

Solderability of Additive Copper Surfaces



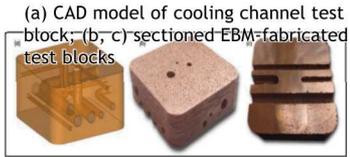
PRESENTED BY

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08 July 2019



Additive manufacturing (AM) involving copper increases design freedom

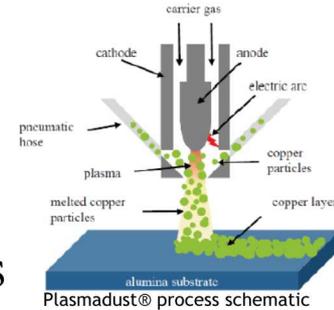


P. Frigola, et al., "Fabricating Copper Components with Electron Beam Melting", 2014.

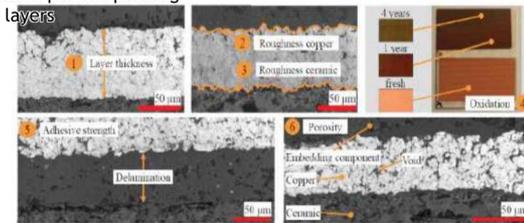


AM of copper components, Fraunhofer Institute for Laser Technology ILT, www.ilt.fraunhofer.de, DQS certified by DIN EN ISO 9001, Reg.-No.: DE-69572-01, 2010.
[40] Additive Manufacturing of Copper Components with Selective Laser Melting, Fraunhofer Institute for Laser Technology ILT, www.ilt.fraunhofer.de DQS certified by DIN EN ISO 9001, Reg.-No.: DE-69572-01, 2011.

- **Complex, novel geometries** for thermal management
- Nonlinear and tapered geometries in extended structures
 - Fins
 - Vane blades
- Capillary wicking structures
- Internal passages
 - Heat pipes/**specialized** plumbing, tubing
 - **Specialized** induction coils
- **Delicate, complex** electrical components in **small batches**
- Jewelry design



Process factors that affect quality of bondable plasma-printing copper layers



(a) Wire bond loops on copper layers (b) cross-section of a bond loop on a printed copper layer on alumina

The first full-scale Cu engine part, a combustion chamber liner that operates at extreme temperatures and pressures (fabricated by NASA). Cooling inlets are visible along the rim



3T RPD® pure Cu concept heat exchanger fabricated by 3T using direct metal laser sintering (DMLS)



<http://www.3trpd.co.uk/3t-success-with-pure-copper-am-production>



C. Kaestle et al., "Evaluation of Influencing Factors on the Heavy Wire Bondability of Plasma Printed Copper Structures", 978-1-4244-5100-5/09/\$26.00©2009 IEEE, 2015 17th Electronics Packaging Technology Conference.

Additive manufacturing (AM) involving copper has not developed as fast as with other alloys (where laser processing is required)

AM “workhorse” alloys, to date:

- Al-2024
- Al-6061
- Al-7075
- CMSX-4 (Ni-base superalloy)
- Inconel 625 (Ni-base superalloy)
- Inconel 718 (Ni-base superalloy)
- Rene 142 (Ni-base superalloy)
- 17-4 PH SS
- 304 SS
- 316L SS
- Co-Cr/Co-Cr-Mo (Co-base superalloy)
- Ti-6Al-4V

Ti2448
Not one Cu alloy

- Most AM processes for metals involve laser processing
- The intrinsic properties that make Cu desirable in many applications (thermal conductivity, ductility, reflectivity) make it undesirable for laser processing
 - Low initial laser absorption accompanied by a step increase at the melting point promotes an unstable melt pool
 - Reflected radiation can be dangerous and damaging to AM instrumentation/components
 - Deformation under residual stresses can be an issue in geometries

Murr, L.E., “A Metallographic Review of 3D Printing/Additive Manufacturing of Metal and Alloy Products and Components”
 Metallography, Microstructure, and Analysis (2018) 7:103-132



laser power significantly, the centre part of the set will soon go into the keyhole operation, often leading material exploding from the weld spot.

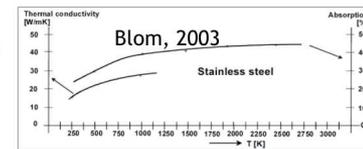


Figure 3 Thermal conductivity and absorption properties for stainless steel

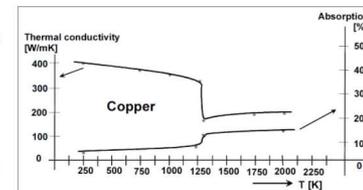
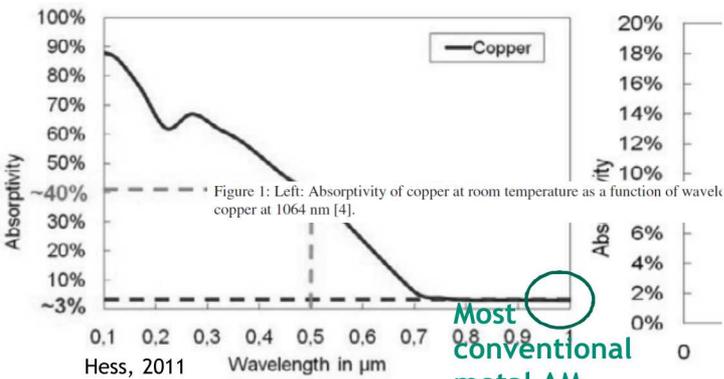


Figure 4 Thermal conductivity and absorption properties for copper

Phase 2, is the melting phase, where the top material within the spot area is initially partly solid and partly liq



Fig. 35 Reticulated mesh Ti-6Al-4V skull replacement fabricated by EBM



Schematic of low absorption/high reflectivity then switch to high absorption and unstable melt pool

4 The field is progressing, and advancement is inevitable

- Alloying alters absorption and conduction properties to provide a more stable melt pool
 - CuNi₂SiCr
 - CuCrZr (C18150)
- But altering these properties limits the applications
- AM with pure Cu is often desirable over alloys
 - Decreasing the wavelengths
 - Pulse processing
- Eventually, fabrication and assembly processes will require soldering and/or brazing*

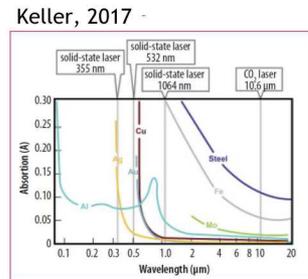
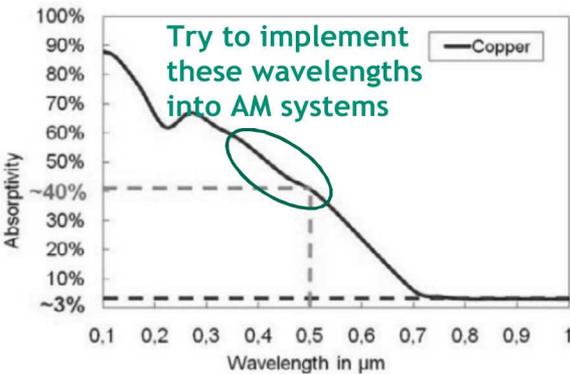
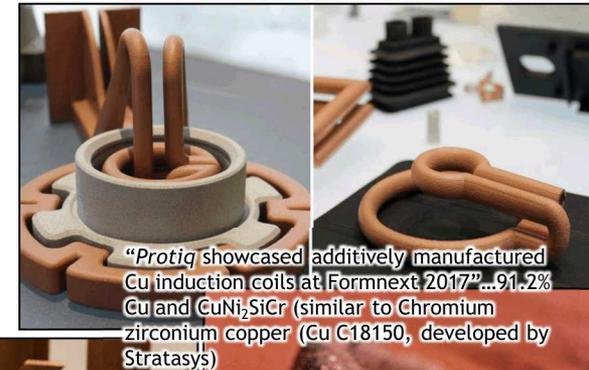
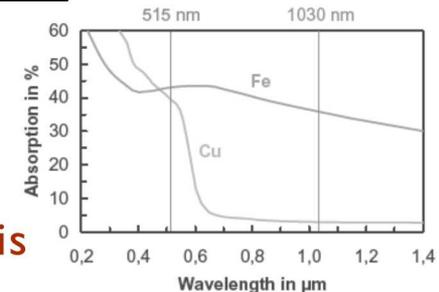


Fig. 2 Absorption coefficient of typical laser-processed materials at different wavelengths. [1]

30 Laser Technik Journal 4/2017

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Engler, 2011

Can we study solderability as the technology is **evolving**, before it is **embedded** in industrial processes?

To provide input on how to tweak processing if needed to promote solderability?

Ink printing/sintering processes are currently more established

- These AM coatings are the basis of this initial solderability study
- The ultimate goal is to perform solderability studies on bulk AM Cu pieces manufactured with various processes.

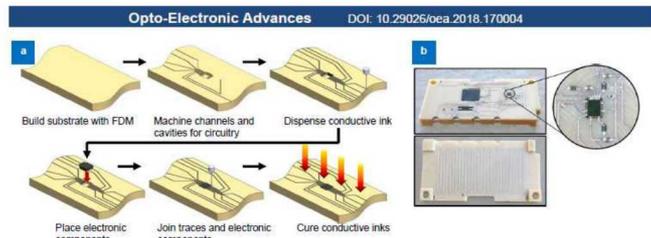


Fig. 2 | (a) Process flow of the multi-3D system. (b) Fabricated parts. Figure adapted from ref. ¹, Springer International Publishing AG.

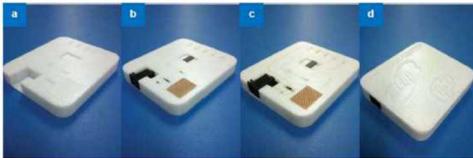


Fig. 3 | Fabrication procedure of fully encapsulated capacitive sensor with 3D printing. (a) Polycarbonate (PC) substrate with recesses designed for all electronic components. (b) Components arranged in the PC substrate. (c) Electrical components with corresponding embedded wiring. (d) Completed capacitive sensor with fully embedded wiring, diodes, LEDs, resistors, and a microcontroller. Figure reproduced from ref. ²¹, IEEE.

Figure adapted from Espalin D, Muse D W, MacDonald E, Wicker R B. 3D Printing multifunctionality: structures with electronics. *Int J Adv Manuf Technol* **72**, 963–978 (2014).



Fig. 4: Cellular hollow Cu structures fabricated using the binder jetting AM process [44].

<http://www.me.vt.edu/dreams/693/>

Table 1. Comparison of printing techniques (Shtein *et al.* 2004, Sakai *et al.* 2005, King *et al.* 2009, Rapp *et al.* 2009, Basiricò *et al.* 2011, Goth *et al.* 2011, Hrehorova *et al.* 2011, Sridhar *et al.* 2011, Hedges and Marin 2012, Paulsen *et al.* 2012, Prudenziati and Hormadaly 2012, Zhao *et al.* 2012, Kang *et al.* 2013, Cai *et al.* 2014, Suganuma 2014, Khan *et al.* 2015).

Printing techniques	Ink viscosity (cP)	Minimum line width (µm)	Layer thickness (µm)	Speed (m/min)	Advantages	Disadvantages
Flexographic printing	10–500	45–100	0.8–1(solvent) Up to 2.5 (UV-curing)	~500	<ul style="list-style-type: none"> – Very fast printing process – Suitable for flexible substrate due to lower printing pressure 	<ul style="list-style-type: none"> – Practically, all of the ink on the plate/ roller is not transferred to the substrate. – Formation of halo tends around the surface of the printed edges – Not suitable with thick and rigid substrate – High initial cost and complex set-up
Gravure printing	100–1000	10–50	0.8–1(solvent) 5–8 (UV-curing)	~1000	<ul style="list-style-type: none"> – Outstanding for high-speed mass production – Suitable for printing on 3D surface with high height steps – Possible to print different layer thicknesses in a single stroke 	<ul style="list-style-type: none"> – Practically, all of the ink on the plate/ roller is not transferred to the substrate. – An organic solvent that might cause swelling of the roller is normally used – High initial cost and complex set-up
Offset lithography	100–10,000	~10	~10	~1000	<ul style="list-style-type: none"> – Suitable for printing on 3D surface with high height steps – High volume and speed production with less environmental impact – Suitable for mass production 	<ul style="list-style-type: none"> – An organic solvent that might cause swelling of the roller is normally used. – Typically, low film thickness (1–2 µm) which is difficult to achieve the electrical conductivity – The presence of moisture lowers the electrical properties of the printed film. – Not suitable for printed organic material due to the viscoelastic properties of organic materials – High initial cost and complex set-up
Screen-printing	500–5000	30–50	5–100	~70	<ul style="list-style-type: none"> – High aspect ratio of printed object – Possible to print thick layers (1–100 µm) – Variety of ink can be printed on any substrate. – Capable of repeated printing of electronic patterns – Suitable for mass production 	<ul style="list-style-type: none"> – Printing is relatively slow. – A mesh pattern, which is formed by photolithography, is required. – The resolution is limited by the mesh pattern. – High surface roughness – Inks are only high viscous or paste-like materials. – High initial cost and complex set-up
Inkjet	<20	30–50	<1	15–500	<ul style="list-style-type: none"> – Contactless digital printing method – Low possibilities of cross-contamination – Possible to print on various types of substrates, from rigid to flexible – 3D coating with non-contact processing – Lower wastes of costly materials – Possible to print with multi-materials and multilayer patterns 	<ul style="list-style-type: none"> – Nozzle clogging occurs usually. – Sometimes, spread-out dots can be found. – Constrain in rheological properties of ink formulation – Formation of coffee stain pattern (Coffee-ring effect) prevents the deposition uniformity. – Not suitable for printing on non-planar surfaces – Lower throughput compared to the conventional printing methods
Aerosol-jet	1–5 (UA) 1–100 (PA)*	>10	0.1–2	Up to 12	<ul style="list-style-type: none"> – Contactless digital printing method – Possible to print on any types of substrate, from rigid to flexible – Capable of printing on non-planar surfaces and 3D surfaces/ structures – High-resolution printing technique with an accurate alignment system – Elimination of nozzle clogging issue – Several options of deposited materials – Decreases the possibilities of cross-contamination – Possible to print with multi-materials and multilayers 	<ul style="list-style-type: none"> – Additional supplying systems are required, for example, sheath gas and cooling system. – Lower throughput compared to the conventional printing methods
OVJC	**	<25	<1	>4 x 10 ⁻⁶	<ul style="list-style-type: none"> – Non-contact, direct-multilayer printing – Free from the solvent orthogonality problems – Variety of materials can be printed 	<ul style="list-style-type: none"> – Additional supplying systems are required. – Relatively slow printing process
LIFT	**	<20	~0.1	***	<ul style="list-style-type: none"> – Non-contact, direct-multilayer printing – No requirement of any mask and vacuum installation – Variety of donor materials can be applied 	<ul style="list-style-type: none"> – Laser irradiation can damage the pattern and reduces the efficiency of devices. – High-power laser consumption is required.

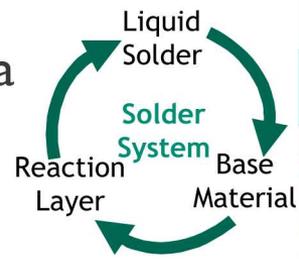
* UA = Ultrasonic Atomizer, PA = Pneumatic Atomiser.

