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Sandia National Laboratories

Microanalysis of Cd Whiskers on Cd Plated Long-Term Used Hardware

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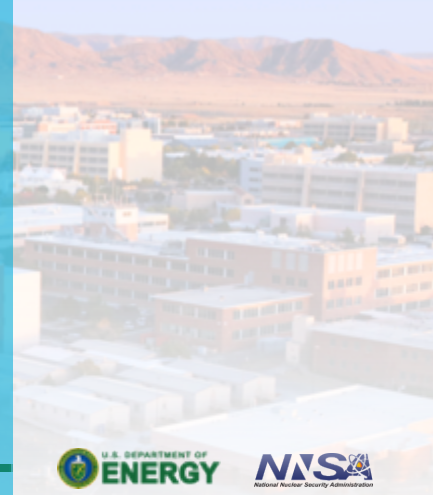

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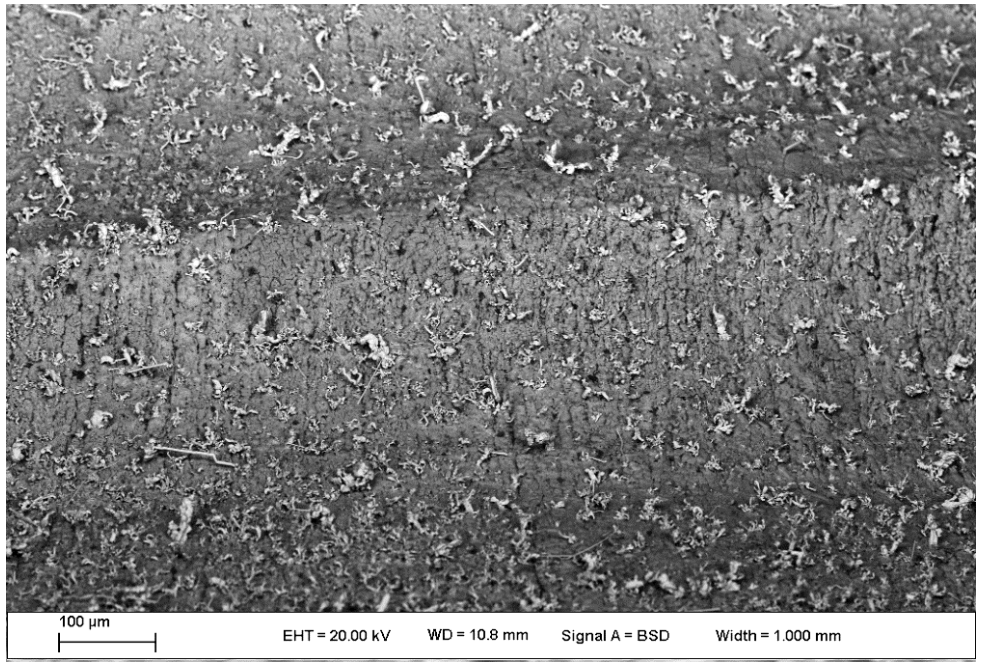
Layout

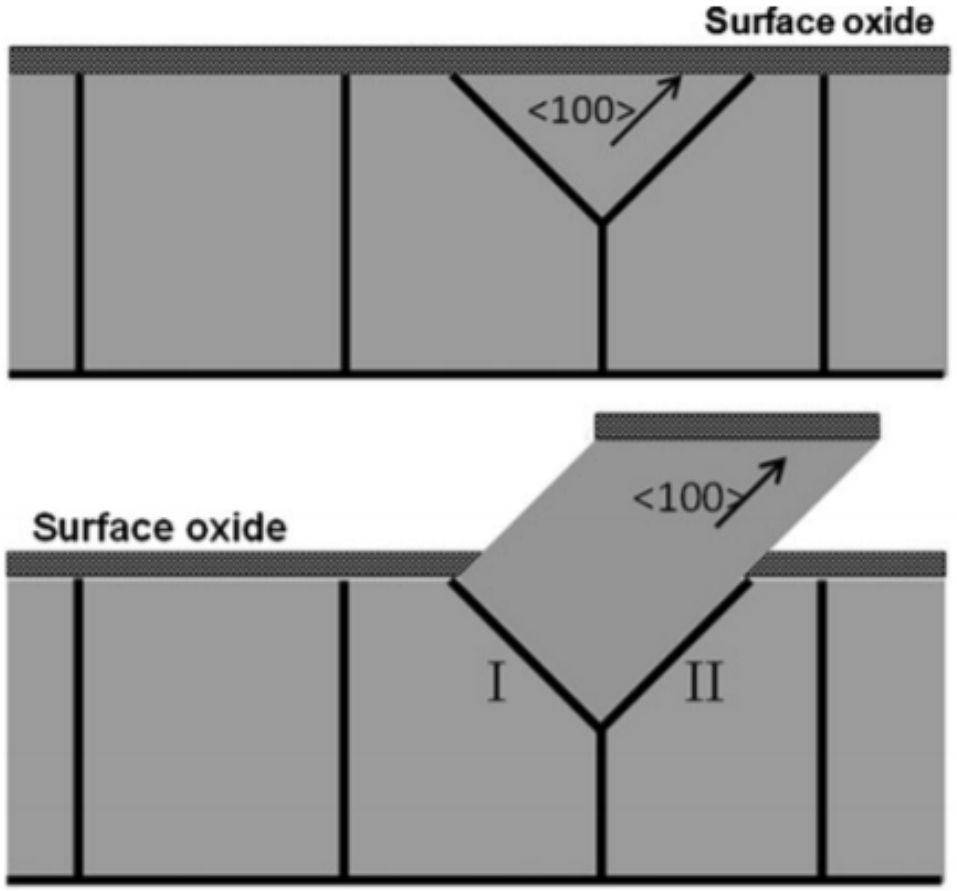
- Metal Whisker Background
- Cd Whisker Morphology
- Microstructural Characterization of Individual Whiskers
  - EDS
  - EBSD/Crystallography
- Goal: contribute to body of knowledge of metal whiskers and evolve whisker evaluation techniques



SEM SE Image of Cd whiskers on cap screw threads

Metal Whiskers

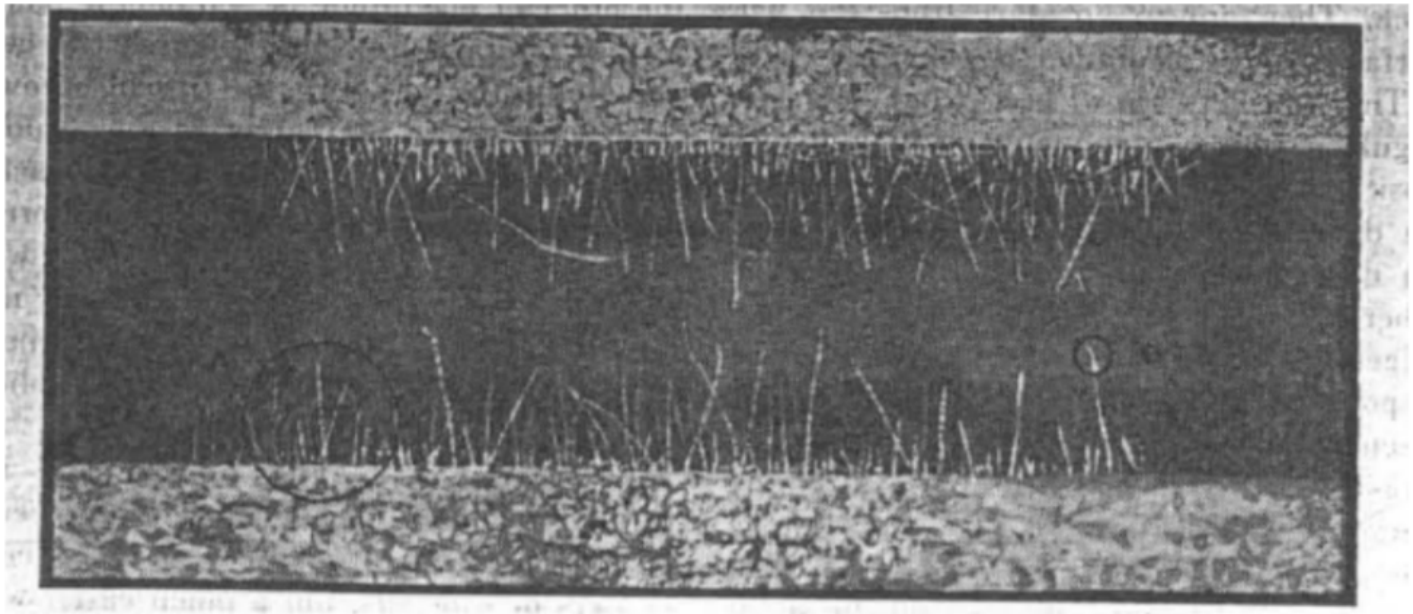
- Whiskering is a stress-relief mechanism for thin (<5μm) electroplated coatings
  - Stresses from plating, mechanical loading, chemical reactions and corrosion, thermal expansion, etc.
- Removing material from stressed location to stress-free location
- Whiskers are generally single crystal with very few defects

