New Perspectives on Tin Whiskers based on Atomistic Modeling

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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
### Engineering use of models

#### Structural and electromagnetic modeling
- **Input:** Finite element mesh, Mechanical and electromagnetic properties, External mechanical strain and EM fields
- **Machinery:** Classical mechanics and electrodynamics
- **Output:** Prediction of mechanical and electromagnetic response

#### Fluid modeling
- **Input:** Finite element mesh, Fluid properties, Flow conditions
- **Machinery:** Navier-Stokes equations
- **Output:** Prediction of flow behavior

#### Atomistic modeling
- **Input:** Chemical elements and initial atom positions, Temperature, stress, electromagnetic field
- **Machinery:** Schrödinger’s equation and statistical thermodynamics
- **Output:** Prediction of materials properties

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**Atomistic modeling provides inputs for FEA and CFD**
The \(100\) model

- **Vacuum**
- **Fixed** \( \{x,-,z\} \)
- **Fixed** \( \{x,y,z\} \)
- **Periodic boundary condition**
Surface oxygen puts whisker in tension

\[ \beta\text{-Sn (1 0 0)} \]

\[ \sigma_a = \sigma_b = -0.16 \text{ (GPa)} \]

\[ I_1 = 0.11 \text{ (GPa)} \]

\[ \varepsilon_v = 0.0025 \]

\[ \varepsilon_v = \text{volume strain} \]

\[ \beta\text{-Sn (1 0 0) + 2 O}_2 \]

\[ \sigma_a = \sigma_b = -2 \text{ (GPa)} \]

\[ I_1 = -2.51 \text{ (GPa)} \]

\[ \varepsilon_v = -0.057 \]

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


Oxide induces ~ 5% volume strain

Can’t stop the driving force! Must control Sn flow to whisker base
\( I_1, \) The first invariant

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

\( I_1 = a_{11} + a_{22} + a_{33} \)

\( I_1 = -1.570 + -0.004 + -0.941 = -2.515 \)

System | \( I_1 \) (GPa)
---|---
\( \text{Sn}_{12} \) (1 0 0) | -0.11
\( \text{Sn}_{12} \text{O}_4 \) (1 0 0) | -2.52

\( \epsilon_V = \frac{I_1}{K} \)

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

\( \begin{array}{llll}
\text{Sn}_{12} \text{O}_4 \) (1 0 0) & K (GPa) & E (GPa) & G (GPa) \\
\text{MedeA} & 14 & 20 & 25 \\
\text{Literature} & 53 & 53 & 19 \\
\beta \text{Sn} & (1 0 0) & \beta \text{Sn}
\end{array} \)
Whisker growth is marginal for stress relaxation compared to *plastic creep*

**Pure tin strain rate vs Stress**

- **Tension**
- **Compression**

Whisker growth due to stress is probable below this line

Max tension @ base

Max compression @ base


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

- 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 without intergranular contact
  - Chen et al 2005
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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.

Sn surface diffusion similar on Pb and Sn

Sn diffusion on surfaces:
- Sn on Sn (1 0 0) || to c-axis = 5 (kJ/mole)
- Sn on Sn (1 0 0) ⊥ to c-axis = 29 (kJ/mole)
- Sn on Pb (1 0 0) = 4.5 (kJ/mole)
- Pb on Pb (1 1 1) = 4.5 (kJ/mole)
- 2 Sn on Sn (100) = 141 (kJ/mole)

Concerted motion.
A really interesting result

Sn is more mobile along the whisker than across it

Sn diffusion on surfaces
• Sn on Sn (1 0 0) || to c-axis = 5 (kJ mole\(^{-1}\))
• Sn on Sn (1 0 0) \(\perp\) to c-axis = 29 (kJ mole\(^{-1}\))
• Sn on Pb (1 0 0) = 4.5 (kJ mole\(^{-1}\))
• Pb on Pb (1 1 1) = 4.5 (kJ mole\(^{-1}\))
• 2 Sn on Sn (100) = 141 (kJ mole\(^{-1}\))

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

Sn is stable at Pb surface and in Pb
Pb stability on Sn

Pb is stable at Sn surface but not in Sn

ΔE 25 kJ/mol  ΔE 2 kJ/mol  ΔE 25 kJ/mol  ΔE 0 kJ/mol
Initial Grain Boundary Model Calculations

Sn-Pb grain boundary collapses
Glues surfaces & Traps Sn

Sn in Sn-Pb (1 0 0)
Pb in Sn-Sn (2 1 0)
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 \( \parallel \) c-axis is 160 times more probable than motion \( \perp \) c-axis

\[
\begin{align*}
\text{C-axis} \\
E_a &= 5 \text{ (kJ mol}^{-1}\text{)}
\end{align*}
\]

- 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!
And now for something completely different….

- 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**
  - $P_c$
    - $\sim 0.5$ for 2D square array
    - $\sim 0.25$ for 3D cubic array
    - **But, Pb inhibits at** $5% < Pb < 10%$ (m/m)........ Hmm....

Adjacent sites may, or may not be connected

A Sn Pb (dark) alloy

An infinite network spans the sample at $P = P_c$

Sn diffuses between Sn grains. . .
Does Pb create a percolation network?
Why does 3% (m/m) Pb not inhibit whiskers?

Inverse Swiss Cheese Model

\[ P_c \approx 3.5\% \text{ (v/v)} \]
creates infinite network

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

Sn-Sn contact
Permits transport

Sn-Pb-Sn contact inhibits transport

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)

Relationship between diffusion and percolation networks established.
ASU: 5 wt% Pb Anode

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

Pb Cluster Sizes (μm²)
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
ASU: 10 wt% Pb Anode

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

Pb Cluster Sizes (μm²)
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)

Material preparation → Indentation of fiducial marks → Polishing

Imaging

3D Microstructure of the solder system → 3D Visualization of lead network → Reconstruction of Lead network → Montage Construction
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
The (1 0 0) model

- Vacuum
- Fixed \(\{x, -, z\}\)
- Fixed \(\{x, y, z\}\)
- Periodic boundary condition
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
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
Why Pb inhibits whiskers…….
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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
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