** Materials are not inks.

*** Depending on the laser's speed.

Tran, T., "A Review: Additive Manufacturing for Active Electronic Components." *Virtual and Physical Prototyping*, 2016 DOI: 10.1080/17452759.2016.1253181

Solderability behavior helps predict the immediate success of a given solder system

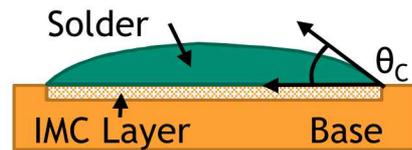


◦ **SOLDERABILITY**: the capability of molten filler metal to **WET** and **SPREAD** over the base material surface

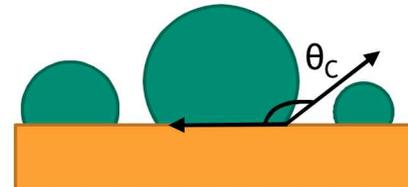
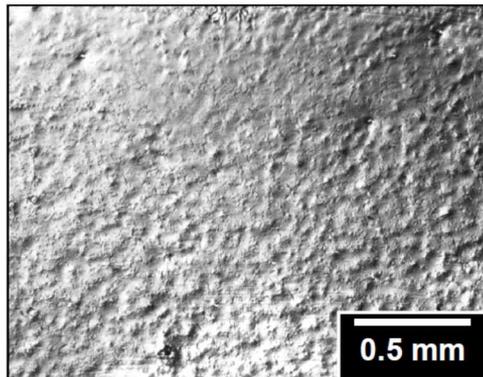
- **Wetting**: forming a metallurgical bond
- **Spreading**: spontaneous coverage by the molten solder and reaction layer

◦ 3 solderability conditions:

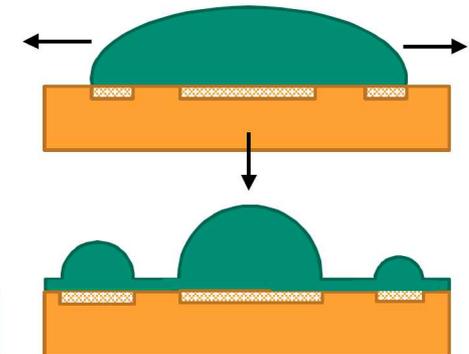
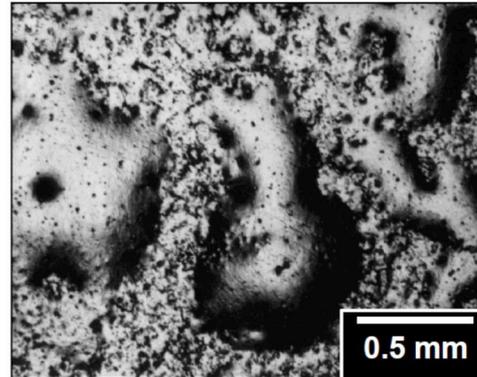
- Wetting
- Non-wetting
- Dewetting



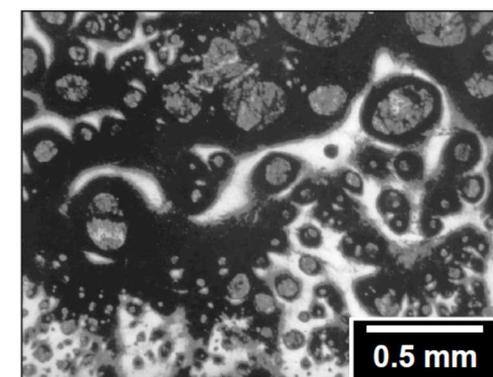
Wetting: metallurgical bond is established by the formation of an intermetallic layer



Non-Wetting: no metallurgical bond is established

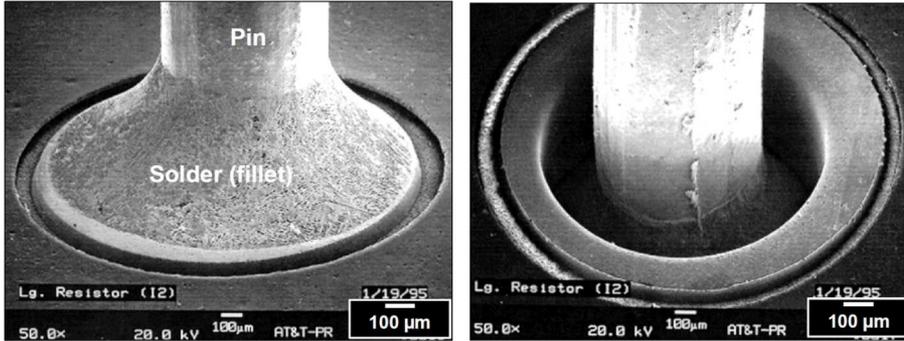


De-Wetting: incomplete metallurgical bonds are established



7 Solderability controls the final joint geometry

Features like **fillet size** and **void content** will impact long-term reliability



58Bi-42 Sn solder

Flux was not properly engineered for a low soldering process temperature (~160 °C). (Courtesy P. Vianco)

Solderability is often quantified by the contact angle (θ_C) from Young's equation

Describes the **equilibrium surface energy relationships** between the liquid solder, liquid flux, and solid base

Maximized by minimizing θ_C (minimize γ_{LF} and/or maximize $\gamma_{SF} - \gamma_{SL}$)

Function of flux and solder combination

Controlled by reaction layer that forms at solder/base interface (more of function of material composition rather than process parameters)

(Courtesy P. Vianco)

Solder (wt.%)	Temp. (°C)	γ_{LF} (dyne/cm)	θ_C (°)
95.5Sn-3.9Ag-0.6Cu	260	497±16	40±1.0
	245	444±17	39±1.0
	230	485±27	42±1.4
96.5Sn-3.5Ag	260	460±30	36±3
60Sn-40Pb	260	380±10	17±4
58Bi-42Sn	215	310±50	37±7

Substrate: OFHC Cu; Flux: RMA, 1:1 IPOH

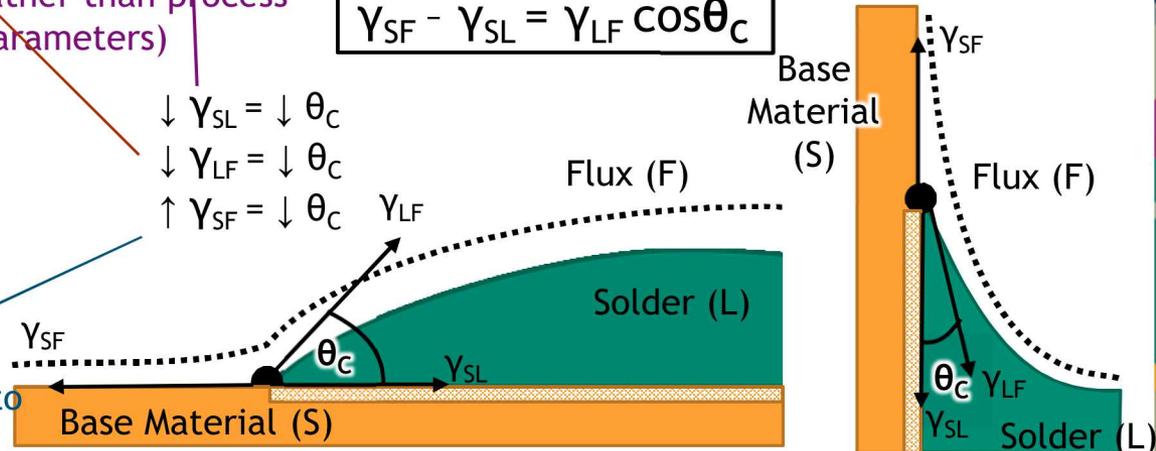
$$\gamma_{SF} - \gamma_{SL} = \gamma_{LF} \cos\theta_C$$

$$\downarrow \gamma_{SL} = \downarrow \theta_C$$

$$\downarrow \gamma_{LF} = \downarrow \theta_C$$

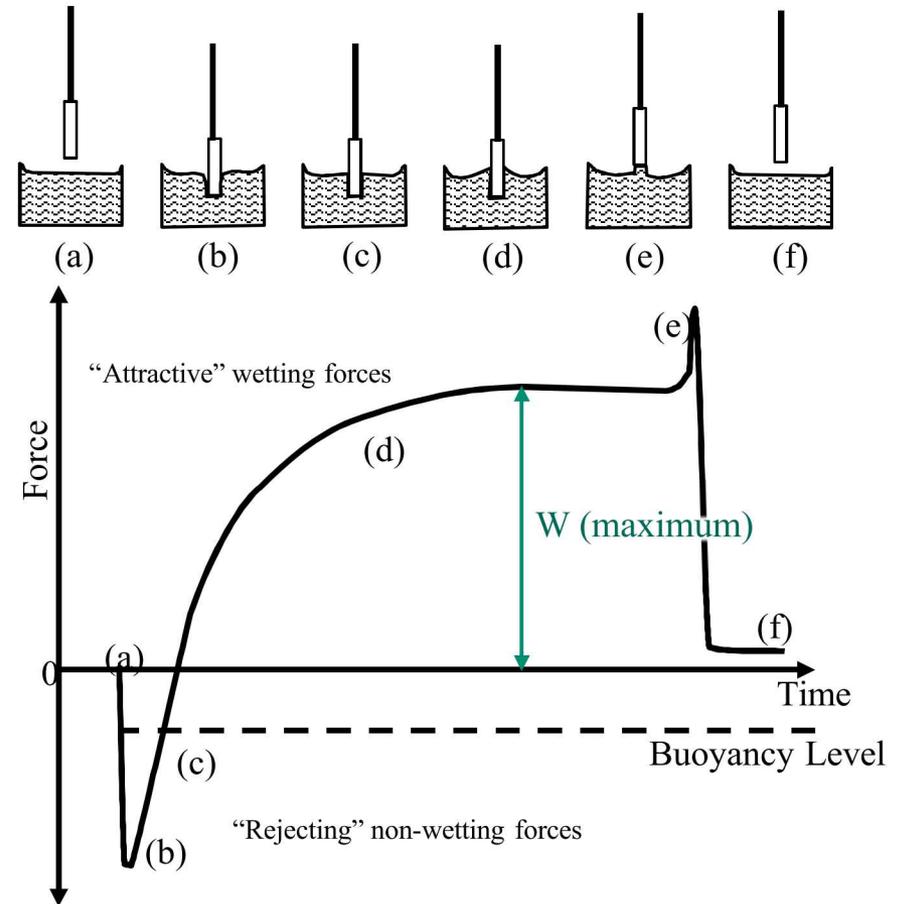
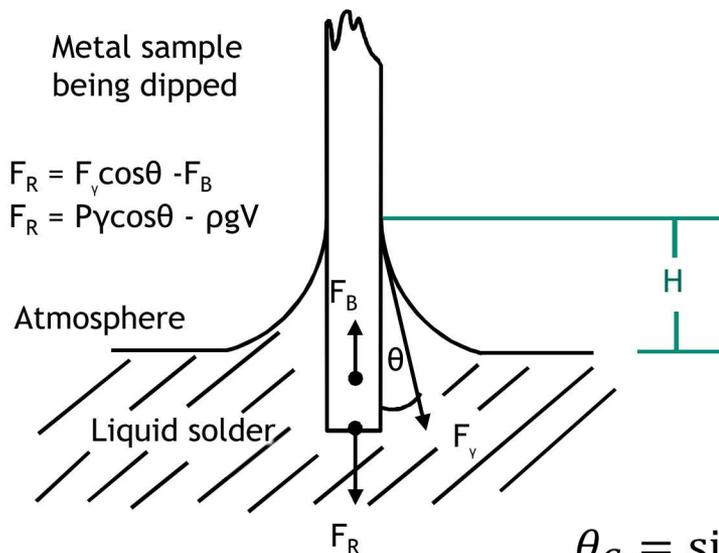
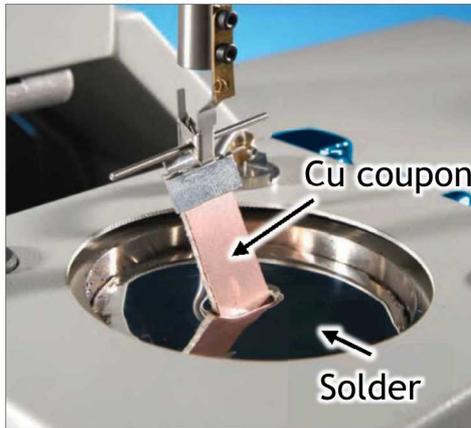
$$\uparrow \gamma_{SF} = \downarrow \theta_C$$

Flux: eliminates oxide layer; fresh surface does NOT want to contact air/flux



Contact angle can be quantitatively evaluated with a wetting balance

- In situ force measurements (weight) as a coupon is dipped into a solder pot
- Allows evaluations for unique material/flux/solder alloy systems



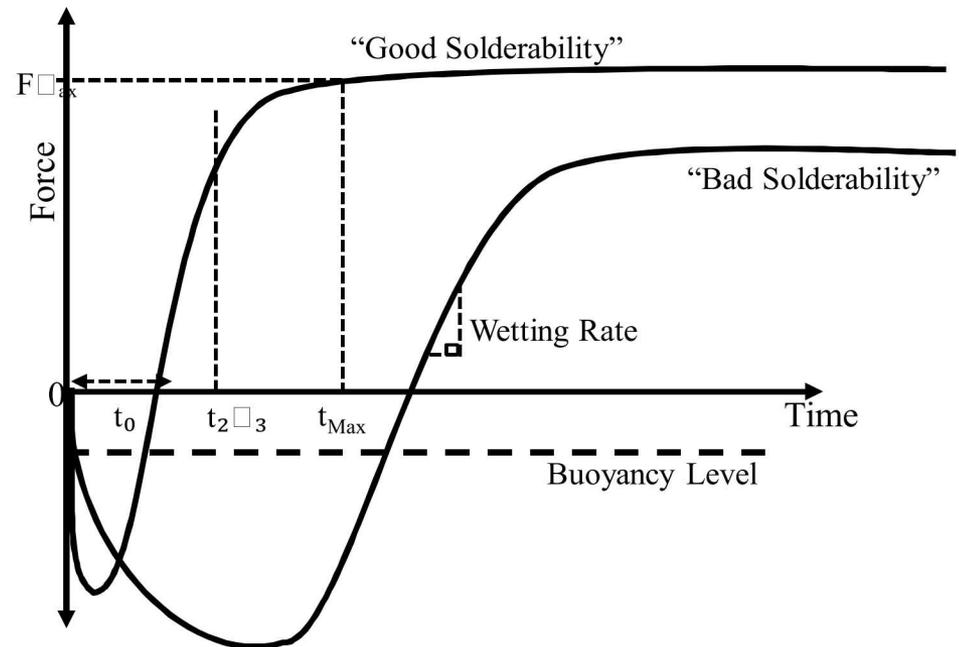
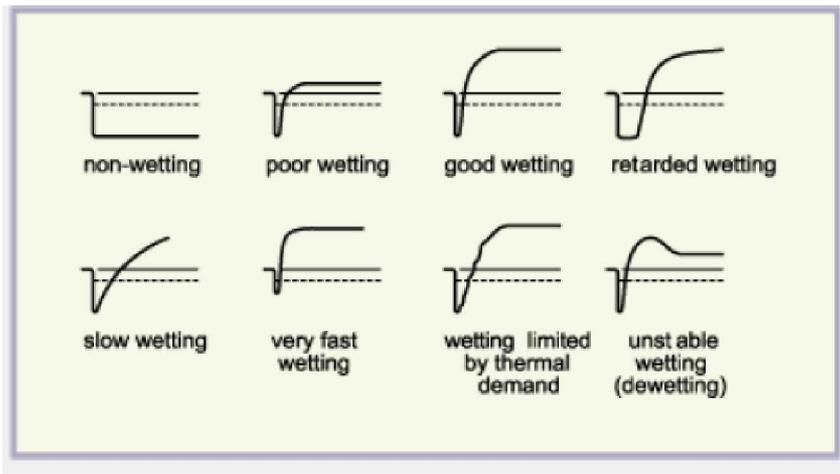
$$\theta_c = \sin^{-1} \frac{(4W^2 - (\rho g P H^2))^2}{(4W^2 + (\rho g P H^2))^2}$$

ρ : solder density
 g : acc. due to gravity
 P : sample perimeter

Wetting curves provide a “fingerprint” for a given system

- Qualitative and quantitative data
- Great for screening, monitoring shelf life

Representative shapes of wetting balance curves



Why might pure Cu exhibit solderability variation between traditionally and additively manufactured substrates?



Composition never changes, so solderability should not change, right?

