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Title: Analysis of Microclad from Several Manufacturing Lots: Summary report

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Analysis of Microclad from Several Manufacturing Lots
Summary report

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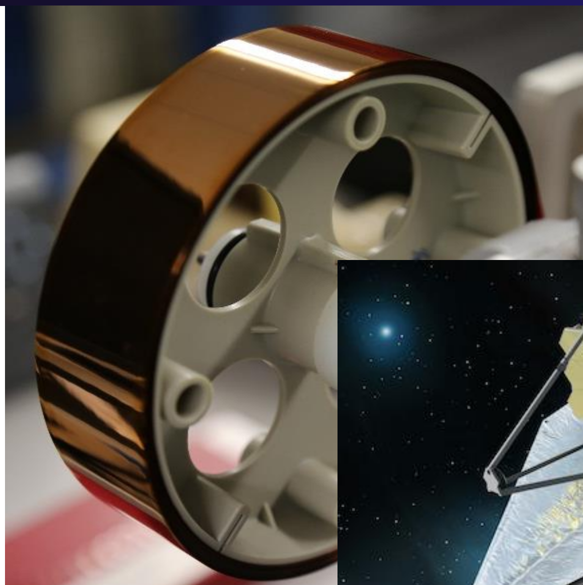
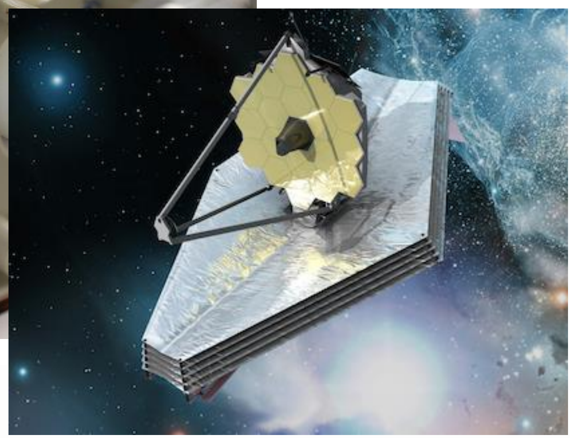
May 11, 2017

Los Alamos NATIONAL LABORATORY EST. 1943
NNSA National Nuclear Security Administration
Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

Background





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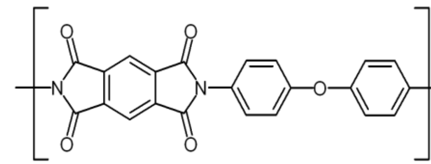
Microclad

Microclad is a Cu-coated polymer (Kapton) tape that is used in the production of detonators.



Issue

Microclad has been produced by several different vendors over the past 20 years, and there is a desire to evaluate differences in the product produced by these vendors.

Goal

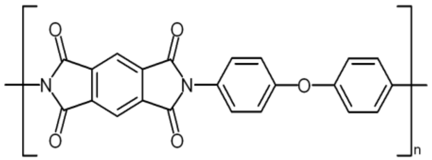
Characterize and document the differences between 4 sets of microclad samples, and provide this information to the detonator Design Agency (Q-6) for the purposes of evaluating “similitude” for stockpile use.

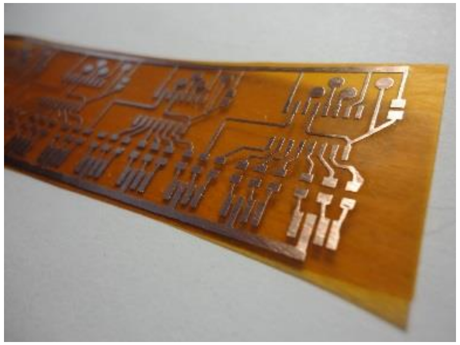
Microclad Material Specification (9Y294599)

Kapton

Polyimide - Dupont Type H (EUC 713)

Thickness: 0.002 ± 0.0002 in





Copper

> 99.8% purity

Thickness: 146 – 180 µin (3.71 – 4.57µm)

< 18 µin (0.46 µm) difference between max. and min. thickness on any given roll

Plating Adhesion

Test according to IPC-TM-650 2.4.10 (cellophane tape test)

Other

No visibly detectable discoloration or contamination

Less than 1 pinhole/foot when inspected using backlit lighting

Cu shall not crack when the foil is bent around a 6 mm radius cylinder (with Kapton located against cylinder)

Surface shall be scratch-free when visually inspecting at 14-16x magnification

MC Characterization – Summary of Efforts

- Assembled team in early December 2016
- Charged with determining "similitude" between sample lots
- Brainstormed key properties to measure
- Recommended analytical techniques to measure these properties
- Down-selected to high-priority measurements
- Weekly meetings to review and share results
- Preliminary results presented to PRT: Feb 1, 2016
- SME presentations: Feb 15, 2016
- Final Report Issued: March 31, 2017
    - LA-UR-17-22647

4 Lots Evaluated

Fortin 1985 – original material

storage conditions varied and not WR

2 versions w/different copper thickness (F160 & F175)

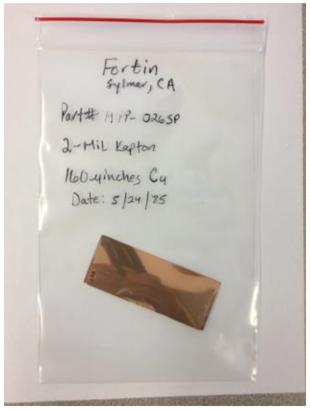
Datex 2003 (D03)

