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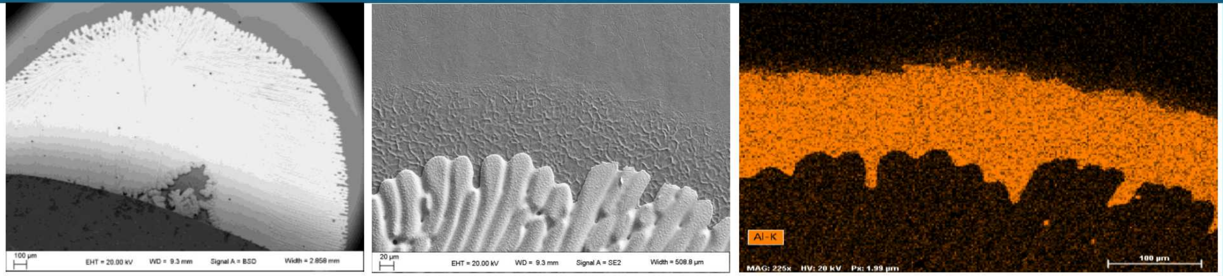
SAND2019-6996C

Preventing active braze filler metal run-out using conformal ALD coatings



PRESENTED BY

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U.S. DEPARTMENT OF ENERGY NNSA

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Outline of the presentation

Problem statement / motivation for the study
- Contained in the presentation title – “active braze filler metal runout”

Why active braze?
- Brief discussion about strengths and weaknesses of active brazing

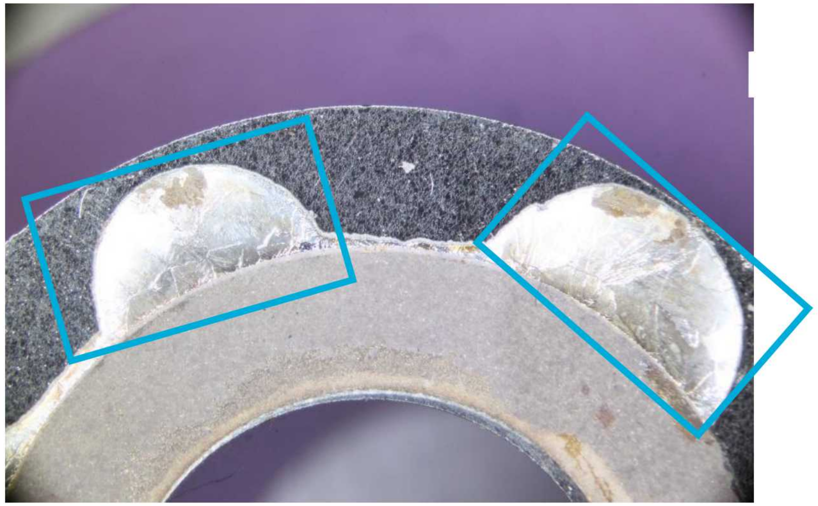
Remedial actions
- Potential courses of action to reduce or eliminate excessive braze filler metal flow

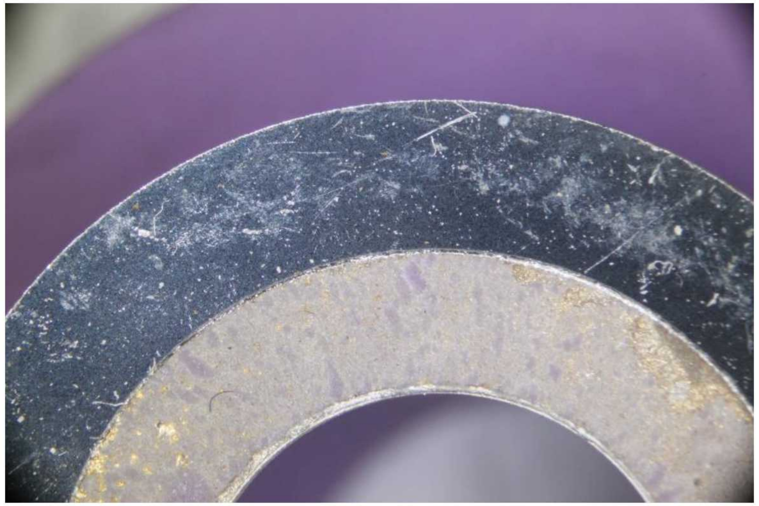
Course of action taken
- Brief description of atomic layer deposition (ALD) and how it can eliminate excess braze filler metal flow