WRONG

1. The composition might actually change

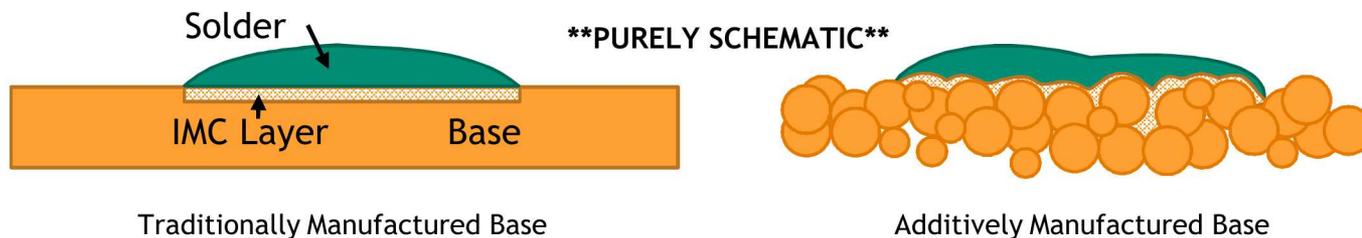
- Binders, different process atmospheres/operating temperatures may result in residual elements/molecules/oxides, affecting surface tension

2. Surface topography may support larger fractions of reaction layers

- If process supports porosity/voids, capillary action may drive the flow of solder into layer (changing the spreading behavior)
- The opposite scenario could also occur, reducing the fraction of reaction layer/substrate intimate contact

3. Process conditions may affect microstructure and hence, surface tension

- Grain size, any potential metallurgical changes imparted from non-equilibrium cooling/sintering conditions



Different wetting behavior may result in different joint systems

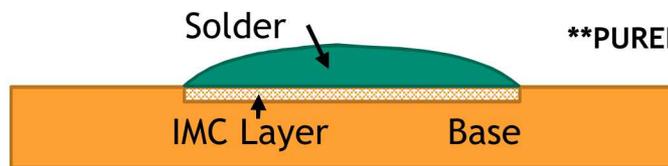


Three consequences of the wetting process:

1. Base metal dissolution
2. Changing the solder alloy composition
3. Reaction layer formation

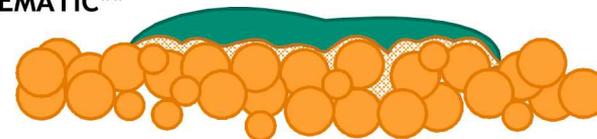


Changing these could produce a different “solder joint system,” potentially affecting solder joint **performance** and **reliability**



Traditionally Manufactured Base

****PURELY SCHEMATIC****

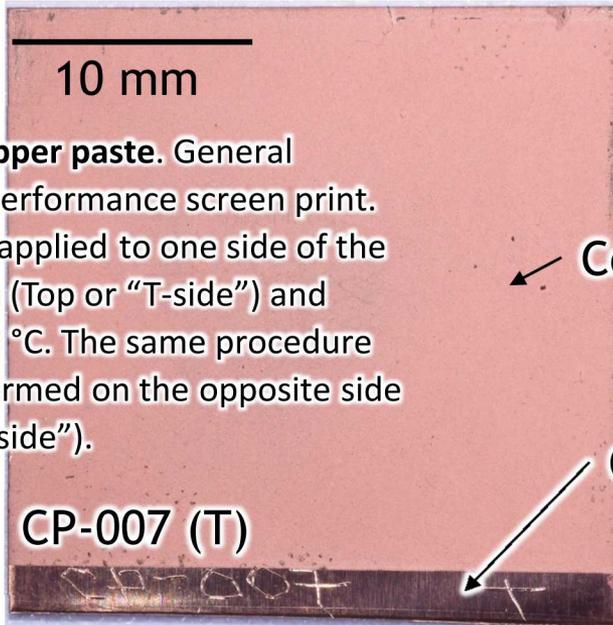


Additively Manufactured Base

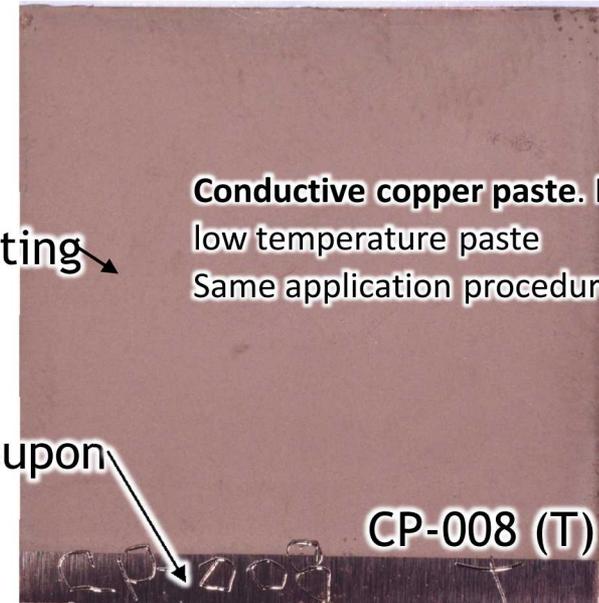
12 Test plan and future outlook

- 1 x 1 x 0.02” oxygen free high conductivity (OFHC) copper coupons coated with AM Cu layer
 - 4 different coating processes were compared (*Intrinsic*)
 - Cleaning procedure (HCl and ultrasonic IPOH)
 - 10 dips per coating?
 - Contact angles, max. force/weight, wetting rate
 - Pre- and post- dip optical and SEM imaging
 - Pre- and post- dip optical and SEM imaging
 - Low cycle and high cycle fatigue studies
 - Interfacial characterization
- Solderability coupons
- Wetting balance
solder dips
- Optical/electron
characterization
- Entirely AM built
coupons; brazing study
- Aging/Reliability

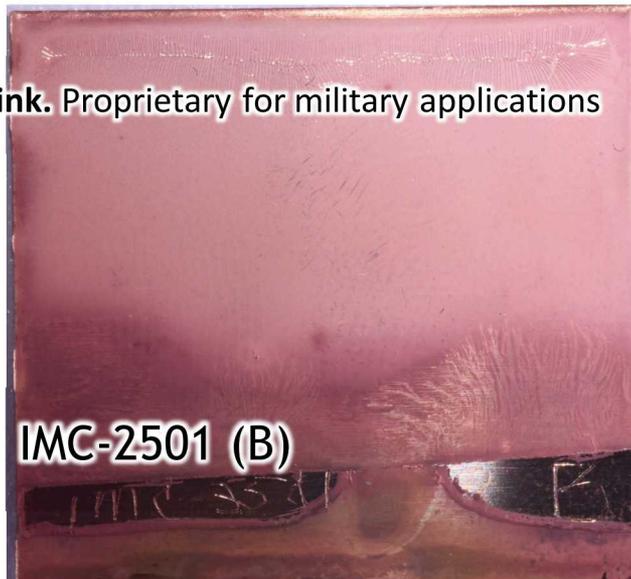
4 Cu coatings were compared



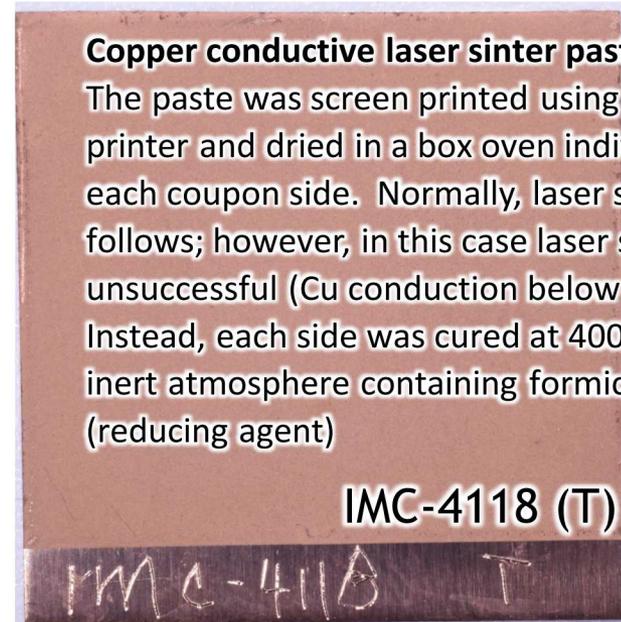
Conductive copper paste. General purpose high performance screen print. The paste was applied to one side of the copper coupon (Top or “T-side”) and sintered at 230 °C. The same procedure was then performed on the opposite side (Bottom or “B-side”).



Conductive copper paste. High copper, low temperature paste. Same application procedure as CP-007.



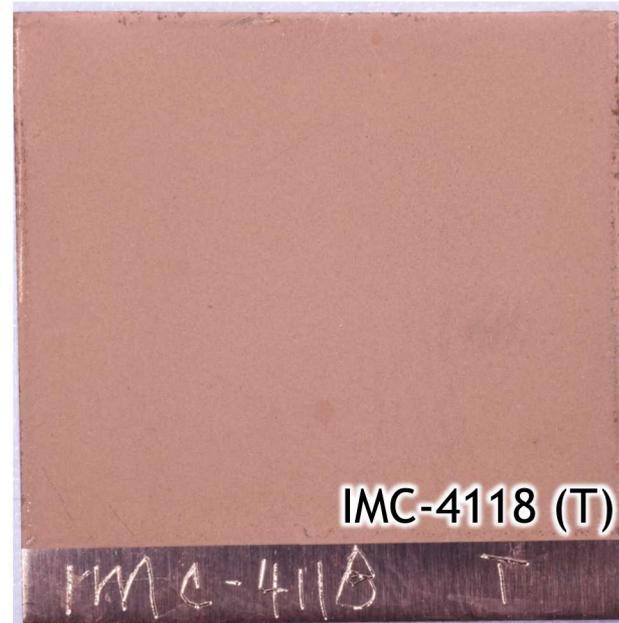
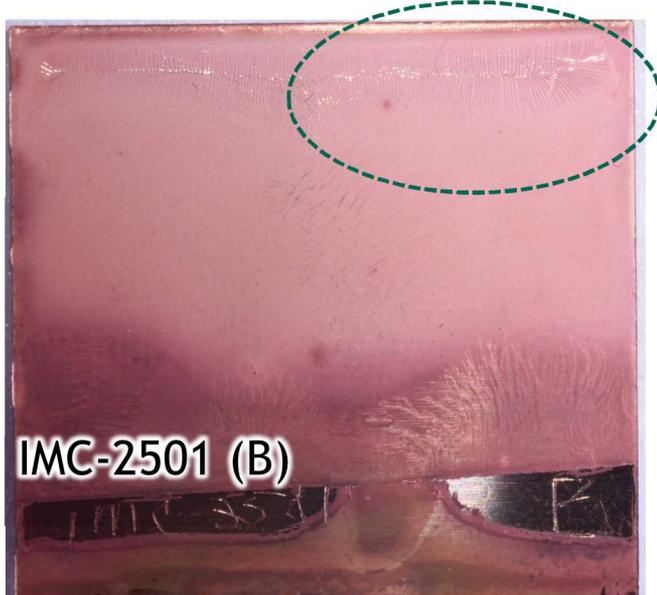
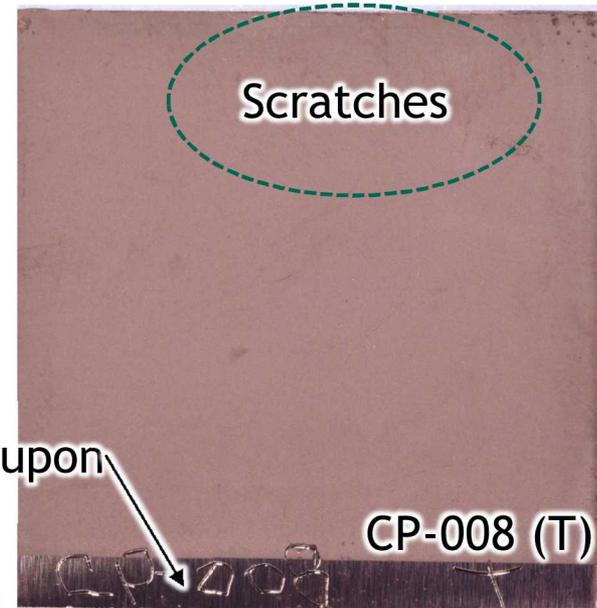
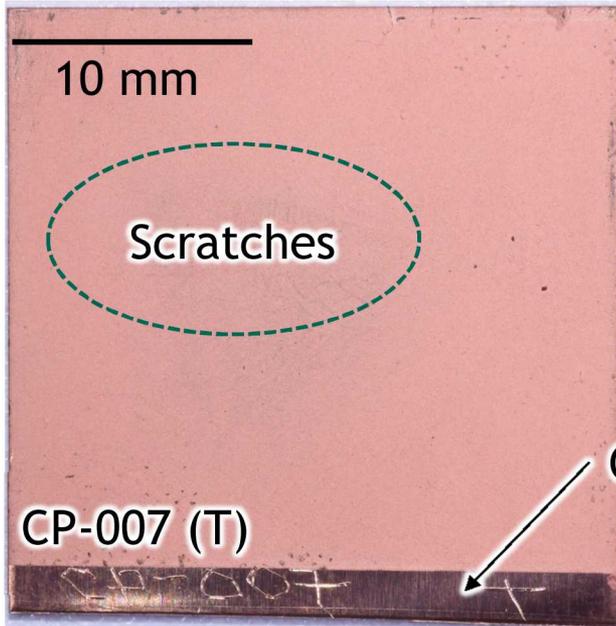
Copper ink. Proprietary for military applications



Copper conductive laser sinter paste.

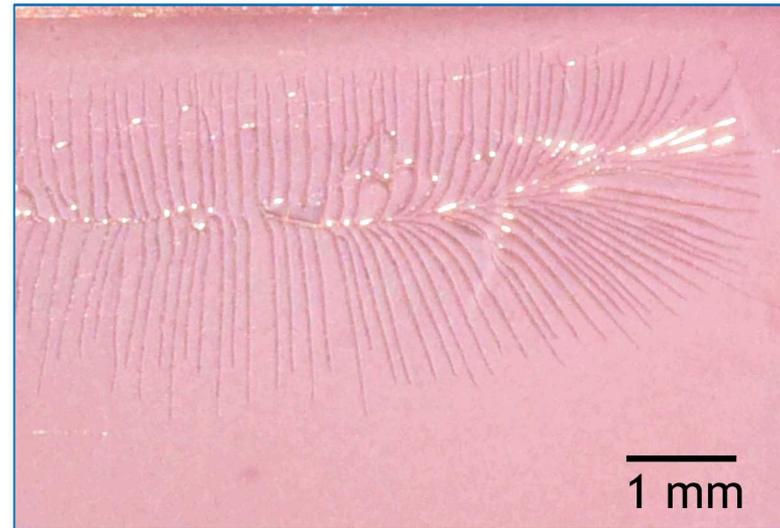
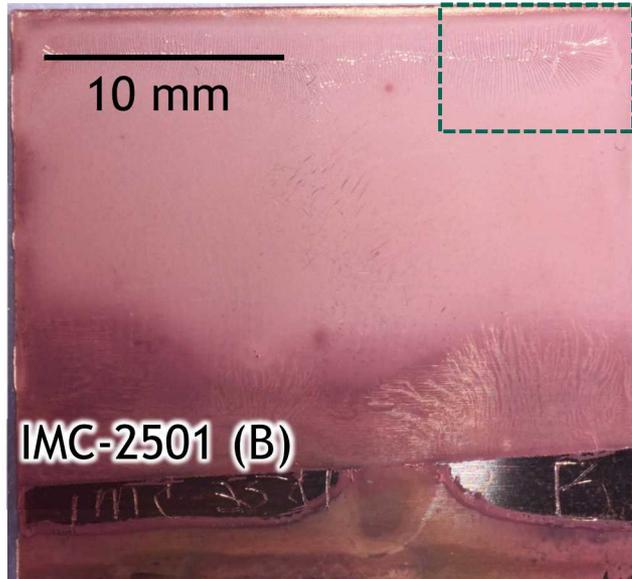
The paste was screen printed using a Dek printer and dried in a box oven individually for each coupon side. Normally, laser sintering follows; however, in this case laser sintering was unsuccessful (Cu conduction below coating). Instead, each side was cured at 400 °C in an inert atmosphere containing formic acid (reducing agent)

Except IMC-2501, surface applications appeared even, though often scratched



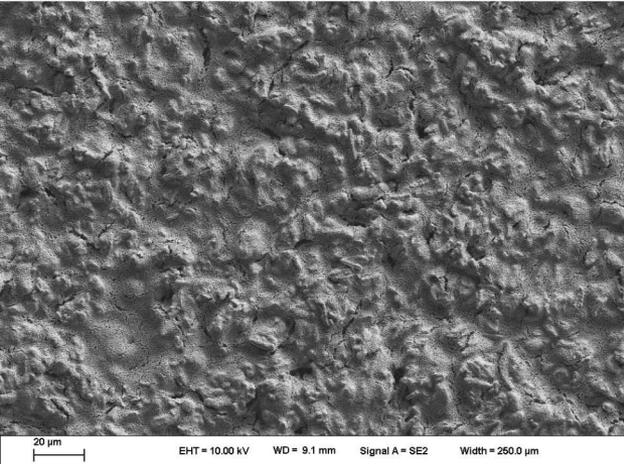
Except IMC-2501, surface applications appeared even, though often scratched

Areas where surface appears feathery, textured

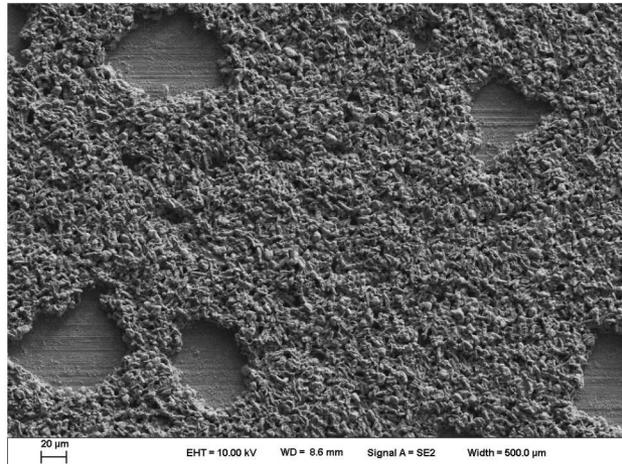
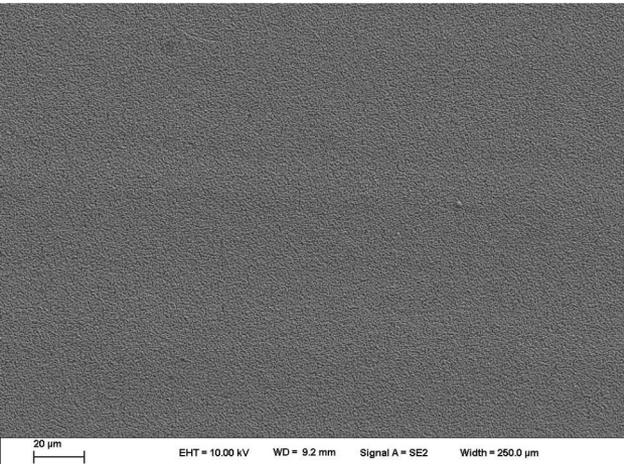
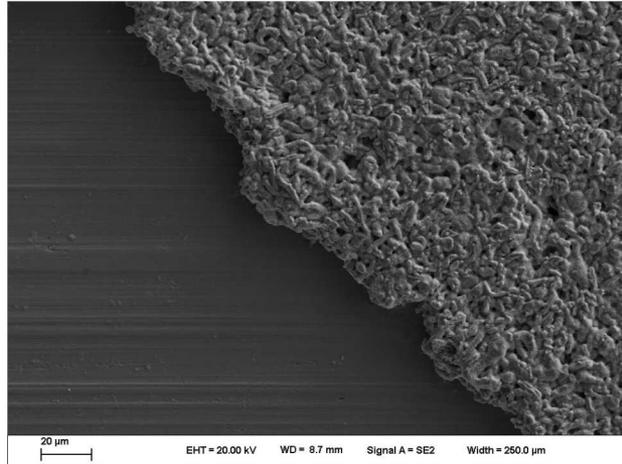