Datex 2013 (D13)

Datex 2016 (D16)

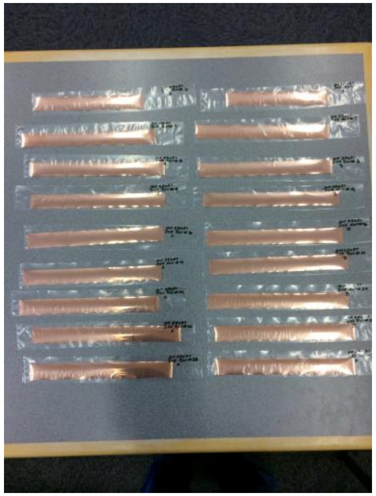
controlled WR storage

two 12" strips from selected roll



Fortin 85

Datex 2016



Datex 2003

Final Report: LA-UR-17-22647

Comparative Assessment of Copper-Coated Kapton: Analysis of Microclad from Several Manufacturing Lots

March 31, 2017

Microclad – Initial Evaluation Matrix

Technique (SME, Org)

Kapton	Radiography (B. Patterson, MST-7)	FTIR (C-CDE)	ICP/MS (D. Kelly, C-CDE)	NMR (A. Labouriau)	GPC	SEM/µ-probe/met. (McCabe & Livescu, MST-8)	XRF (D. Kelly, C-CDE)	TEM	TGA (C-CDE)	DSC (C-CDE)	AFM (J. Tokash, SIGMA)	Spectral Reflectometry (M. Beaux, MST-7)	Optical Microscopy	Profilometry (M. Beaux, MST-7)	Load Testing (C. Sandoval, MST-7)	4-Point Probe (MST-7)	Eddy Current	ECR	XPS (D. Kelly, C-CDE)	SIMS (C-NR)	Adhesion Testing (D. Vodnik, MST-7)	Bend Test
thickness	high					high						high	medium									
density	low																					
composition		high	low	medium	low	medium																
polymer structure	low			medium	low								low									
thermal									medium	medium												
modulus											medium				low							
refractive index												high										
dielectric constant												low										
surface roughness						high					high		medium	high								
tensile strength															medium							

Copper	Radiography (B. Patterson, MST-7)	FTIR (C-CDE)	ICP/MS (D. Kelly, C-CDE)	NMR (A. Labouriau)	GPC	SEM/µ-probe/met. (McCabe & Livescu, MST-8)	XRF (D. Kelly, C-CDE)	TEM	TGA (C-CDE)	DSC (C-CDE)	AFM (J. Tokash, SIGMA)	Spectral Reflectometry (M. Beaux, MST-7)	Optical Microscopy	Profilometry (M. Beaux, MST-7)	Load Testing (C. Sandoval, MST-7)	4-Point Probe (MST-7)	Eddy Current	ECR	XPS (D. Kelly, C-CDE)	SIMS (C-NR)	Adhesion Testing (D. Vodnik, MST-7)	Bend Test
thickness	high					high					high		high	high		high	high		high			
resistivity																high	high	low				
density	low																		high			
composition			high			high	high													medium		
microstructure/grain orientation/morphology						high		low														
surface roughness						high					high		medium	high								

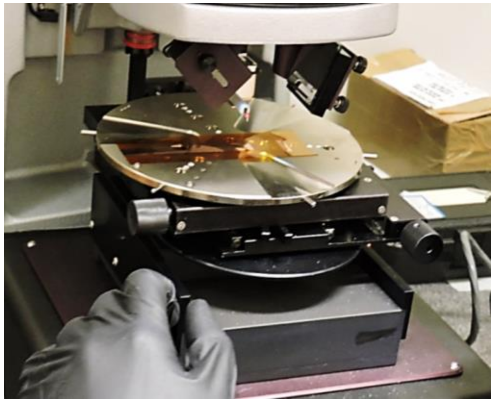
Integrated Microclad	Radiography (B. Patterson, MST-7)	FTIR (C-CDE)	ICP/MS (D. Kelly, C-CDE)	NMR (A. Labouriau)	GPC	SEM/µ-probe/met. (McCabe & Livescu, MST-8)	XRF (D. Kelly, C-CDE)	TEM	TGA (C-CDE)	DSC (C-CDE)	AFM (J. Tokash, SIGMA)	Spectral Reflectometry (M. Beaux, MST-7)	Optical Microscopy	Profilometry (M. Beaux, MST-7)	Load Testing (C. Sandoval, MST-7)	4-Point Probe (MST-7)	Eddy Current	ECR	XPS (D. Kelly, C-CDE)	SIMS (C-NR)	Adhesion Testing (D. Vodnik, MST-7)	Bend Test
interface		medium				high	high	low			high		low					low	high	medium		
bond strength/adhesion																					high	high
chemistry		medium	low			medium	medium												high	medium		
bridge geometry	high					high							high	medium								

high priority - will do	(green)
medium priority - may do	(yellow)
low priority - could do	(pink)

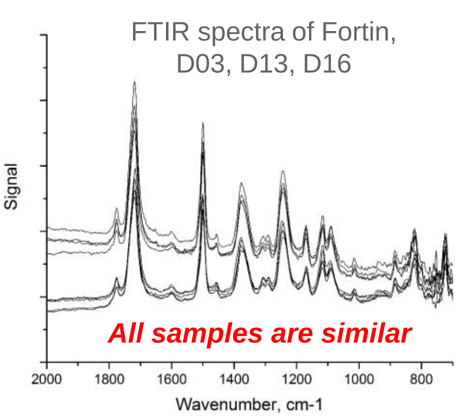
MC Characterization – Summary of Findings Part 1