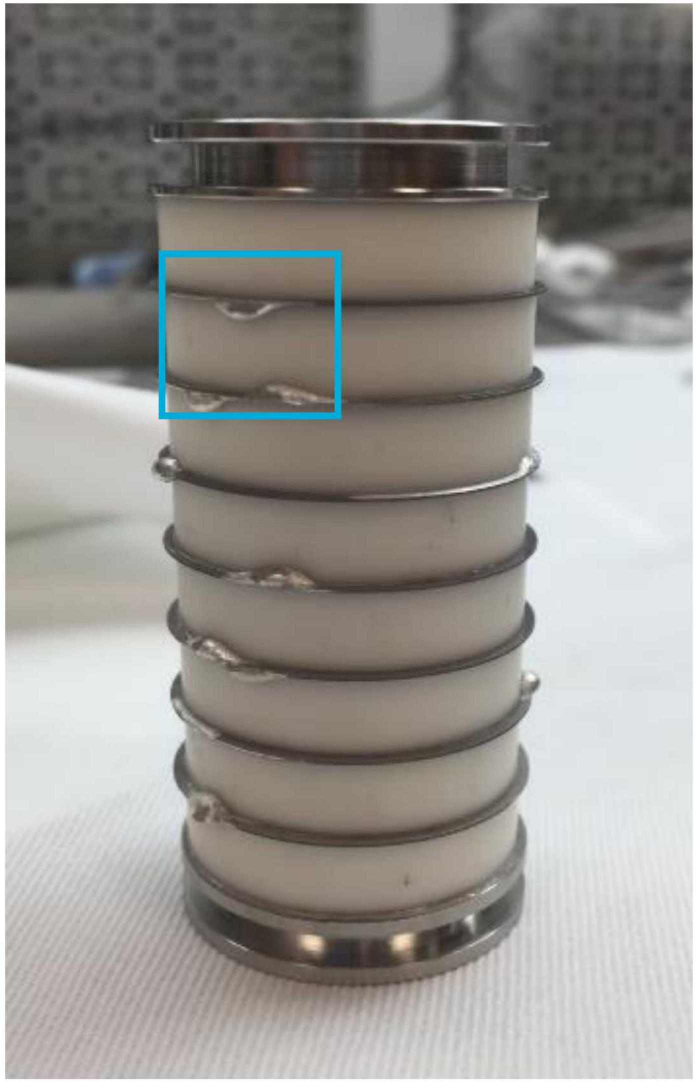
Experiments performed
- Three experimental sets of samples were brazed and tested

Results, discussion and conclusions
- Discussion of sample inspecting, testing and conclusions

Problem statement - Brazing Kovar to alumina ceramic with Zr-based ABA filler metals leads to excessive brazing filler metal flow.







Samples having excessive filler metal flow or spreading compared to those without.
The samples were brazed in vacuum using Ag-1Cu-2Zr ABA

Why active braze?

Pros:

