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Cadmium Whisker Growth on Cd-Plated Steel Fastener Hardware

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Outline

This is an overview of observed Cadmium whiskers. More detailed characterization work to be covered in follow-on presentation (Z. Ghanbari).

- Historical background
- Initial observations
- Surveys of Cd-plated fasteners for whiskers
- Attempts at growing Cd whiskers in the lab

Historical Background

- Cadmium whisker growth was first reported in 1946 (H.L. Cobb)
- Whisker growth between plates of air capacitors used in military equipment. During World War II.
- Interest in Cd whiskers faded due to overwhelming focus on tin whiskers in microelectronics. For example, nepp.nasa.gov compiles literally hundreds of papers on tin whiskers; Only 3 papers for Cd whisker growth.
- *Metallic whiskers represent a conductive debris hazard (short circuit hazard), especially if present near sensitive electronics.*

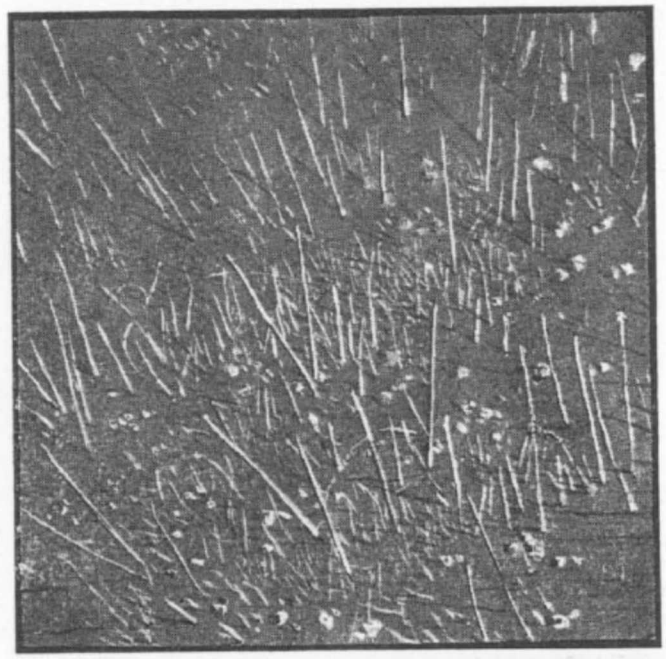


Fig. 4. Perspective view of cadmium whiskers. Found in the square shown in Fig. 1. Hand drawn. X22.

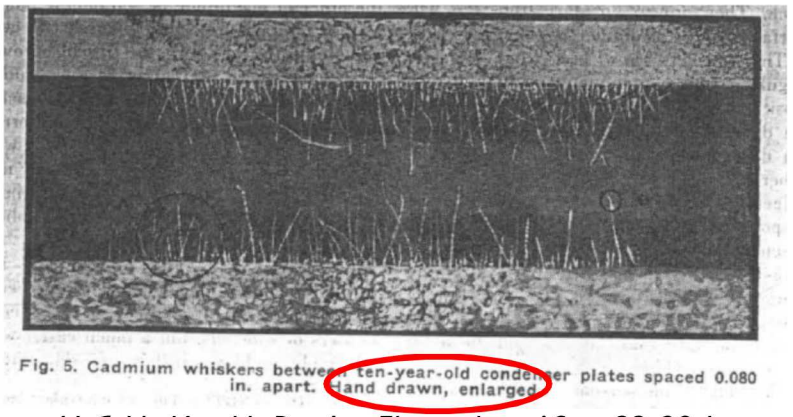
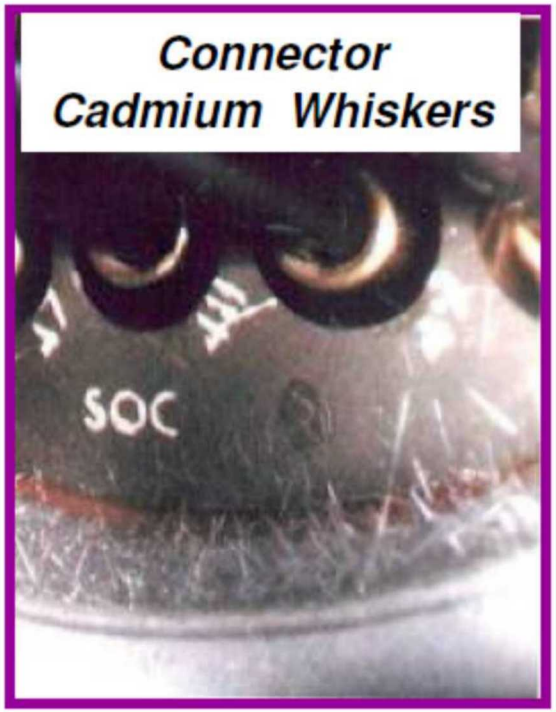


Fig. 5. Cadmium whiskers between ten-year-old condenser plates spaced 0.080 in. apart. Hand drawn, enlarged.

H. Cobb, Monthly Rev. Am. Electroplaters' Soc., 33, 28, Jan. 1946.

Background (continued)



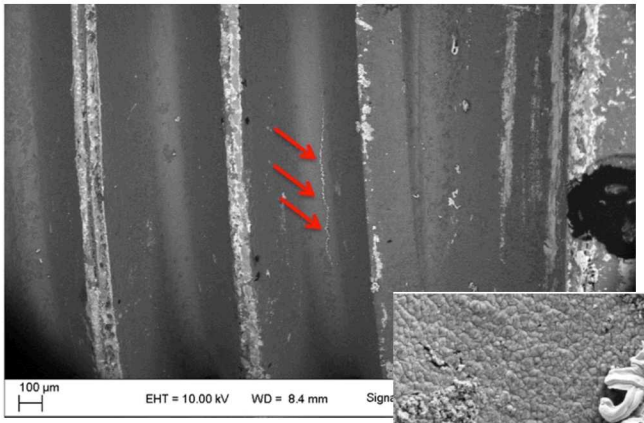
J. Brusse et al., 2007 (NASA)

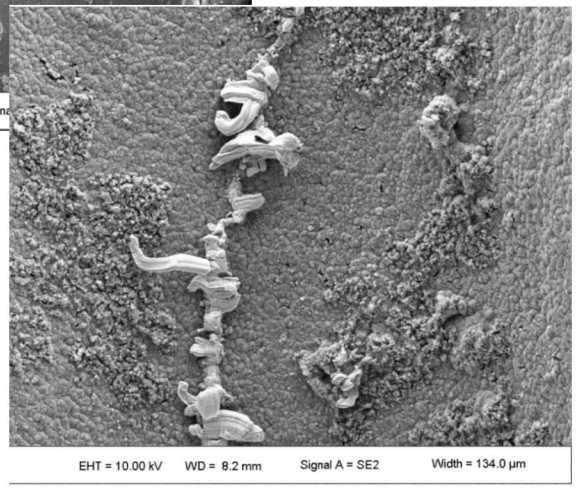
Work by NASA 2007-present:

- Cd whiskers on a feedthrough connector for a thermal-vacuum chamber. Several mm long, produced electrical shorts from shell to pins that interrupted testing of a spacecraft system
- NASA prohibits Cd in all spaceflight systems
  - Cd sublimates in vacuum environments (the main reason for the ban)
  - Cd is toxic
  - NASA also mentions Cd subject to whisker growth
- The NASA ban mentions that Cd is used on fastener hardware. However, to date, no literature found specifically on the subject of Cd-plated ***fasteners…***