- We have completed the work as specified in our original evaluation plan
- In general Datex (D03, D13, D16) specimens look similar (Differences noted below)
- Kapton chemistry appears quite similar between samples
  - FTIR, DSC, Swelling all show similar response
  - DSC/TGA data shows exotherm & small weight loss in some D16 samples at ~130 °C (hypothesized to be due to continued reaction of monomers in these young samples).
- Kapton thermomechanical properties vary slightly, both inter- and intra-sample
  - All samples show shrinkage when exposed to heat. All Datex samples shrunk 1-5% upon heating to 160°C, while Fortin shrank 10-20%.
  - Datex samples all behave similarly from a tensile and thermomechanical standpoint.

Sample Name	Average Peak Load (N)	Stiffness (N/in)
D03	**153.31** ± 26.34	**645.79** ± 107.00
D13	**152.96** ± 18.20	**711.77** ± 251.24
D16	**172.68** ± 8.45	**664.54** ± 112.03



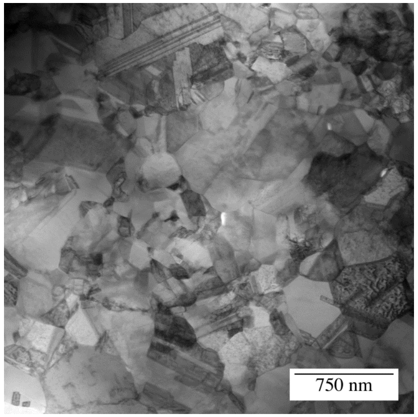
Zygo profilometer measurement of Kapton substrate



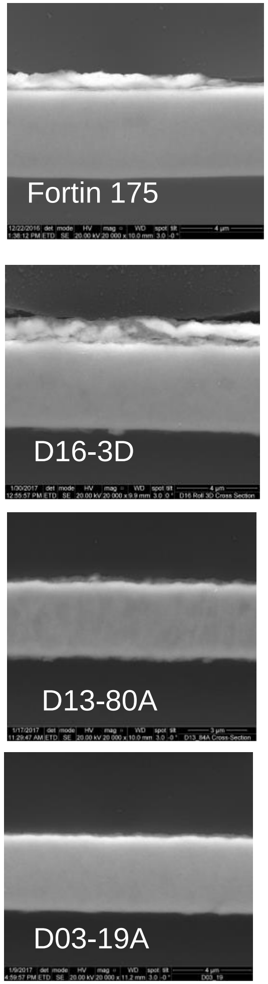
MC Characterization – Summary of Findings Part 2

- Copper morphology varies widely among all samples, both inter- and intra-
  - D16 shows a slightly larger copper surface roughness
  - Datex have very small grain sizes compared to Fortin
  - Copper thickness is consistent among Datex samples, varies slightly from Fortin
  - ICP-MS shows ~10% copper mass/area for D16 compared to D03 and D13
- Surface layers varies between batches
  - Fortin and D16 show visible surface (contamination?) layer, lesser amounts on D03 and D13
- There are slight variations in chemistry of the interface
  - All samples show Pd and Sn (Cu plating catalyst).
  - D03 and D13 show a 3:1 Sn:Pd ratio
  - D16 shows a 2:1 ration of Sn:Pd

	Cu Wt% of Microclad Average +/- Std. Dev.	**Cu Coverage (mg/cm^2) Average +/- Std. Dev.**
D03	35.56 +/- 0.98	3.71 +/- 0.15
D13	34.55 +/- 2.10	3.63 +/- 0.37
D16	*32.91 +/- 0.83*	*3.26 +/- 0.12*
Fortin	34.59 +/- 1.45	3.55 +/- 0.32



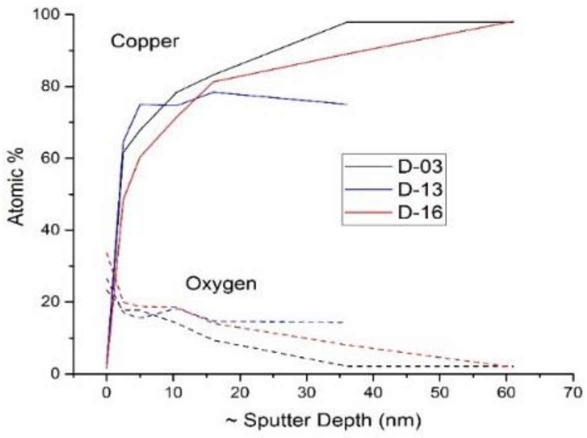
TEM Micrograph of D16



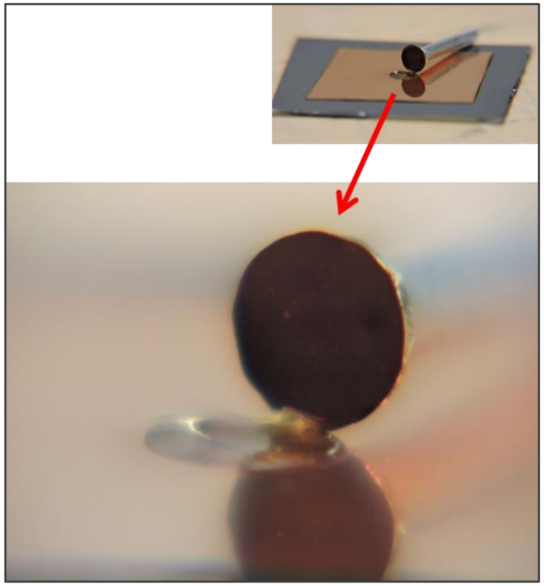
Surface Layers – SEM

Data Courtesy Of:
R. McCabe, R. Spillers, C. Miller (MST-8)