Reduced number of ceramic preparation processes

Reduced processing time

Broader thermal processing range

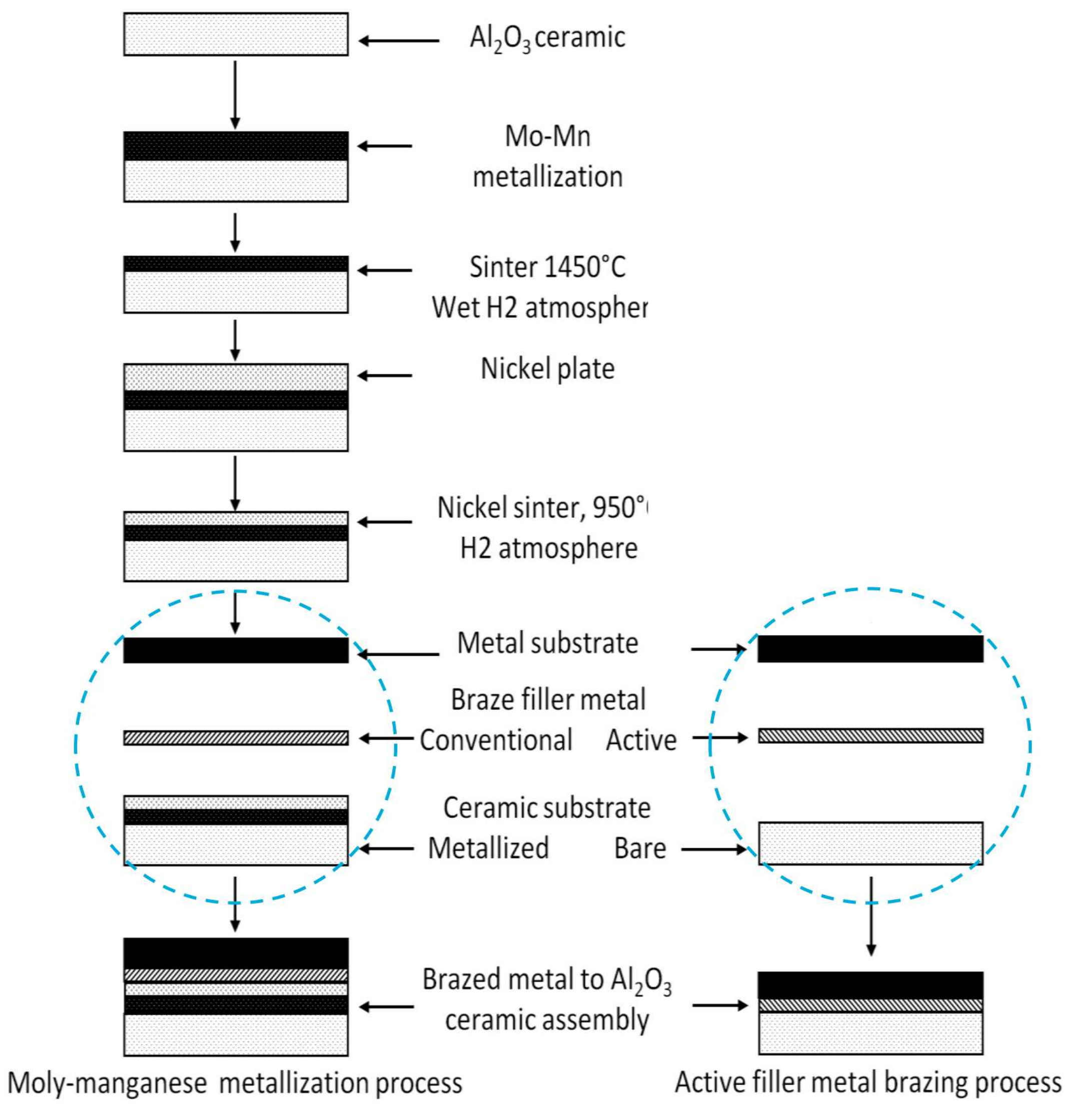
Increased brazement performance
- Higher tensile strengths

Cons:

May require braze joint redesign

More stringent atmosphere requirements
- Less tolerant of oxygen and carbon contaminants

Higher tendency for excessive filler metal flow



Brazing process comparison, Conventional (left) versus Active Brazing (right)

Potential remedial actions that *can* minimize or eliminate excessive active braze filler metal flow

Use braze flow inhibitors, often referred to as stop-off or braze-stop

- Ceramic powders in various aqueous and non-aqueous based carriers.
- Typically applied by spraying or brushing.
- Can be difficult to apply where needed and can be difficult to remove

Decrease the filler metal volume

Modify temperature profiles

Alter brazement geometry (grooves, chamfers, etc.)

Change surface morphology, i.e. roughen or smooth

Change the surface chemistry with plated or thin-film coatings

- Can be difficult to control (apply only where needed)
- Might require removal from certain regions prior to next assembly

Braze stop-off is unacceptable for product.

These other methods were tried and failed to ***consistently*** prevent excessive flow.

Epiphany*

Determined a **metallurgical solution** was required…

- Develop new active braze filler metal alloy?
- Try a barrier layer?