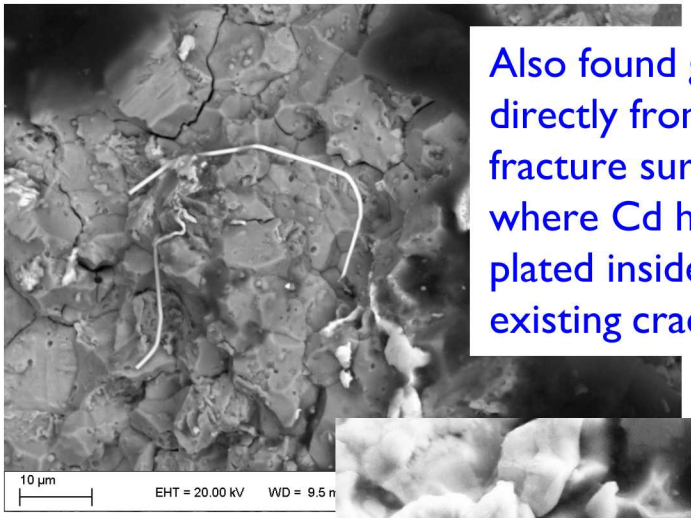
Initial Observation of Cd Whiskers at Sandia

- Cd plating is used on fasteners for sacrificial corrosion protection (in combination with a thin chromate outer coating…gives characteristic yellow/gold or olive drab surface color) especially in saltwater environments. Cd also provides good lubricity which prevents galling.
- Cadmium whiskers were found in 2016 during a failure analysis of a Cd-plated high strength steel, socket head cap screw (whiskers not related to the failure)

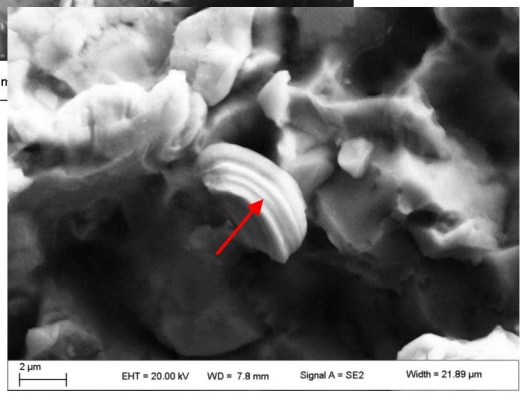




Whiskers initially observed growing from a crack in the thread root



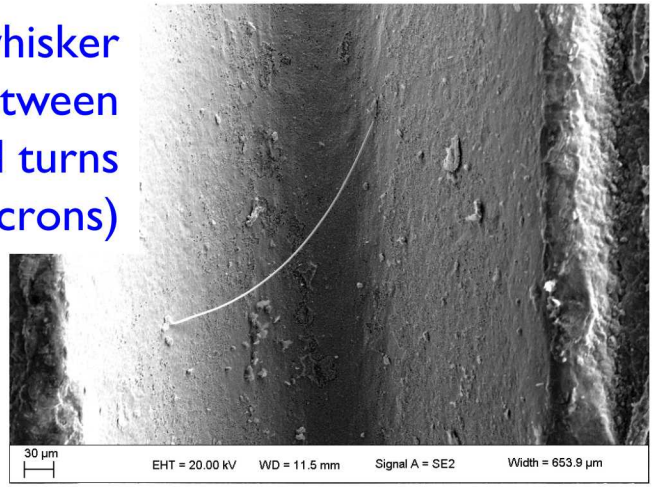
Also found growing directly from the fracture surface, where Cd had been plated inside a pre-existing crack

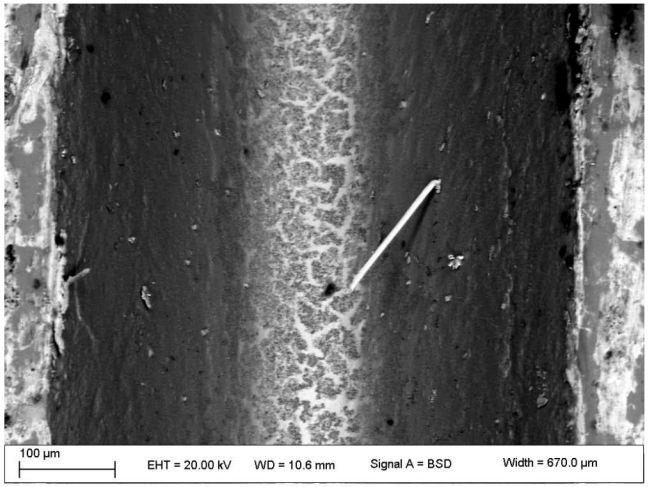


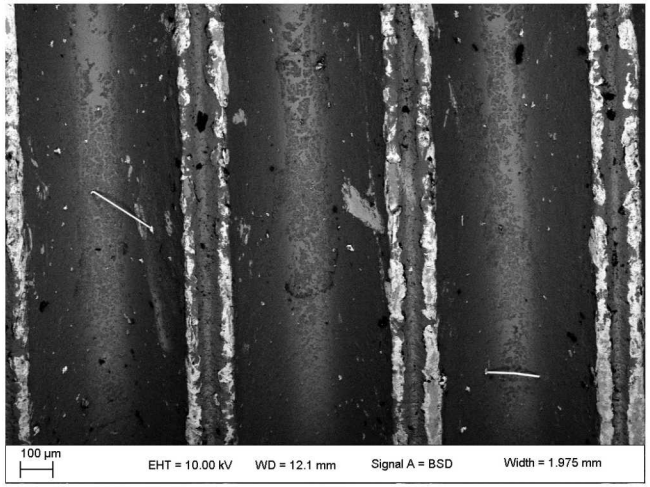
- Long Cd whiskers were subsequently found on the surface of the failed fastener and other fasteners from the same investigation

Bent whisker spanned between thread turns (~300 microns)

Optical (Keyence)



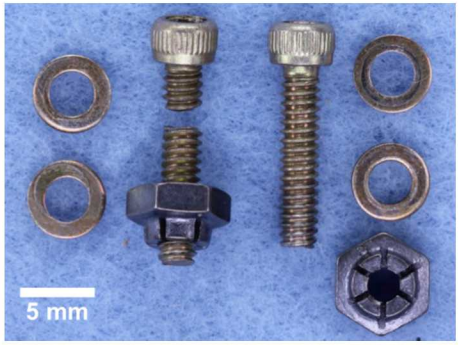


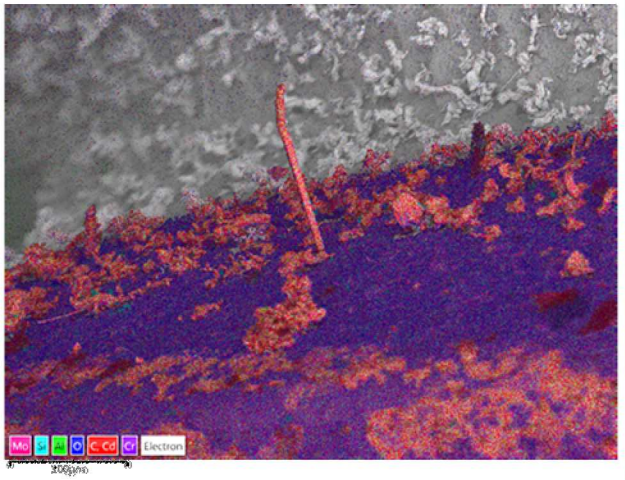


Scanning electron microscopy

Cd Whiskers Observed During Failure Analysis

- In 2016, a failure analysis investigation began on a cadmium- (Cd-) plated, high strength screw failed upon insertion into an assembly
  - **Cause of failure:** Use of incorrect (brittle, high carbon) alloy led to embrittlement and compromised mechanical integrity
  - During the investigation, whiskers were observed growing from a crack in the thread root and on the fracture surface