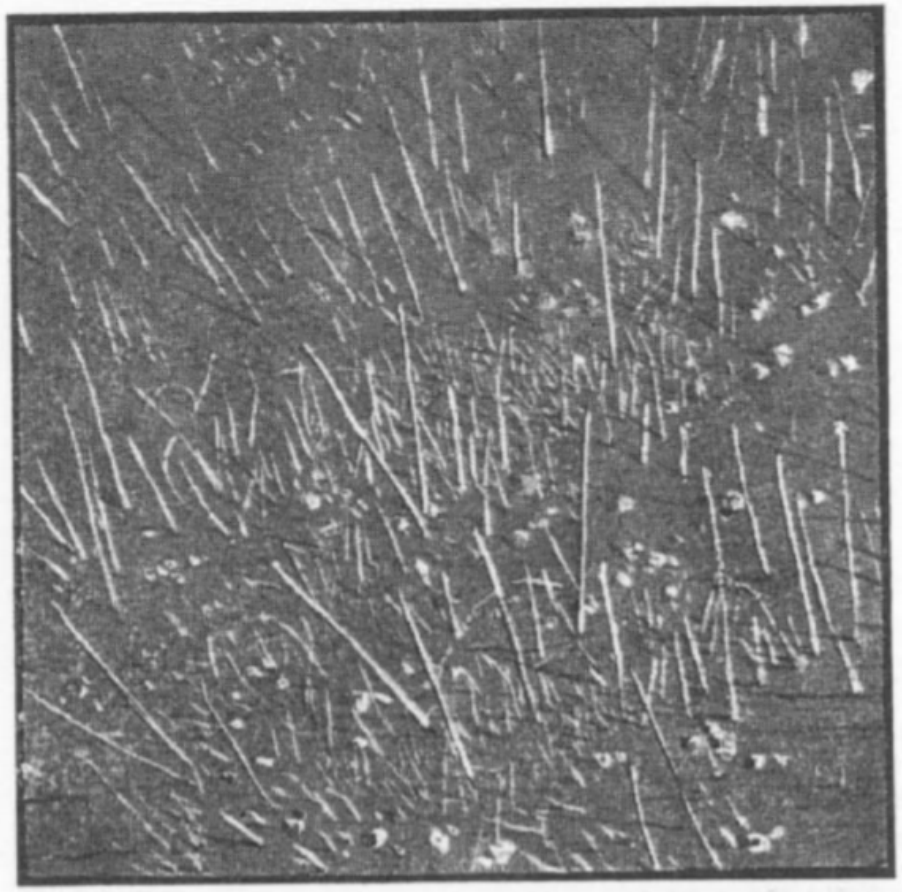


Oblique grain boundaries at the base of a whisker in an otherwise columnar Sn plating
[Susan et al. Met Trans A, 2013]

Cd Whisker History

- Cd whiskers were first discovered in the 1940's between air capacitor plates used in WWII
- Conductive foreign object contamination risk, but not as widely studied as Sn whiskers

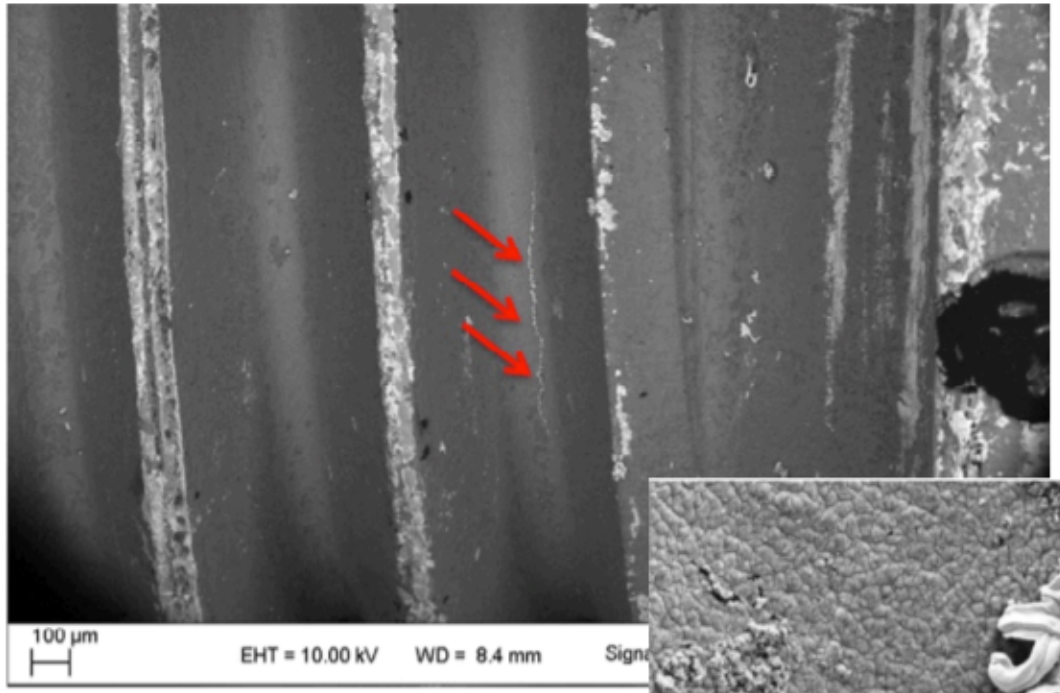




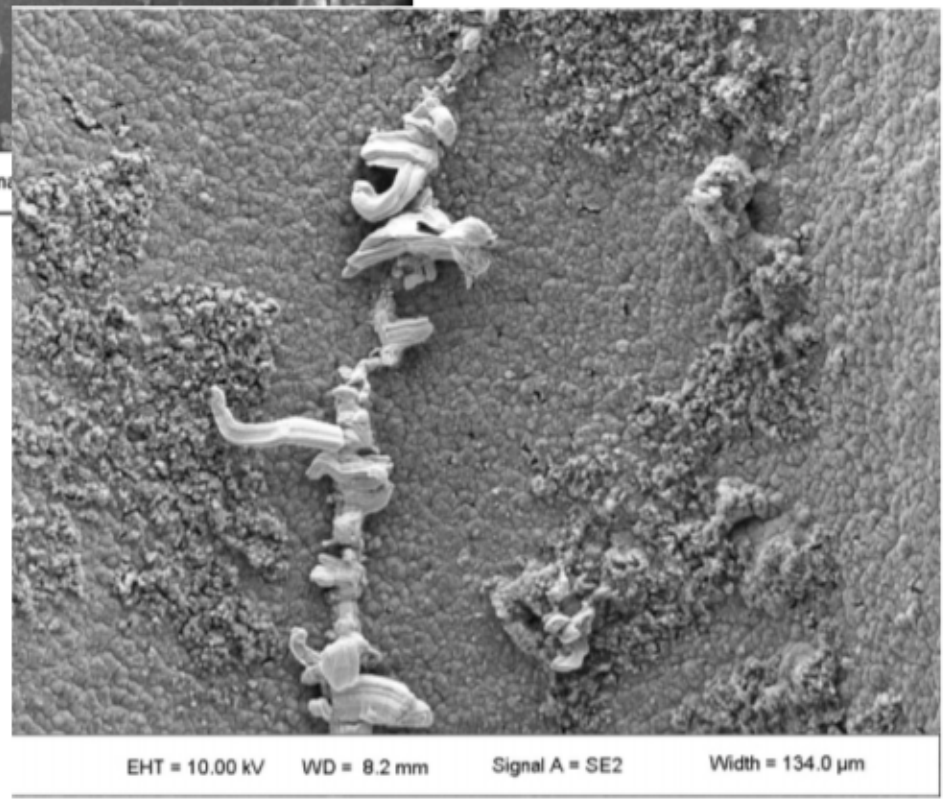
[Cobb. Electroplate Society, 1946]

Cd Whiskers at Sandia

- Observed during an unrelated fastener failure analysis
- Cd whiskers were found growing from a crack in the thread root
- Hardware of indeterminate age found in tool boxes also contain Cd whiskers

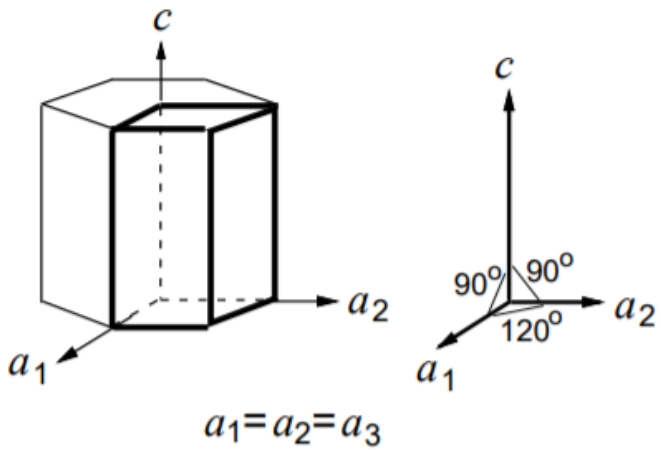


[Rodelas, RGSAM 2013]