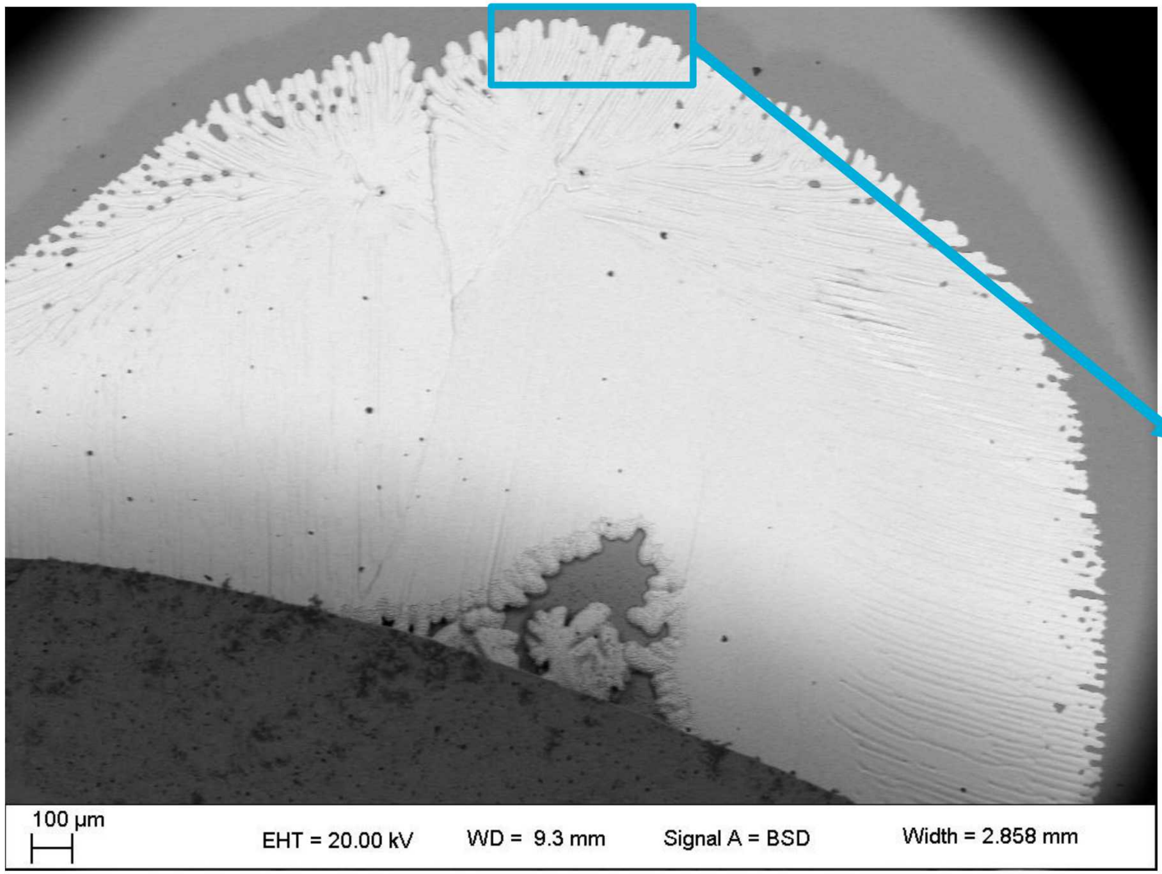
Not enough $$ for active braze filler metal development