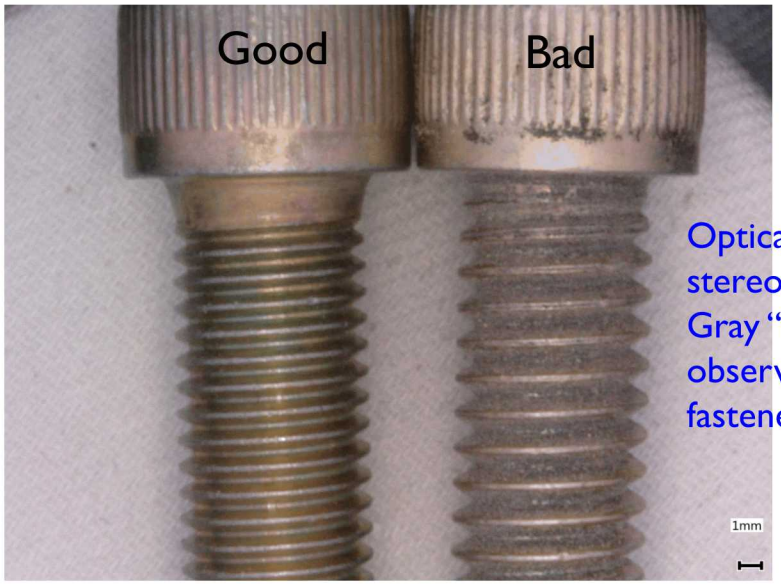
EDS mapping confirmed whiskers as pure Cd.

(Cr signal confirms chromate coating)

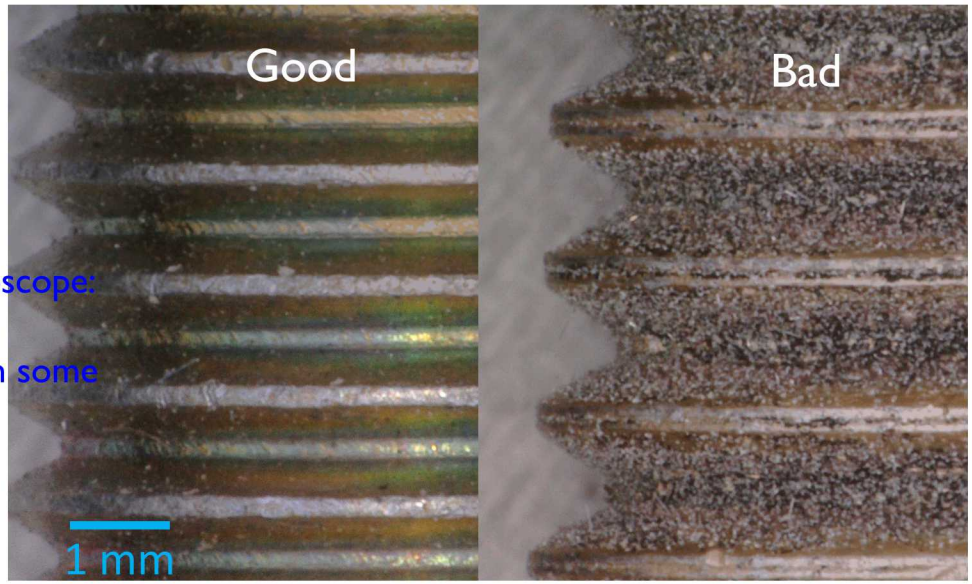
- Though not the cause of failure, long, straight whiskers pose a conductive foreign object debris (FOD) hazard (similar to tin (Sn) whiskers):

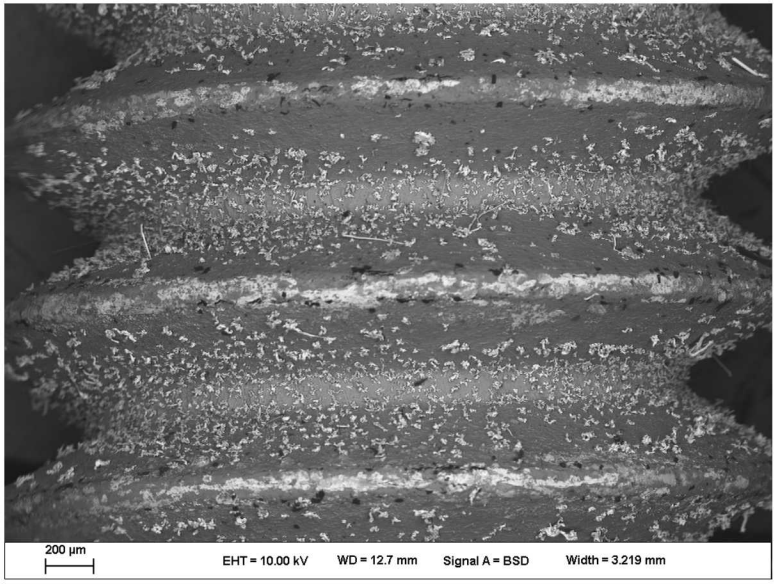
If whiskers become detached, the whiskers could short out nearby circuits - especially when fasteners are used near microelectronics

Fasteners found in laboratory drawers. Unknown age… probably 20 years or more.