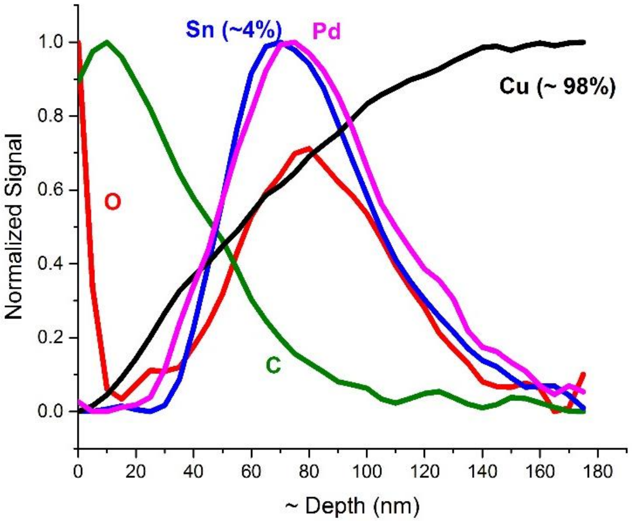
XPS depth profiling



XPS survey scans of copper side of Datex D03 sample, as-received and after ~ 50 nm of material is removed;



Stud-Pull test. Failure occurred at Cu-Kapton interface. A small piece of Kapton keeping the stud from being completely separated from the sample.

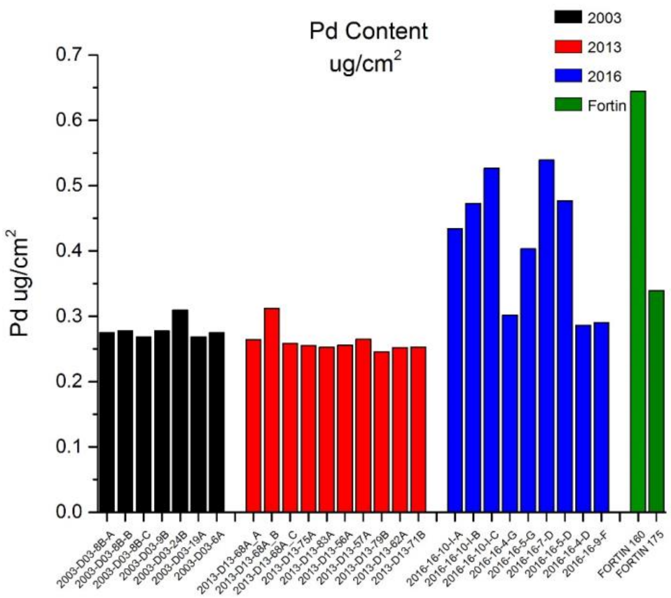


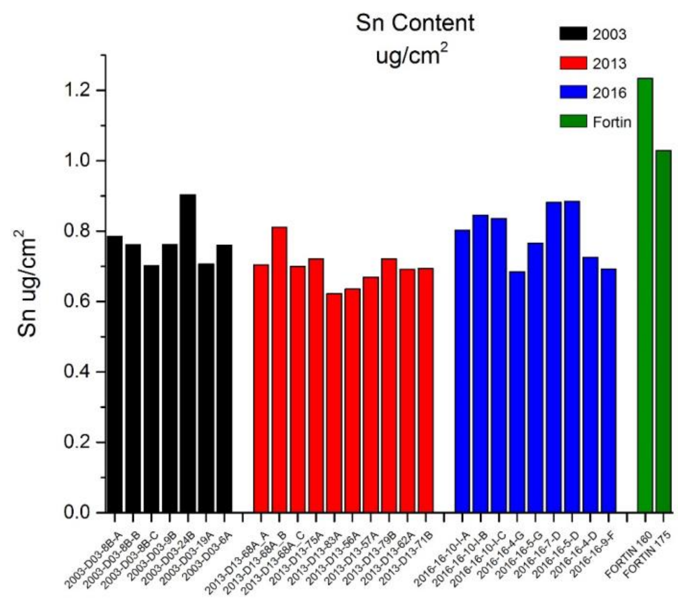
XPS depth profile of the "copper side" of a Datex microclad sample that has been pulled apart (separating kapton from copper) during adhesion strength testing.