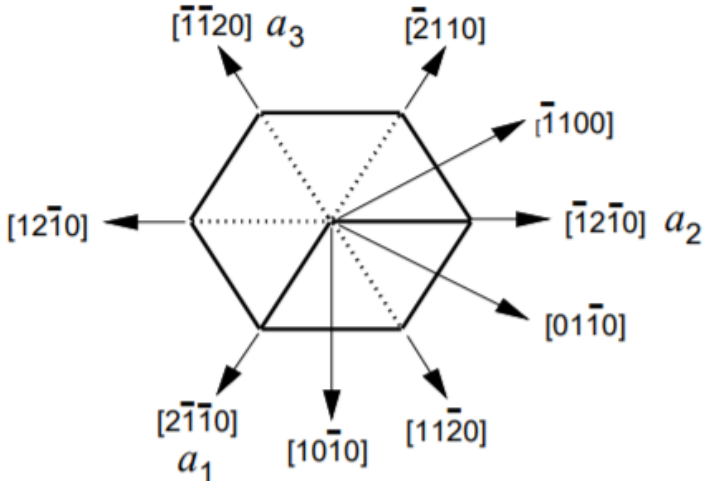
Hexagonal Crystal Structure

- Three main directions
- Growth directions are normal to identical planes for three main axes
- Cd exhibits high c/a ratio



$a_1 = a_2 = a_3$

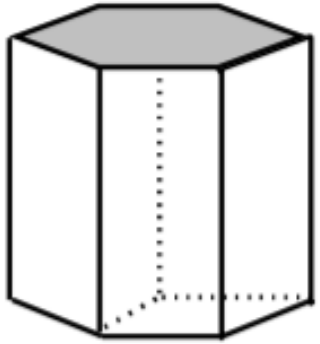
Types of directions



Cd: P63/MMC (194)	
a	0.2979nm
c	0.5618nm
c/a	**1.866**
α	90°
β	90°
γ	120°

Ideal c/a = 1.633

(0001)



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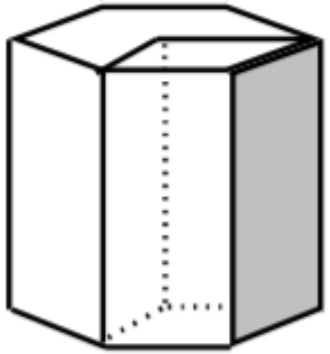

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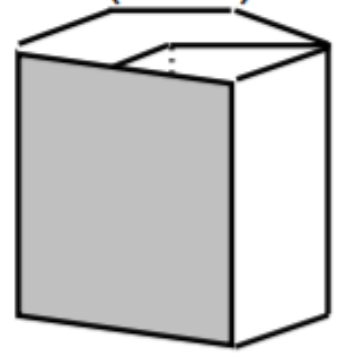
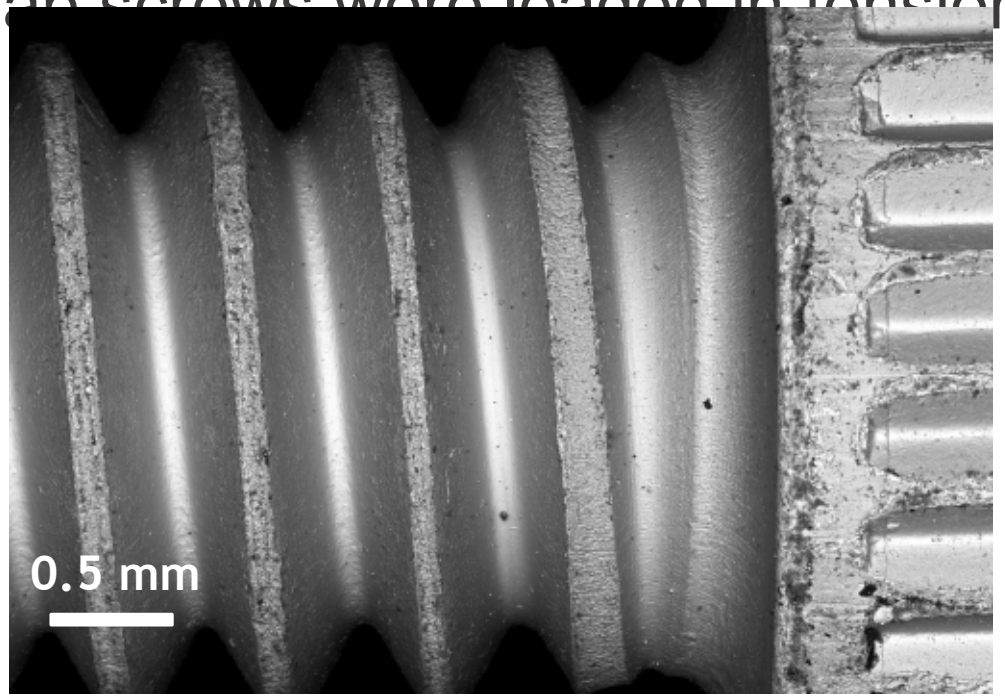
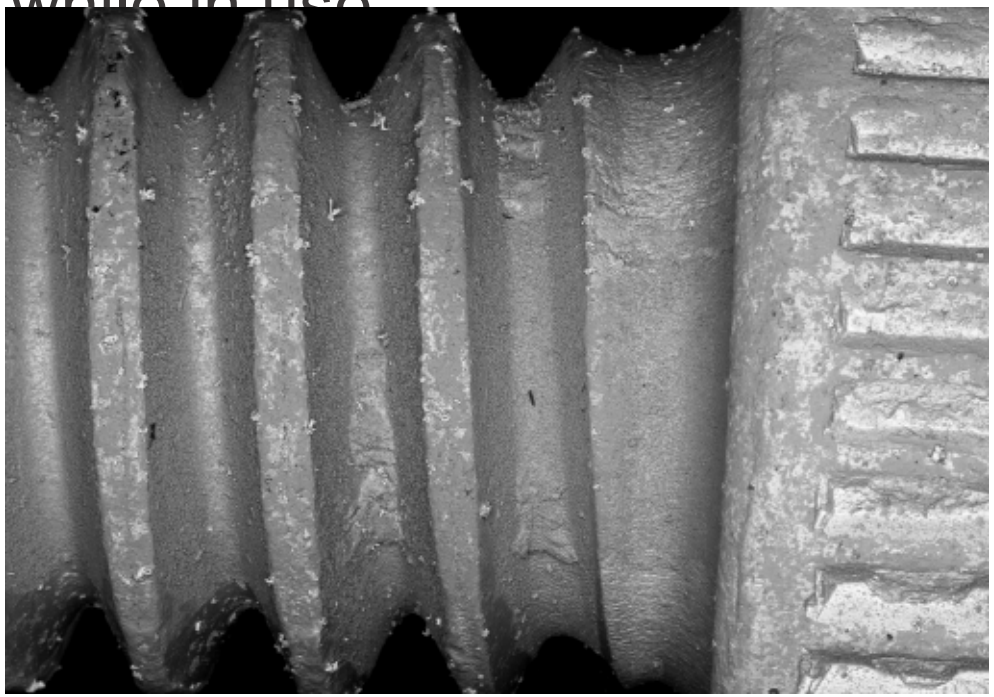


[Tromans. IJRRAS, 2011]