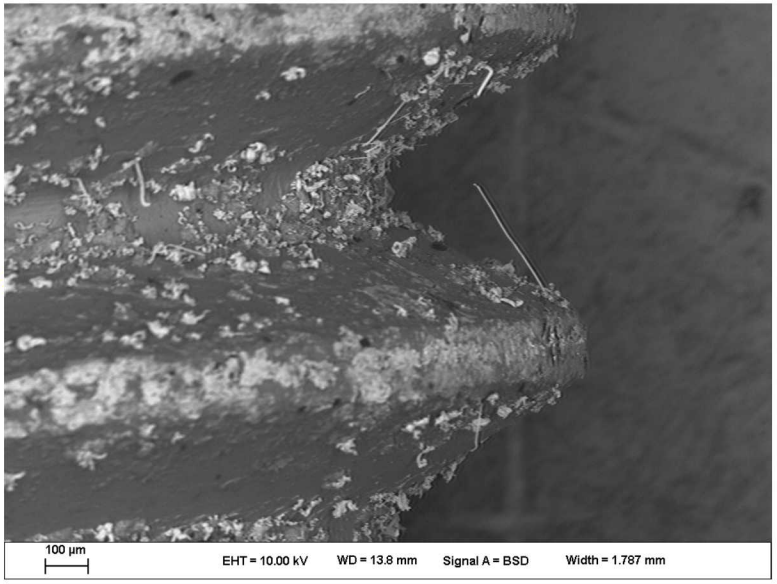


Optical stereomicroscope: Gray "fuzz" observed on some fasteners

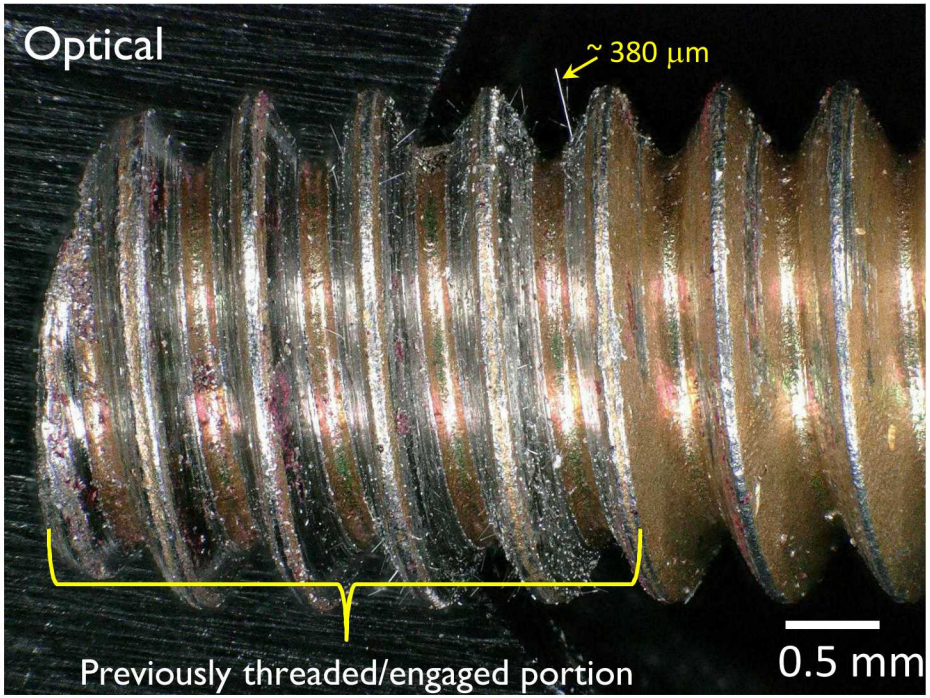




SEM: Ubiquitous Cd nodules and some long whiskers



- In 2017, a project was initiated to collect Cd-plated fastener hardware. Abundant Cd whiskers were found, i.e. Cd whiskers on fasteners are commonplace, not unique.



- Whiskers were found mainly, though not exclusively, in the worn previously engaged regions of threads, suggesting that majority of growth may occur *after* disassembly. Whisker growth from externally applied stress or deformation is well-known for tin whiskers.

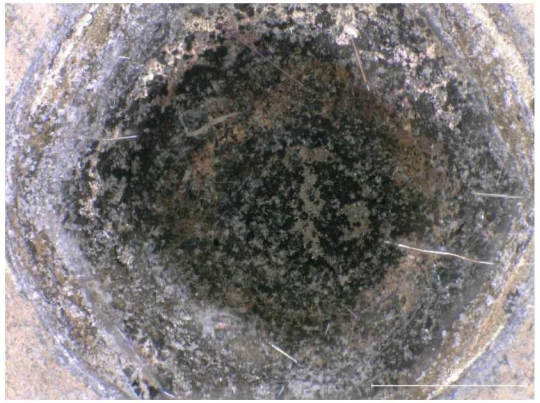
J. Cheng, S. Chen, P.T. Vianco, and J.C.M. Li, J. Appl. Phys., Vol. 107, 074902, 2010. S-K Lin et al., J. Elect. Mat., Vol. 36, No. 12, pp 1732-1734, 2007.

Morphologies of Cd whiskers and nodules are identical to those observed for Sn whiskers

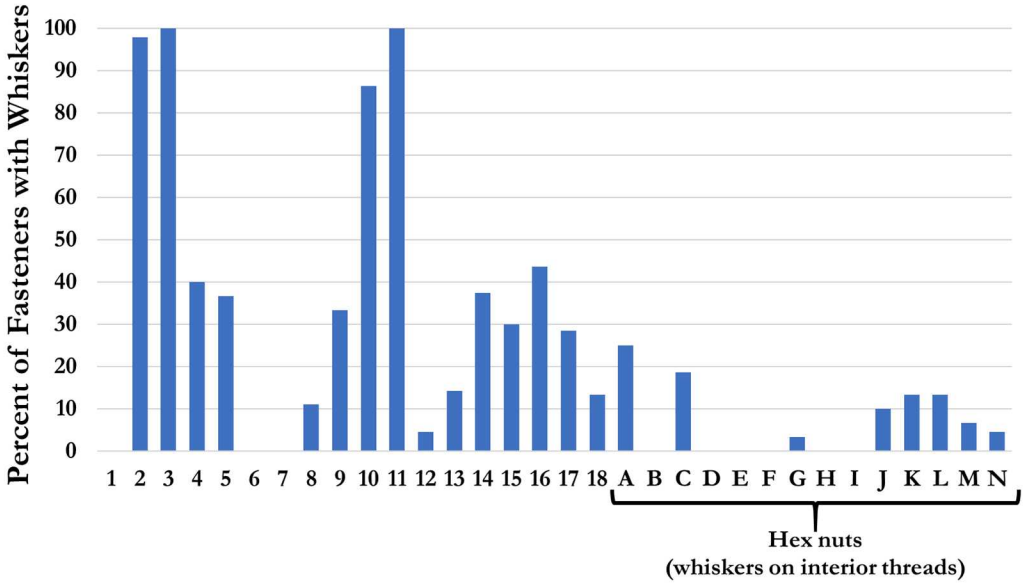
2017-2019 Fastener Survey Shows Whiskers are Common (in aged/old hardware)

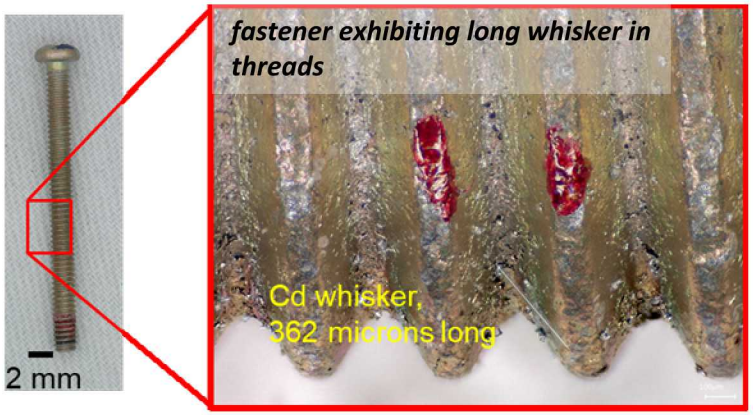
- Over the past year, a survey of fasteners was initiated
  - 668 of 2075 parts surveyed
  - 26% (175 of 668) of parts exhibited whiskers
  - 74% (23 of 31 bags) of hardware types/groups exhibited whiskers

Abundant Cd whiskers were found on the majority of fasteners surveyed, i.e. Cd whiskers on fasteners are commonplace, not unique.



Head of field returned fastener exhibiting numerous whiskers



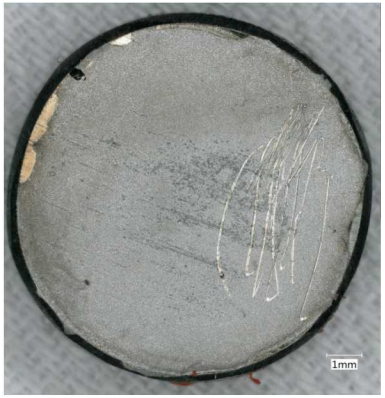


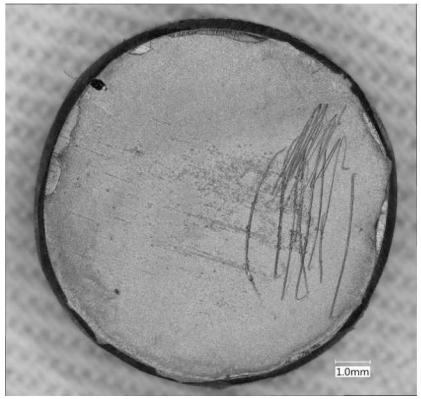
- To date, we have only seen Cd whiskers on old hardware (field return or stored in lab drawers). > 20 years old…
- Can we grow whiskers on “new” Cd-plated fasteners by applying stress, temperature, humidity, etc. i.e. accelerating the aging process? Plans for 2020 fiscal year
- Can we Cd-plate flat coupons in the laboratory that grow Cd whiskers? Flat coupons would make whisker growth experiments and characterization much easier.