Chemical Purity

	Cu Wt% of Microclad Average +/- Std. Dev.	Cu Coverage (mg/cm^2) Average +/- Std. Dev.
D03	35.56 +/- 0.98	3.71 +/- 0.15
D13	34.55 +/- 2.10	3.63 +/- 0.37
D16	32.91 +/- 0.83	3.26 +/- 0.12
Fortin	34.59 +/- 1.45	3.55 +/- 0.32

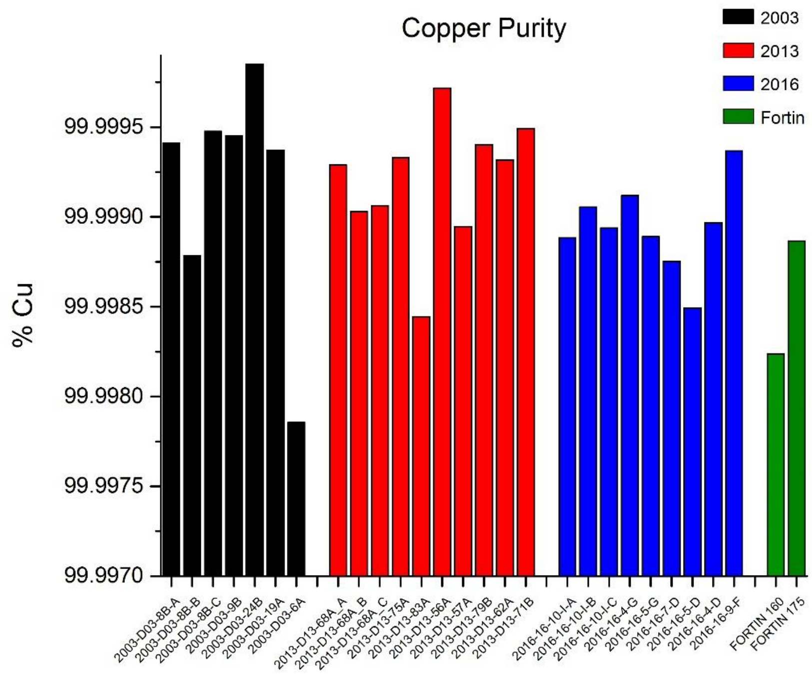
Average mass of copper etched per lot reported as a weight percent (wt%) of the microclad and as a mass per area (mg/cm^2).





Palladium (left) and tin (right) mass per area (μg/cm^2) per lot. The bar graphs represent the different lots: black - D03, red – D13, blue – D16, and green – Fortin.

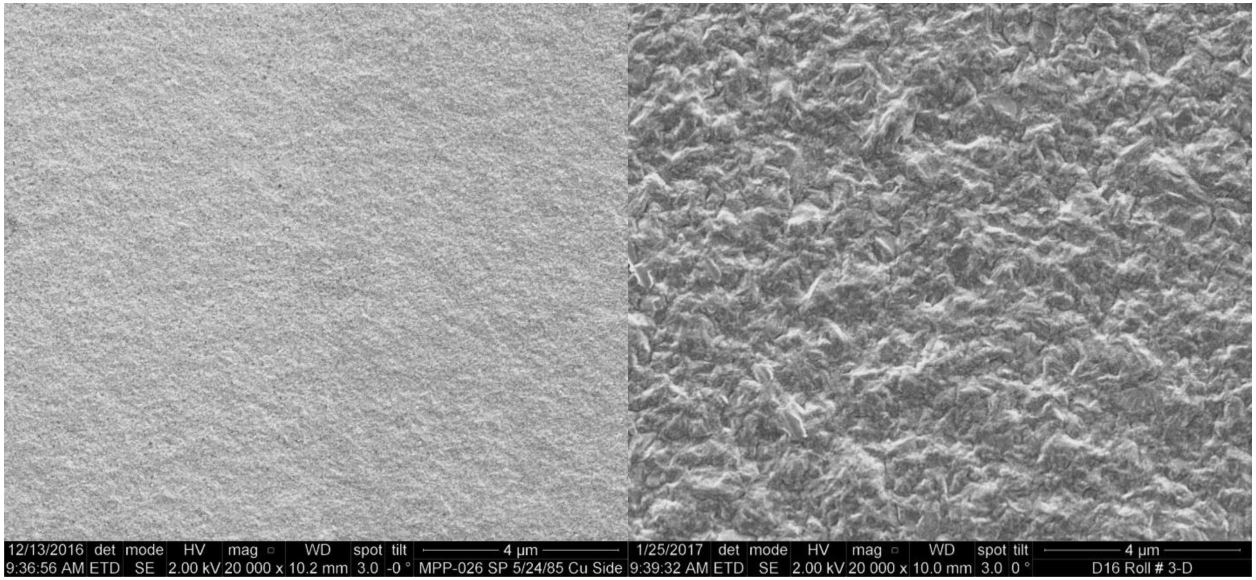
Chemical Purity continued



	Average Cu Purity (wt%)	Std. Dev (wt%)
D03	99.9992	0.0007
D13	99.9992	0.0004
D16	99.9989	0.0002
Fortin	99.9986	0.0004