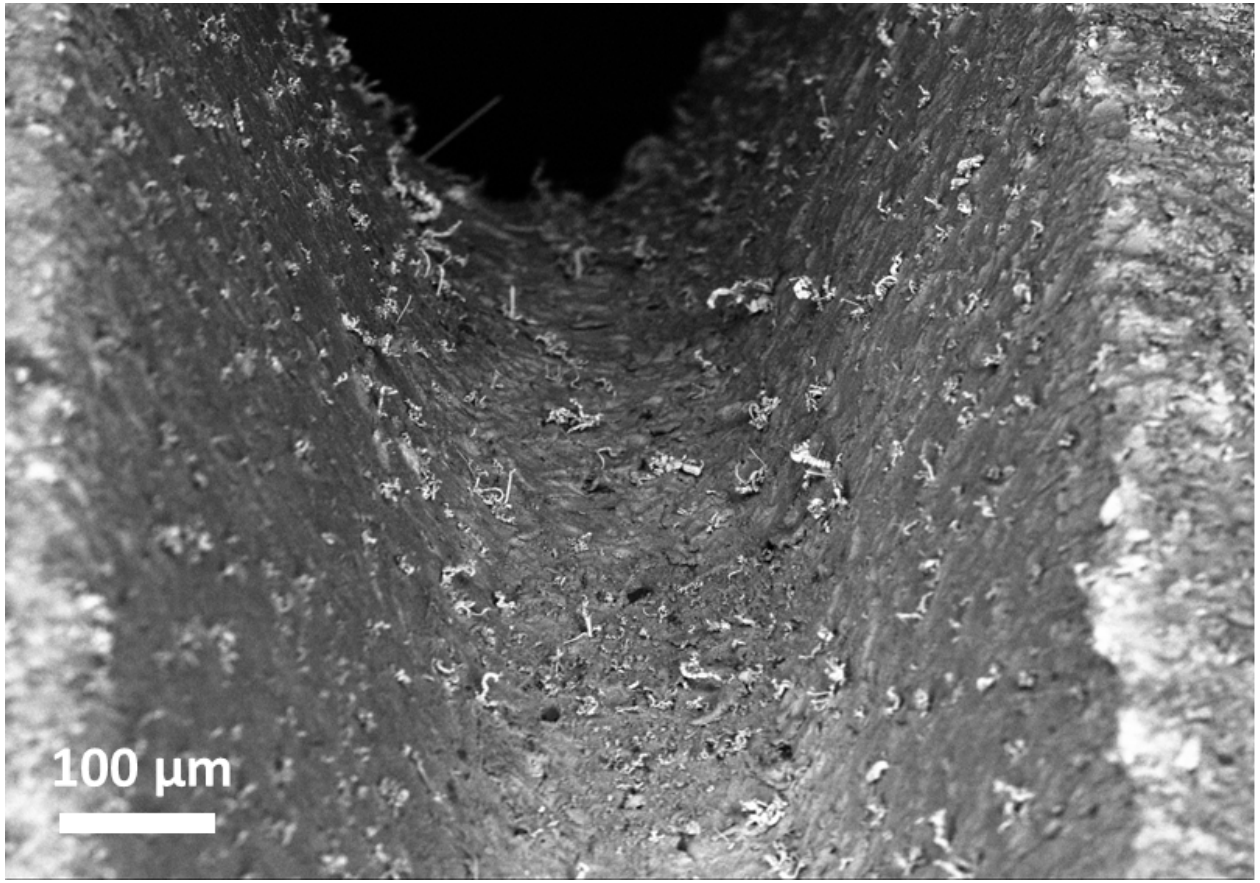
Example of Cap Screws Studied

- Backscatter (BSE) SEM images of
  - [Left Image] an uncontaminated cap screw showing a smooth appearance with very little wear and debris
  - [Right Image] a contaminated cap screw showing uneven contamination (low Z), increased wear (high Z) on the head and threads
- Cap screws were loaded in tension while in use

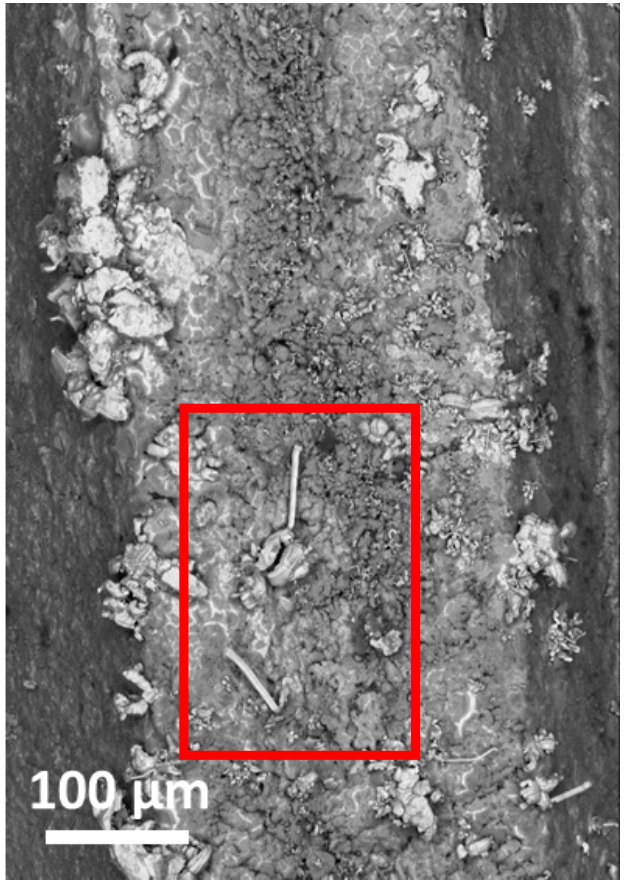




Example Cd Whisker Features on a Cap Screw



SEM BSE image of a thread root (left)



SEM BSE image on the crest of a thread (right) with a box indicating where long, straight whiskers have grown

Example Cd Whisker Features on a Cap Screw

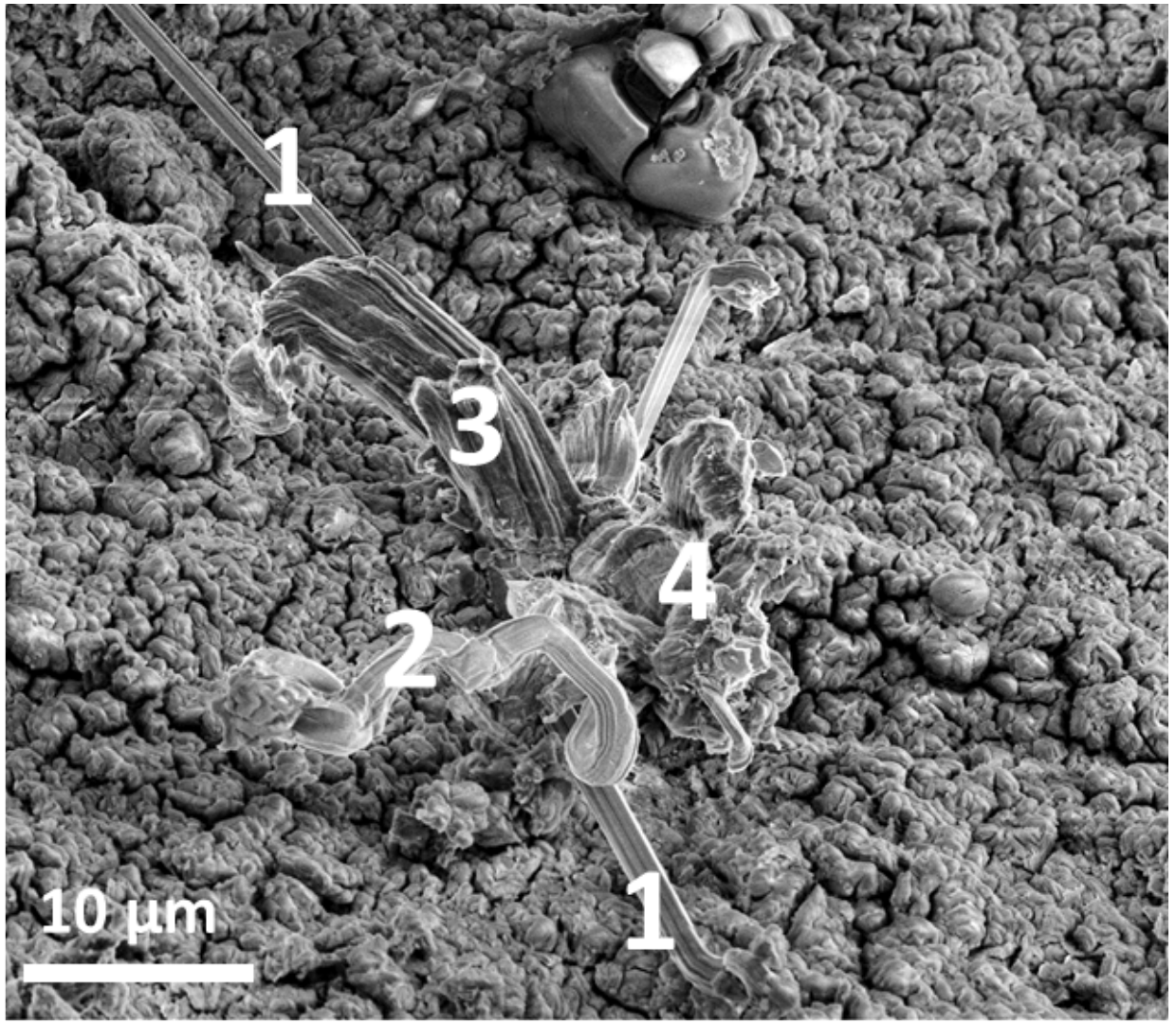
SE image of an agglomerate with several different Cd morphologies

1. Straight and/or kinked whiskers
   - High aspect ratio
   - Single crystal

2. Curly whiskers

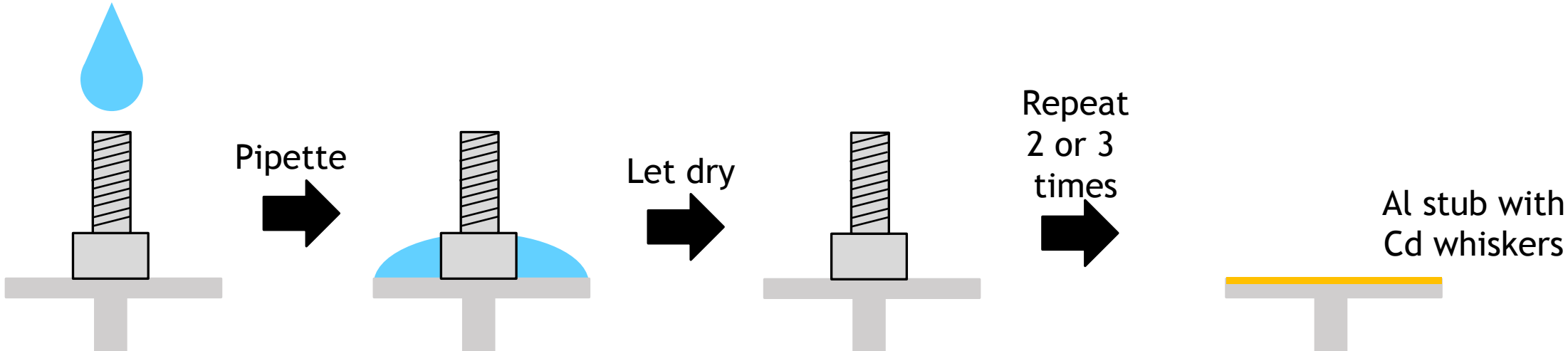
3. “Multi-stranded” whiskers (possibly)