16 AM Cu Surface Comparison

CP007



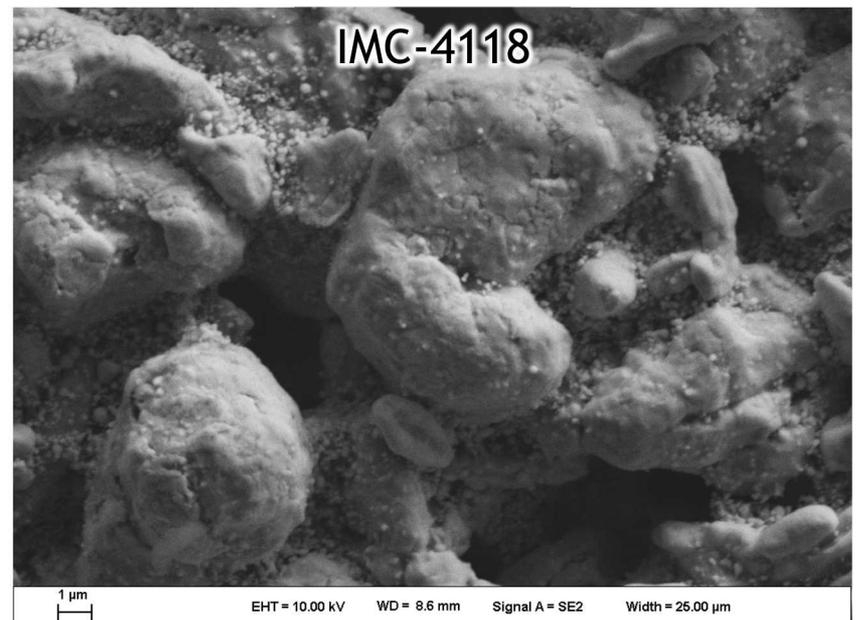
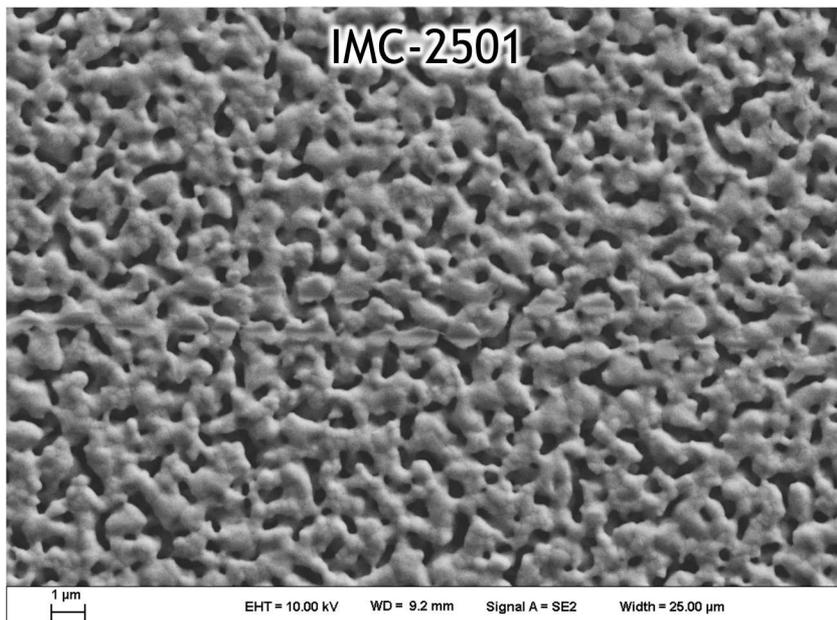
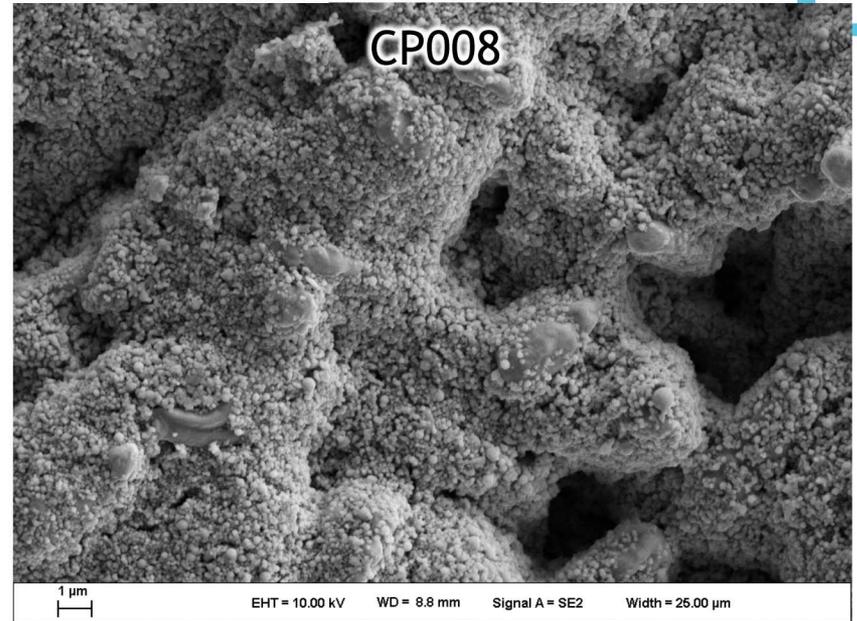
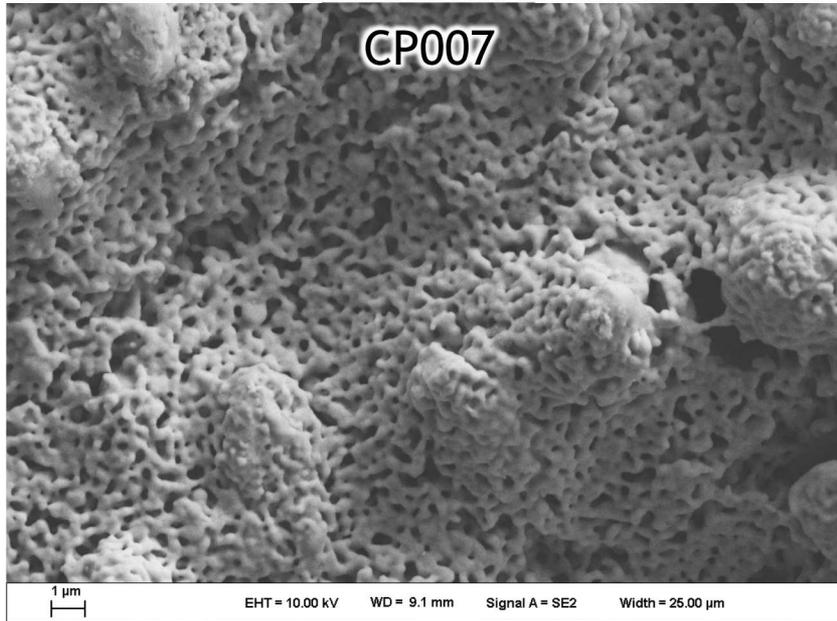
CP008

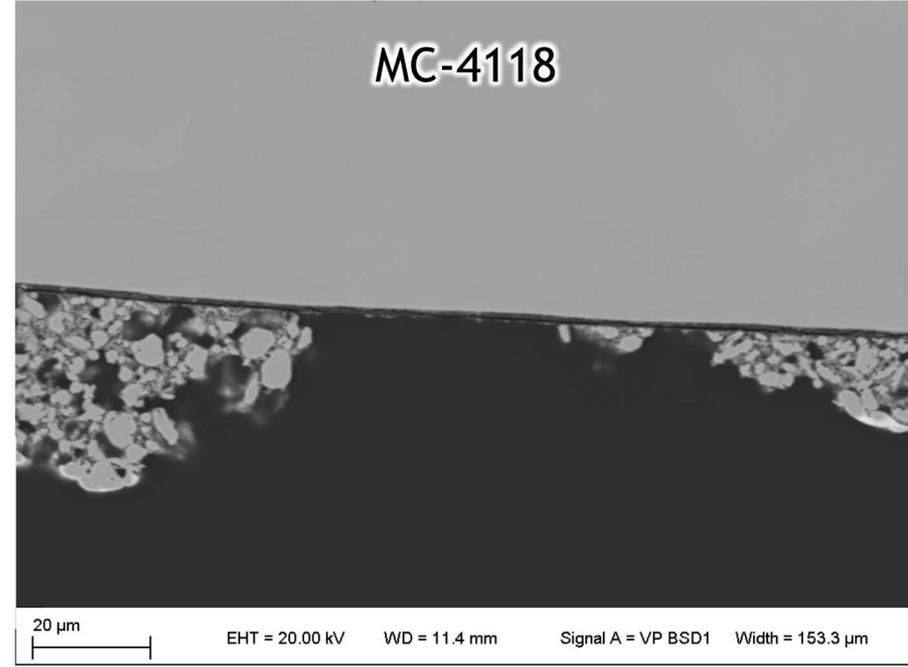
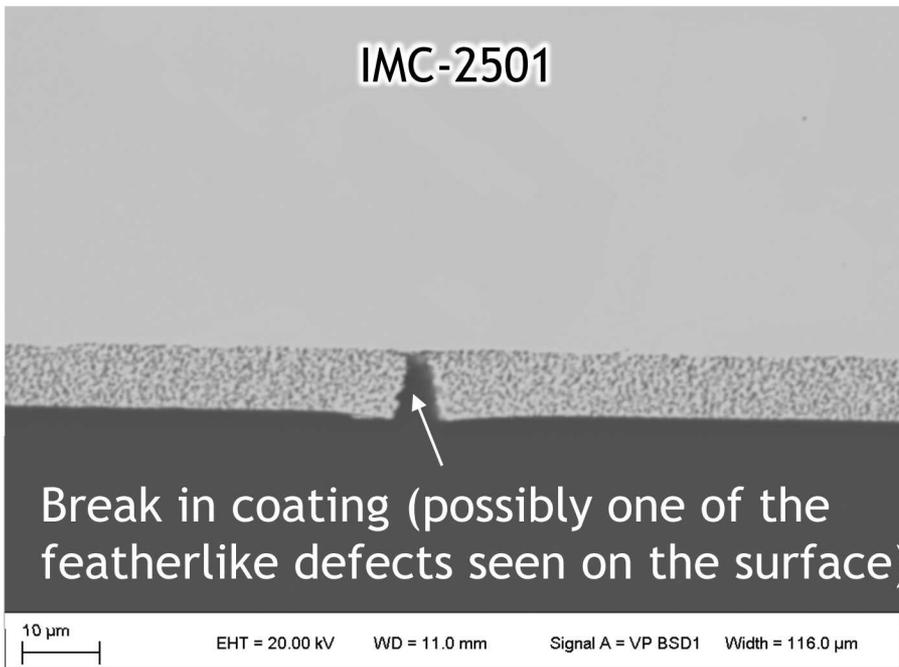
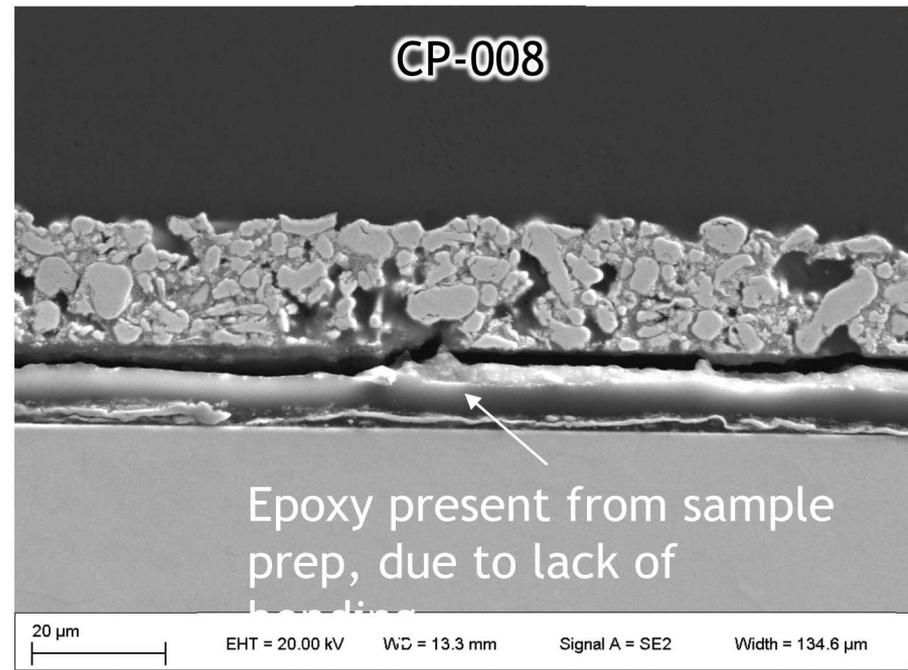
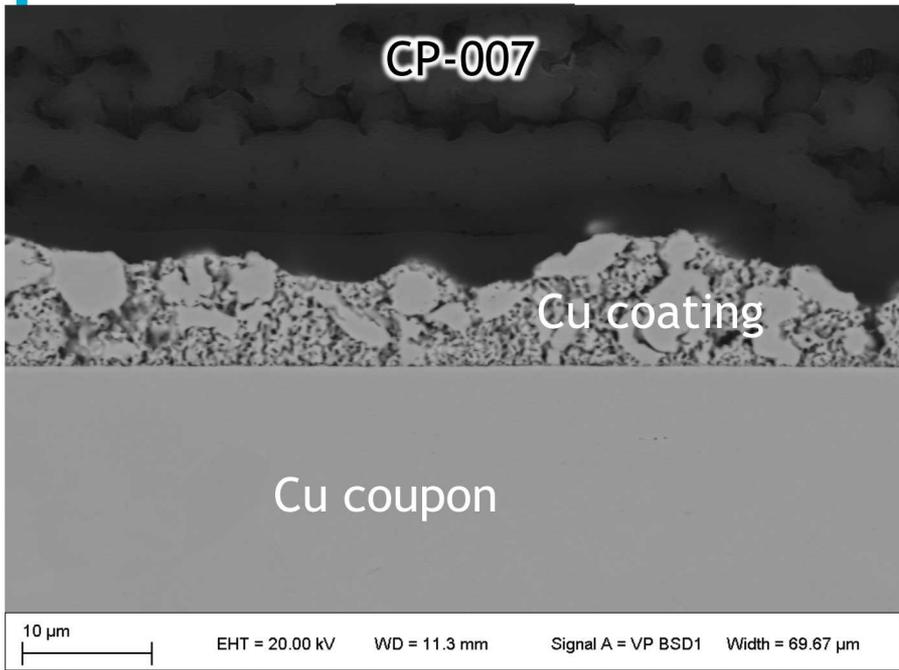


