Understanding and Mitigating the Risks Associated with Lead-Free Electronics

March 5, 2015

SERDP DOD • EPA • DOE | ESTCP

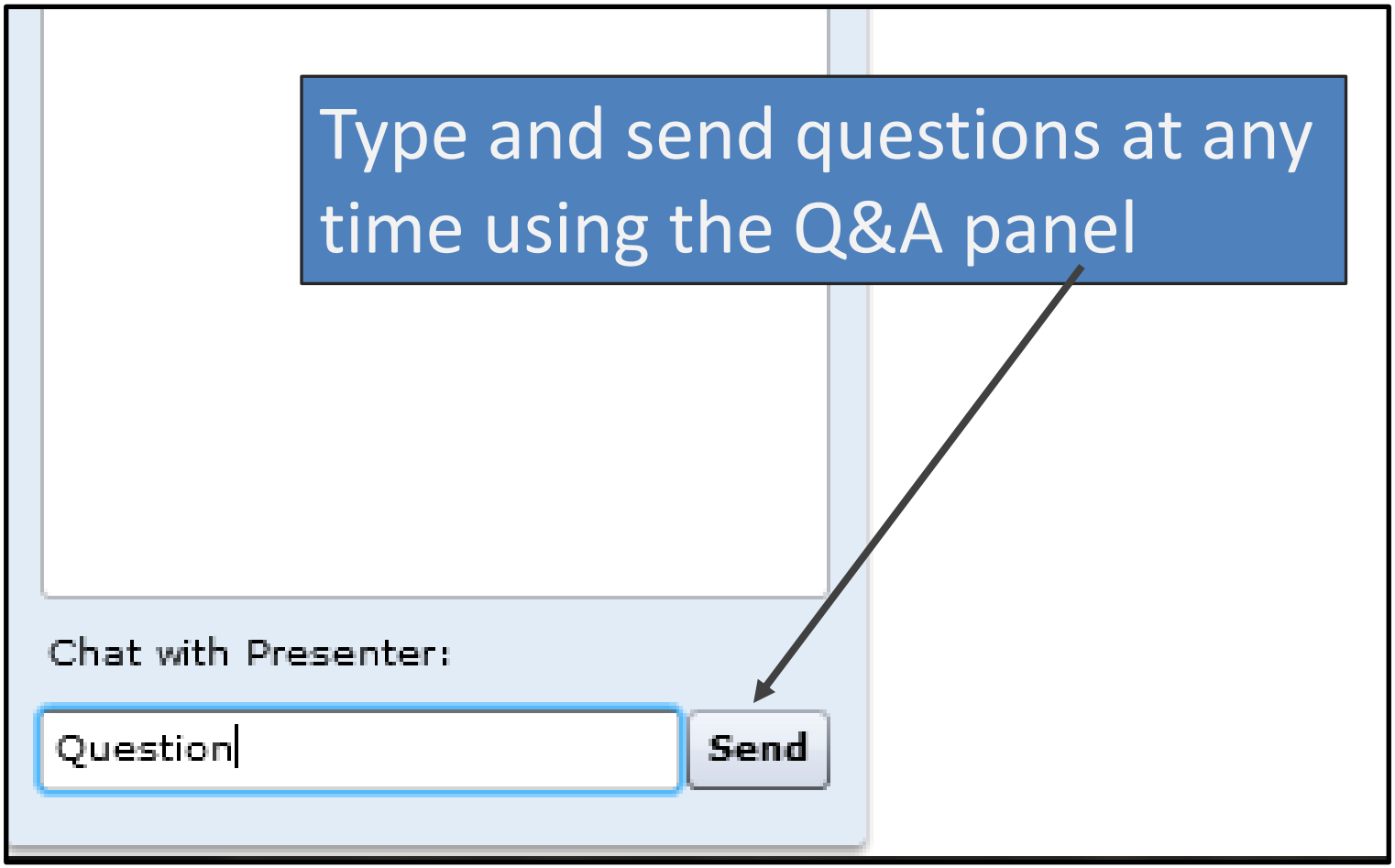
Welcome and Introductions

Rula Deeb, Ph.D.
Webinar Coordinator

Webinar Agenda

- Webinar Overview and ReadyTalk Instructions
  Dr. Rula Deeb, Geosyntec (5 minutes)
- Overview of SERDP and ESTCP
  Dr. Robin Nissan, SERDP and ESTCP (5 minutes)
- Microstructurally Adaptive Constitutive Relations and Reliability Assessment Protocols for Lead Free Solder
  Dr. Peter Borgesen, Binghamton University, The State University of New York (25 minutes + Q&A)
- Whisker Mitigating Composite Conformal Coat Assessment
  Dr. Stephan Meschter, BAE Systems (25 minutes + Q&A)
- Final Q&A session

How to Ask Questions



SERDP and ESTCP Overview

Robin Nissan, Ph.D.

Weapons Systems and Platforms Program Manager

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SERDP

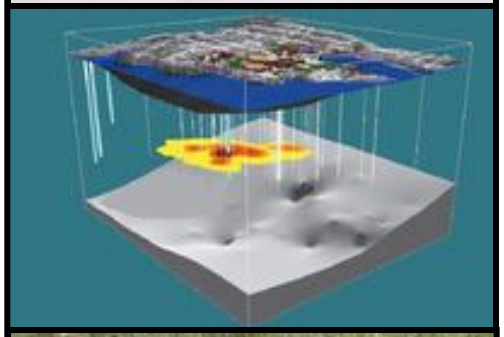
- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management

ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance

Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Climate Change
5. Weapons Systems and Platforms



Weapons Systems and Platforms

- Major focus areas
  - Surface engineering and structural materials
  - Energetic materials and munitions
  - Noise and emissions
  - Waste reduction and treatment in DoD operations
  - Lead free electronics

SERDP and ESTCP Webinar Series

DATE	WEBINARS AND PRESENTERS
March 19, 2015	**Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches at Chlorinated Solvent Sites** • Dr. John Wilson, Scissor Tail Environmental • Ms. Carmen Lebrón, Independent Consultant
March 26, 2015	**Environmental DNA: A New Tool for Species Inventory, Monitoring and Management** • Dr. Caren Goldberg, Washington State University • Dr. Lisette Waits, University of Idaho
April 16, 2015	**Blast Noise Measurements and Community Response** • Mr. Jeffrey Allanach (Applied Physical Sciences Corp.) • Dr. Edward Nykaza (U.S. Army Engineer Research and Development Center)
May 7, 2015	**Munitions Mobility**
May 28, 2015	**Managing Munition Constituents on Training Ranges** • Dr. Paul Hatzinger (CB&I Federal Services) • Dr. Thomas Jenkins (Thomas Jenkins Environmental Consulting)

http://serdp-estcp.org/Tools-and-Training/Webinar-Series

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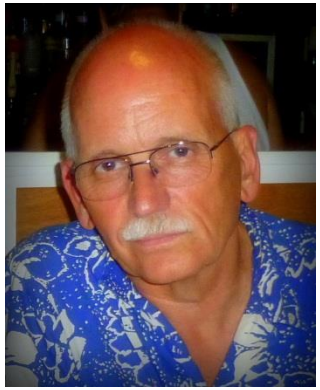
Microstructurally Adaptive Constitutive Relations and Reliability Assessment Protocols for Lead Free Solder



Dr. Peter Borgesen,
Binghamton University,
The State University of New York

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Assessment of Lead Free Solder Reliability

SERDP Project WP-1752

Peter Borgesen
Binghamton University

Agenda

- Motivation
- Challenges
- Approach
- Results (constitutive relations and protocols)
- Benefits
- Conclusions

Problem: Electronic Waste Contains Hazardous Materials

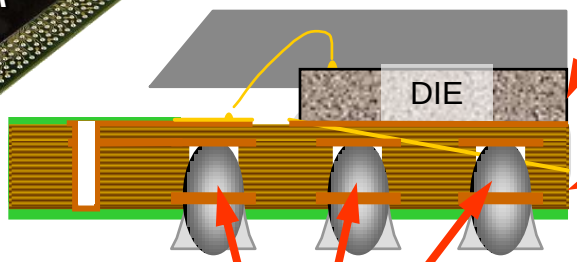
- Lead, Barium, Beryllium, Mercury, Cadmium, ...
- Pb (Lead) Hazard known since Roman times (Pb=Plumbium)
- Mentioned in Old Testament - Jeremiah, 6:29 - get the lead out

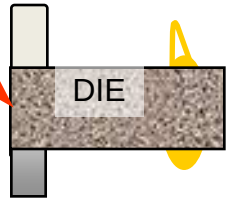
Goal: reduce hazard risk to humans & environment

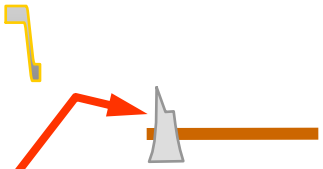
Where is Pb Used in Electronics?

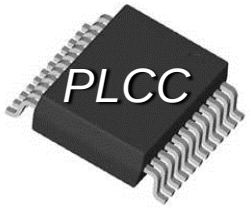
Inside component packages:
Semiconductor Die Attachment

Lead-frame Finish
(pre-tinning)







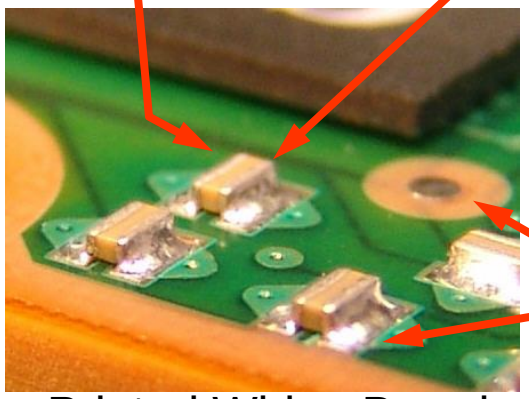


Solder Ball Grid Array
(BGA)

Component -to- PWB
attachment

Component Terminals
Finish (pre-tinning)

Plating on Mounting Hardware



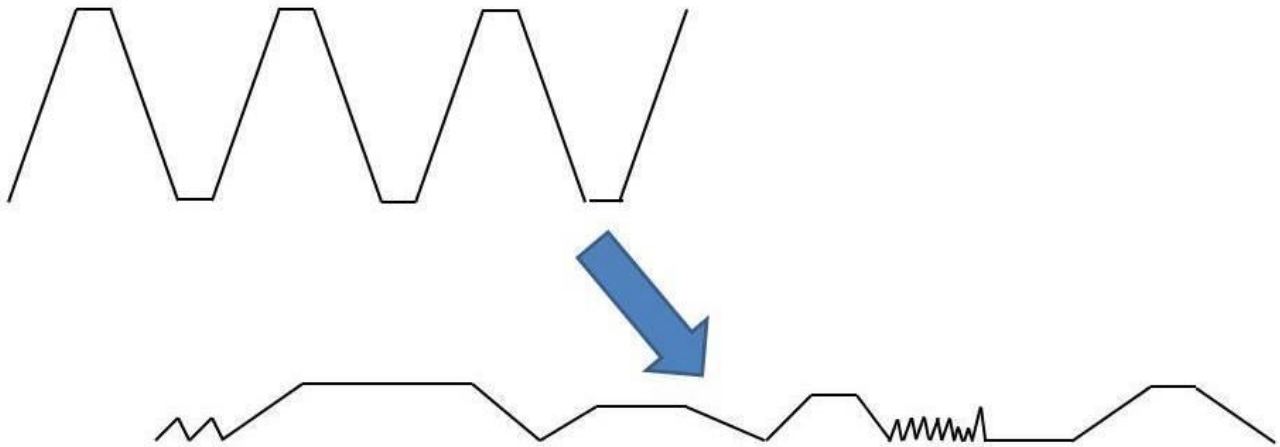
Printed Wiring Board
Surface Finish (pre-tinning)

Solder

- Electronics manufacturing was built up around SnPb solder (37% Pb)
  - Lots of experience, behavior relatively simple, semi-empirical models with ‘calibration’
- Legislation forcing elimination of Pb
  - Commercial sector doesn’t care about same service conditions and life as DoD
- Long term life of electronics commonly limited by fatigue

Reliability (Life in Cycling)

- Assessed by accelerated testing and extrapolation
  - Actual life in service
  - At least optimize (compare alternatives)
- Acceleration