Attempts to plate Cd for whisker growth in-house on flat coupons

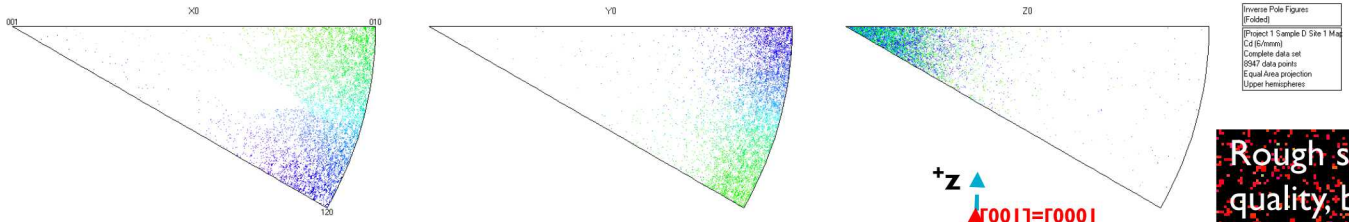
- Cadmium sulfate base plating bath

As-plated+abrasion | 48hr at | 96hr at | 144hr at 83°C

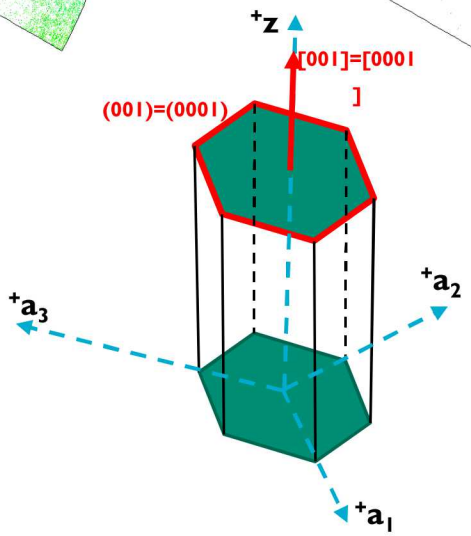


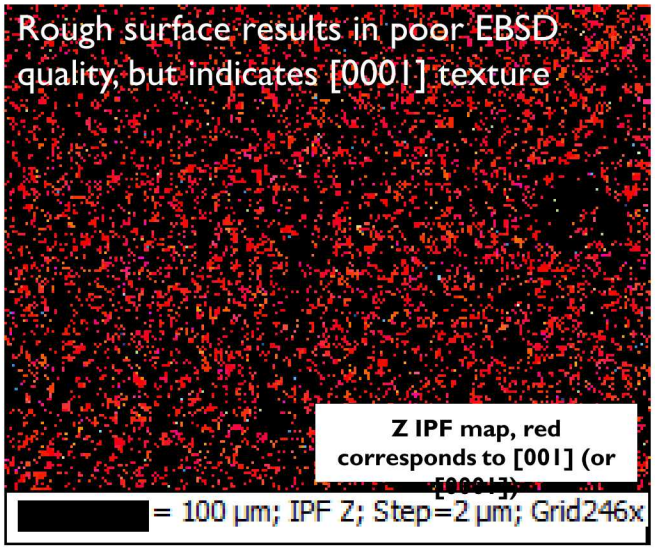


Sample D

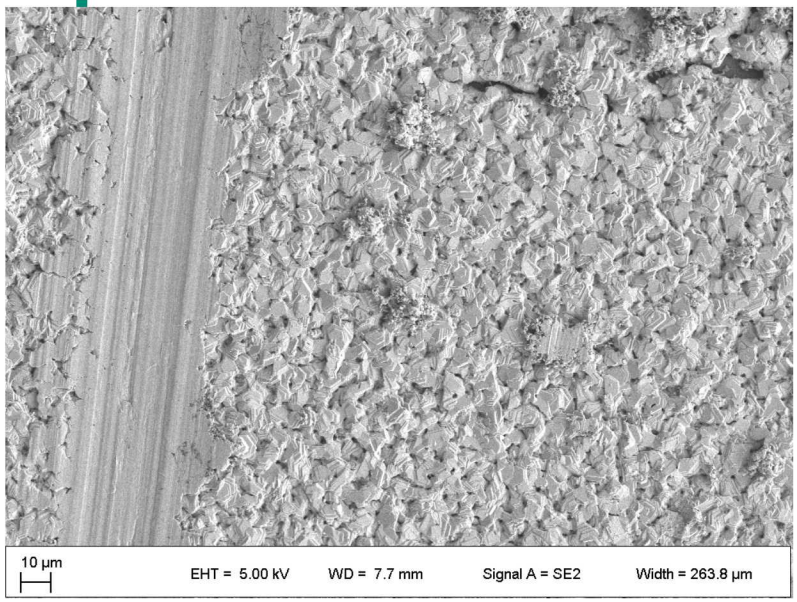


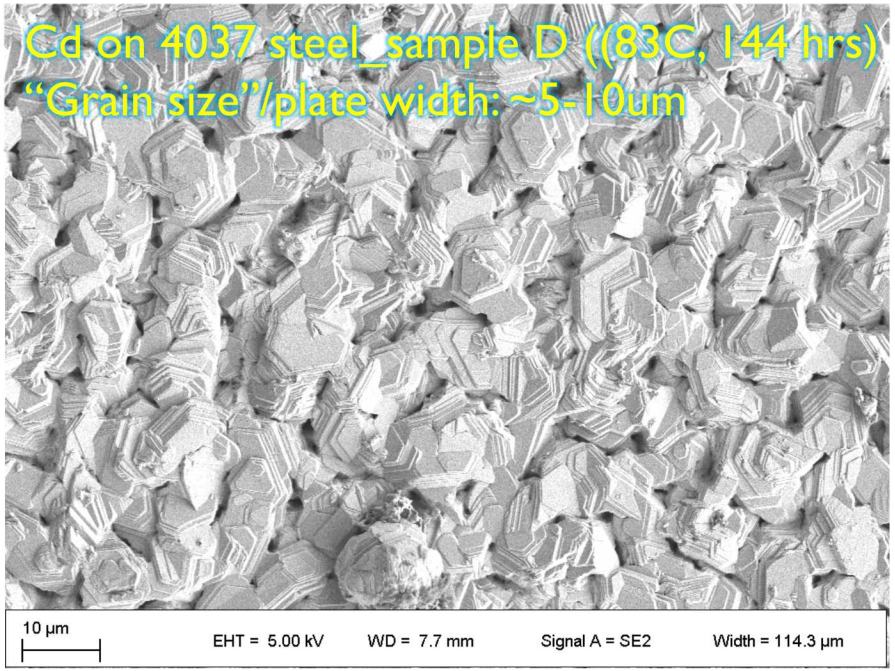
EBSD performed after heat treatment for a total of 144hr at 83°C. Uniform plating texture is not obvious, although many points correspond to [001] (or [0001]) in Z-direction (ie basal plane growth in HCP system)