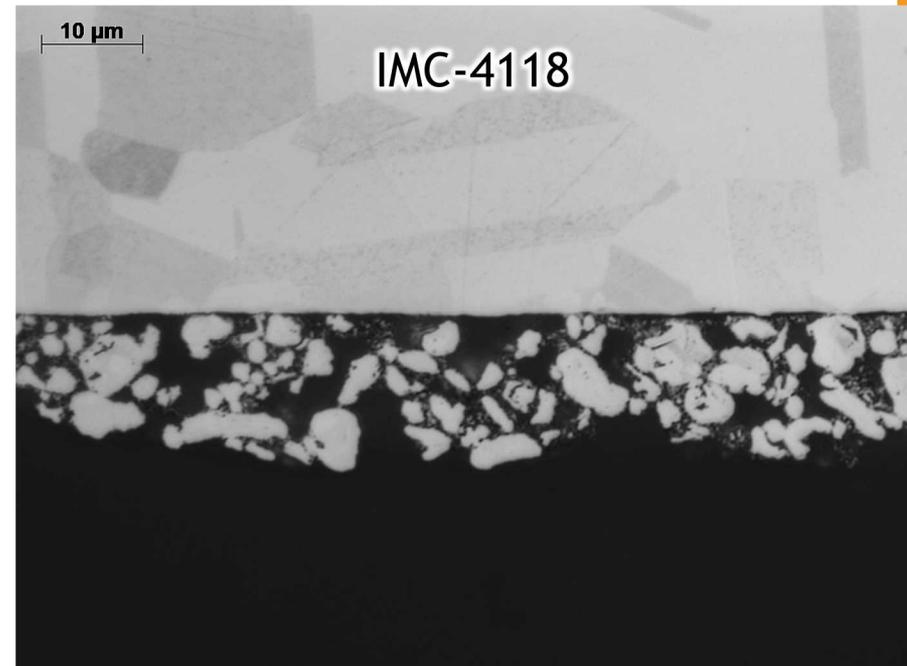
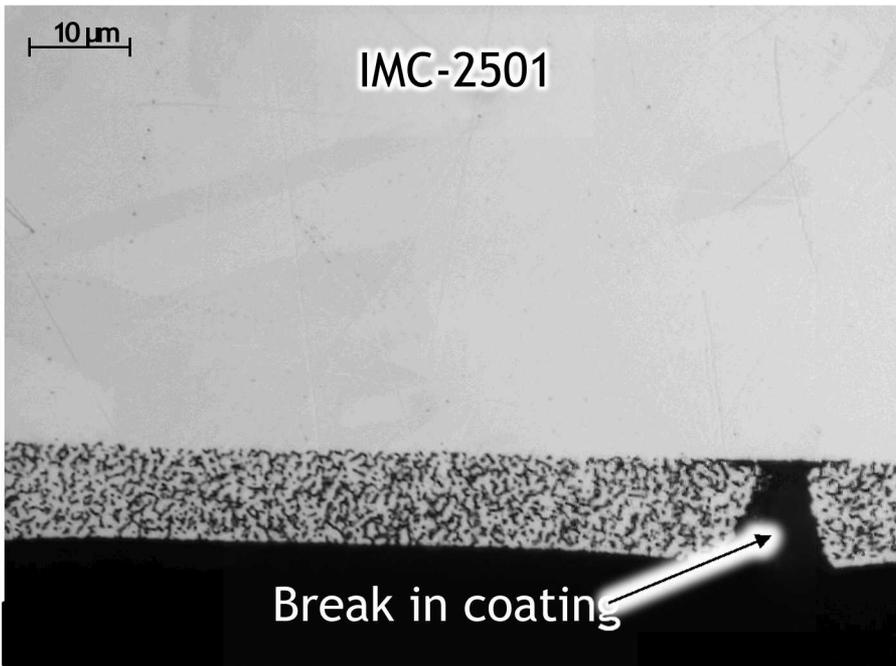
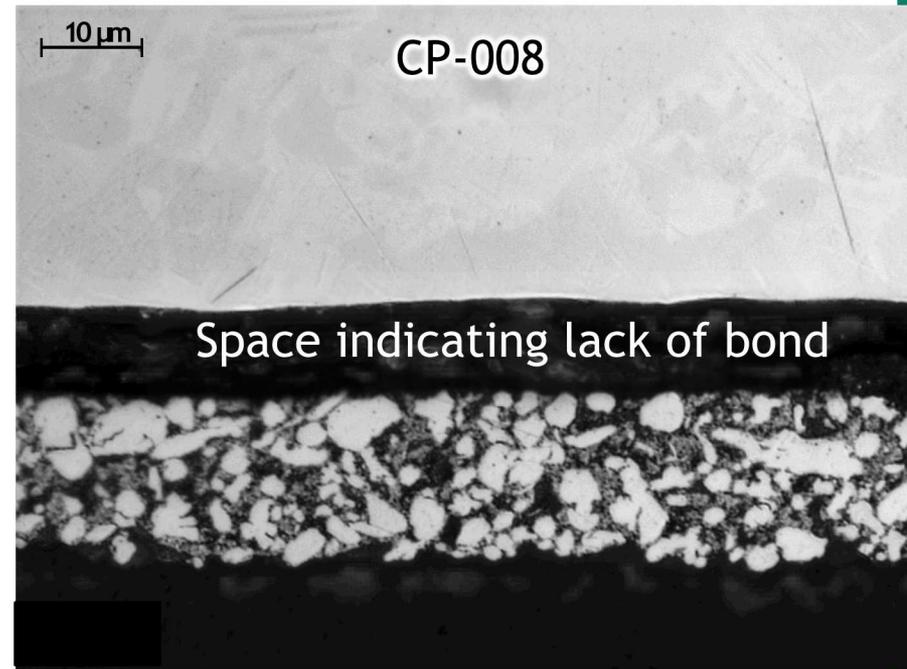
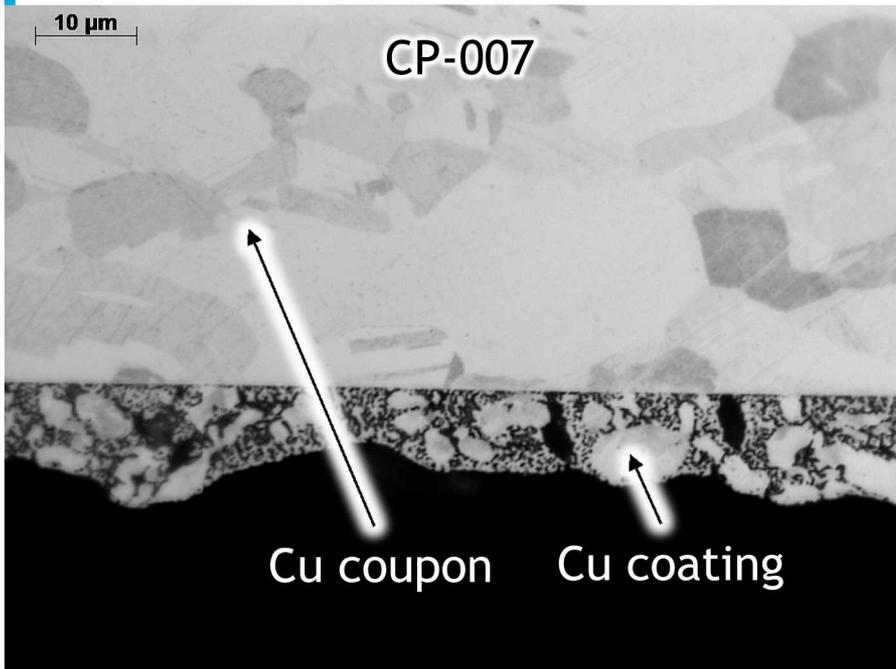
IMC-4118 (scale isn't the same)

IMC-2501

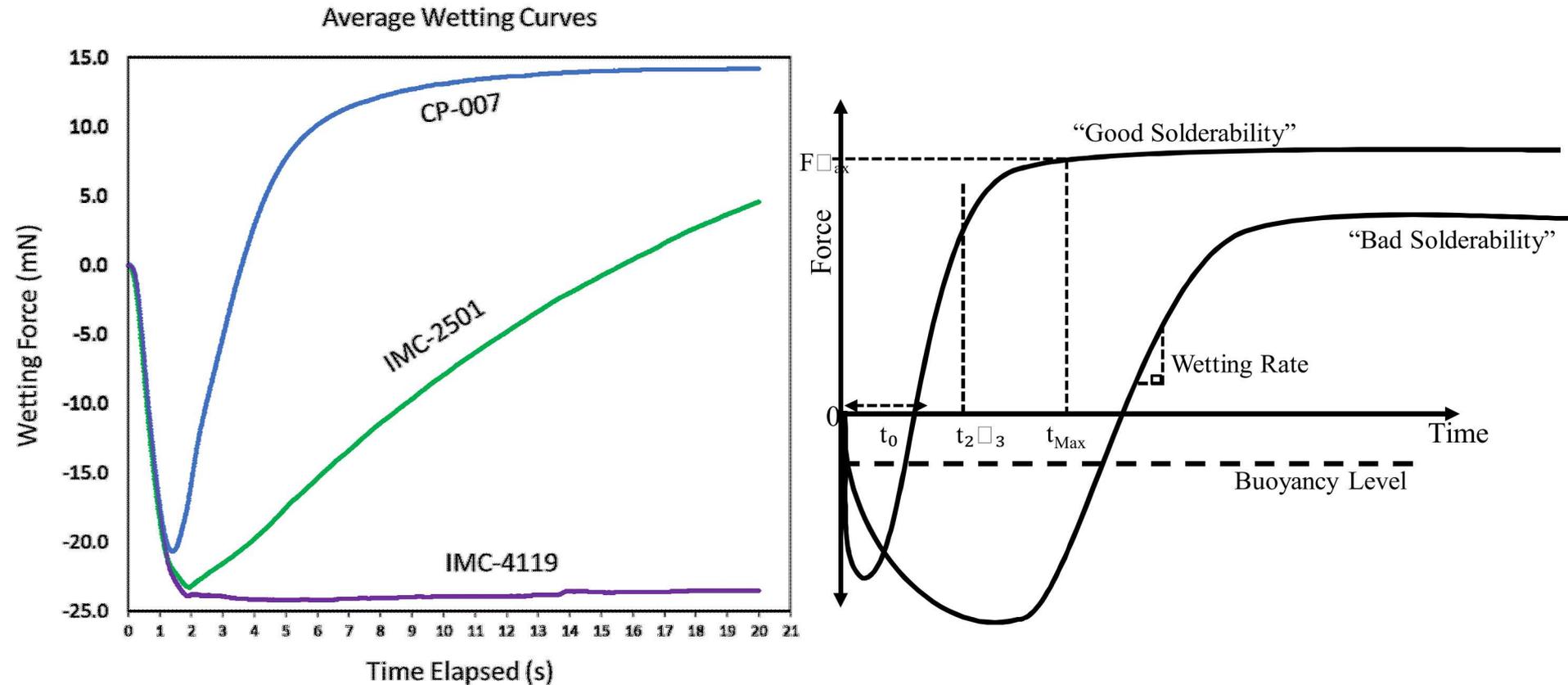
IMC-4118 (shrunk to match the scale)







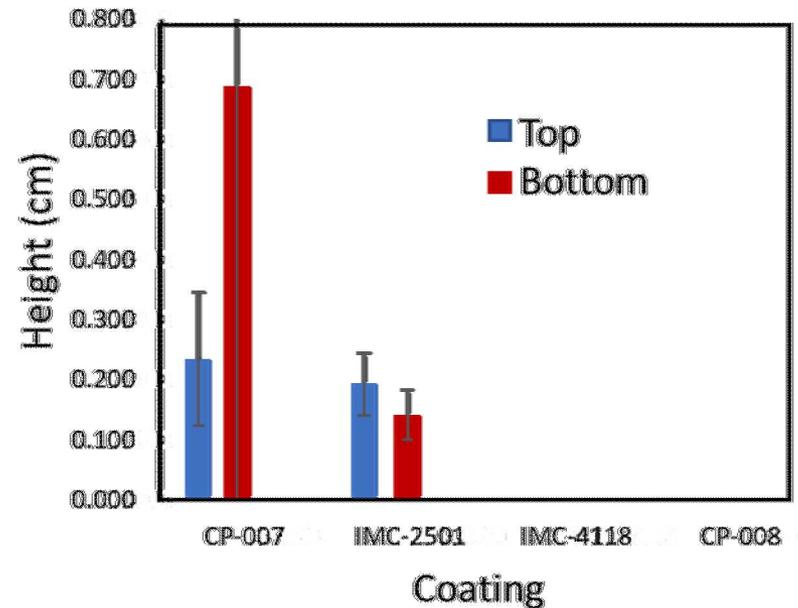
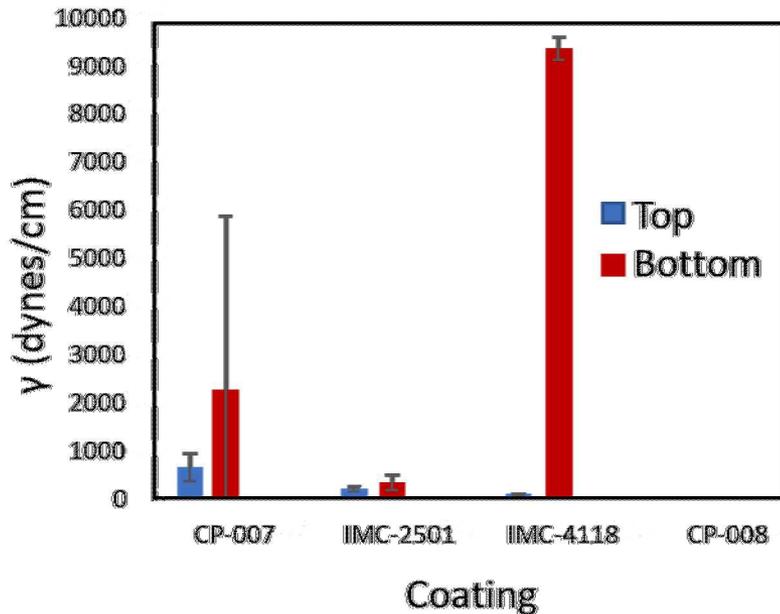
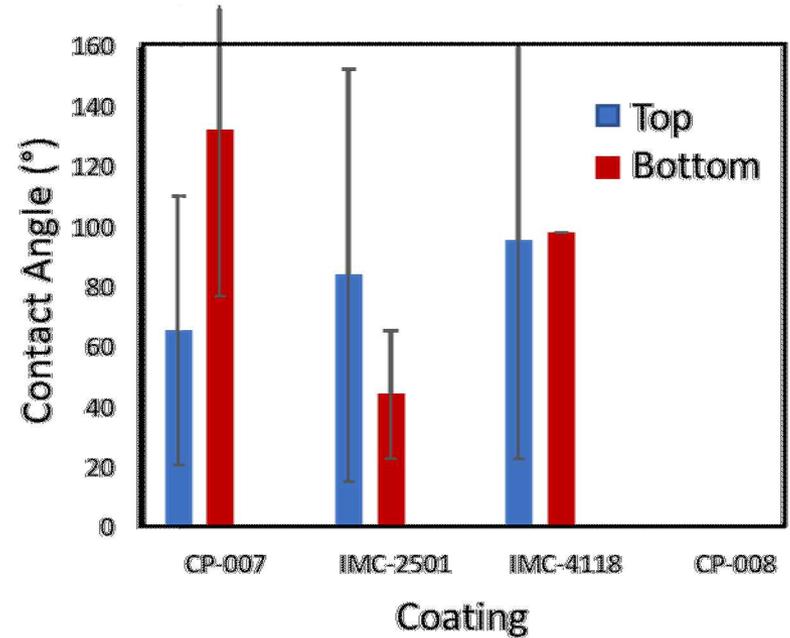
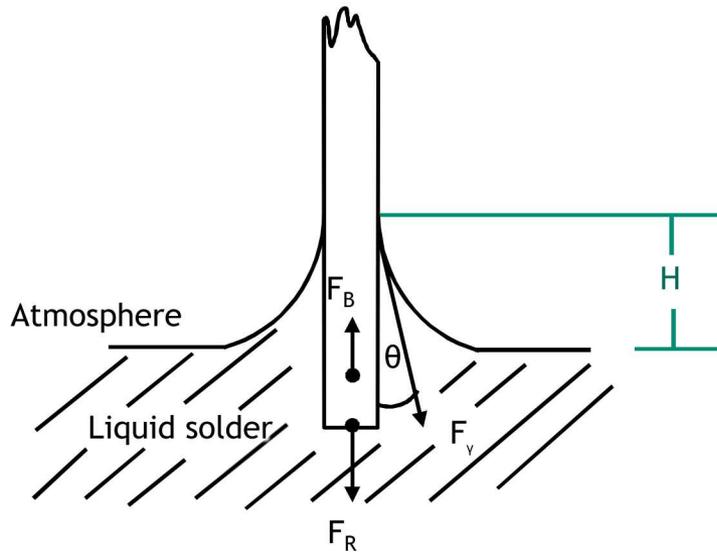
The 3 testable coatings reflected very different wetting curves