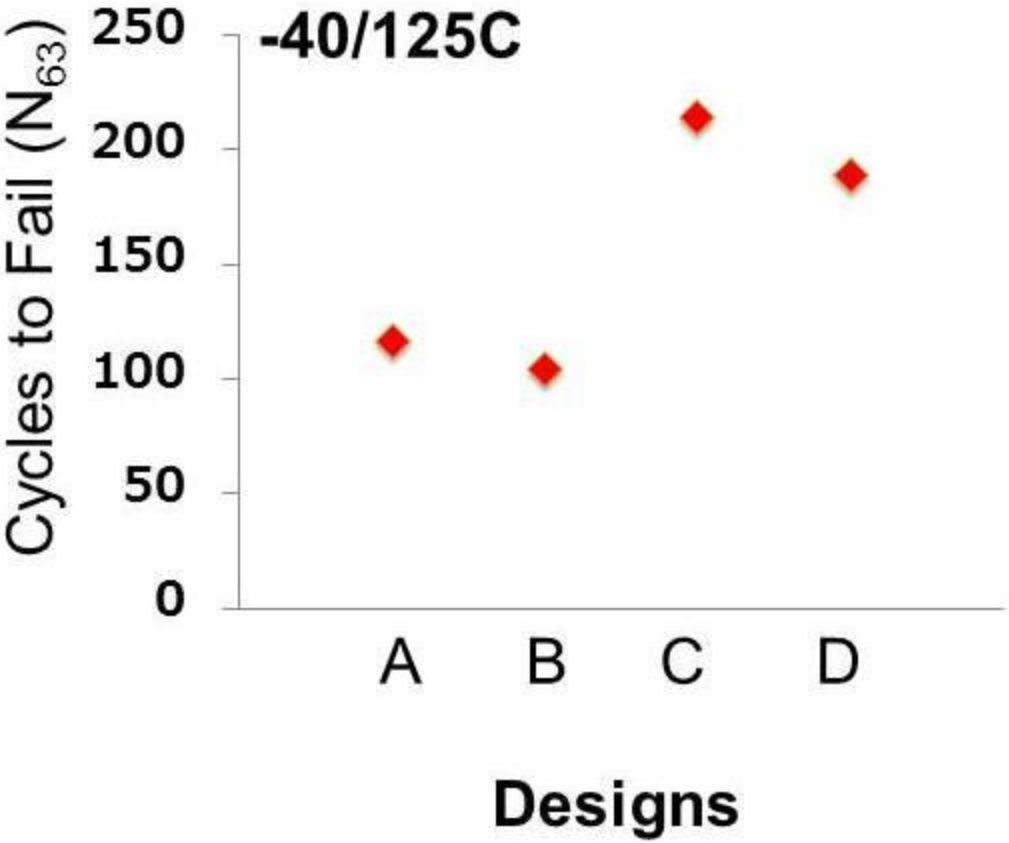


Reliability Concerns

- Predictions cannot be directly verified
  - Need ‘faith’ (mechanistic understanding)
- Concerns
  - Same damage mechanism in test and service?
  - What are acceleration factors?
  - Even if we don’t know them, are they the same?
    - Best in test = best in service?

Example: Optimize (Compare) Reliability

- Want to know best life in service



Example: Optimize (Compare) Reliability

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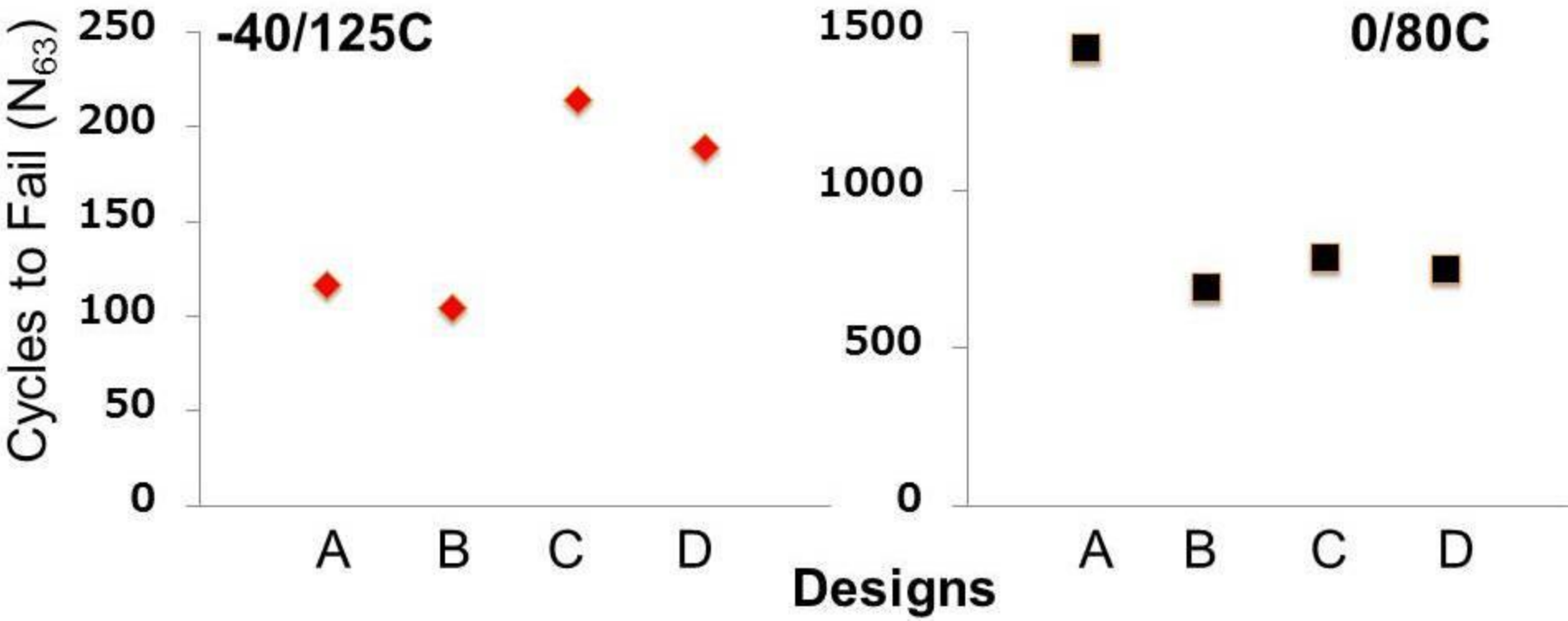

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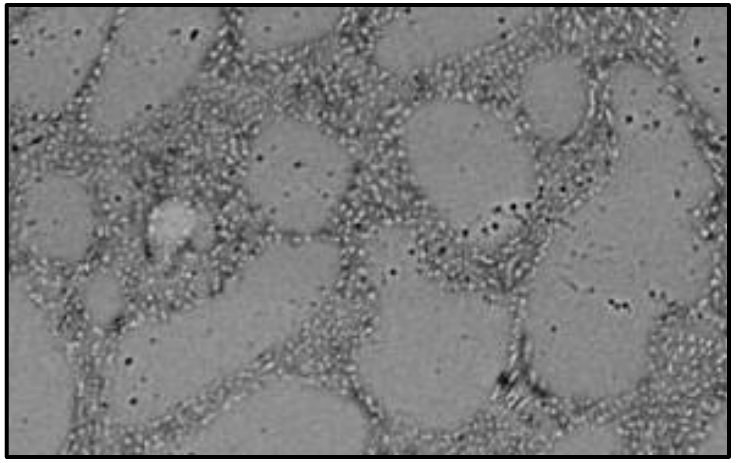
Acceleration factors?

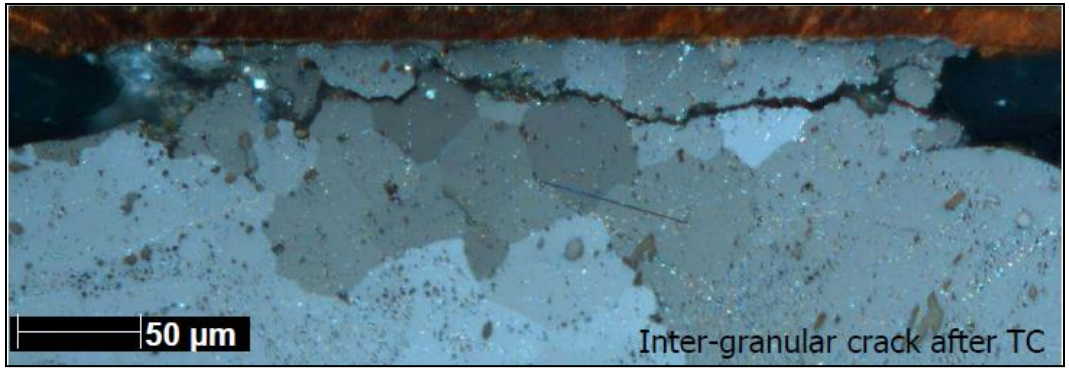
Extrapolate/Interpret Test Results (Model)

- Standard industry approach
  - Calculate stresses and strains vs. time and temperature (FEM)
  - ➡ Calculate rate of damage vs. time and temperature
- Constitutive relations
  - Creep vs. stress, temperature, time (solder properties)
  - Damage vs. stress and temperature (solder properties)
- **Problem**: Pb-free properties not stable!!

Constitutive Relations (Fatigue)

- Solder properties vary with precipitate distributions – quantify relationship
- Predict initial distribution and evolution
- Predict ***damage*** evolution vs. stress and temperature





Creep vs. Microstructure

- Showed creep rate to vary with precipitate spacing, λ (stress, T, t):

$$\gamma_{creep} = \alpha\left(1 - e^{-\beta t}\right) + \dot{\gamma}_{ss} t$$

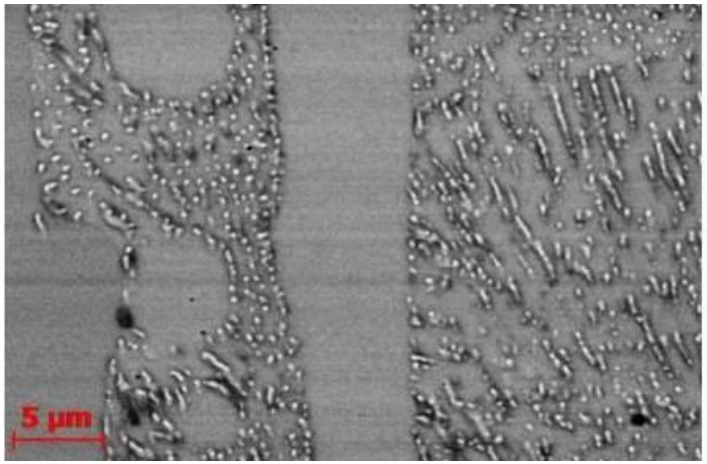
$$\alpha = C_1\left[\tau_{eff} / G\right]^2 \qquad \beta = C_2\left[\tau_{eff} / G\right]^{n'}(1/T)e^{-Q/RT}$$

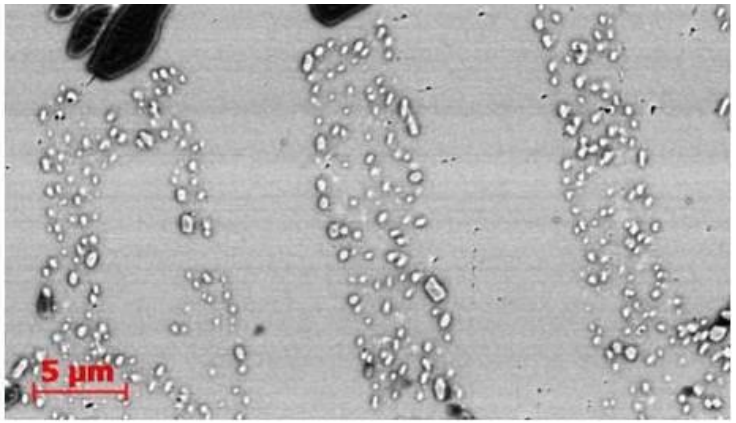
$$\dot{\gamma}_{ss} = B\frac{Gb}{kT}\left[\frac{\tau_{eff}}{G}\right]^n \lambda e^{-Q/RT}$$

- 'All' we need is to calculate λ

Precipitate Spacing

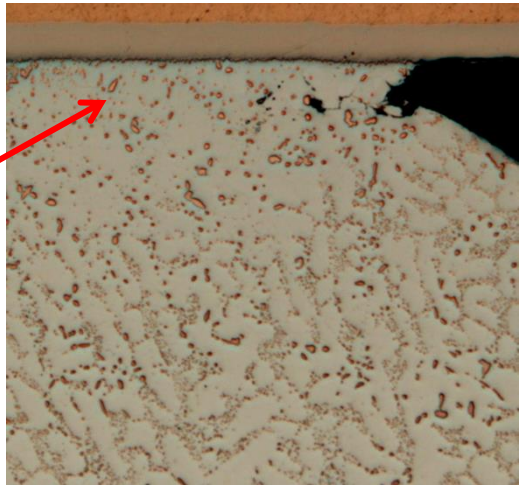
- Precipitate spacing λ result of reflow
  - Predict or measure from cross section
- Effects of solder joint size, pad finish, alloy and process
- Effects of aging (T, t)





Predict Microstructure (λ) Evolution

- Effects of thermal cycling (strain enhanced 'aging')