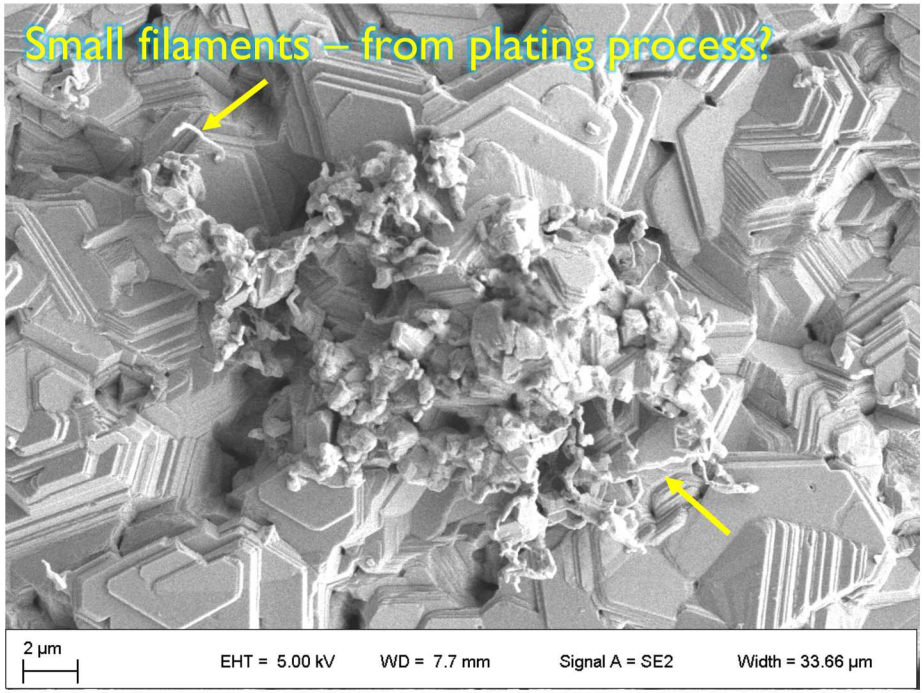


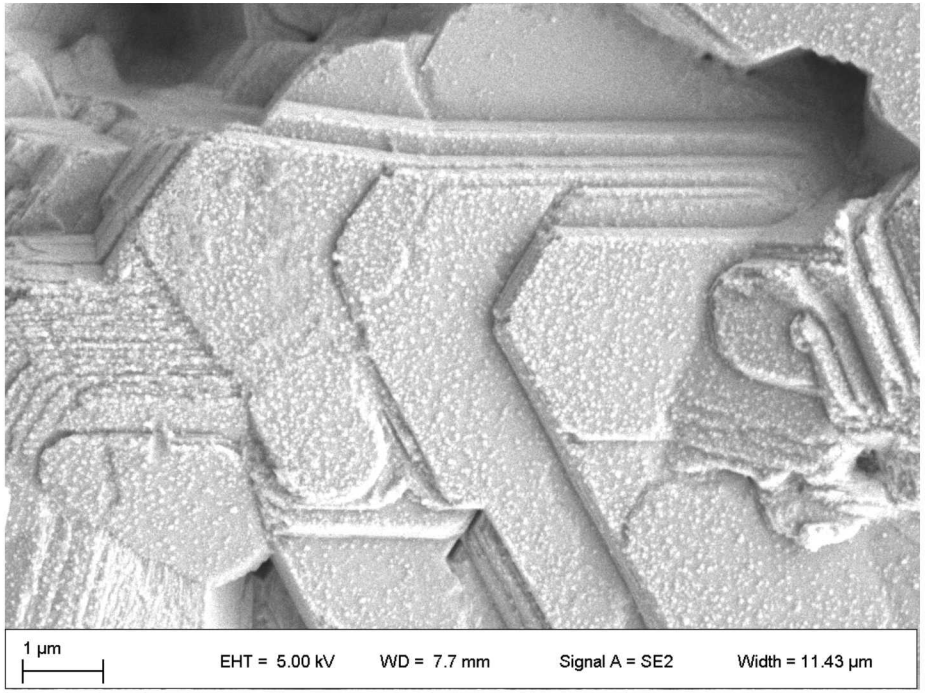


Coarse crystalline plating results



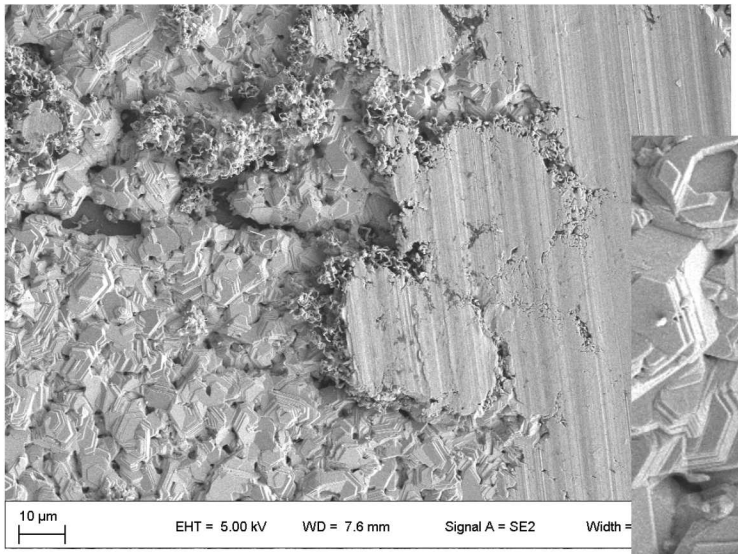


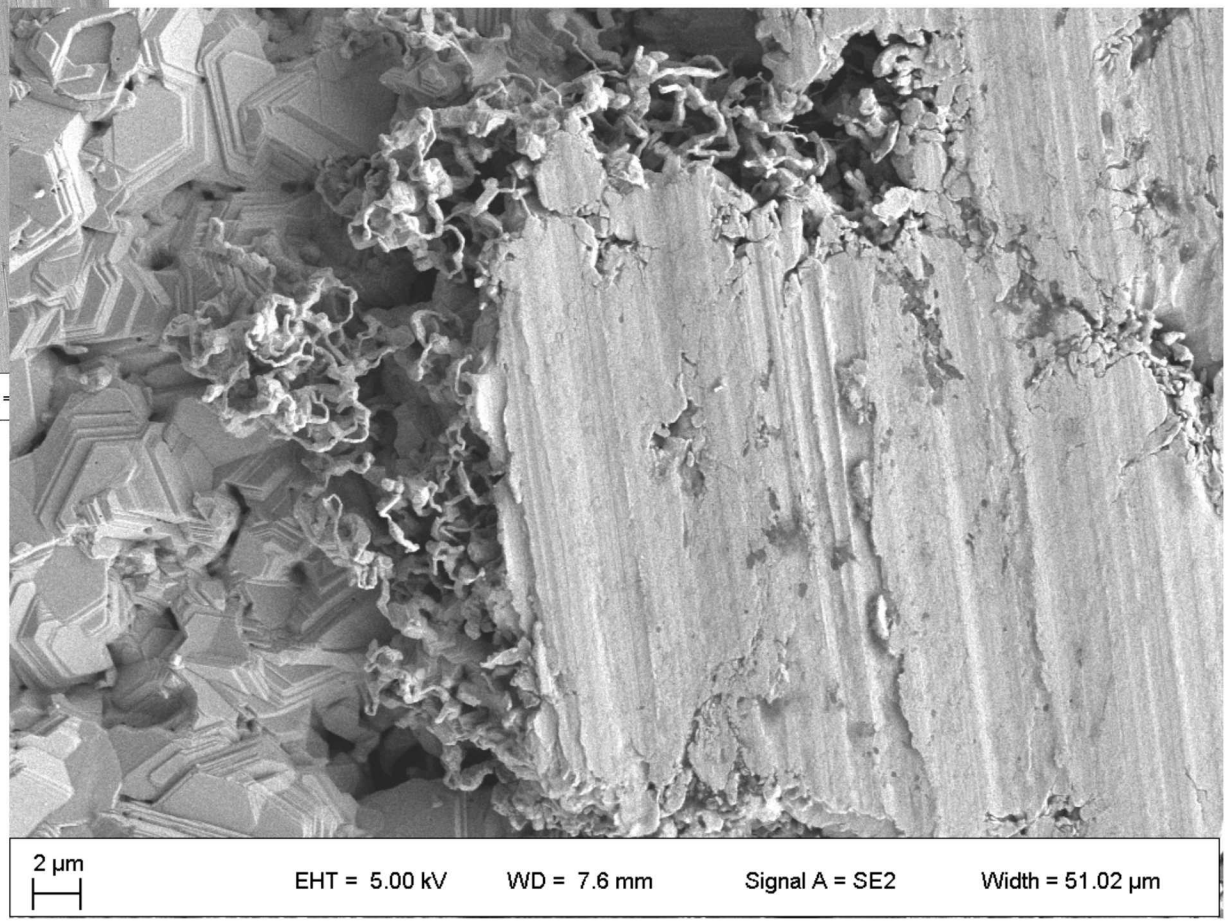




Cd on 4037_sample D (83C, 144 hrs)
"Grain size"/plate width: ~5-10um

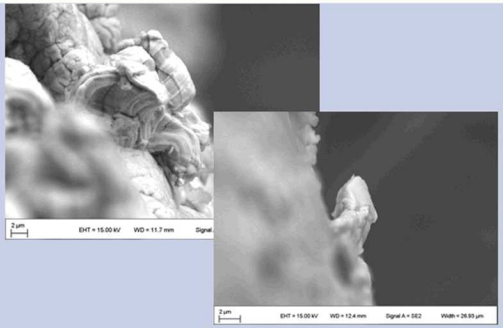
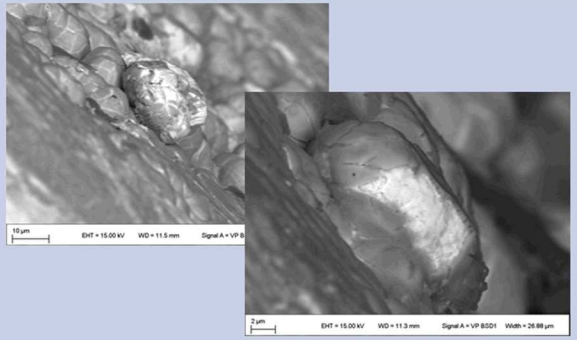
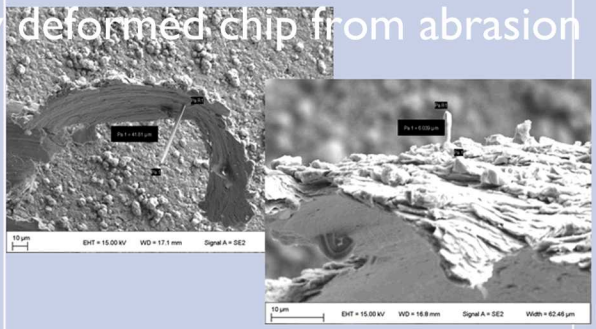
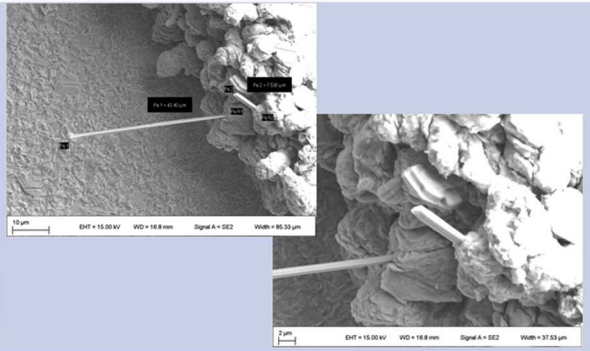
"spaghetti-like" filaments, primarily near scratched/highly deformed region





