

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