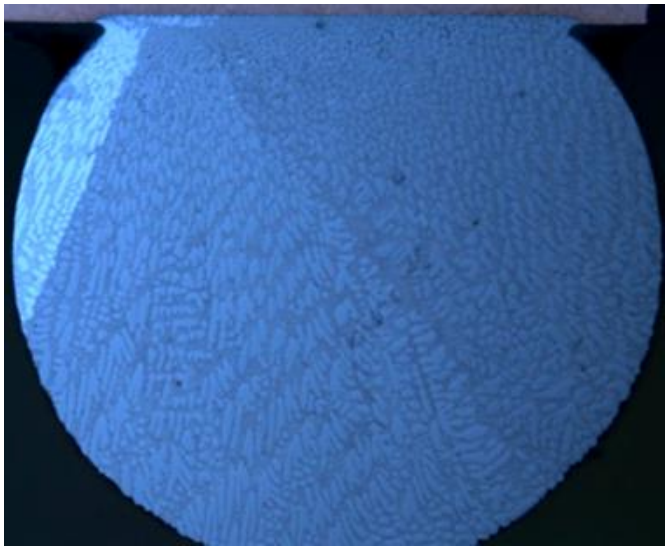


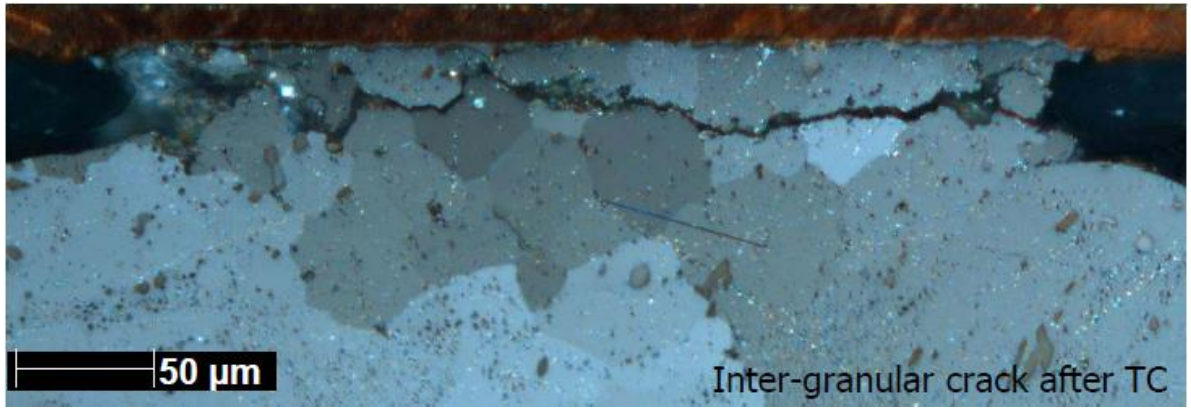
$$\lambda^2 - \lambda_0^2 = K \frac{\overline{C_{sol} D_{sol}}}{T} t$$

$$\begin{aligned}
\overline{C_{sol} D_{sol} t / T} \;=\; & \nu_C \left\{ \frac{D_{o,sol} C_{o,sol}}{T_{\max} - T_{\min}} \left[Ei\left(\frac{Q_{sol} + Q'_{sol}}{RT_{\max}} \right) - Ei\left(\frac{Q_{sol} + Q'_{sol}}{RT_{\min}} \right) \right] \left(1 + N\dot{\gamma}_{TMC}\varphi\right) t_{ramp\,up} \right. \\
& + \frac{C_{sol}^{\max}}{T_{\max}} D_{sol}^{T_{\max}} t_{dwell} T_{\max} + \frac{C_{sol}^{\min}}{T_{\min}} D_{sol}^{T_{\min}} t_{dwell} T_{\min} \\
& \left. + \frac{D_{o,sol} C_{o,sol}}{T_{\max} - T_{\min}} \left[Ei\left(\frac{Q_{sol} + Q'_{sol}}{RT_{\max}} \right) - Ei\left(\frac{Q_{sol} + Q'_{sol}}{RT_{\min}} \right) \right] \left(1 + N\dot{\gamma}_{TMC}\varphi\right) t_{ramp\,down} \right\}
\end{aligned}$$

Damage Evolution

- Damage ~ recrystallization
  - Large Sn grains:





- Cycling → recrystallization → cracking
- Same mechanism in test and service (25/60C)

Damage Evolution

- The rate of damage per thermal cycle

$$(\partial D/\partial N)_{eff} = \Phi_o * \psi^n * e^{\Delta E/kT} * (1 + \xi * t_{dwell})$$

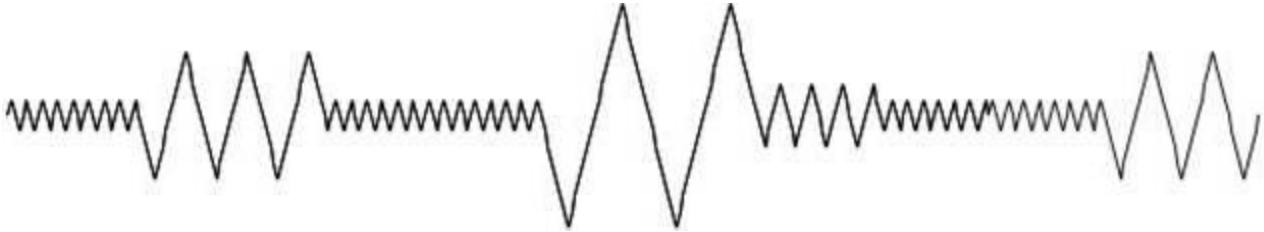
- All we need is to calculate work ψ from stresses and strains at high T (above)

- Vibration etc. different (no recrystallization):

$$\partial D/\partial N = D_o * \Delta W * \acute{\varepsilon}^{0.13}$$

Complication (Vibration etc.)

- Realistic service conditions not only lower, but also varying, amplitude



- Constitutive relations vary with loading history – further research needed
- For now we developed semi-empirical model:
  - Predict life in random vibration based on life with fixed amplitude/frequency

Test Protocols

- Aging
  - Minimum of 2 weeks @ 100C before cycling
  - Ignore any improvements in test performance
- Vibration etc.
  - Fixed frequency (avoid random vibration)
  - Limit amplitude to avoid resonance shifts
  - Compare materials, designs, processes at fixed and varying amplitudes

Test Protocols

- Thermal cycling:
  - Accelerated test life > 200 cycles
  - Don’t count on better in test = better in service. 3 or more different tests for safe comparisons
  - Recommended dwell times and ramp rates
  - Establish own parameter values in damage function if possible

Test Protocols

- Combined vibration and thermal cycling
  - Design test to account for relative severity of each in actual service.
  - Account for sequence: simultaneous or sequential, …
  - ‘Worst case’ test is thermal cycling followed by vibration

Test Protocols

- ESS
  - Screen in vibration (do not screen in thermal cycling)
  - Make screening amplitude as gentle as practical
  - If actual concern in service is vibration more than thermal cycling, effect of screening on life is stronger than indicated by acceleration testing

Benefits of Our Results

- Understand, generalize, optimize
  - Without this almost all testing is worthless or misleading
- Predict life (FEM)
- Basis for realistic comparisons to new alternatives (alloys or Ag or Cu)
  - Without this, comparisons are misleading

Conclusions

- DoD is following the commercial sector, changing electronic interconnect material
- Understanding of reliability insufficient for DoD, assessment protocols misleading
- Understanding, constitutive relations and protocols established
- More work needed on vibration and on protocols (ESS, vibration-thermal cycling combinations)

Next Steps

- Constitutive relations can be used by subject matter experts
- Someone needs to develop ‘cook-books’, demonstrate modeling
- FEM guidelines?
- Parameter values can be improved
- Extension to other (high-T?) alloys
- Develop design rules for representative examples
- Smaller dimensions (3D assembly)

Performers

- Peter Borgesen, Professor, Systems Science and Industrial Engineering Department, Materials Science Program, Binghamton University
- Eric Cotts, Professor, Physics Department, Binghamton University
- Indranath Dutta, Professor, Mechanical and Materials Engineering Department, Washington State University

For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Lead-Free-Electronics/WP-1752/WP-1752

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Q&A Session 1

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Whisker Mitigating Composite Conformal Coat Assessment

Dr. Stephan Meschter
BAE Systems

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Whisker Mitigating Composite Conformal Coat Assessment

SERDP WP-2213

Dr. Stephan Meschter

Agenda

- Tin whiskers - new (old) lead-free failure mode
- Conformal coating enhancement for whisker mitigation
- Microscopic examination of nanoparticles in coating
- Mechanical properties evaluation
- Assembly coating mitigation results
- Conclusion/DoD Benefits

Project Team

Dr. Stephan Meschter
BAE Systems
Electronic Packaging Failure Analysis and Mechanical Engineering

Dr. Polina Snugovsky and Jason Keeping
Celestica, Toronto, Ontario Canada
Chief metallurgist and Conformal coating specialist

Kevin Elsken
Bayer Material Science, Pittsburgh, PA
Polymer scientist

David Edwards
Henkel Electronic Materials, Irvine, CA
Senior Engineer

Dr. Junghyun Cho
Mechanical Engineering Department
Binghamton University, Binghamton, NY

Pb-Free Electronics: New (Old) Failure Modes

- "Tin whiskers"
  - Discovered in the 40s-50s
    - Shorts
    - Contamination
    - Arc flash - metal vapor plasma
    - SERDP WP-1753 Research
- Pb in Sn inhibits whiskers
  - Late 50s Tin whisker solution
- Zn and Cd also whisker
- Environmental effects
  - Fractures in thermal cycling, shock and vibration

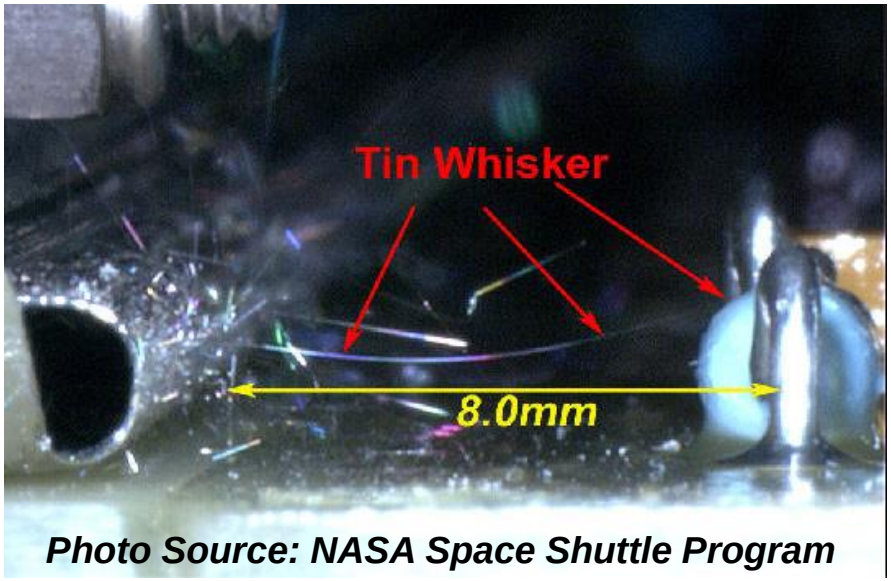


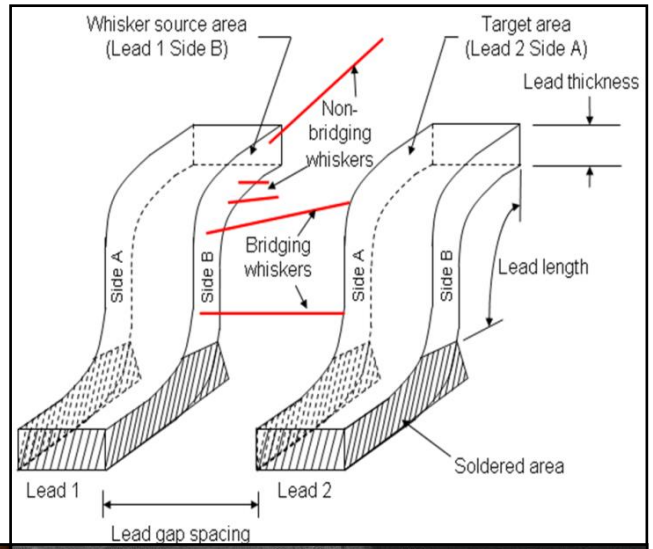
Photo Source: NASA Space Shuttle Program

Electromagnetic Relay Short Circuit

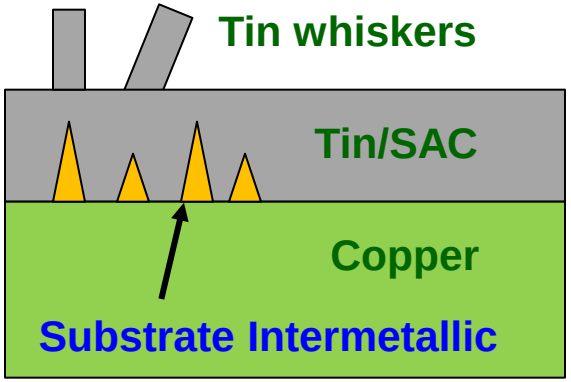
Cracked Solder Joint Open Circuit

Tin Whiskers

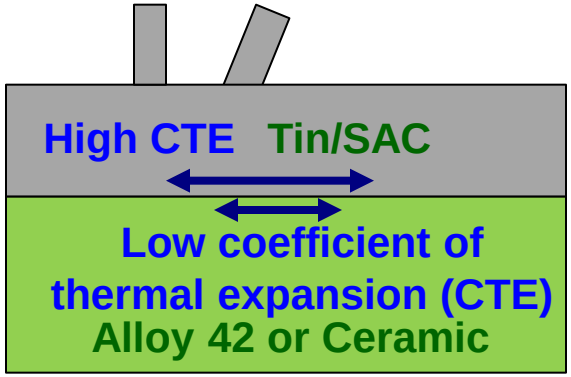
- Electrical short circuits
  - Intermittent
  - Permanent
  - Found recently in accelerator pedal position sensor (Leidecker et al., 2011, http://nepp.nasa.gov/whisker/)
- Debris/contamination
  - Interferes with optical paths and MEMS
- Metal vapor arc
  - Whiskers vaporize into a conductive plasma
  - Power applications