4. Hillocks/Nodules
   - Low aspect ratio



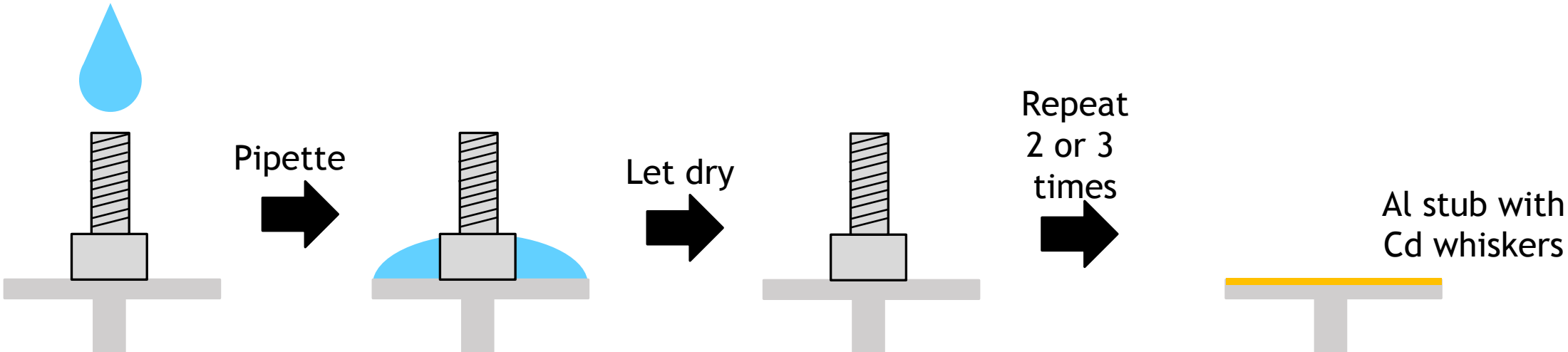
Cd Whisker Study - Approach

- Approximately 200 cap screws and 400 nuts were surveyed
- To study whiskers individually, they were washed from cap screws onto Al stubs using the following protocol:
  - Cap screws were set vertically in the center of a 2 cm diameter Al stub, with the cap screw head down.
  - One or two drops of alcohol were dropped onto the end of each cap screw using a pipette.
  - Once the cap screws dried, step 2 was repeated two or three more times.



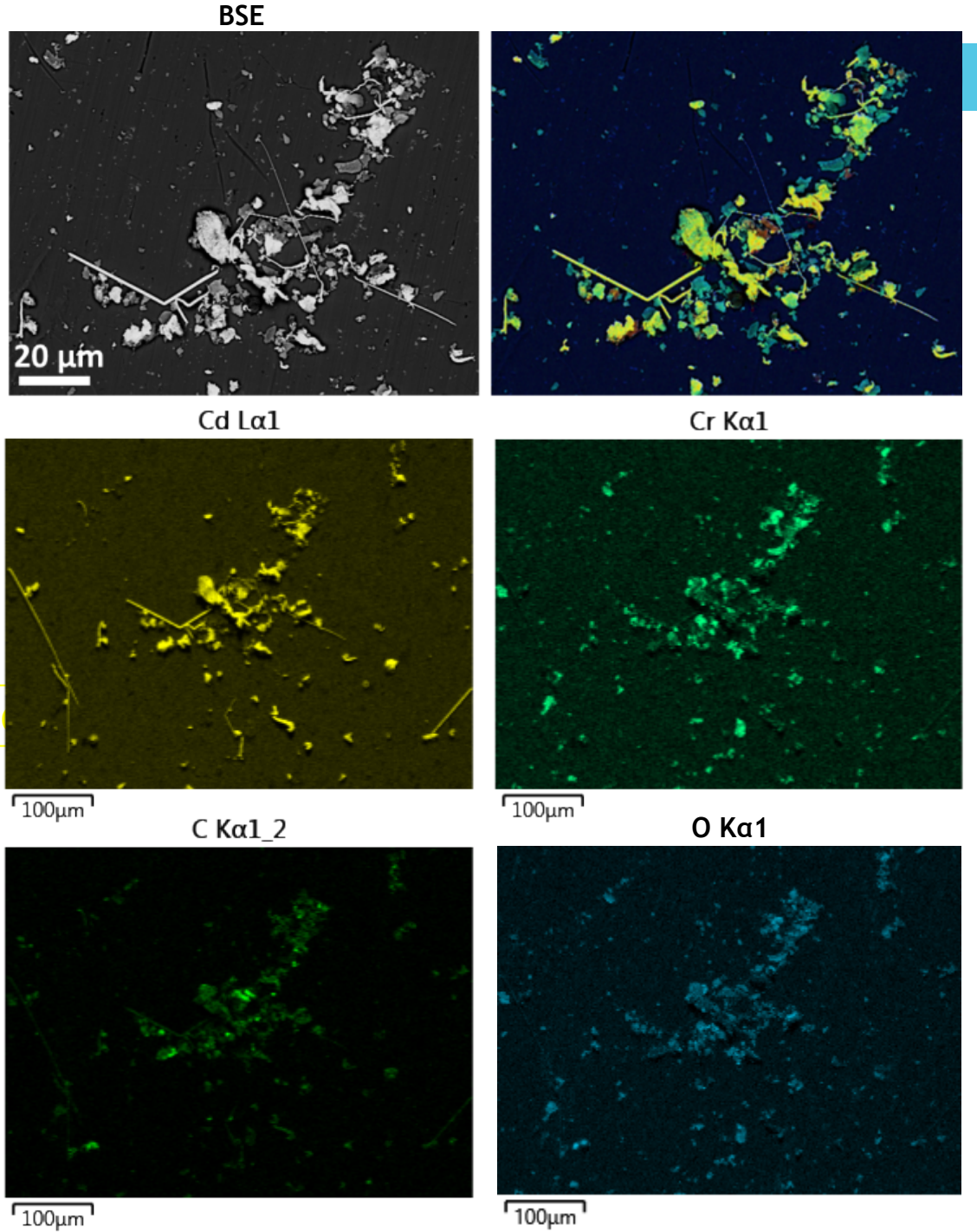
Additional Study Details

- This technique results in minimal distortion of the whiskers, which was confirmed by a lack of plastic deformation in the whisker EBSD maps.
  - Many kinks were very abrupt and had crystallographic significance
  - Kinks likely present in the original whisker
- Hardware may be up to 40-50 years old
  - Exact age, service timeline, and storage conditions of various sets is unknown.



Cd Confirmation on Al Stub

- Energy dispersive spectroscopy (EDS)
  - Most dense concentration of whiskers were found on most visibly contaminated cap screws
- Pure cadmium (yellow) and chromate (teal) were found as well as possible organic contamination, cadmium oxide and/or cadmium carbonate from environmental contamination.
- Debris morphology and composition appear to vary between hardware sets
  - Possibly from different environmental exposures.



Representative Whisker with Kink

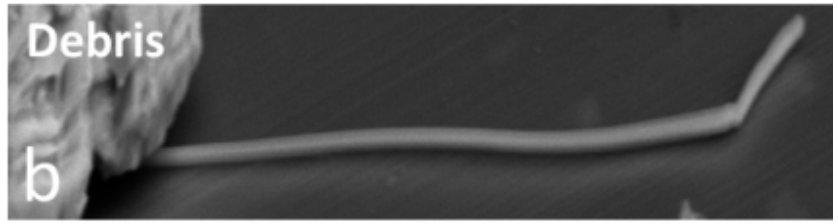
The kink of a whisker studied in detail

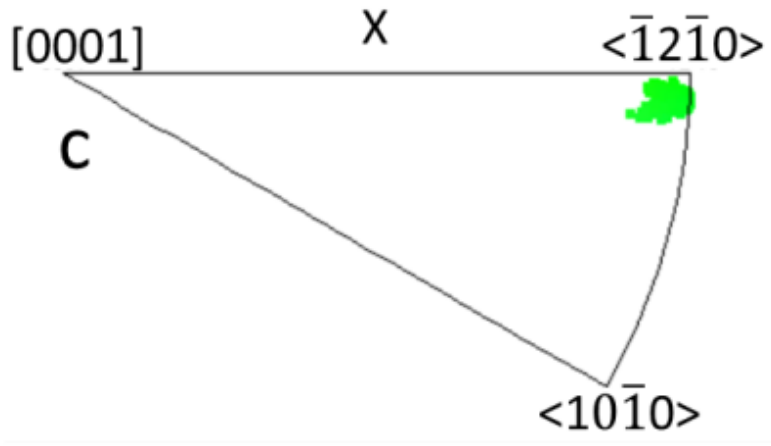
(a) EBSD IPF X map

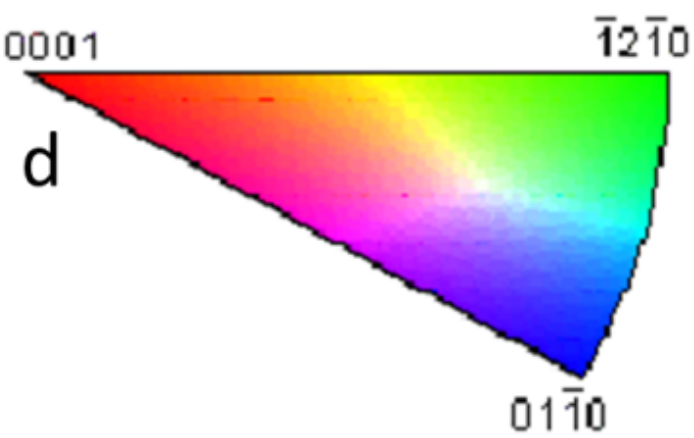
(b) secondary SEM image

(c) IPF of the whisker showing a single crystal with a <$\bar{1}2\bar{1}0$> type growth direction