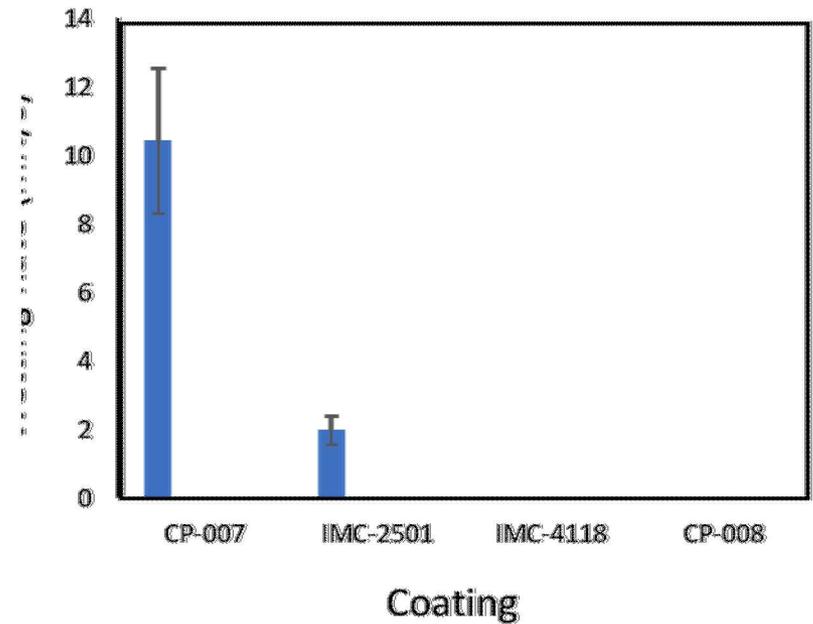
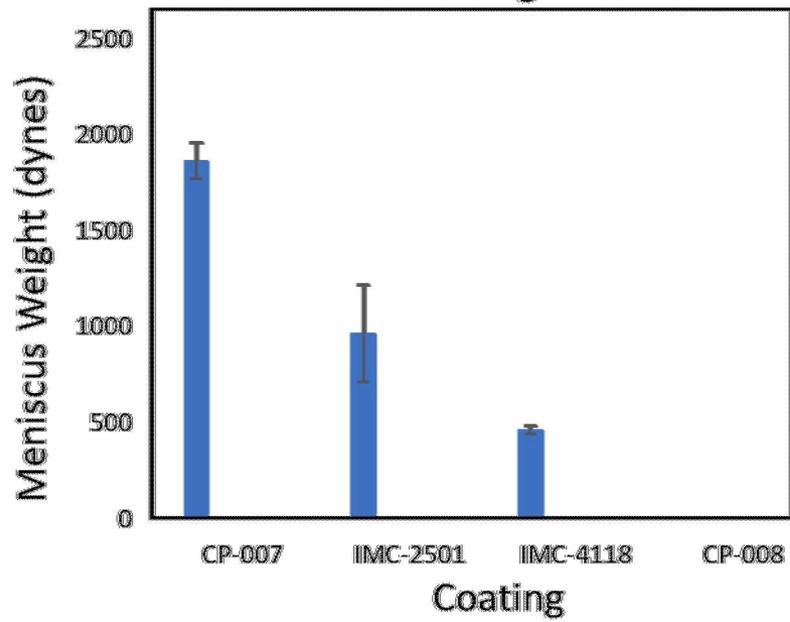
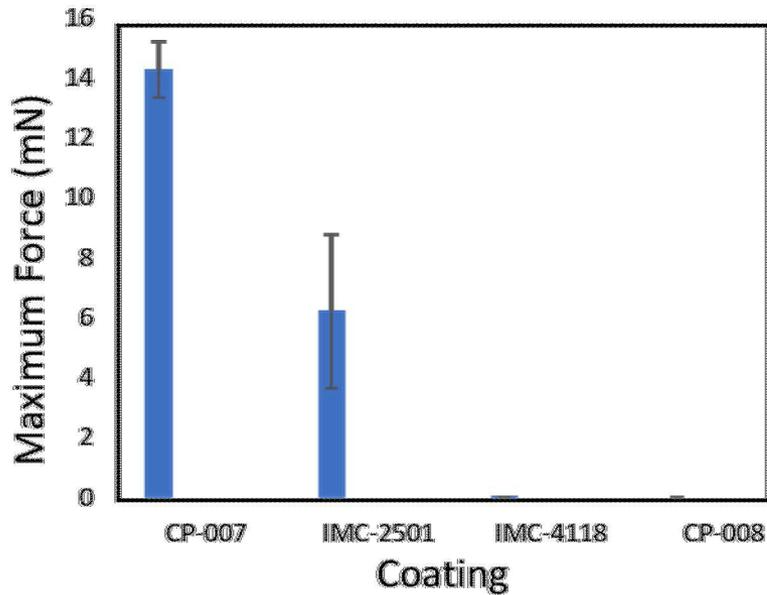
All 3 coatings were meant to produce a pure, high conductivity Cu coating, but the difference in wetting behavior is clear

CP-007 appears to be the top performer, qualitatively, from the wetting curves

Side-Specific quantitative data doesn't reflect clear trends

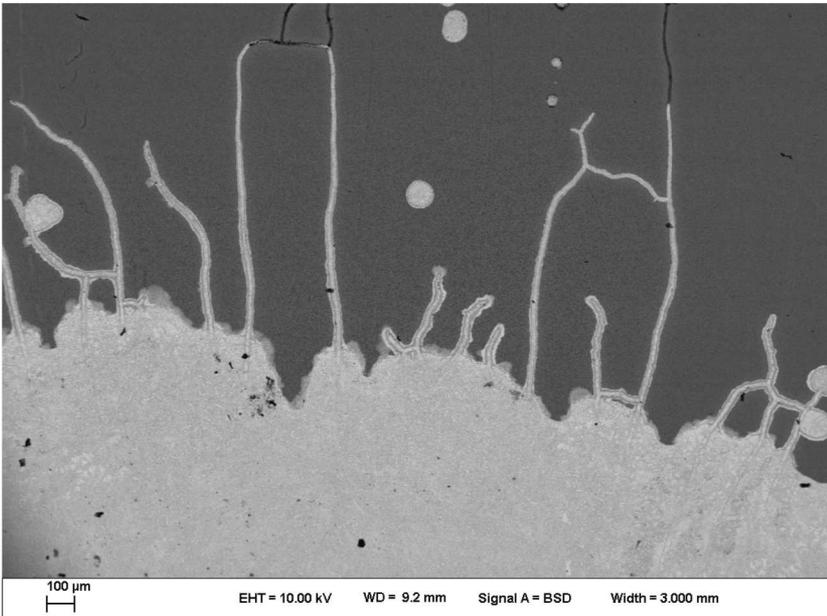
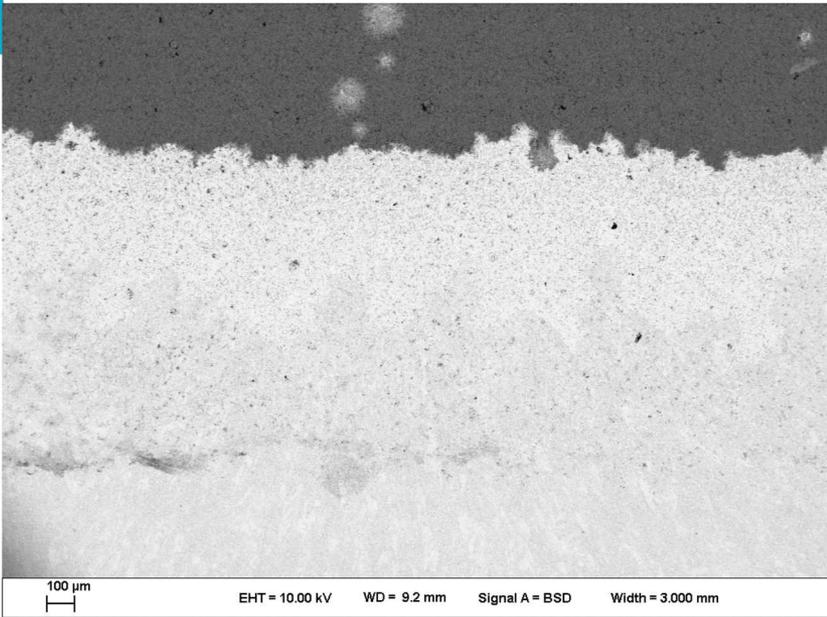


Non-side specific data exhibits clearer trends

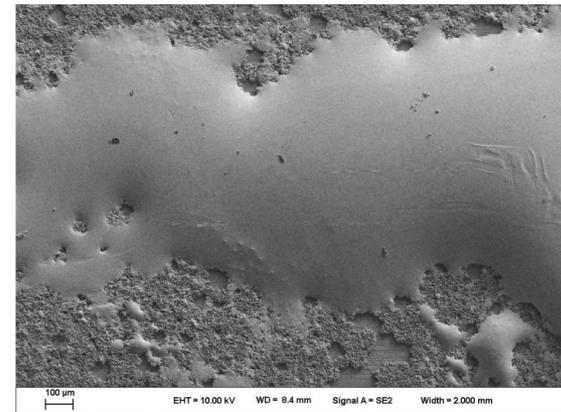
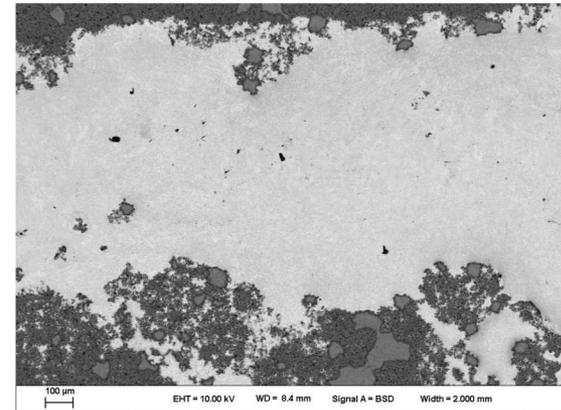


CP007

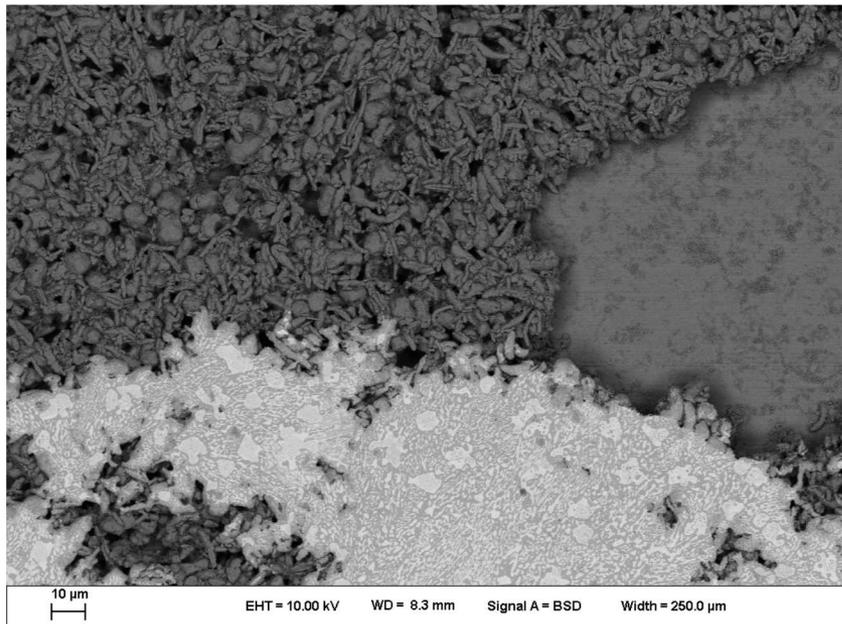
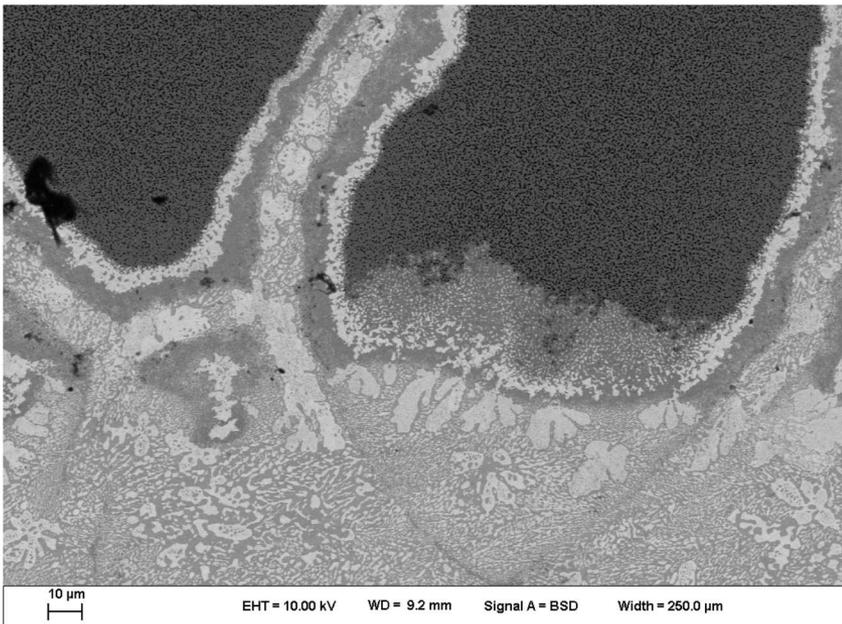
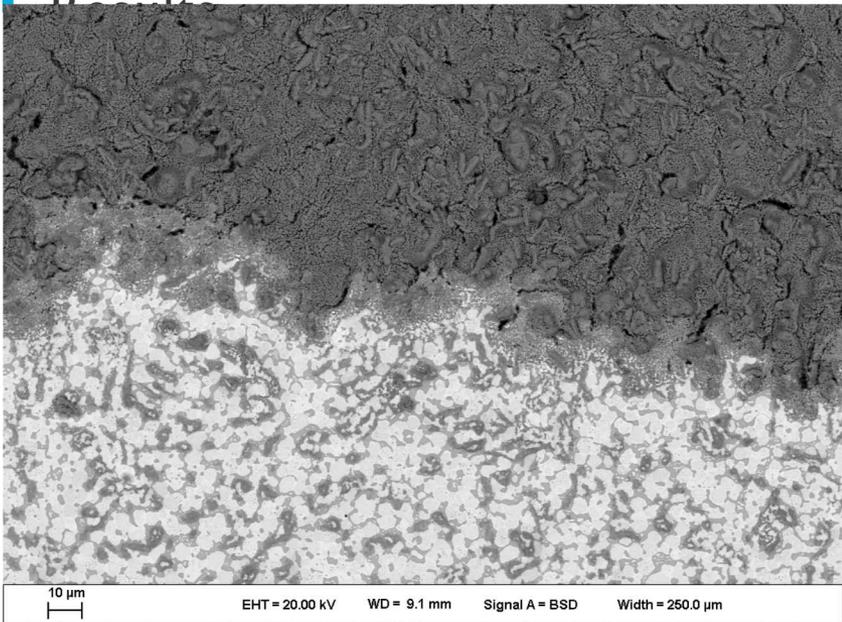
23



IMC-2501



IMC-4118 (shrunk to match the scale)