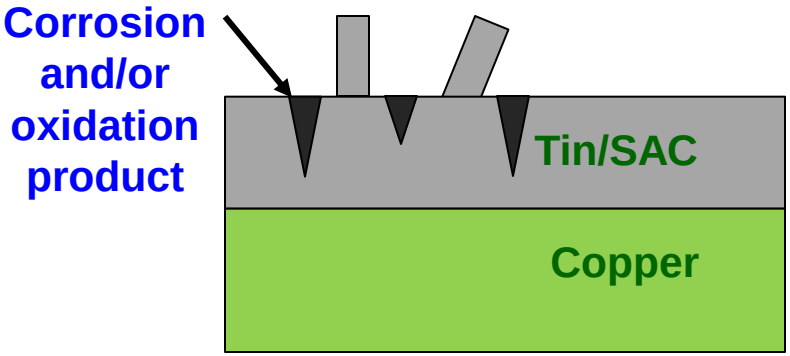
Factors Contributing to Whisker Growth



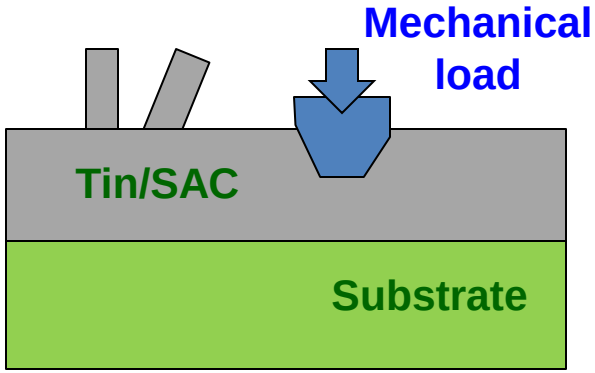
Use, storage and thermal cycling



Thermal cycling



Corrosive and/or high humidity atmospheres



Clamping screws, connector contacts, etc.

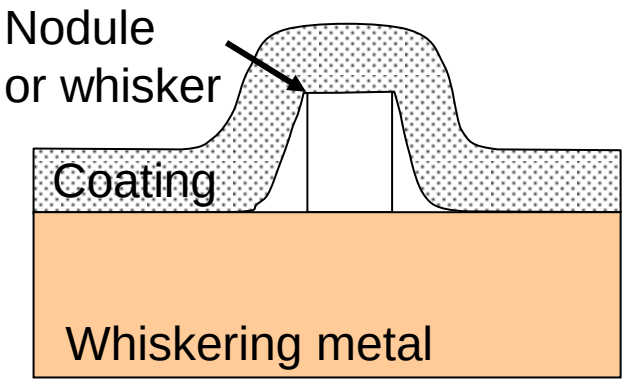
Compressive stresses believed to cause whisker growth

DoD applications have many of these

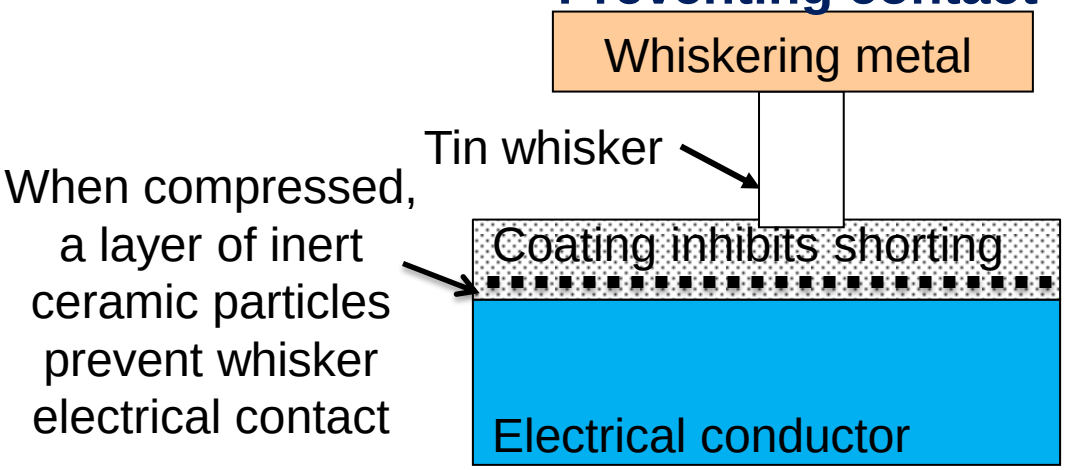
SAC=Sn-Ag-Cu solder

Coating as a Whisker Mitigation

Containing whiskers

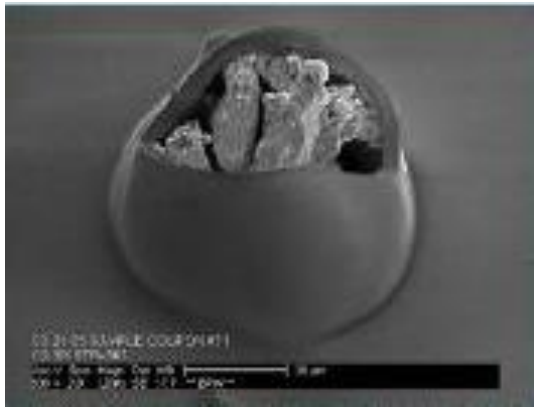


Preventing contact

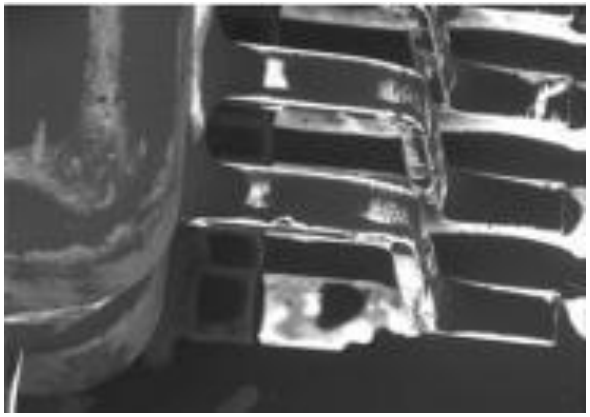


Coverage and strength/toughness needed

Documented issues

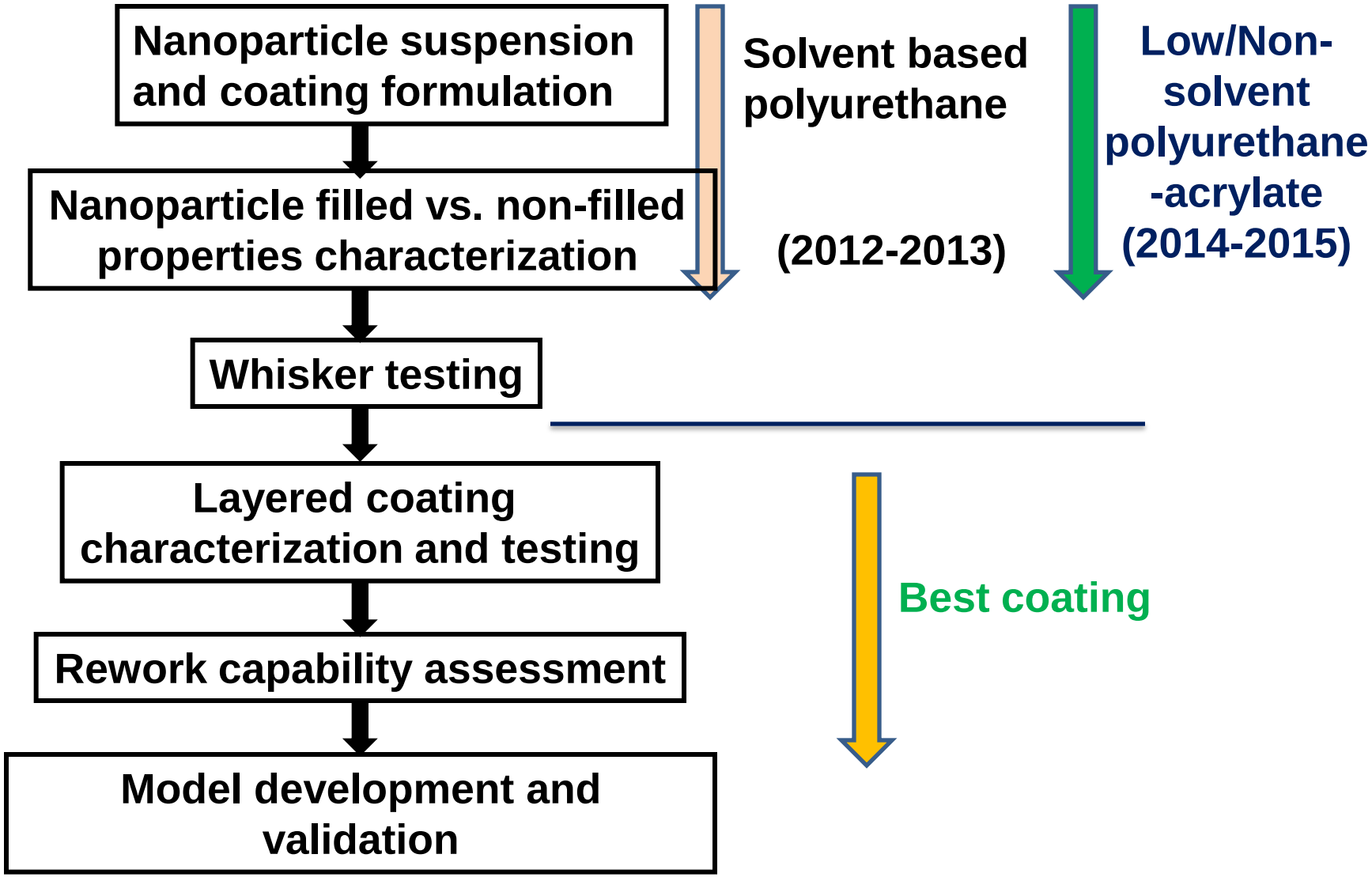


Ruptured coating (Woodrow, 2006)



Thin coverage (CALCE, 2010) (light areas =thin coating)