(d) the IPF map orientation color key

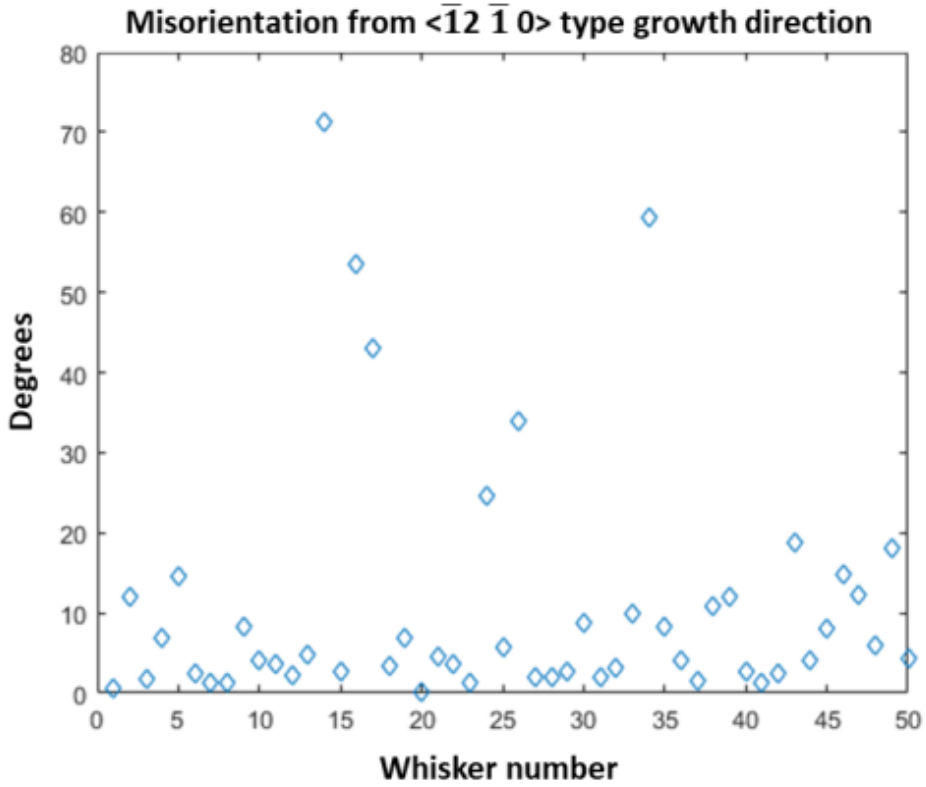


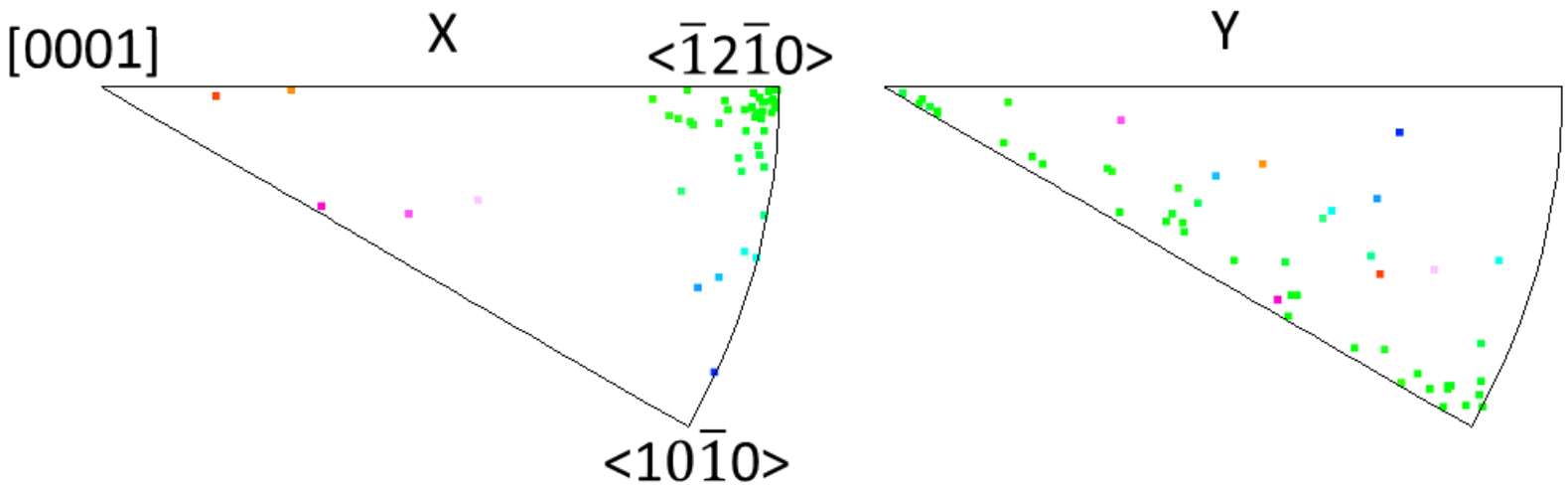


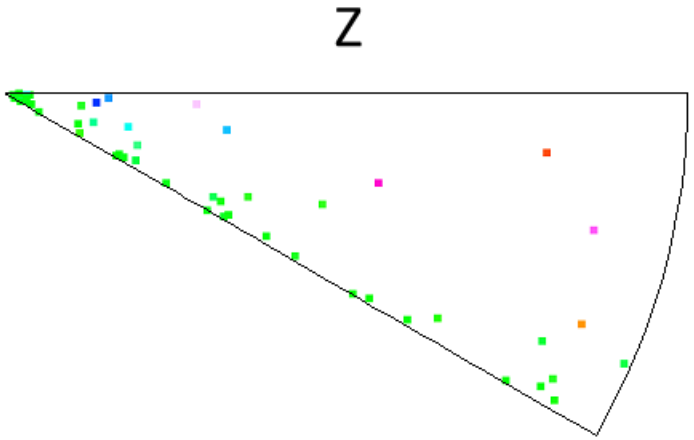


Whisker Growth Orientation

- 50 straight, x-oriented, whiskers were compiled into one pole figure
  - 80% were within 15° of a <$\bar{1}2\bar{1}0$> type growth direction
  - 20% grew in directions other than the {$\bar{1}2\bar{1}0$} type
    - → less favorable growth directions are possible
  - Perhaps only if the plating stress is very high in these locations (i.e. there exists a very high thermodynamic driving force)
- Sn has been shown to grow in a variety of directions including <100>, <210>, <001>, <101>, and <110>