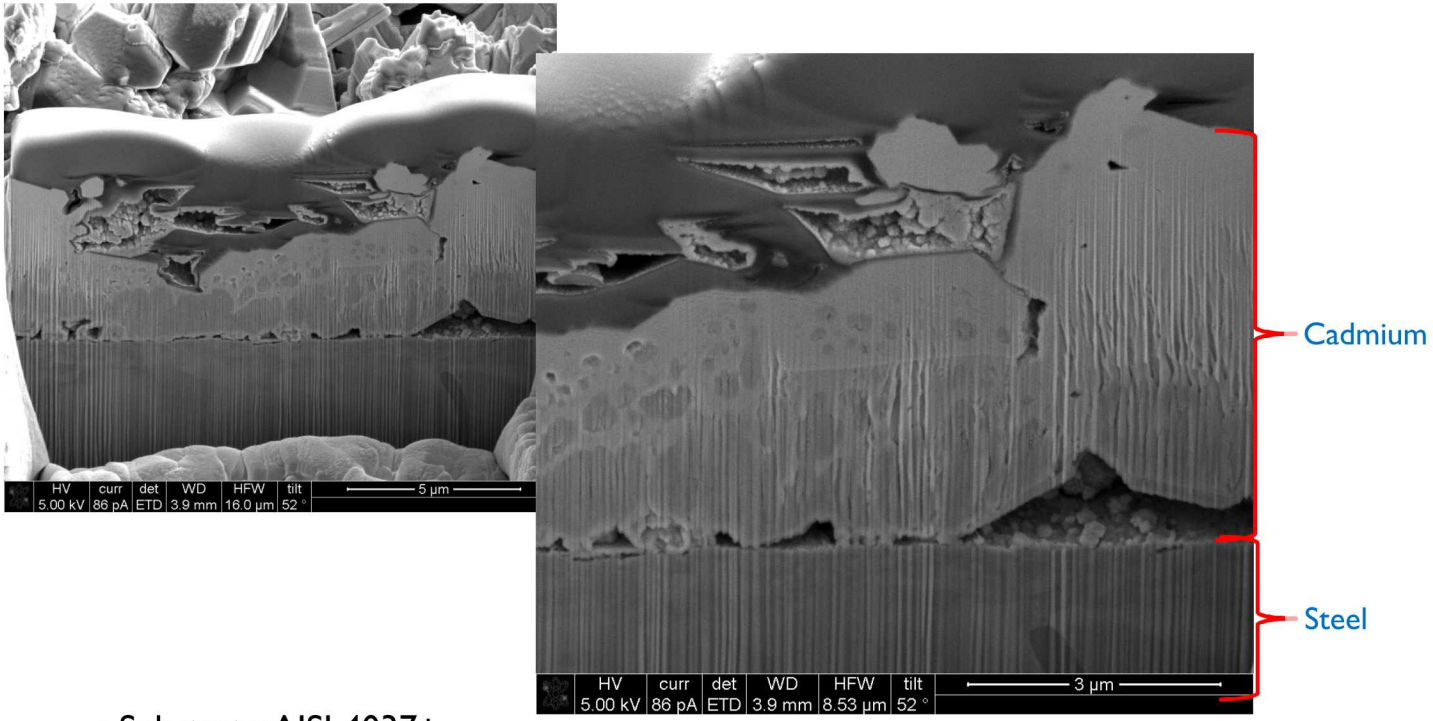
Heat treatment of in-house Cd-plated coupons

- Heat treatment of multiple Cd platings (and multiple substrates) has yielded a few Cd whiskers.
  - Observations of whiskers or nodules forming on each Cd plated washers or Cu coupons suggest that temperature range needed to promote accelerated whisker growth may be near 138°C-170°C (for 6-9 days). Deformation appears to play a key role in promoting whisker growth.