Technical Approach: Coating Development

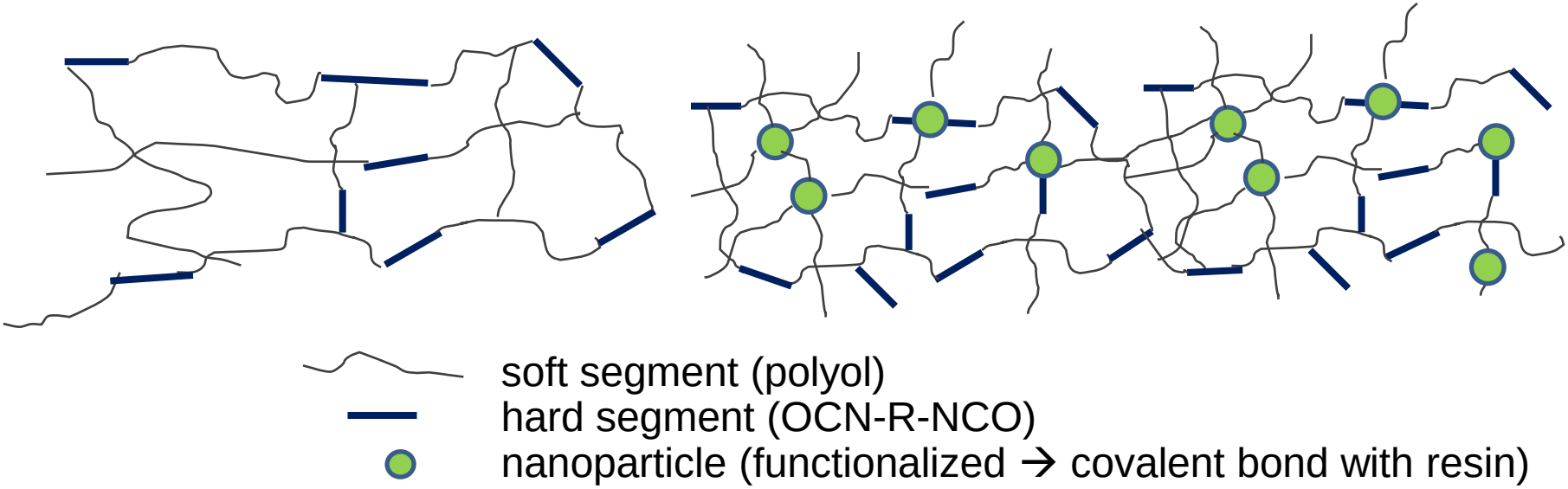


Enhancing Coating Properties

Polyurethane: Segmented Block Copolymer

Basic polyurethane

Polyurethane with nanosilica reinforcement



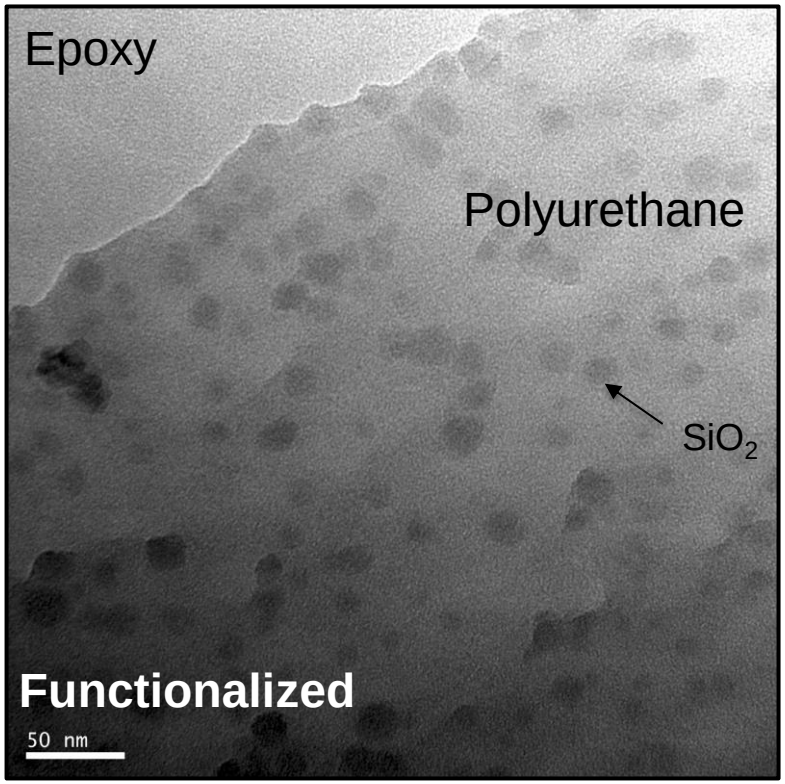
Improve coating properties to provide long term whisker penetration resistance and good coverage

Functionalized Particles → Good Distribution

TEM Observations

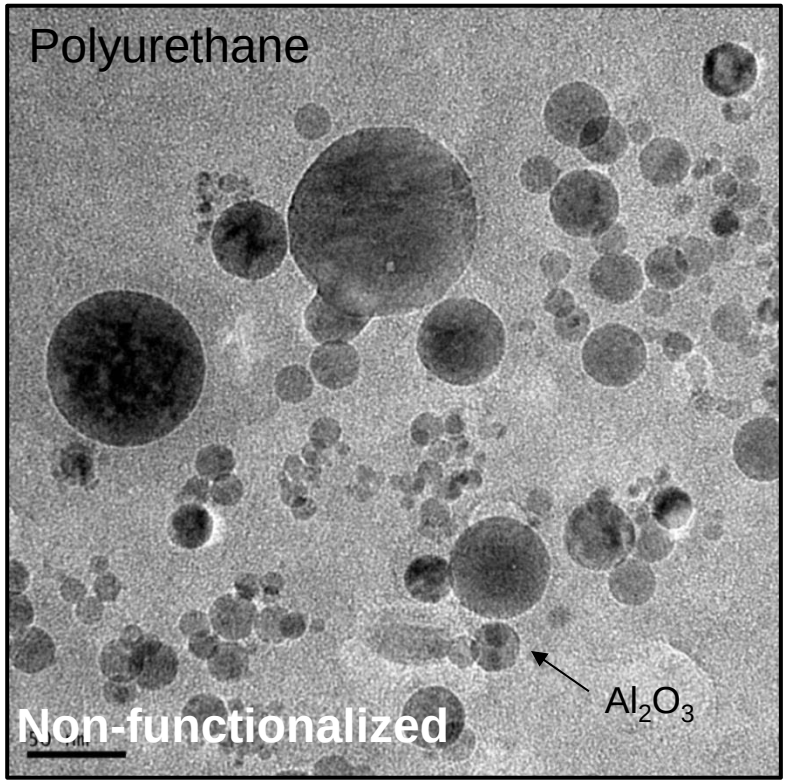
Cryo-TEM at 120 kV (on cold stage at < -176˚C)

PC18M+50% XP2742
(15.17 wt% SiO_2) (~80 nm thick slice)



Nanosilica **singly distributed** in polyurethane matrix (also, narrow size distribution)

PC18M+20% X11102PMA
(13.04 wt% Al_2O_3) (~50 nm thick slice)



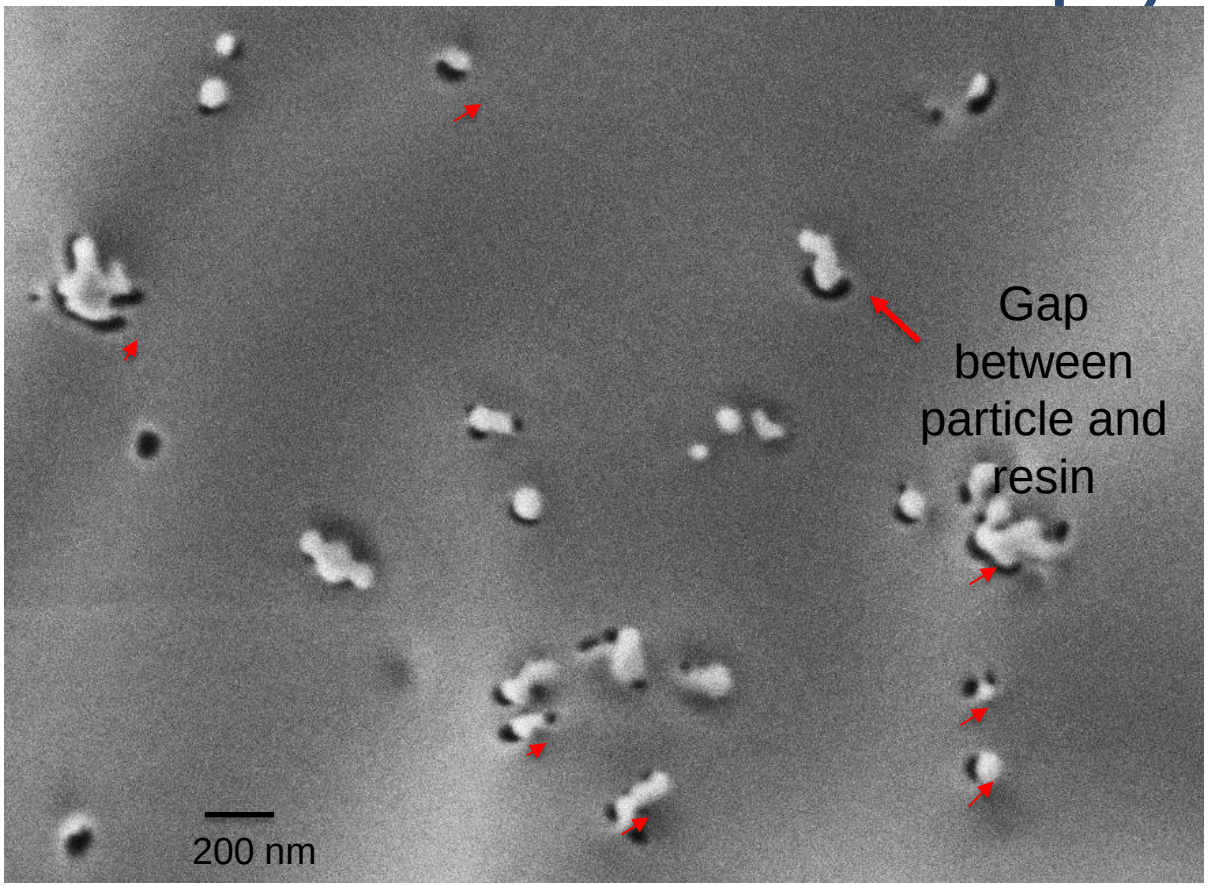
Nanoalumina **strongly agglomerated** in polyurethane matrix (also, wide size distribution)

Non-Functionalized Particles Found: Poor Resin Adhesion

FE-SEM at 2 kV (on microtome cross-sectioned sample)

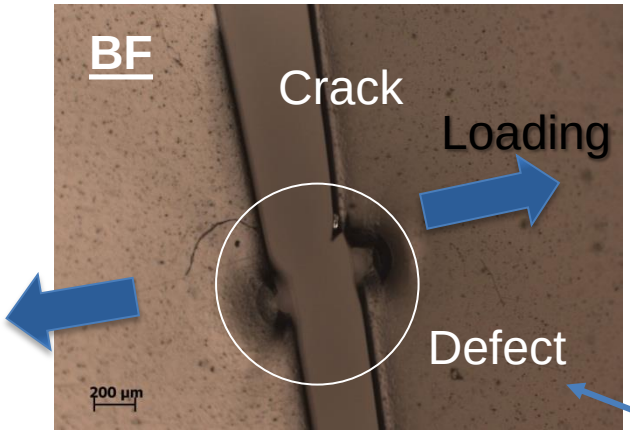
4% X11102PMA (2.44 wt.% Al_2O_3)

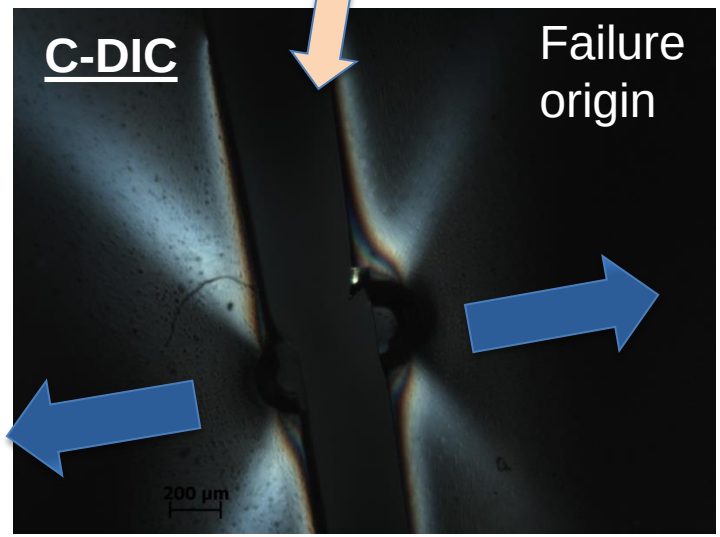
- Nanoalumina particles separated from polyurethane matrix
- Poor adhesion (indicated by arrows)

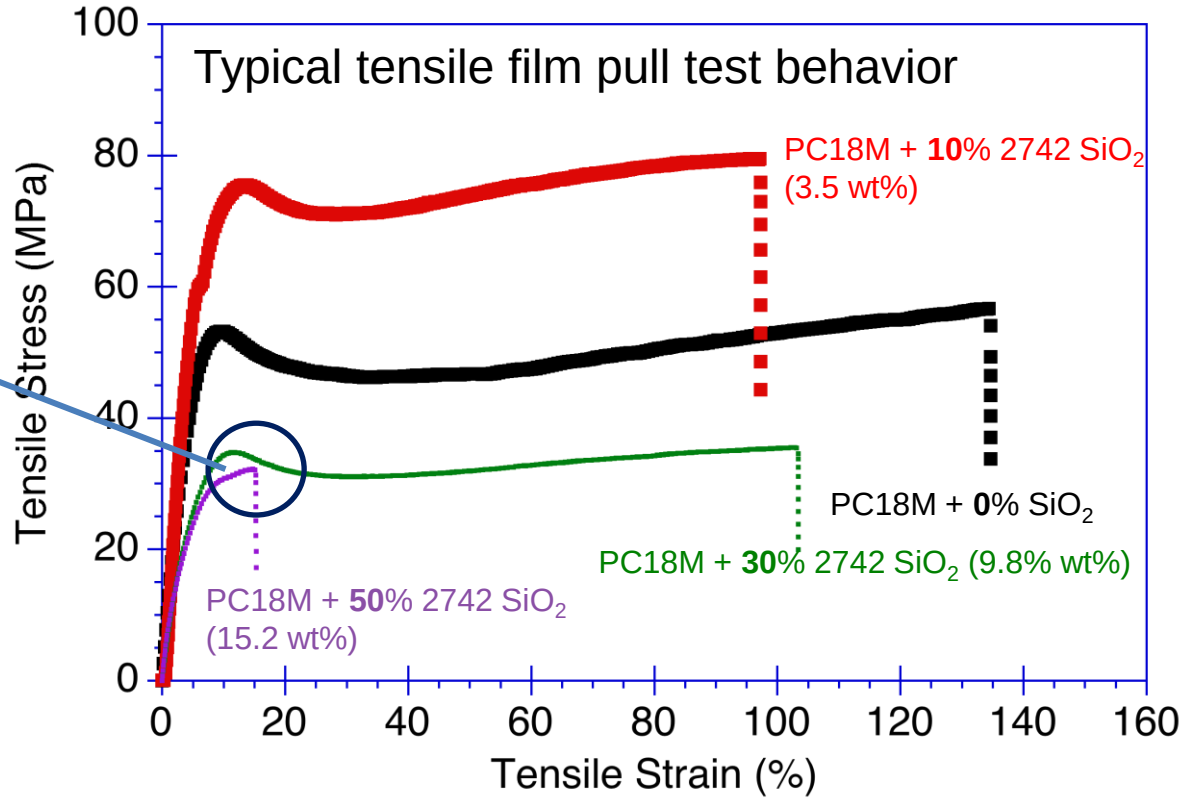


Microtome sectioning exposed that the nanoalumina particles were not functionalized