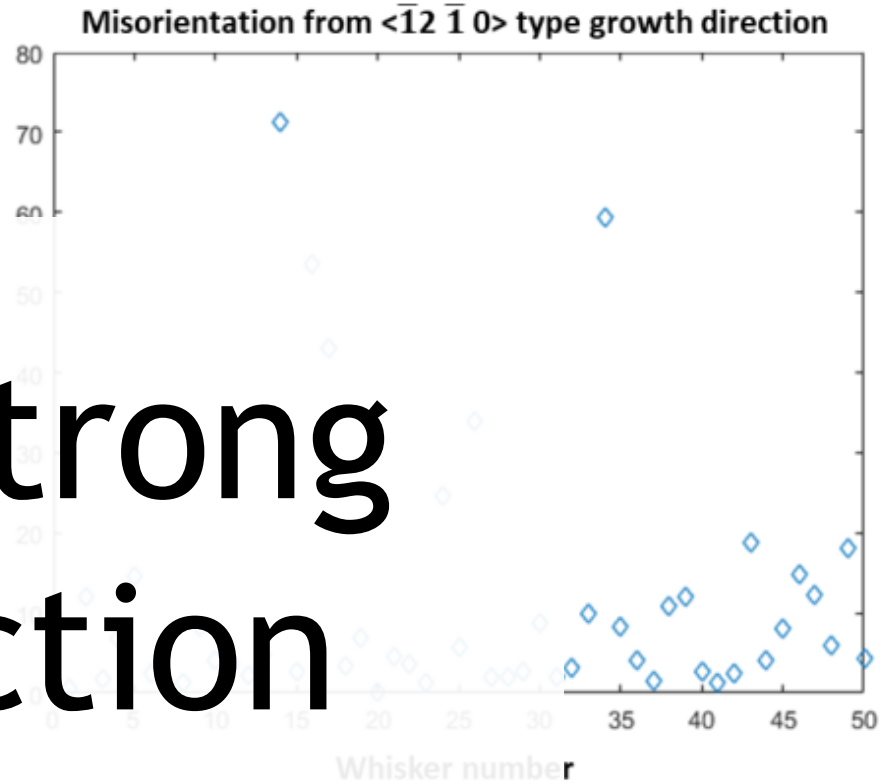




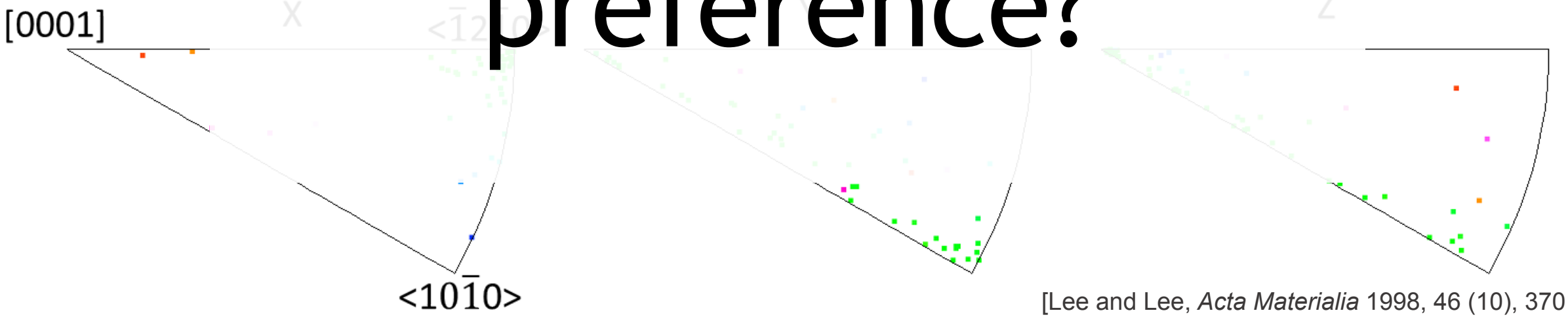
[Lee and Lee, *Acta Materialia* 1998, 46 (10), 3701-371
[Susan et al. Sandia LDRD Report 1998]

Whisker Growth Orientation

- 50 straight whiskers were compiled into one pole figure
  - 80% were w
  - 20% grew ir
    - → less
    - Perhaps or locations (driving for
- Sn has been including <1(



Why such a strong growth direction preference?



[Lee and Lee, *Acta Materialia* 1998, 46 (10), 3701-371
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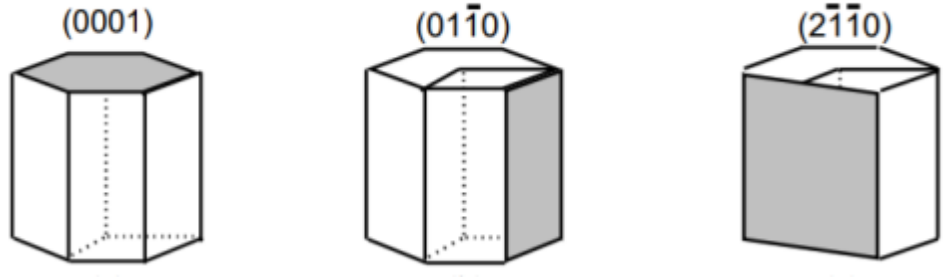
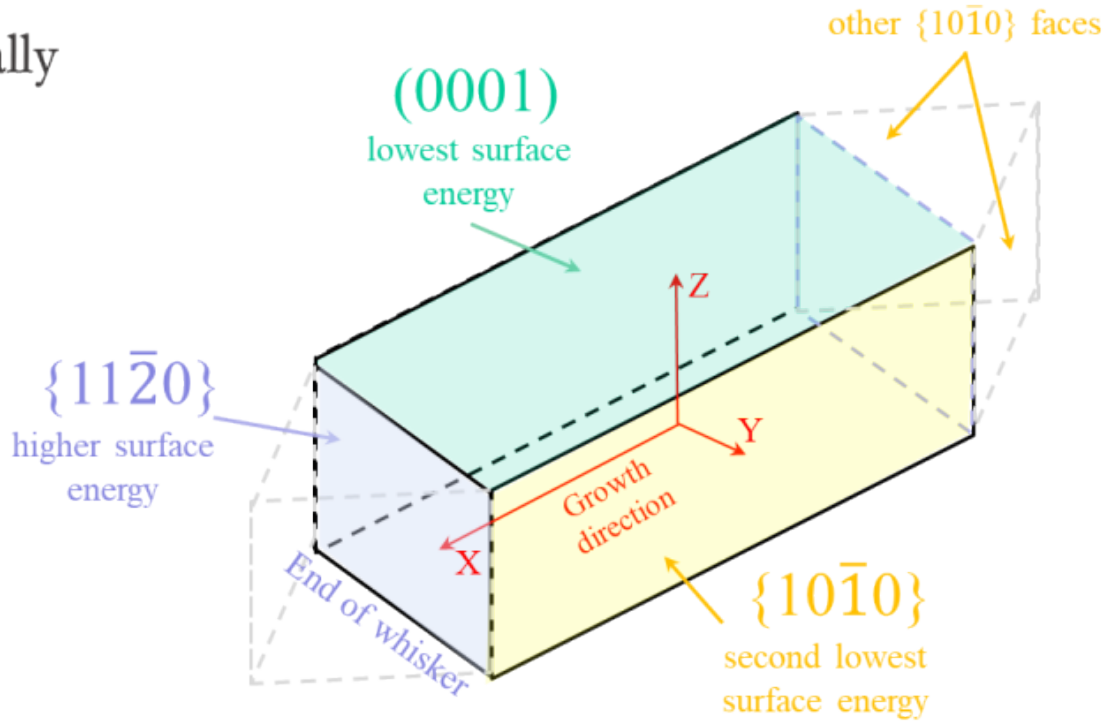
Energetically Optimized Whisker

- Growth direction sets the whisker side faces
  - Energetically optimized with (0001) and {10$\bar{1}$0} side faces!
- This data shows that Cd whiskers grow to minimize their surface energy.
  - Gibbs free energy minimization by stress relief and energetically stable whiskers
  - This crystal growth optimization is more energetically consequential for anisotropic materials like Sn, Cd, and Zn
  - Cd and Zn have high c/a ratio which results in unideal atomic packing and anisotropic properties.
  - As the c/a ratio increases, the formation of low energy planes becomes more important



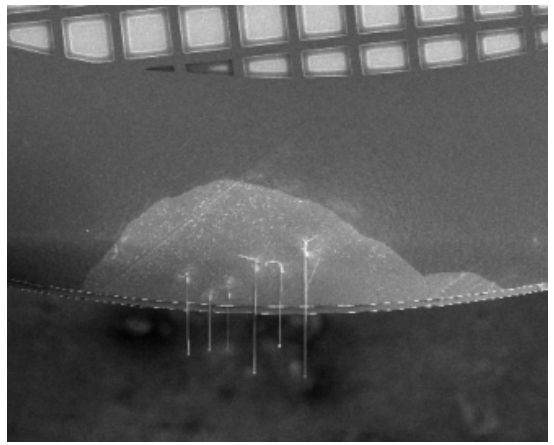


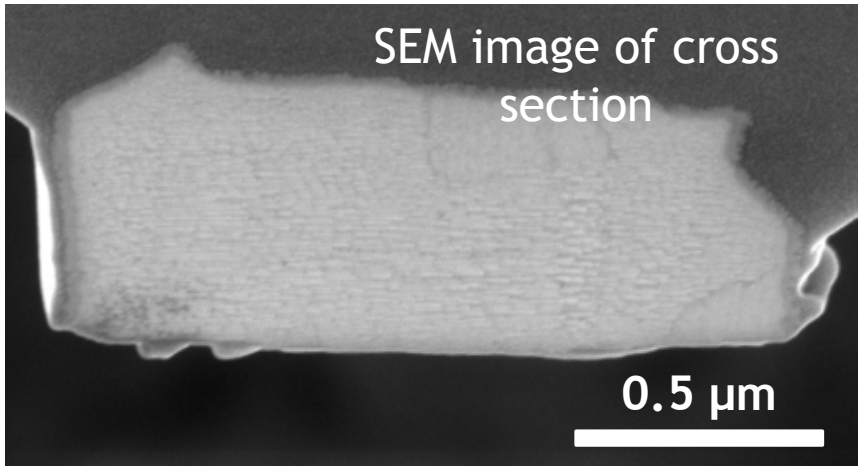
Material	(0001)	{10$\bar{1}$0} type	{$\bar{1}$2$\bar{1}$0} type
Be (c/a=1.568)	1.00	1.00	1.00
Ideal (c/a=1.633)	1.00	1.06	1.20
Cd (c/a=1.886)	1.00	1.50	1.95

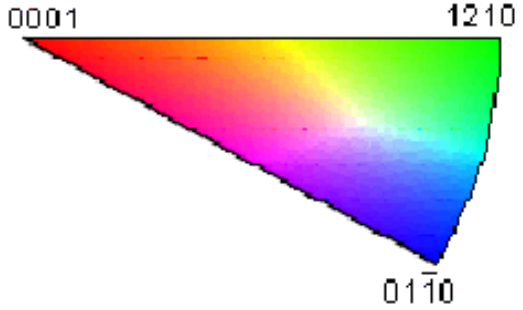
[Matysina, Mat. Chem. And Phys. 1999.]