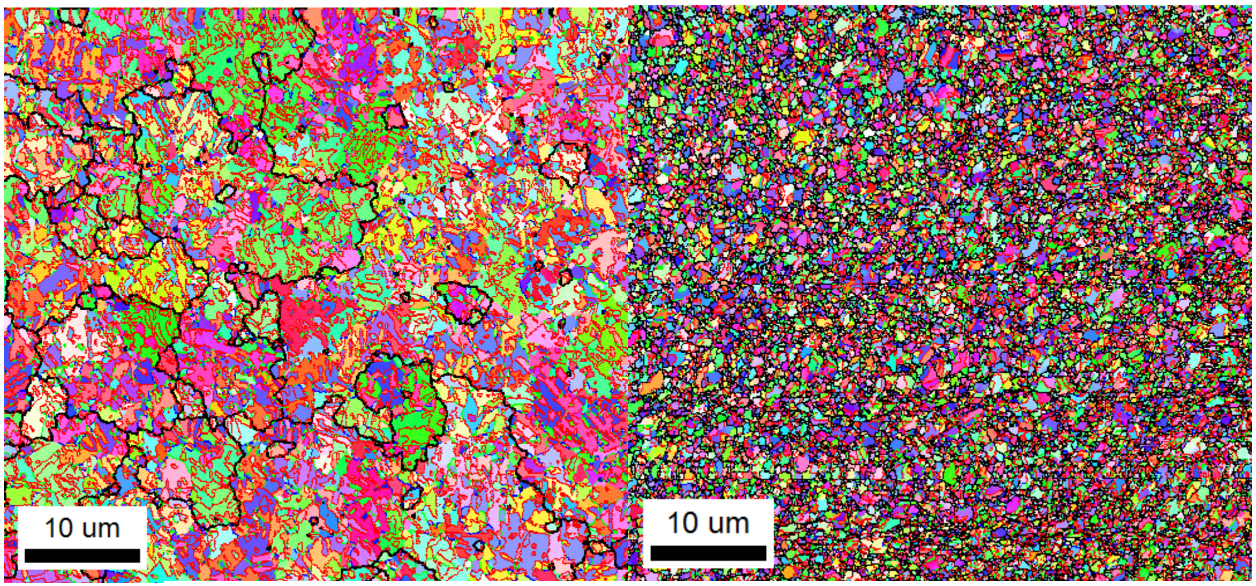
Average Copper purity for each lot based on impurities detected

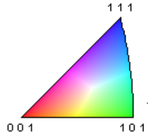
SEM of Cu surface structure



Copper surfaces for a) Fortin 16 and b) D16 3D. The Fortin 160 has the finest scale surface roughness and Fortin 175 has a similar though slightly rougher appearance. Fortin 160, D03, and D16 exhibited similar surfaces with a fine scale roughness. Fortin 175 and D13 exhibited similar cracked surfaces.

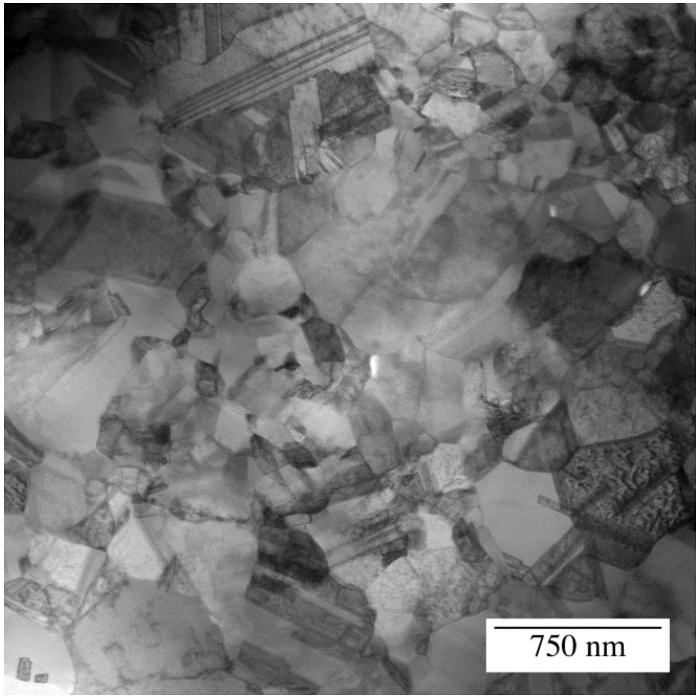
Crystallographic Orientation map



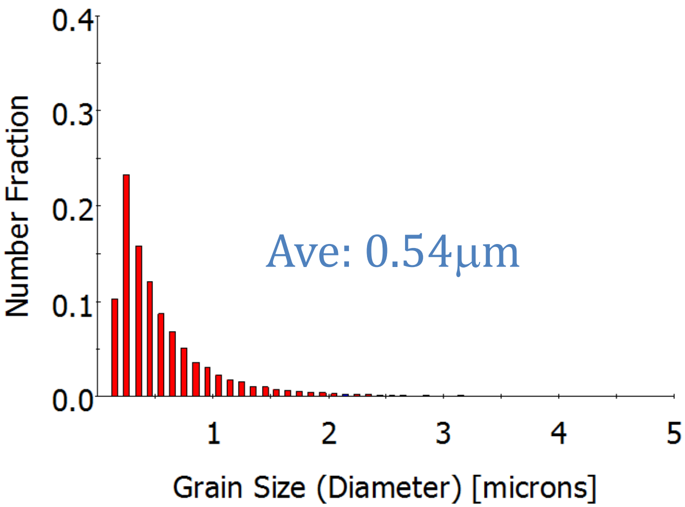


EBSD based inverse pole figure (IPF) orientation maps for a) Fortin 160 and b) D16-2F. The colors in the map indicate the copper grain crystal direction in the foil plane normal direction. The black boundaries are general high angle grain boundaries. The red, green, and blue boundaries are special low energy boundaries (also known as twin or coincident site lattice (CSL) boundaries) that are common in copper. Fortin 175 appears similar to the Fortin 160 with some clustered regions of grains with general high angle grain boundaries. D03 and D13 look similar to the D16 with slight differences in average grain size.