Defects Limit Coating Elongation in Tensile Test





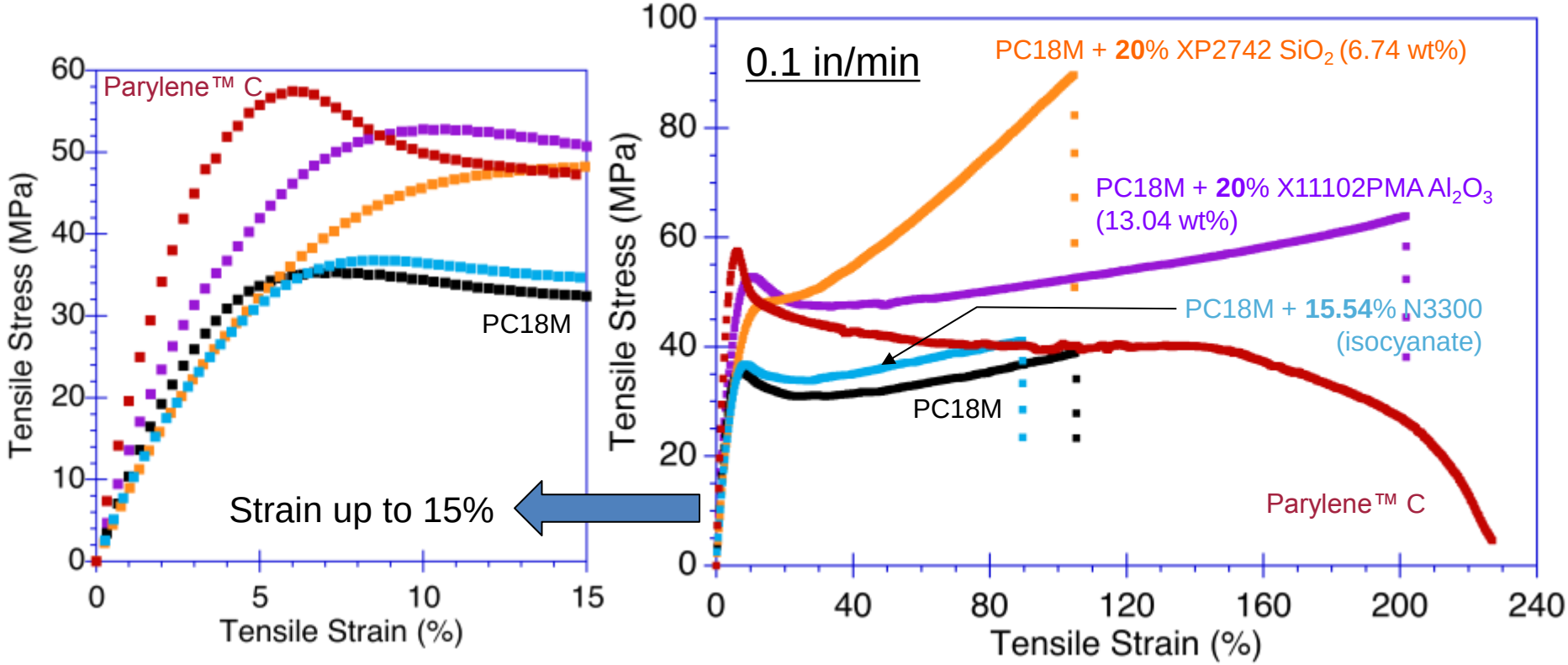


Sample dimension: 2.5 in x 0.5 in, Gauge length: 0.5 in
Testing conditions: displacement control at 0.1 in/min

Defects reduce mechanical properties: Factor must included in electronics coating standard

Tensile Testing Summary

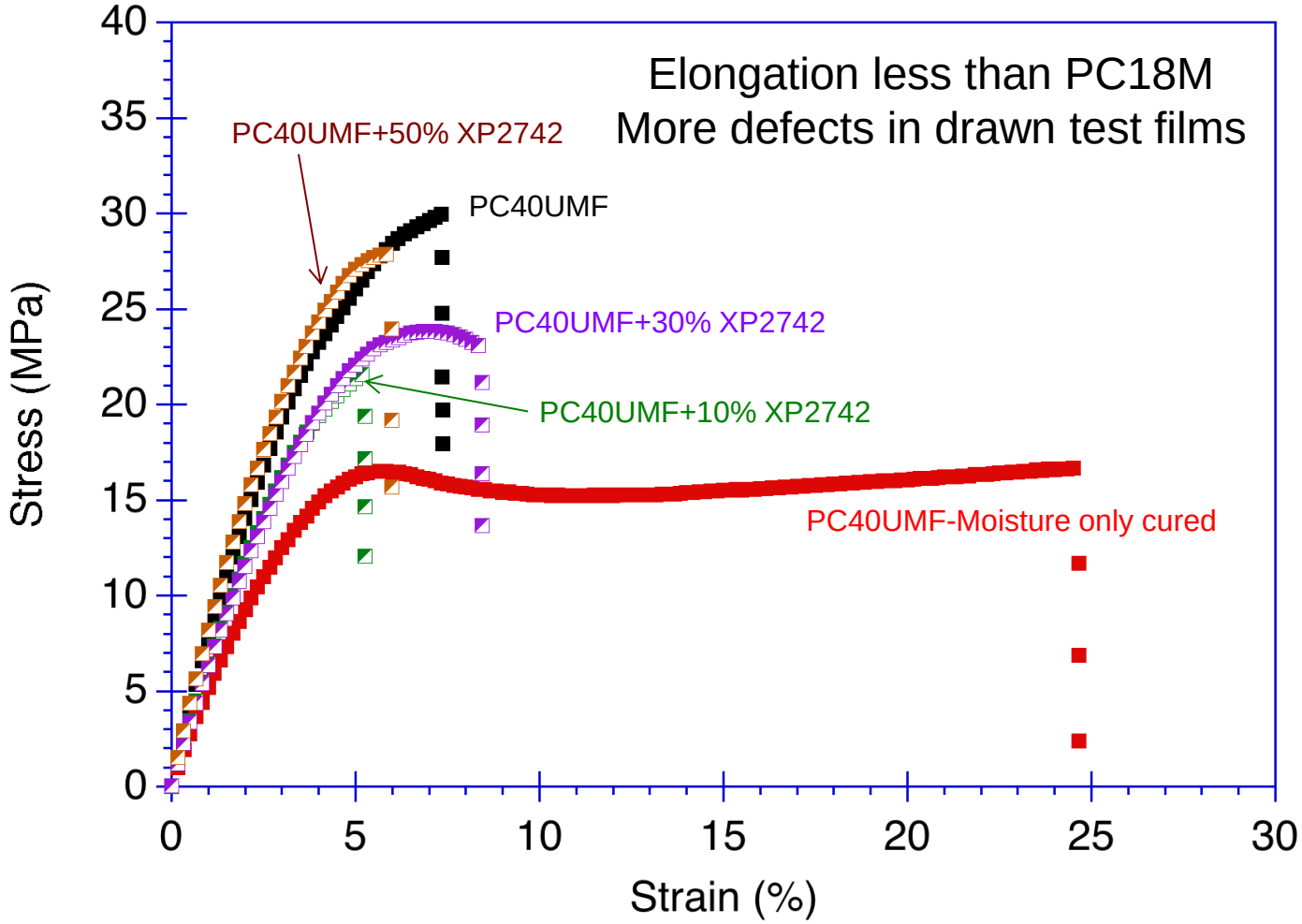
PC18M with Nanoparticles/additives vs. Parylene™ C (25-mm thick film)



PC18M with nanoparticles sprayable coating shows comparable mechanical properties with the Parylene™ C films vacuum deposit

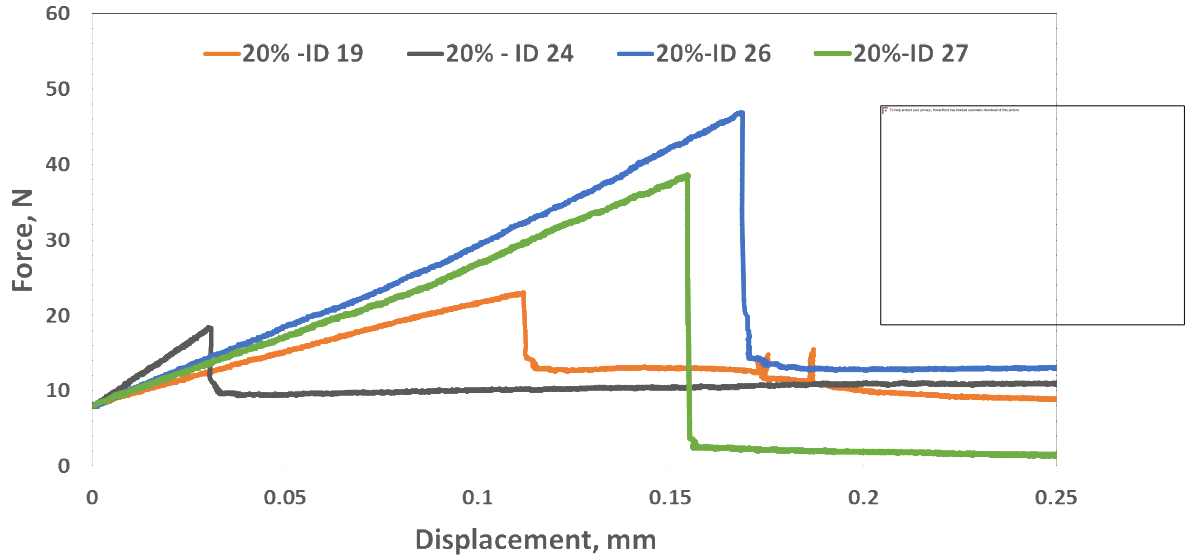
UV-Cured Low VOC Polyurethane (PC40UMF)

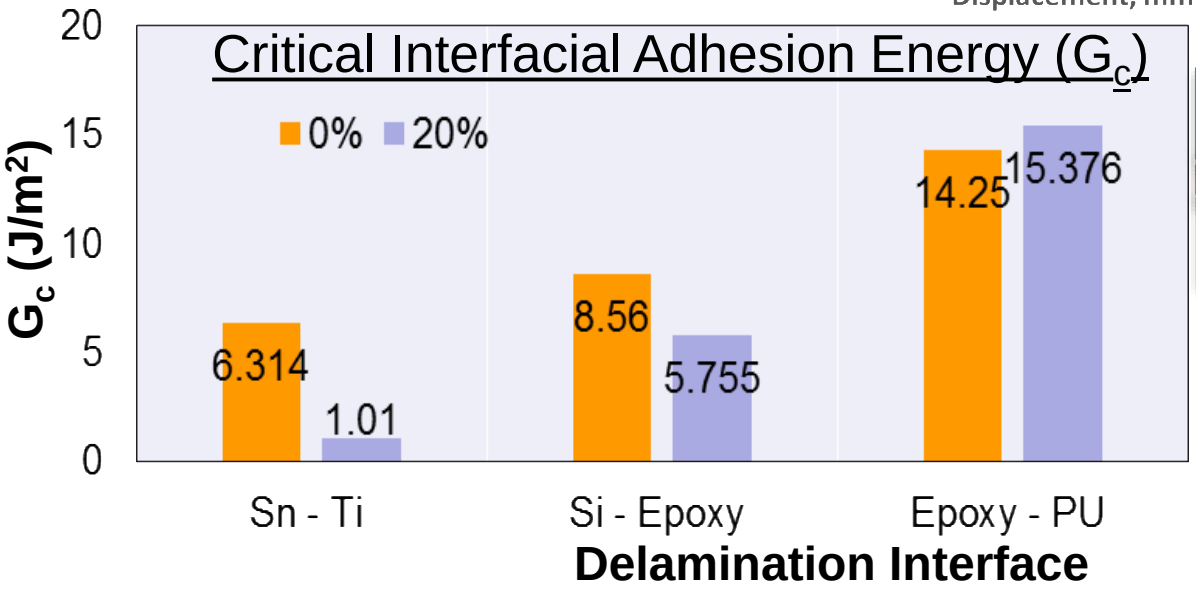
- **Rapid curing and low energy consumption** (compared to thermal curing)
- **Environmental friendly process**: No or little VOCs, reduction of green house gas emissions