CP007

CP-007

Cu coupon

Solder

100 μ m

EHT = 20.00 kV

WD = 11.4 mm

Signal A = SE2

Width = 3.267 mm

IMC-2501

100 μ m

EHT = 20.00 kV

WD = 11.8 mm

Signal A = SE2

Width = 2.854 mm

MC-4118

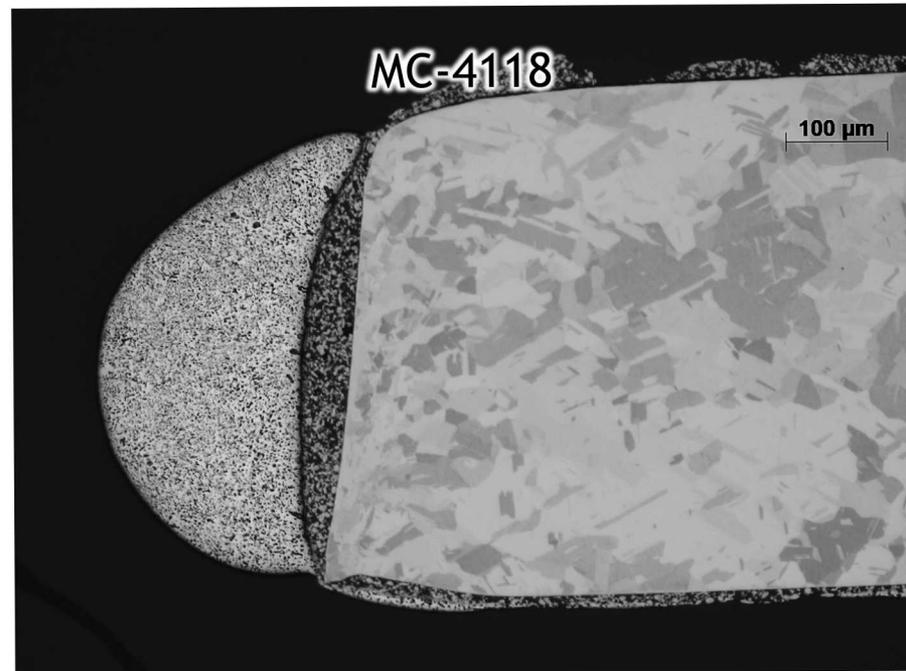
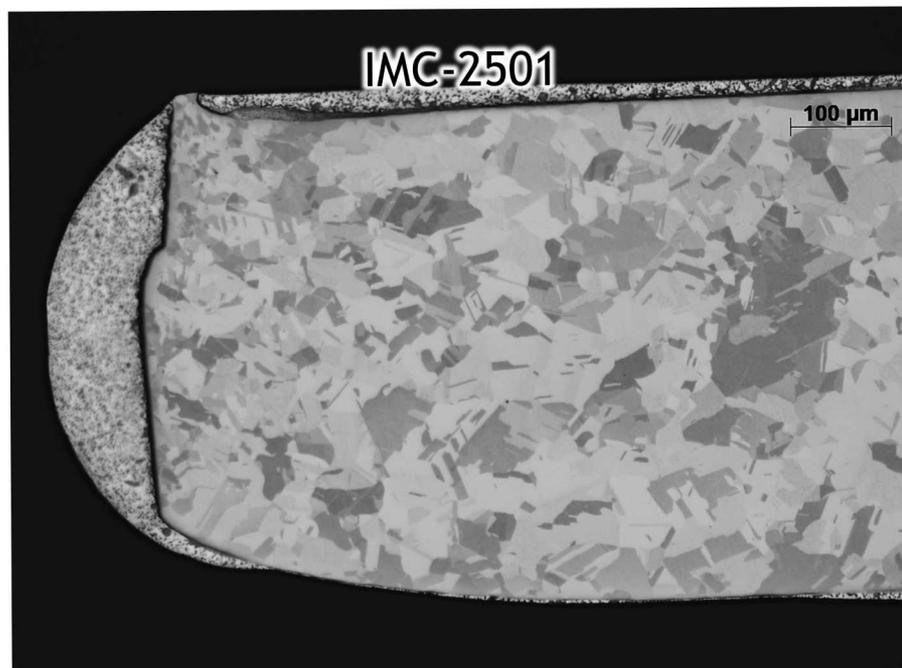
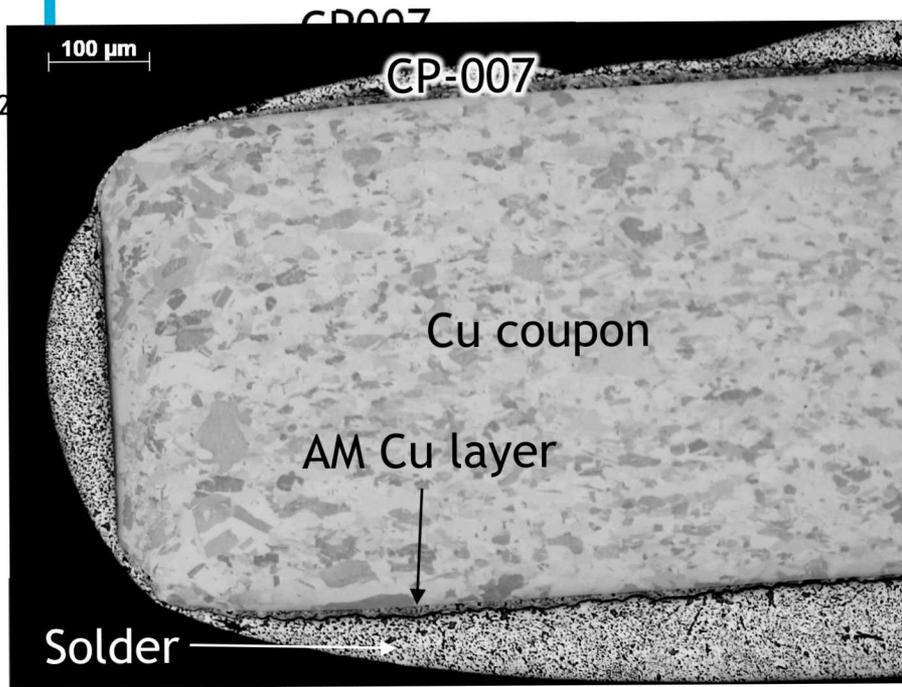
100 μ m

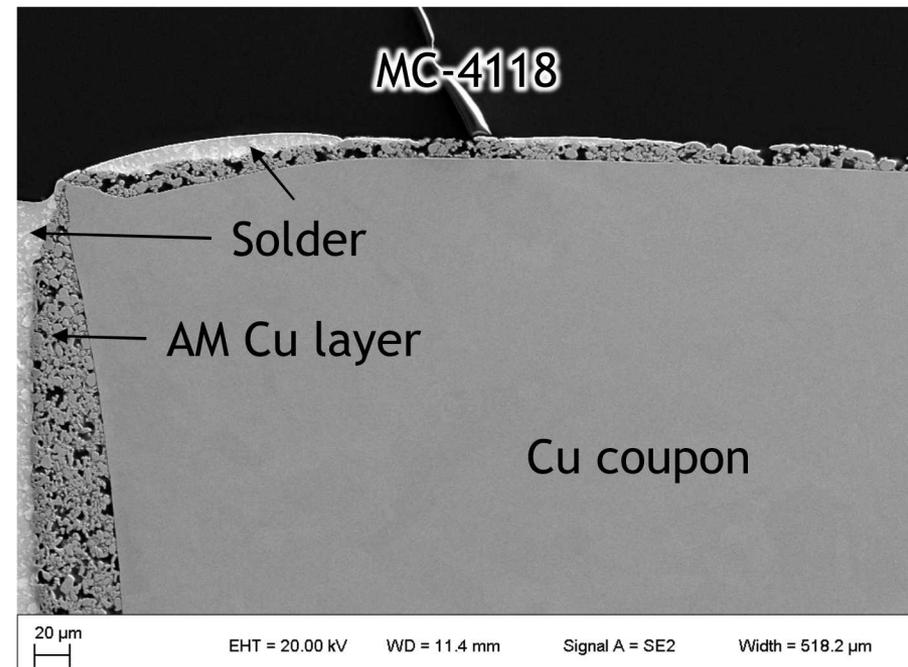
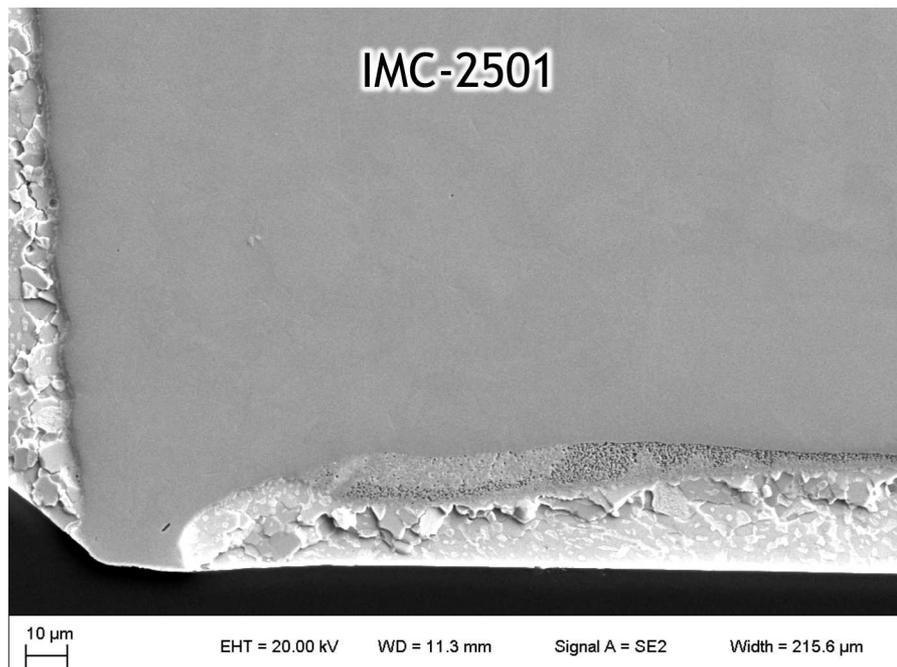
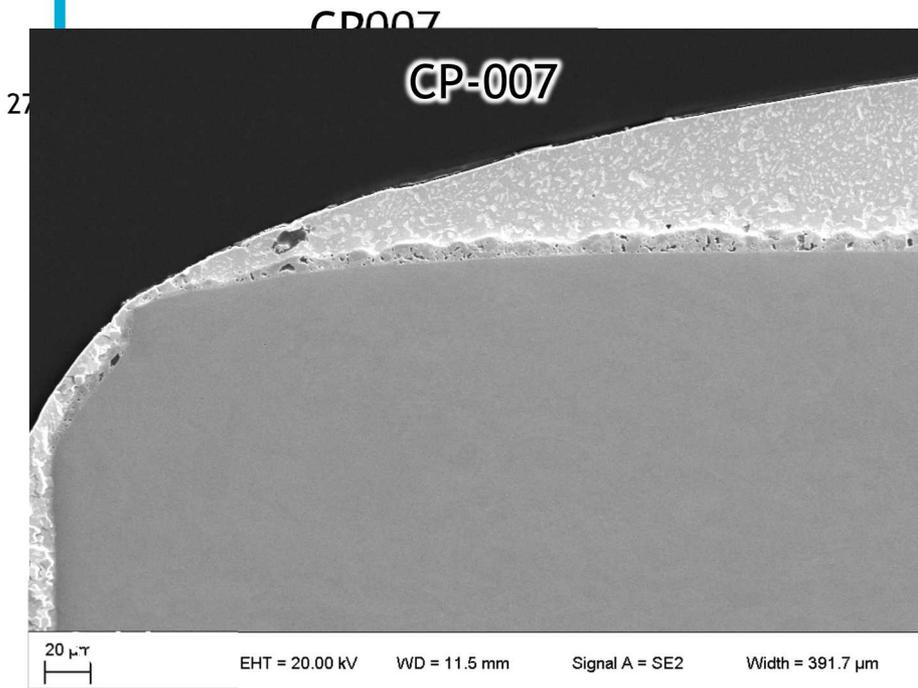
EHT = 20.00 kV

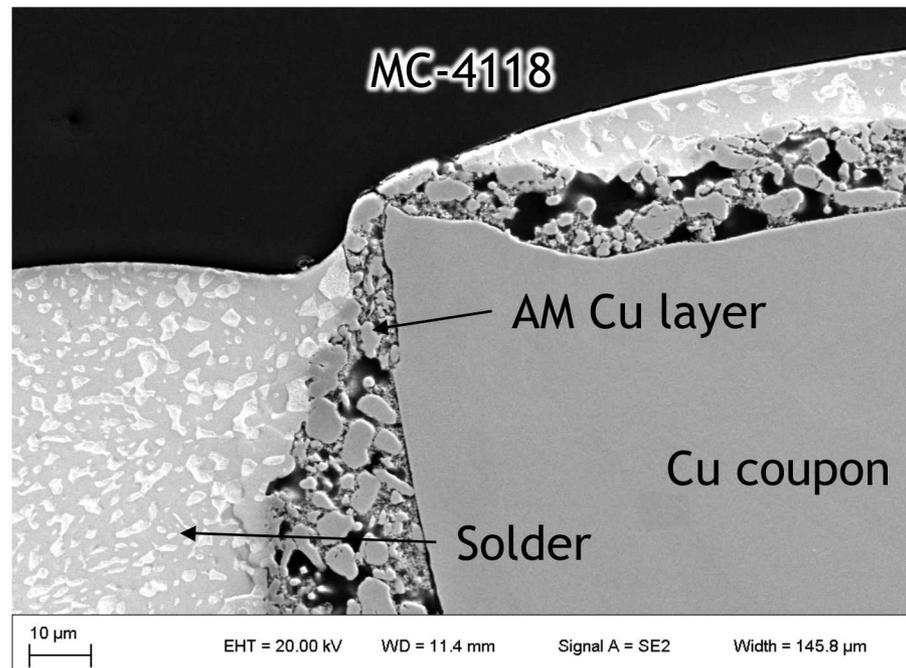
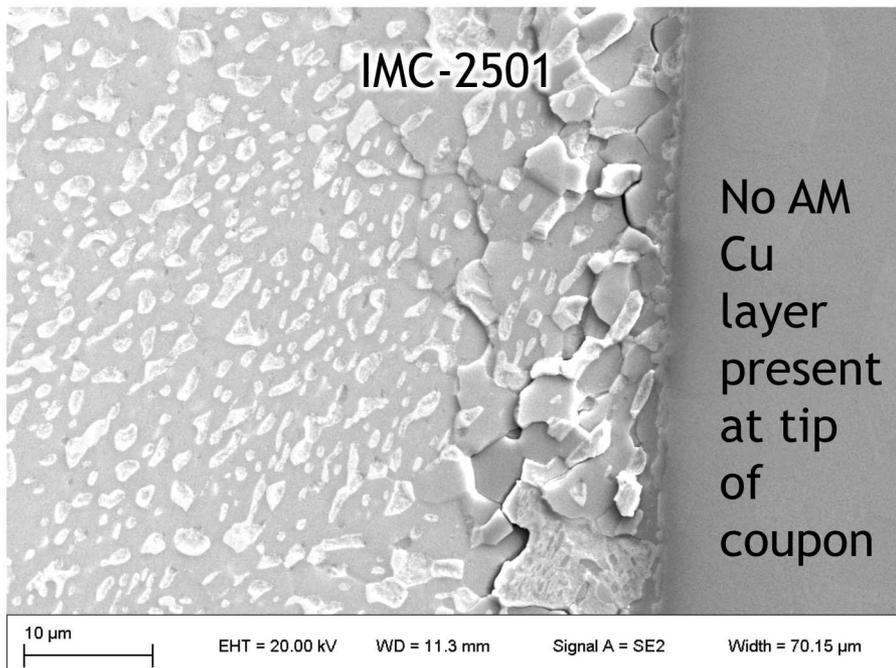
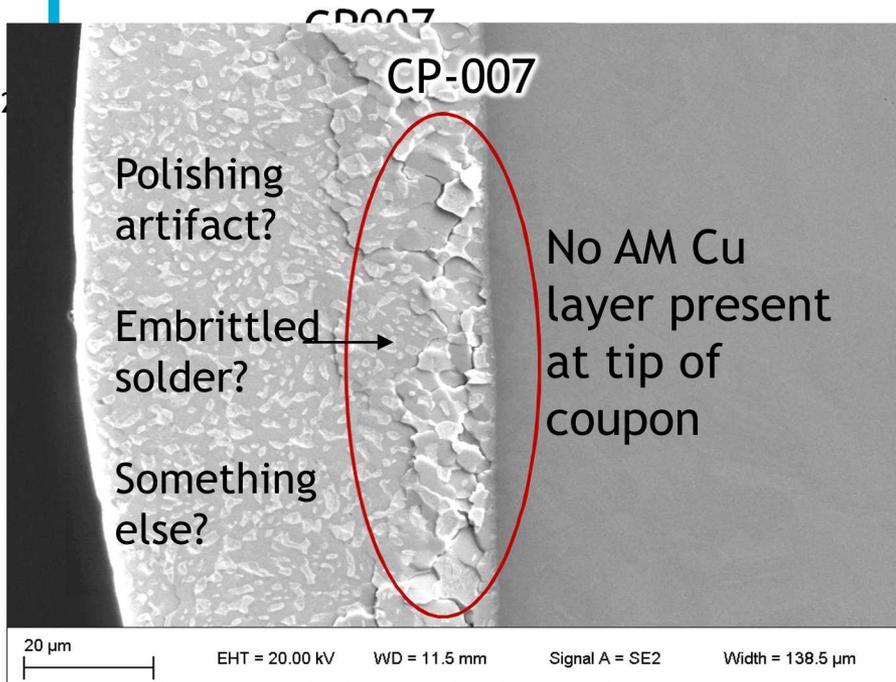
WD = 11.0 mm