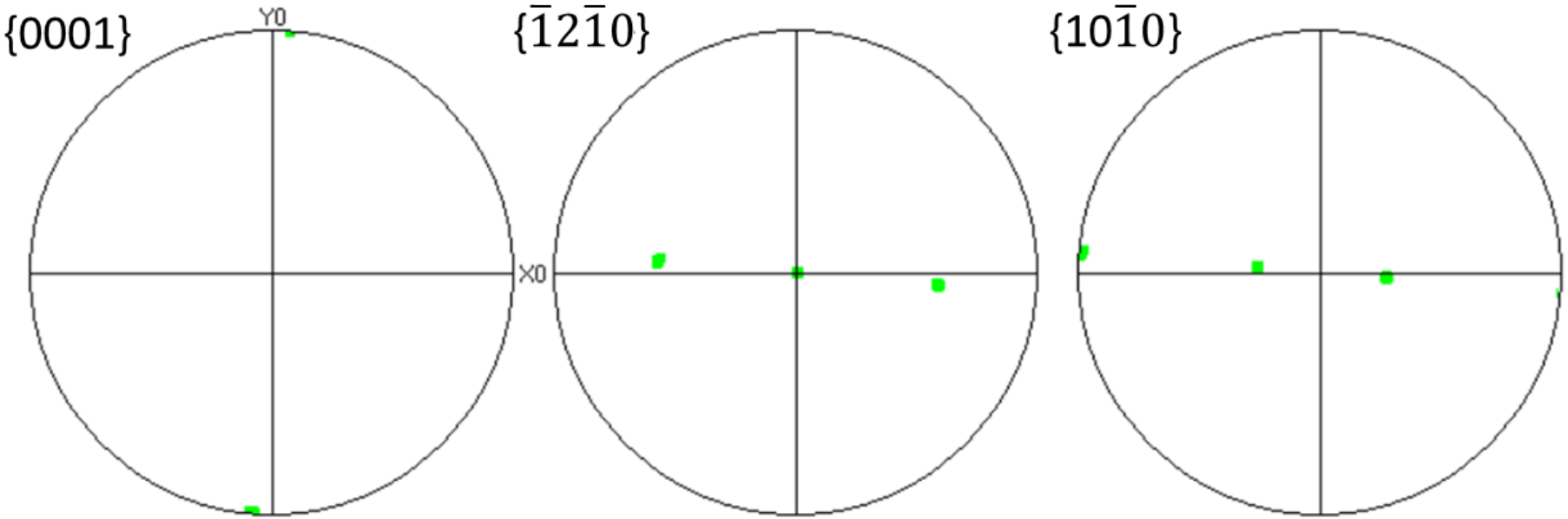
“Nearly Ideal” Whisker

- Focused ion beam (FIB) cross section on end of whisker and EBSD to determine growth direction and side faces
- Does this energy optimization actually happen?
  - ~50% of surface area of five <$\bar{1}2\bar{1}0$> type whiskers
  - 87% of surface area of “nearly ideal” whisker





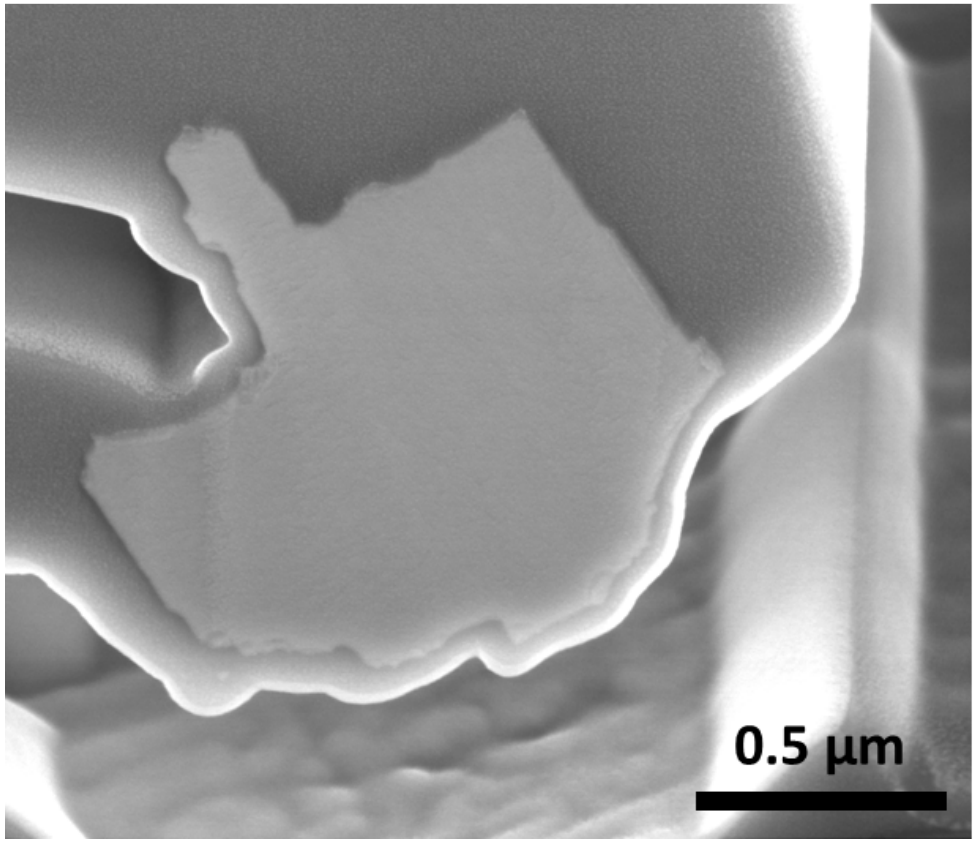


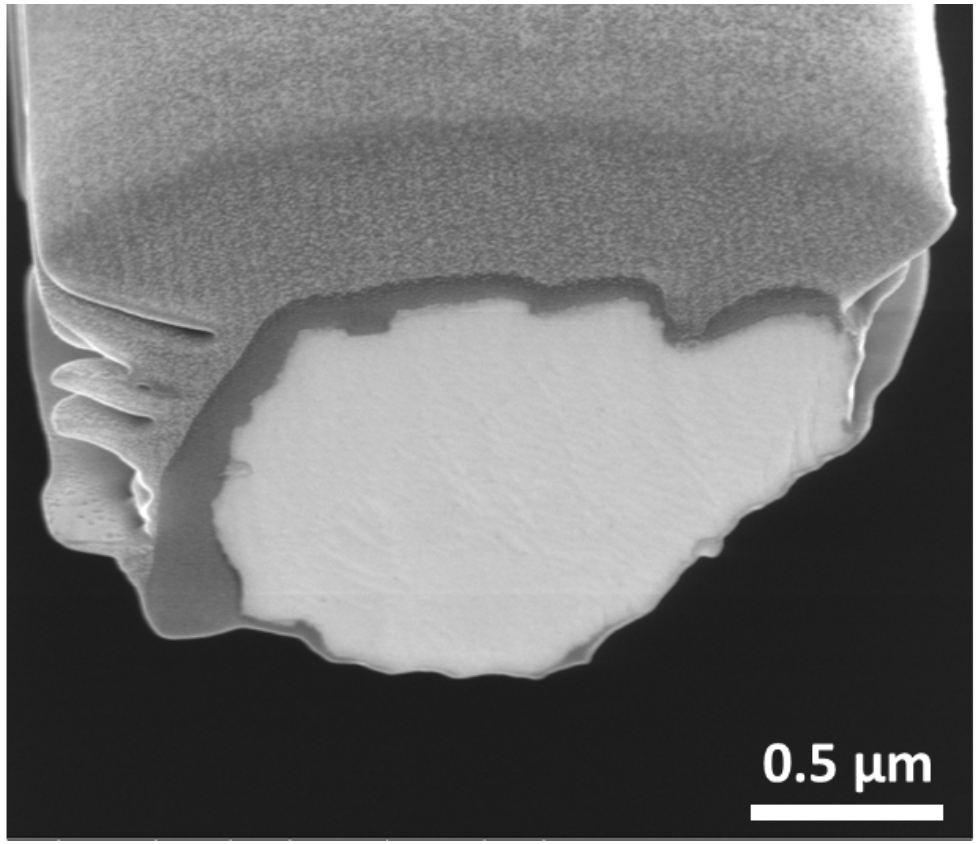


Surface energy is only *one* of the factors

With a high driving force to reduce stress in plating, whiskers of all shapes and sizes can form

- Are influenced by plating (voids, grain shape, etc.)





Conclusions

- Cd whiskers on old, used cap screws are very common. More contaminated and worn hardware exhibits more whisker growth. The contamination appears to be both organic and inorganic ("dirt", cadmium oxide and/or carbonate).
- Similar to other metal whisker systems, there are many morphologies of Cd features including straight and kinked whiskers, curly whiskers, and nodules. Cd features are often agglomerates of these morphologies.
- EBSD analysis showed that 80% of 50 Cd whiskers grew in a $<\bar{1}2\bar{1}0>$ type direction, consistent with previous studies of Cd whiskers grown from the vapor phase. Many of the whiskers exhibited cross sectional features biased toward the formation of (0001) and $\{10\bar{1}0\}$ side faces. These low energy side faces minimize the energy of the system and are one of the many factors which influence the geometry of whiskers and nodules.

Acknowledgements

- Joe Michael for detailed crystallography discussion
- Mark Rodriguez for XRD analyses

- This work was funded by Sandia National Laboratories Aging and Lifetime program