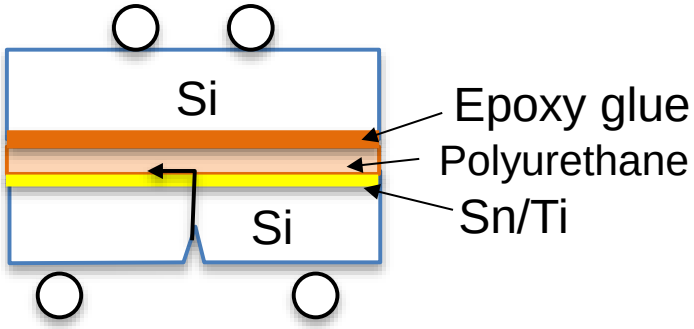


4 Point Adhesion Test Result

PC18M
+ 20% XP2742 SiO_2





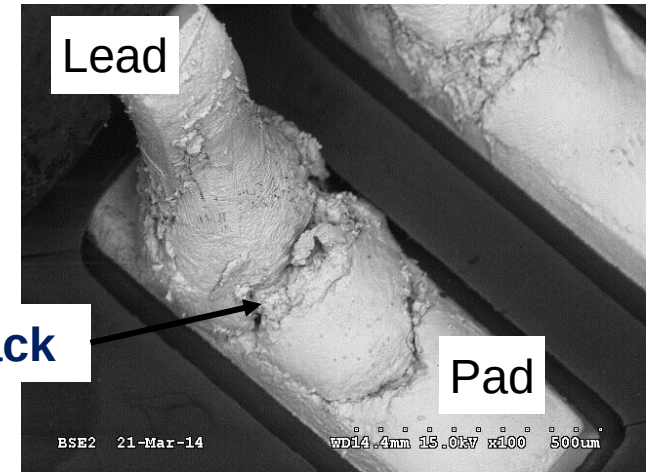


* G_c of Polyurethane/Sn should be > 14-15 J/m²

Coating Stressed by Solder Deformation (1)

Uncoated SAC305 solder joints

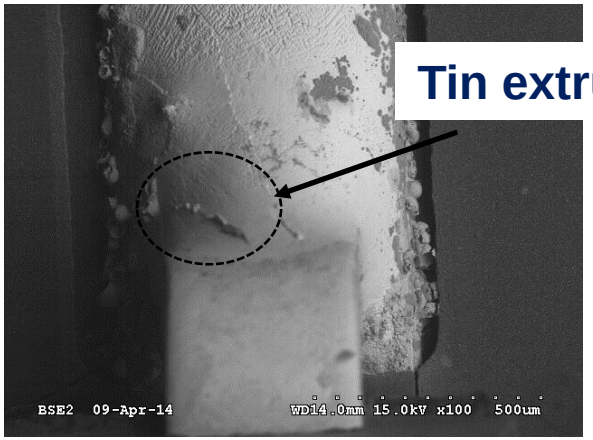
Alloy 42 leads: Thermal shock cycles (1)



Solder crack

WP1753 Thermal cycling result

Copper leads: Thermal cycles followed by 85C/85%RH (2)



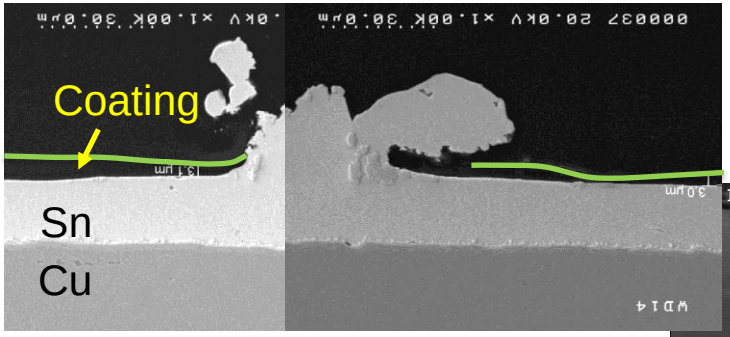
Tin extrusion

(1) 2,110 JESD201 cycles -55 to +85°C 3 cyc/hr
(2) 100 cycles -55/125°C, then 233 cycles -20/80°C, thermal cycles, then 1,000 hours 85°C/85%RH

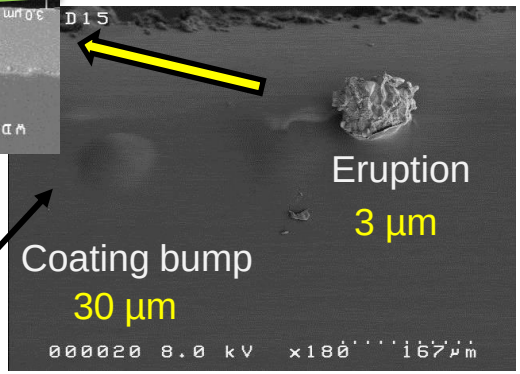
Thermal cycling coating survival is key for DoD harsh environment whisker mitigation and moisture protection

Coating Stressed by Solder Deformation (2)

Eruption cross-section

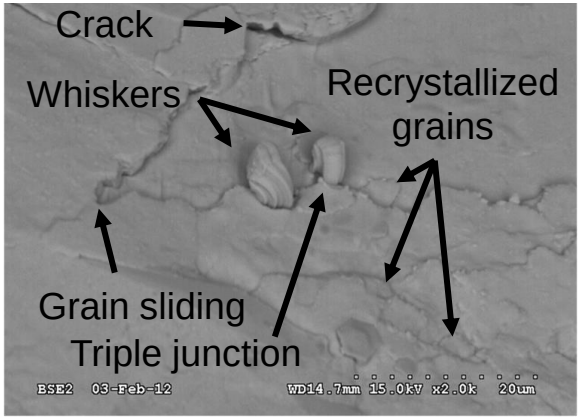


Tin eruption
3 µm thick coating

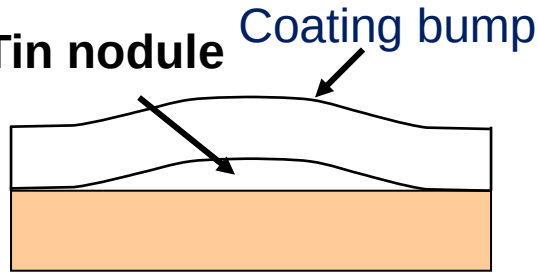


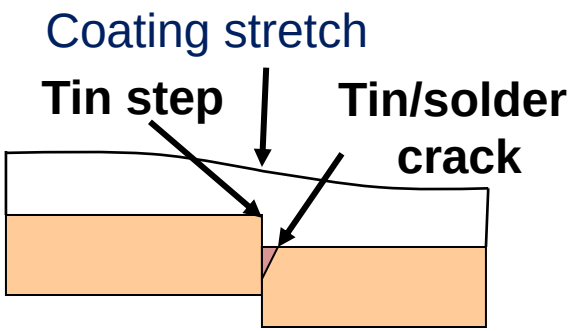
PC18M + 30% XP2742 (9.75% SiO2) after 2500 hours at 60^{0}C/60% RH

Thicker coating retarded penetration

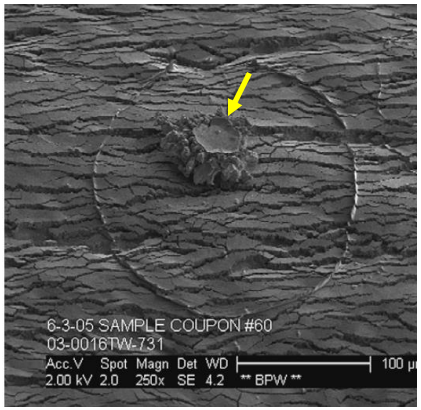


Step and crack formation

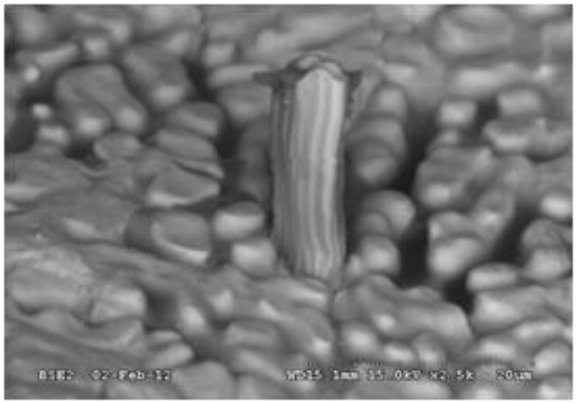




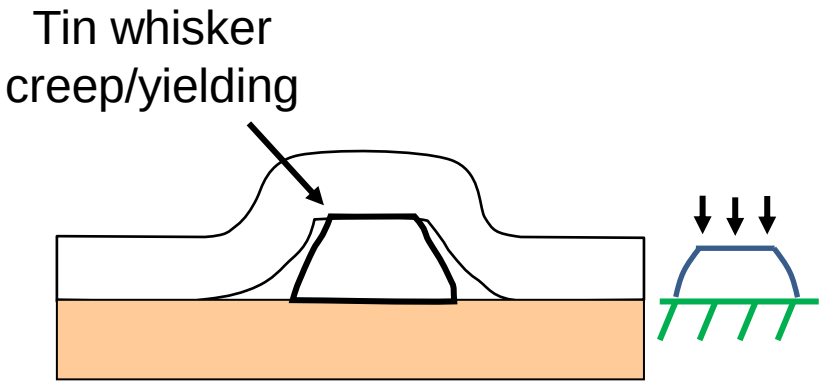
Tin Yielding Under Coating

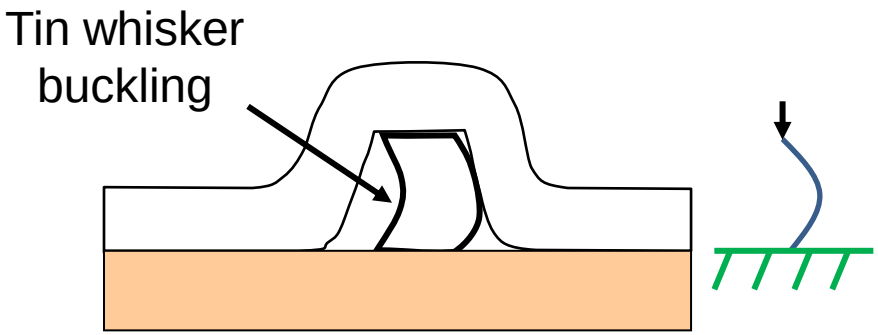


Tin nodule yielding under Parylene™ C coating (removed) (Woodrow 2006)



Whisker growth from Sn3Ag0.5Cu solder

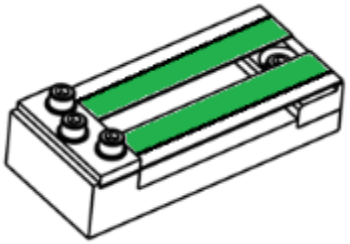




Tin whisker mitigation involves an interaction between coating strength, modulus, elongation and adhesion

Coating Reduces Whisker/Nodule Density

PC18M+30% XP 2742 (9.75% SiO_2) after 2500 hours at 60°C/60% RH



Cantilever coupon screening experiment: **bright tin** over Cu with bending preload

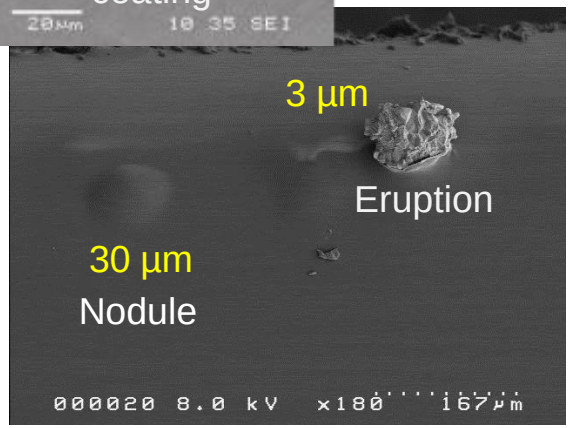
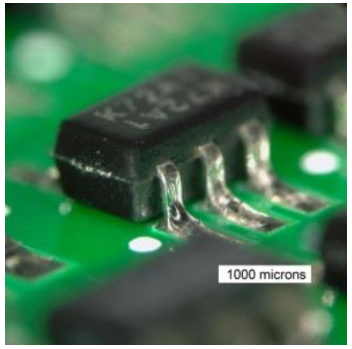


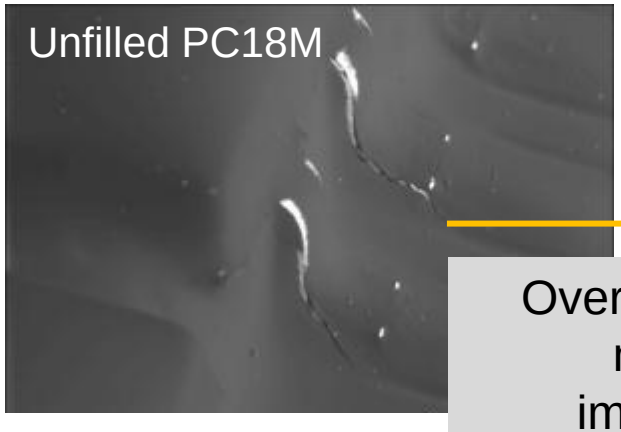
Image after coating removed

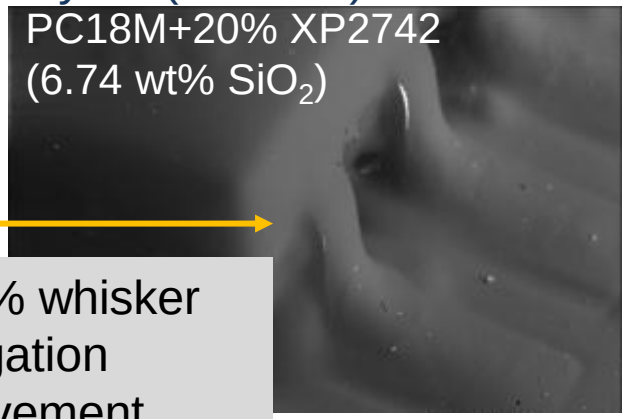
Filled Coating Performed Best After TC

Thermal cycles from -55 to +125˚C (100 cycles), followed by from -20 to +80˚C (200 cycles)