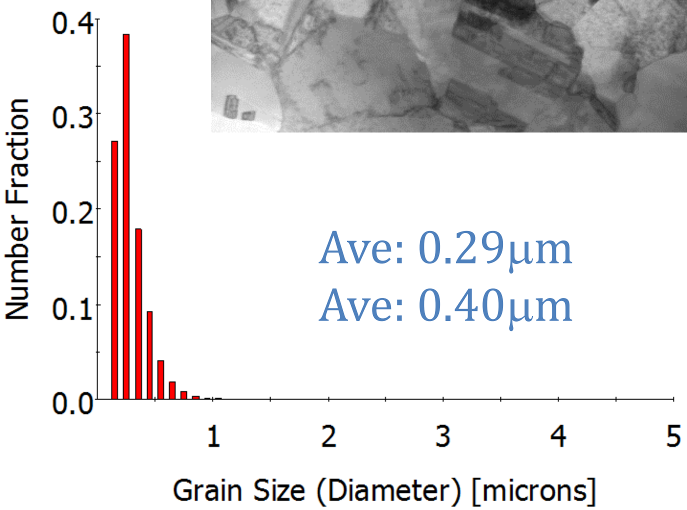
Grain size



Fortin 160

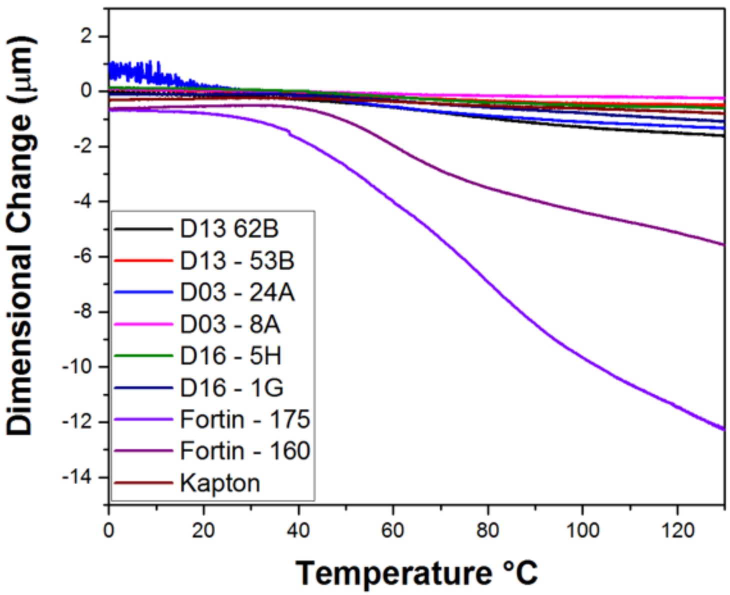


D03-16



Unclassified

Thermal Mechanical Analisys



Ssummary of the TMA measurements. All samples shrunk as they were heated. D03, D13, and D16 samples all have similar shrinkage values: 1-5%. The Fortin samples have larger shrinkage values: 10-20%.

Peel test

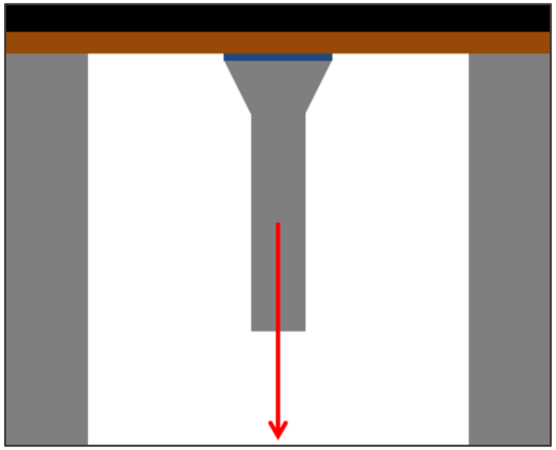
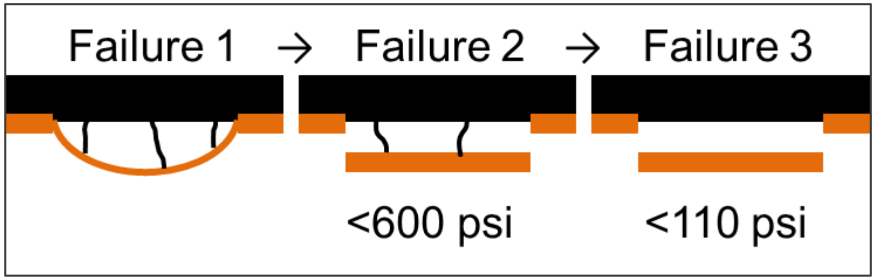
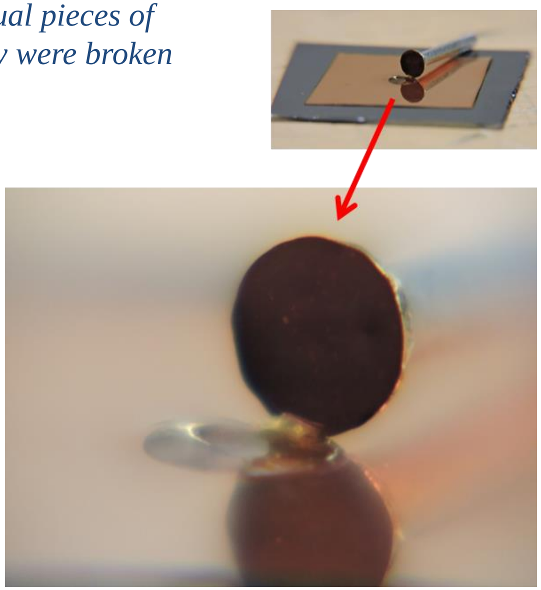