	138°C, 9 consecutive days	170°C, 9 consecutive days
Undeformed Cd coating (w/chromate layer) on steel washer		
	138°C, 6 days (3 cycles x 2 days each)	170°C, 6 days (3 cycles x 2 days each)
Abraded Cd on Cu coupon	Highly deformed chip from abrasion 	

Characterization of Lab-Plated Steel Coupons

- AISI 4037 steel was plated with Cd at SNL to simulate Cd on a typical fastener steel
  - The Cd plating was quite rough compared to industrially plated Cd and showed intermittent adhesion to the substrate
- Cd plating thickness of 4.5 ± 1.7µm measured from focused ion beam (FIB) cut

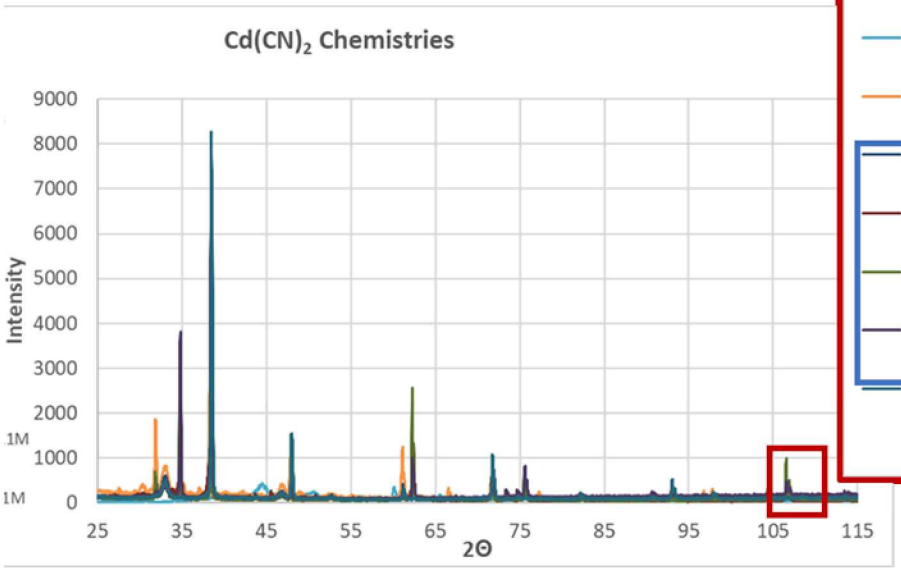


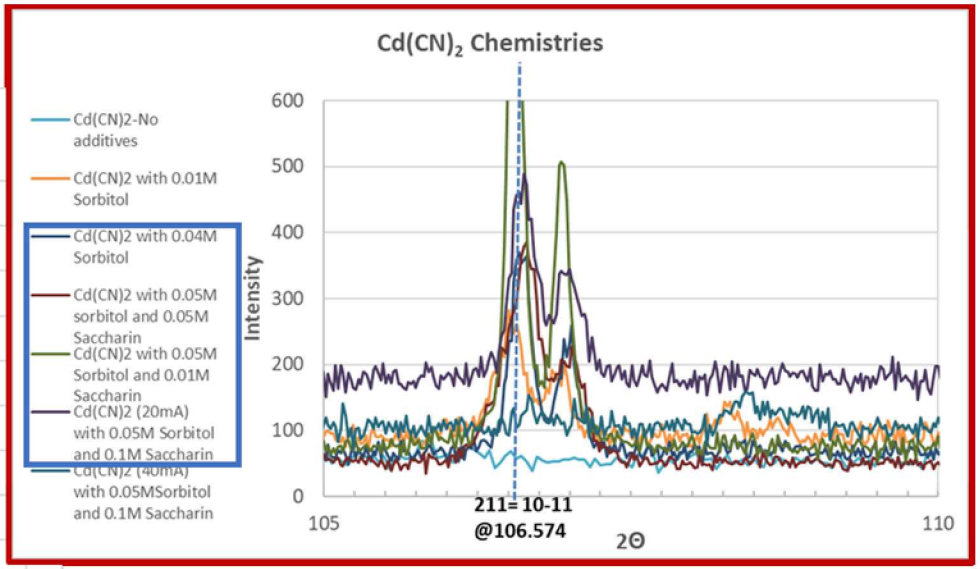
- Substrate: AISI 4037+
- Cadmium Sulfate-based bath chemistry
- Measured Cd thickness: 4.5 ± 1.7 µm

+low-alloy steel commonly used in fasteners
⁺FIB cross-sections courtesy of Daniel Perry, Sandia National Laboratories

More Recent Cd Plating Experiments

- Commercial (MIL-STD-870C) plating of Cd utilizes a cyanide based plating bath, sodium cyanide NaCN based
- Amount and types of additives (brighteners, levelers) are largely unknown
  - Sorbitol, Saccharin
- Can we reproduce the smooth morphology and crystallographic texture of commercially plated Cd?
  - Texture on both Cd-plated washers was identified as 58 degrees from <0001> direction, **or** 10$\bar{1}$1
  - Lab-plated coupons that exhibit increased 10$\bar{1}$1 peak intensity in XRD spectra have been prioritized for SEM examination

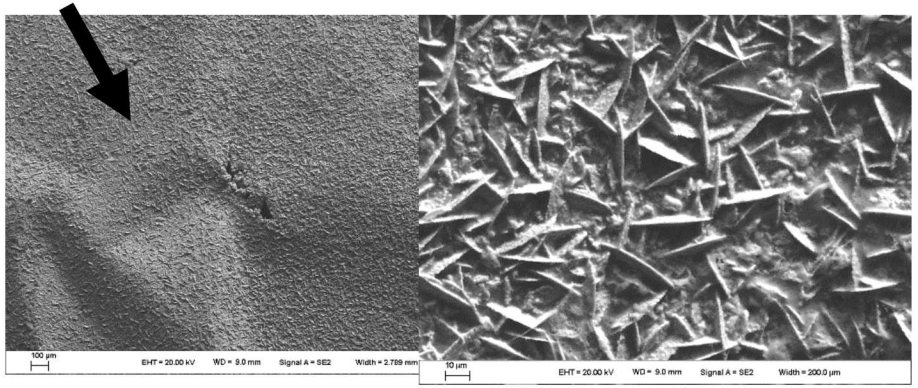




More Recent Cd Plating Experiments

Coupon plated in a CdCN bath (0.03M Saccarin) exhibited delamination and plate-like Cd on surface. The lack of contact between the coating and substrate and surface roughness are expected to be undesirable for Cd whisker growth.

Delamination



- Morphology of CN bath specimens much different from previous sulfate-based platings.
- Poor adhesion still a concern

The best candidates for whisker growth experiments have continuous, flat coatings.

				Morphology	
Sample	**Adherent**	**Continuous**	**Flat**	**Platelets/Crystalline**	**Rough/Bumpy**
Cyanide with Sorbitol 0.04M	X	X			X
Cyanide 0.03M Saccarin		X		X	
Cyanide with 0.01M Sorbitol	X	X			X
Cyanide 0.05M Saccarin, 0.05M Sorbitol					X
Cyanide 0.1M Saccarin, 0.05M Sorbitol, 20mA/cm2		**X**	**X**		
Cyanide 0.01M Saccarin, 0.05M Sorbitol	X			X	
Cd Sulfate Ruzzy IDD with BA	X	X		X	
Cd Sulfate Ruzzy IDD with SDS	**X**	**X**			**X**
Cd Sulfate IDD No Additives	X	X		X	X
Cd Sulfate Ruzzy IDD No Additives	X	X			X
Cd Sulfate IDD with Saccarin	X				X

Concluding Remarks

- Although Cd whiskers have been known for a long time, there has been little interest compared to tin whiskers. Cadmium whiskers were found recently on Cd-plated steel fasteners. This represents the only documentation of Cd whiskers *on fasteners*, notwithstanding the NASA Cd ban.

- Cd whiskers on Cd-plated fasteners appear to be commonplace on *old/aged hardware*. Cd whisker growth may be enhanced by stress and deformation, due to mating and de-mating of threaded connections.

- Preliminary results on laboratory Cd plating have shown only small, filamentary whiskers, some related to the plating process itself and some associated with *extreme deformation* of the coatings. The commercial (Mil-Spec) cyanide bath chemistry is currently being investigated; addition of leveling agents/brighteners is being studied to simulate the commercial plating morphology and crystallographic texture.