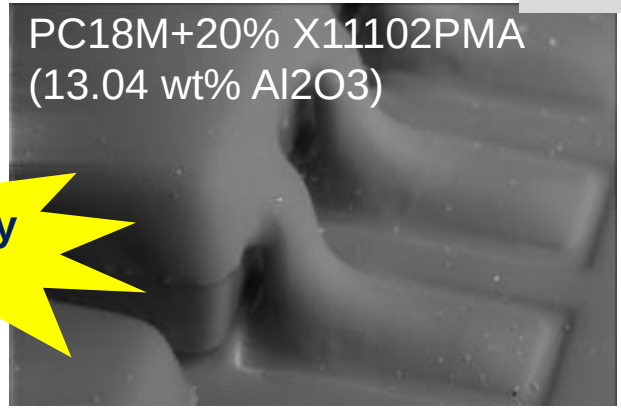
SOT6 with low CTE alloy 42 (Fe-42Ni) leads







Over 90% whisker mitigation improvement

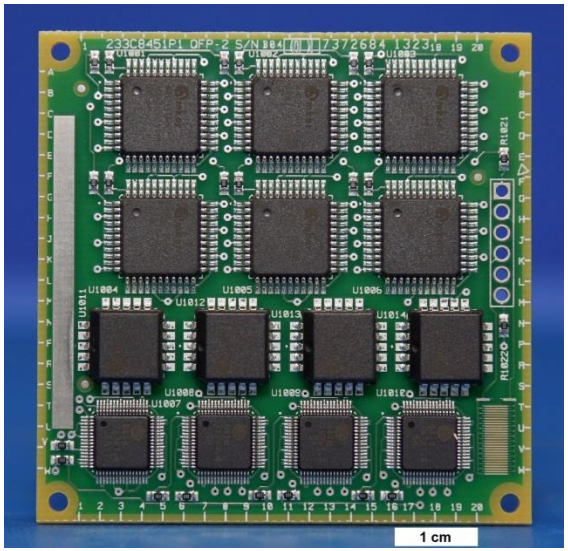


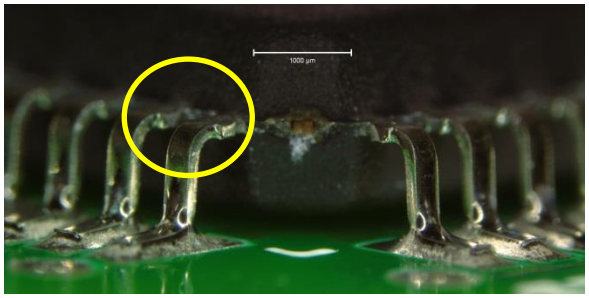
Best spray coverage

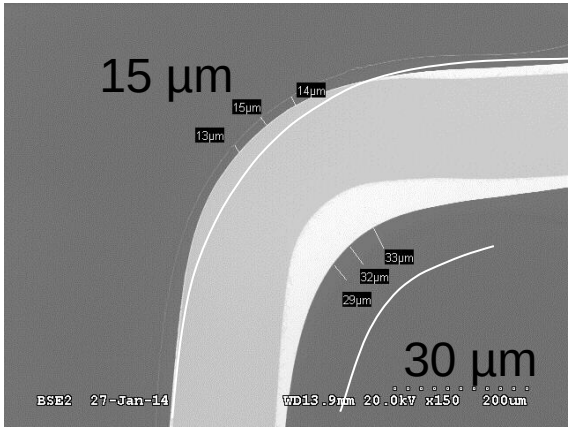
Unfilled PU: coatings cracks; whisker growths within cracked areas

Nanoparticle-filled PU: more crack resistant; no whisker growth under or through any coating

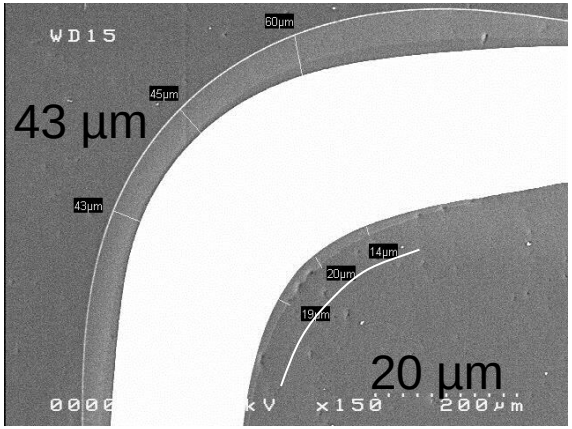
Quantifying Coating Coverage on Quad Flat Pack



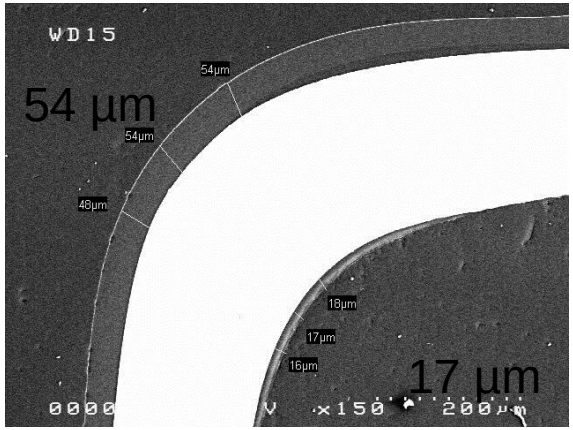




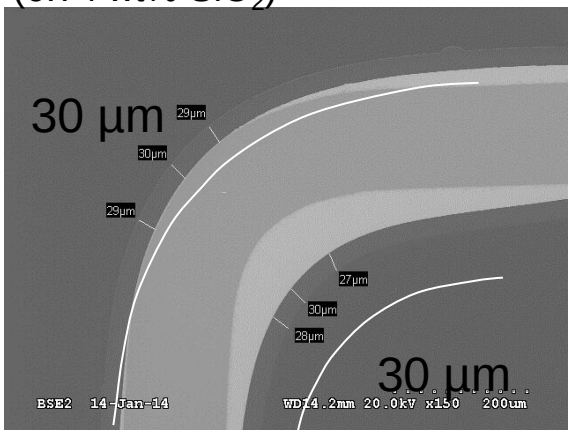
Unfilled PC18M



PC18M with 20% XP2742 (6.74 wt% SiO_2)



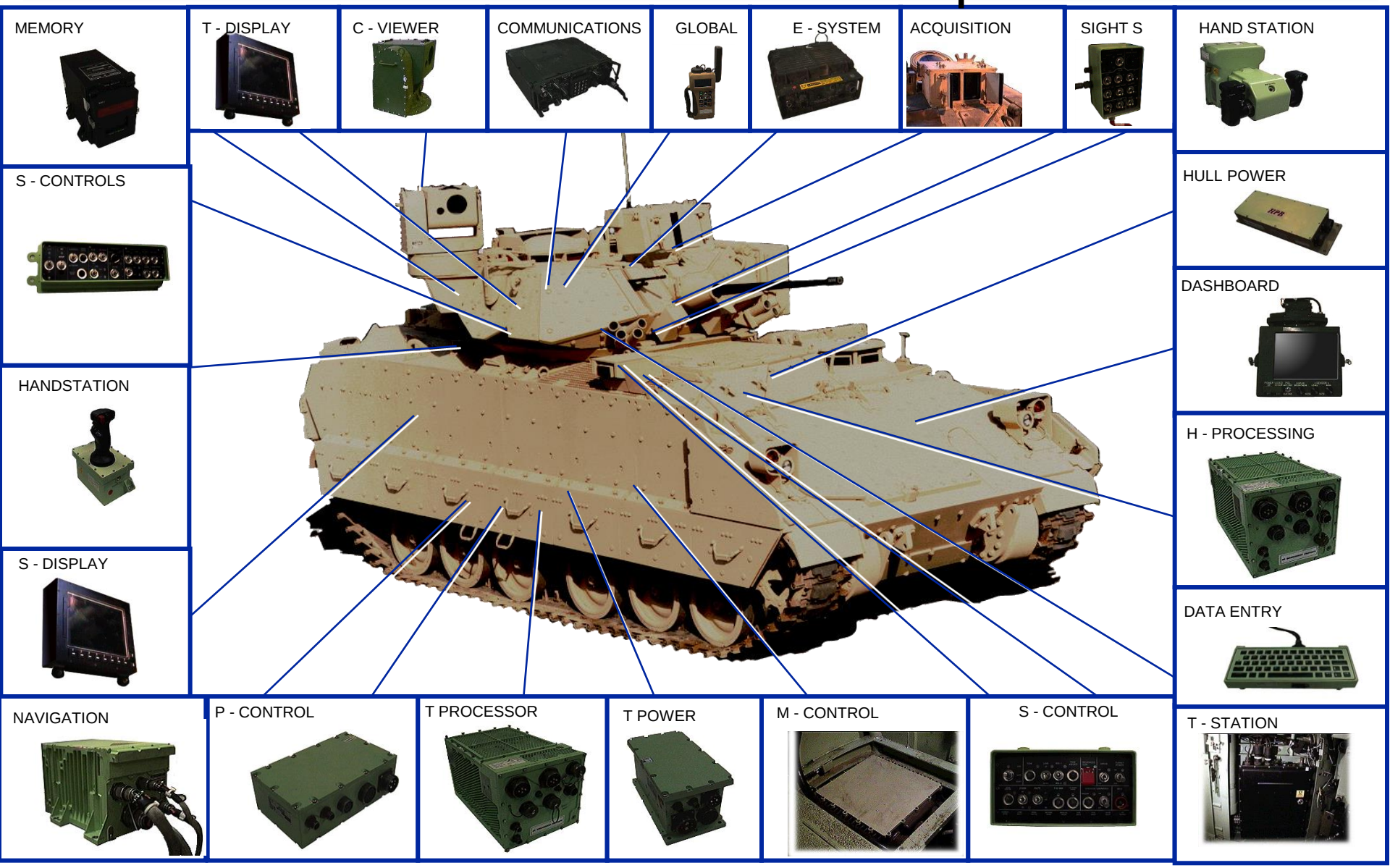
PC18M+20% X11102PMA (13.04 wt% Al_2O_3)



Parylene™ C

Cross-section shows actual coverage

Combat Vehicle: No Whisker Surprises Wanted



Failure Modes and Effects in DoD and Aerospace Products

- Environmental stresses are more extreme
  - Outdoor operation: day/night thermal cycles
  - Direct sunlight, rain, salt water, space
  - Shock and vibration
- Multiple mission-critical systems on board make a single-point failure more likely
- Product life is long
  - Design life of 25 years is common, actual use past 75 years
- System must survive repairs

User must survive failure events

Equipment must survive repair events

Conclusions

- PC18M with nanoparticle properties approach Parylene™ C films
  - Optimal properties: PC18+20%XP2742 (6.74 wt.% SiO_2)
  - Functionalization of nanoparticles
    - Reduced particle agglomeration
    - Strong nanoparticle-polyurethane matrix interface
  - Defects remain an issue: mechanical properties
  - Good surface coverage and cracking resistance
  - Tin whisker mitigation when thick enough
- Low VOC UV-Curable PC40UMF films
  - Localized properties comparable to PC18M
  - Coverage and macroproperties need further work

DoD Benefits

- Military uses commercial-off-the-shelf lead-free electronics
  - Combinations of environments that promote whisker growth stress
    - Unlike consumer electronics
  - Whisker shorts are very difficult to troubleshoot
    - “Gremlins” in the system
- Mitigate – Mitigate – Mitigate
  - Enhanced coatings provides better whisker mitigation
  - Program need education
  - Require SAE/GEIA-STD-0005-2
    - Standard for Mitigating the Effects of Tin Whiskers in Aerospace In High Performance Electronic Systems

For additional information, please visit https://www.serdp-estcp.org/Program-Areas/Weapons-Systems-and-Platforms/Lead-Free-Electronics/WP-2213/WP-2213

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Q&A Session 2

SERDP DOD • EPA • DOE | ESTCP

The next webinar is on March 19

Quantitative Framework and Management Expectation Tool for the Selection of Bioremediation Approaches at Chlorinated Solvent Sites

http://www.serdp-estcp.org/Tools-and-Training/Webinar-Series/03-19-2015

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Please take a moment to complete the survey that will pop up on your screen when the webinar ends

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