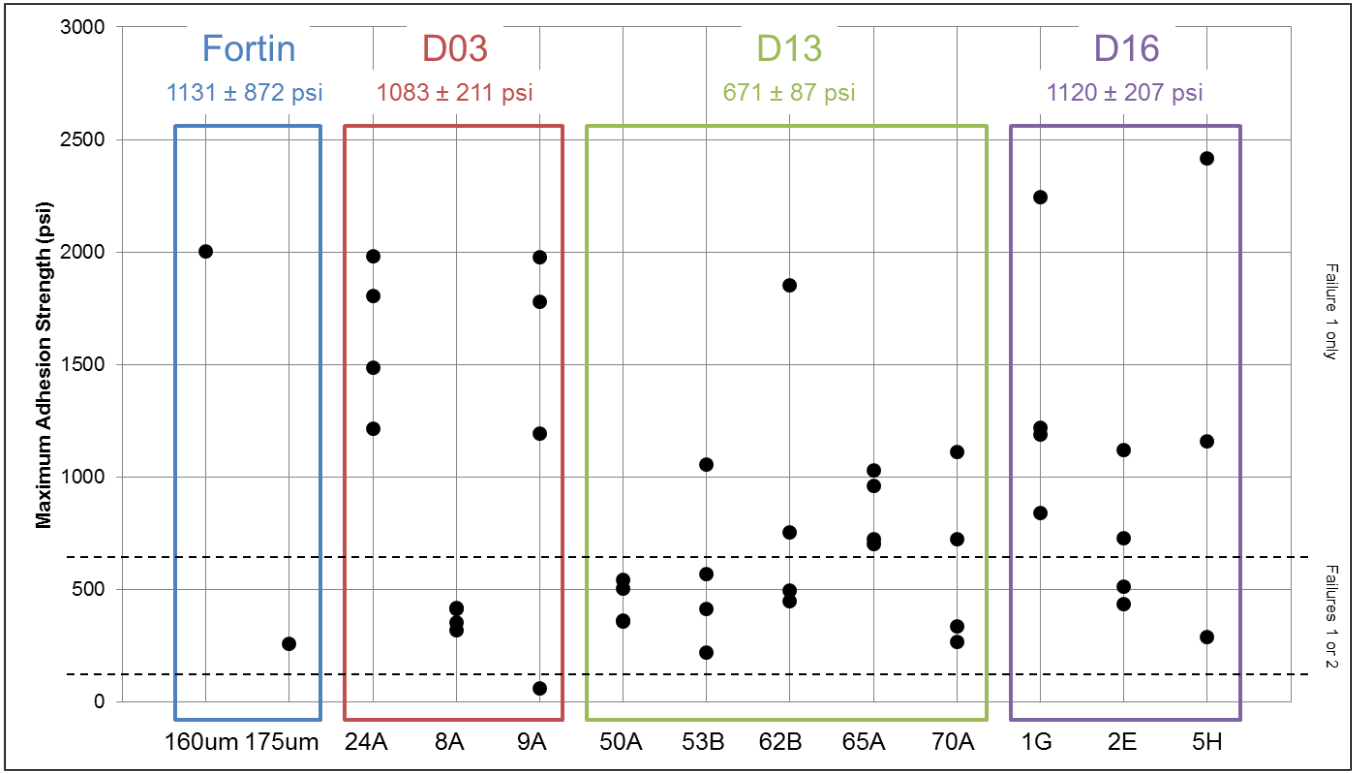
Illustration of the stud pull adhesion test method. The stud is attached to the copper (brown) by an epoxy (blue), and is pulled perpendicularly away from the sample through a hole while the sample rests over the hole.



The three sequential failure modes observed during testing. Failure 1 occurred when the copper (orange) attached to the stud (not shown) delaminated from the Kapton (black) but maintained its connection to the surrounding copper, forming a "blister." Failure 2 occurred when the copper attached to the stud ripped off of the surrounding copper. If there were any residual pieces of Kapton still holding the copper to the sample, they were broken and complete separation was achieved.



Peel test results



Maximum adhesion strength data. Each point corresponds to one run while each column of points corresponds to one roll. Most rolls yielded four samples, which were each run once. The dashed lines correspond to the failure modes: for any points above the top dashed line the maximum adhesion strength measured for that sample corresponded to the first failure mode. For any points between the two dashed lines, the maximum adhesion strength measured for that sample may correspond to either the first or second failure mode. The numbers below the lot names are the average maximum adhesion strength for that lot ± standard error.

Microclad Characterization – Discussion and Recommendations

Conclusions:

- D16 samples are quantitatively similar to D03 and D13 samples in nearly all respects, with four key differences:
  - DSC/TGA data shows exotherm & small weight loss in some D16 samples at ~130 °C (excess polyamic acid?)
  - Copper roughness and grain size and slightly less copper mass.
  - Surface contamination layers vary among all samples. D16 most similar to Fortin samples.
  - Sn:Pd ratio different for D16 (2:1) relative to D03 and D13 (3:1).

- Difference in copper surface and morphology are of possible concern in how the system will age.

- There is considerable intra-sample variability in all Datex lots. Differences in D16 (to D03 and D13) are within the range of variability seen within D03 and D13 lots.

Recommendations:

- Some level of evaluation of corrosion and accelerated aging response of D16 samples is recommended.

- Recommend further characterization based on SME & PRT input and performance testing.

D16 material is of sufficient similitude to D03 and D13 for continued evaluation and use.