Signal A = SE2

Width = 3.267 mm

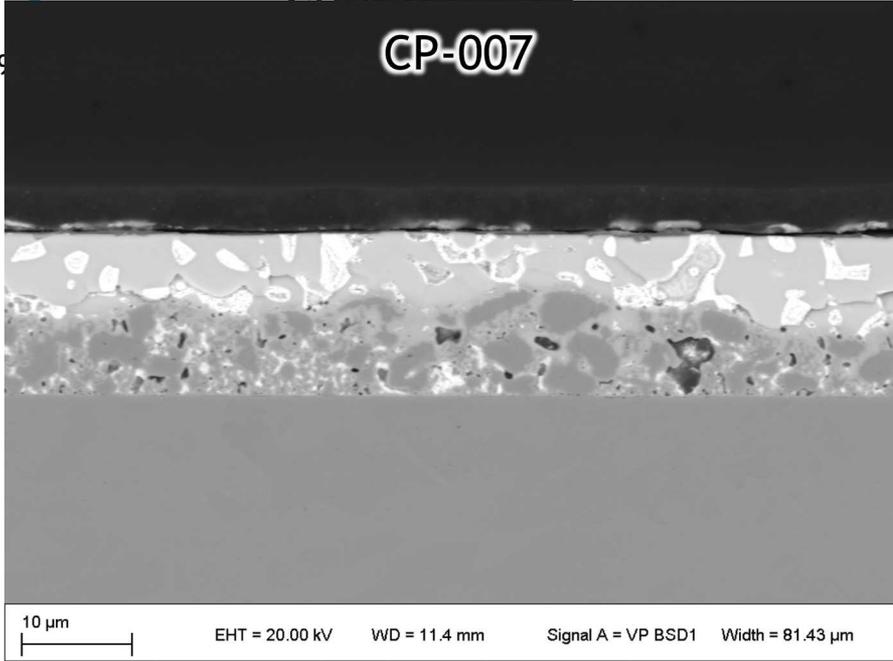






CP007

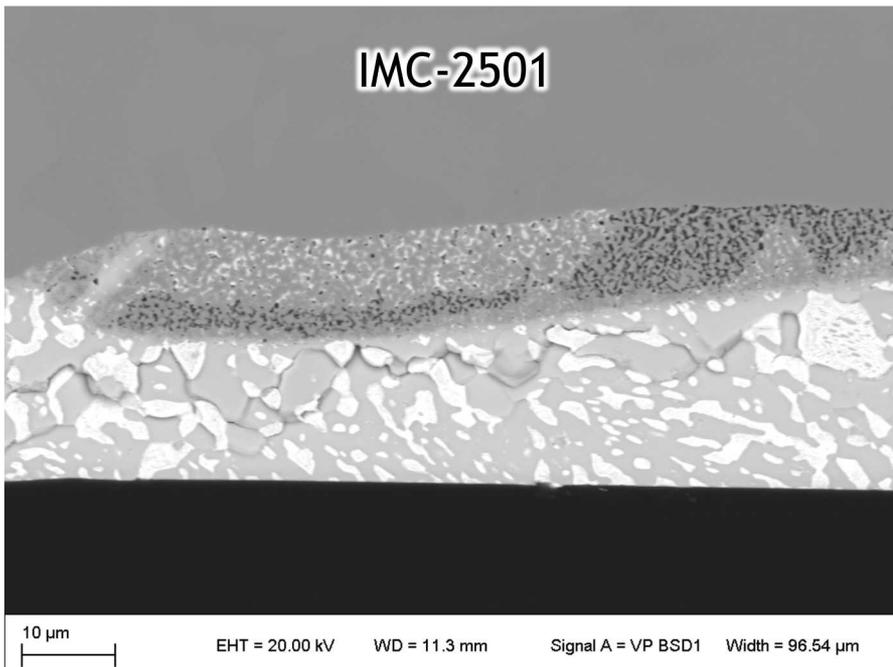
CP-007



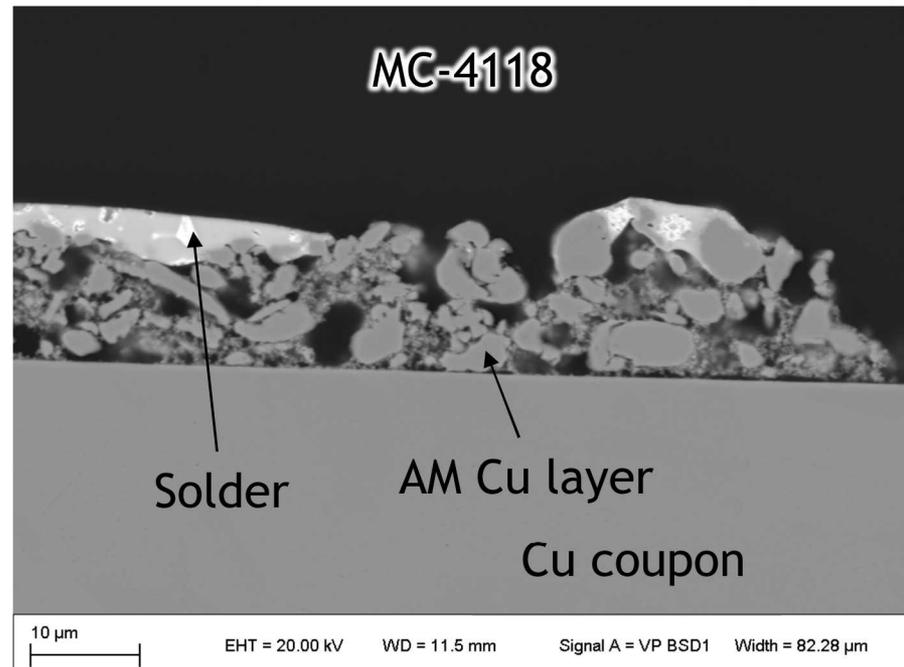
CP-008



IMC-2501

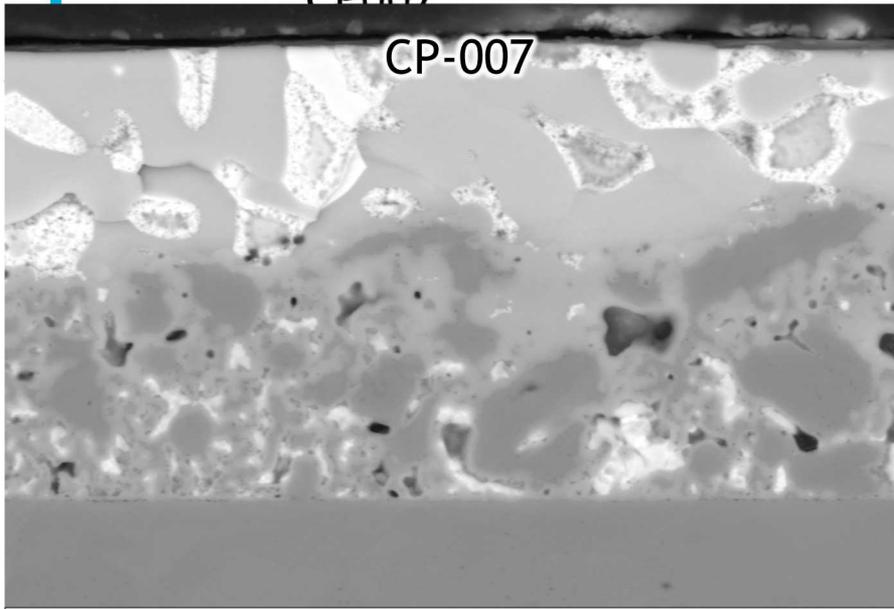


MC-4118



CP007

CP-007



2 μ m

EHT = 20.00 kV

WD = 11.4 mm

Signal A = VP BSD1

Width = 29.39 μ m

Cu coupon

IMC-2501

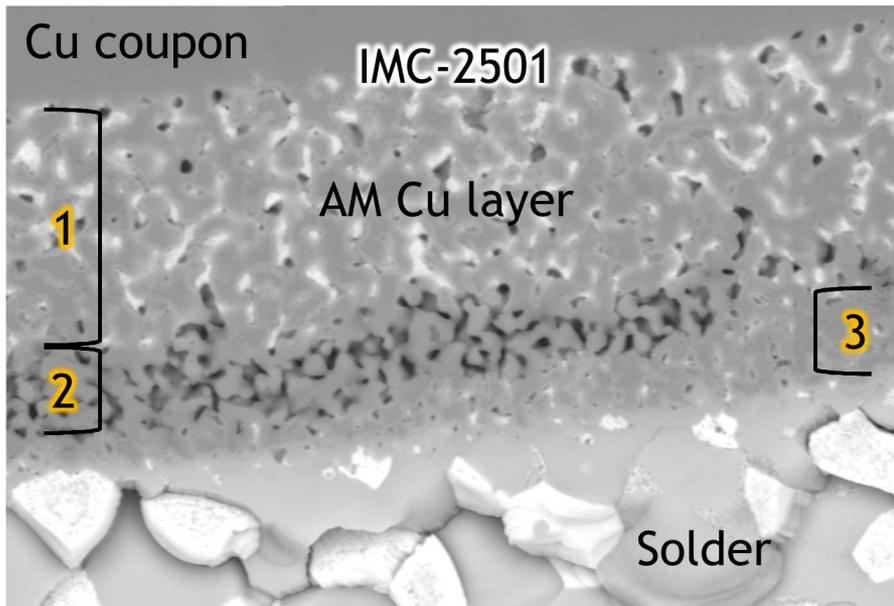
AM Cu layer

1

2

3

Solder



2 μ m

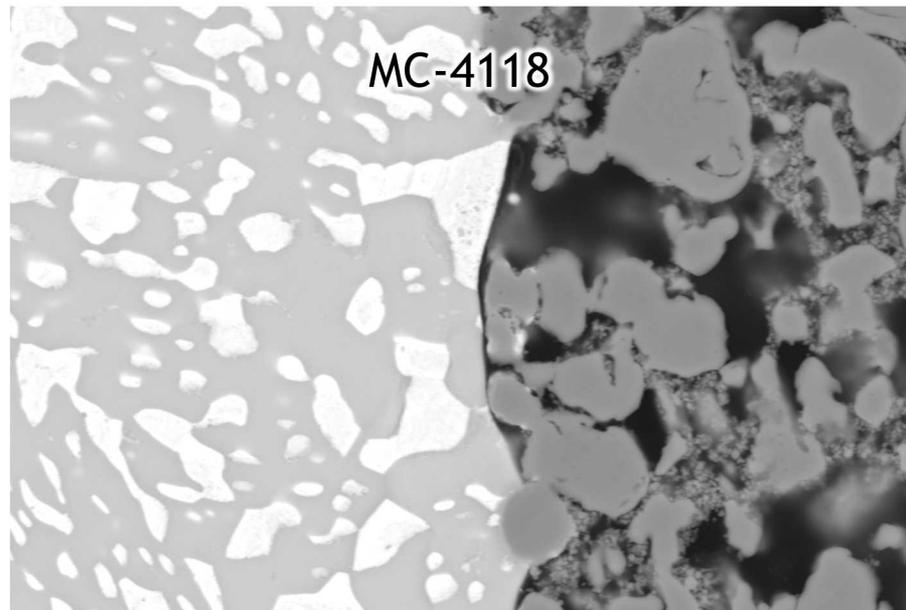
EHT = 20.00 kV

WD = 11.3 mm

Signal A = VP BSD1

Width = 26.87 μ m

MC-4118



2 μ m

EHT = 20.00 kV

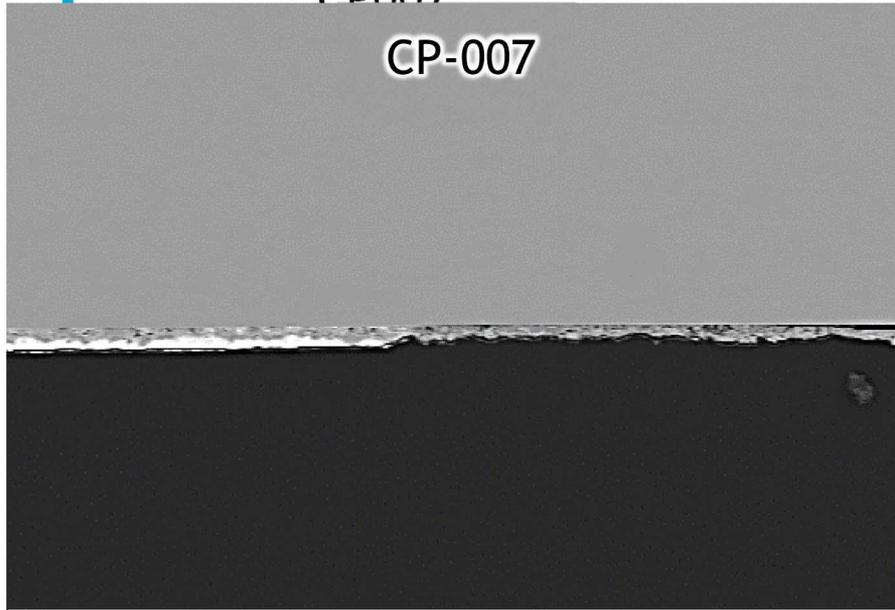
WD = 11.4 mm

Signal A = VP BSD1

Width = 40.15 μ m

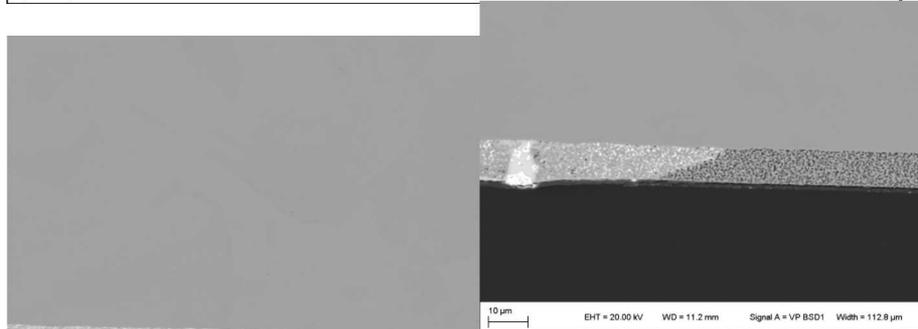
CP007

CP-007



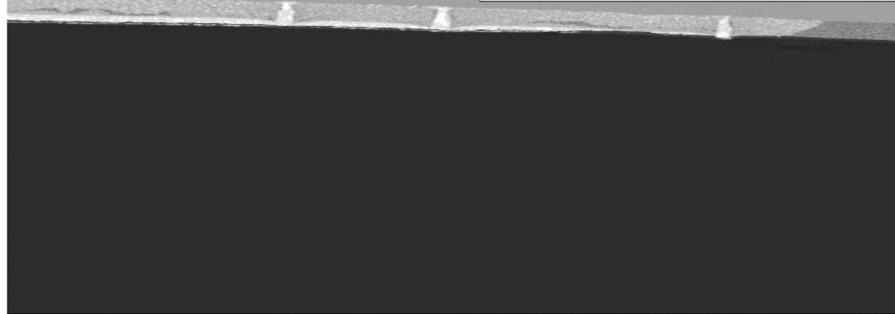
20 μm

EHT = 20.00 kV WD = 11.5 mm Signal A = VP BSD1 Width = 500.0 μm



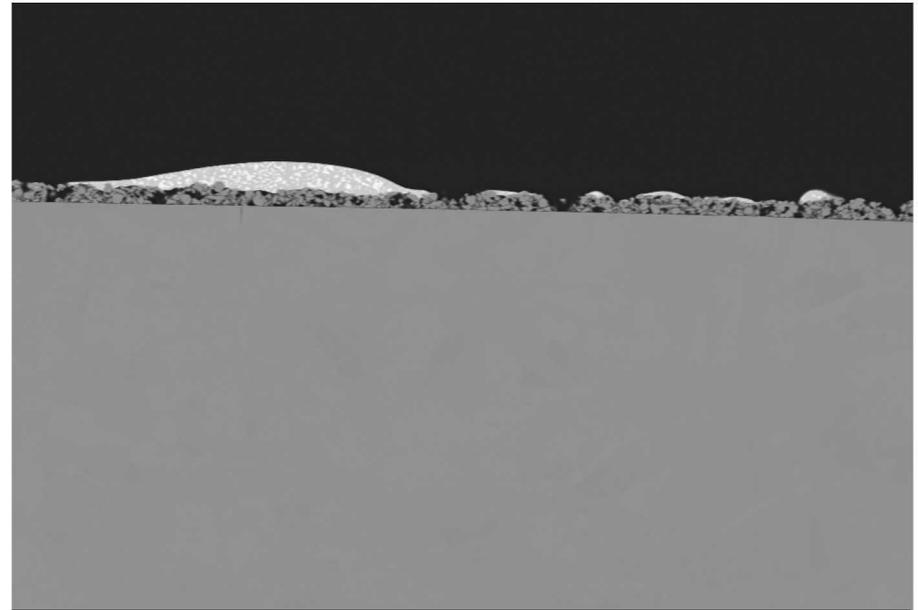
10 μm

EHT = 20.00 kV WD = 11.2 mm Signal A = VP BSD1 Width = 112.8 μm



20 μm

EHT = 20.00 kV WD = 11.2 mm Signal A = VP BSD1 Width = 464.0 μm



20 μm

EHT = 20.00 kV WD = 11.5 mm Signal A = VP BSD1 Width = 587.1 μm

Conclusions: AM Cu Coating Solderability

- Wetting balance data shows that all AM Cu coatings are not equal, in terms of solderability
- The application process may have a significant impact on the final product
- Process consistency is going to be a key part, in order for successful qualification/implementation of AM Cu into high reliability soldering applications
- A better understanding of the wetting mechanisms affecting solderability may provide a foundation for recommending processing changes

Moving forward

- Involve bulk AM coupons into the study
- Thermal spray coatings?
- Involve different AM materials (Nickel)
- Include surface finishes; Do the Cu coating effect surface finish quality, and subsequent solderability?
- Involve brazing (Cu, 304L, KovarTM)

****Continue to emphasize the “as-built” condition, NOT “as-polished”****

In search of collaboration

Continue and expand current coating study

- Intrinsic merged as of 2018 and has NOT regained previous formulation and distribution capabilities, yet

Expand study to include bulk AM processing methods

- Most of AM Copper (pure Cu) work is flourishing outside the U.S.

Start simple, work from there

- Looking for pretty “simple” geometries
- 1 X 1 X 0.02”
- Washer-like geometries

Thin-wall geometries



Sandia's plasma arc process CANNOT build the thin walled structure; Sandia's LENS process CANNOT build with pure copper

Thank you

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