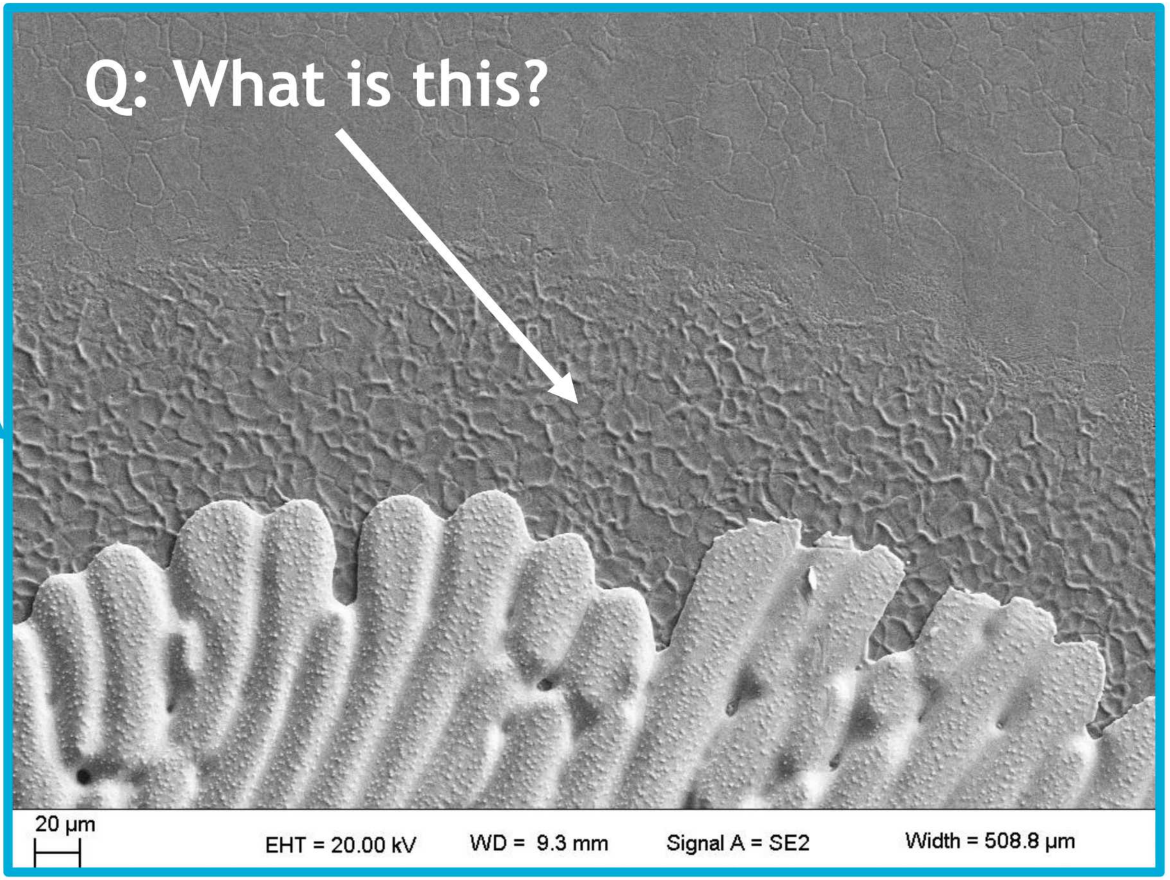
ALD alumina could meet product requirements

*blinding flash of the obvious

Potential remedial actions that can minimize or eliminate excessive active braze filler metal flow

Epiphany



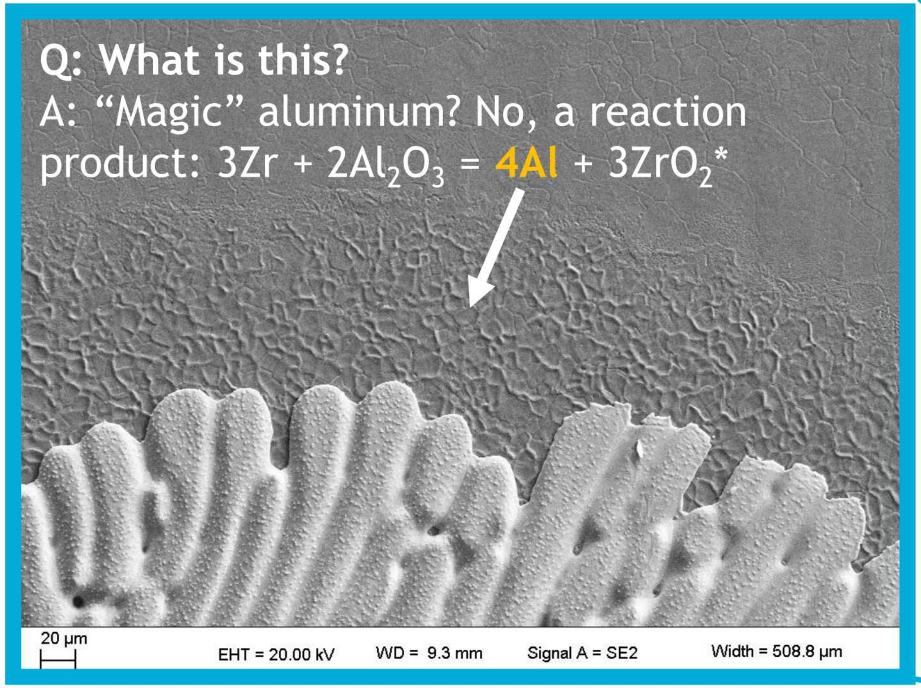


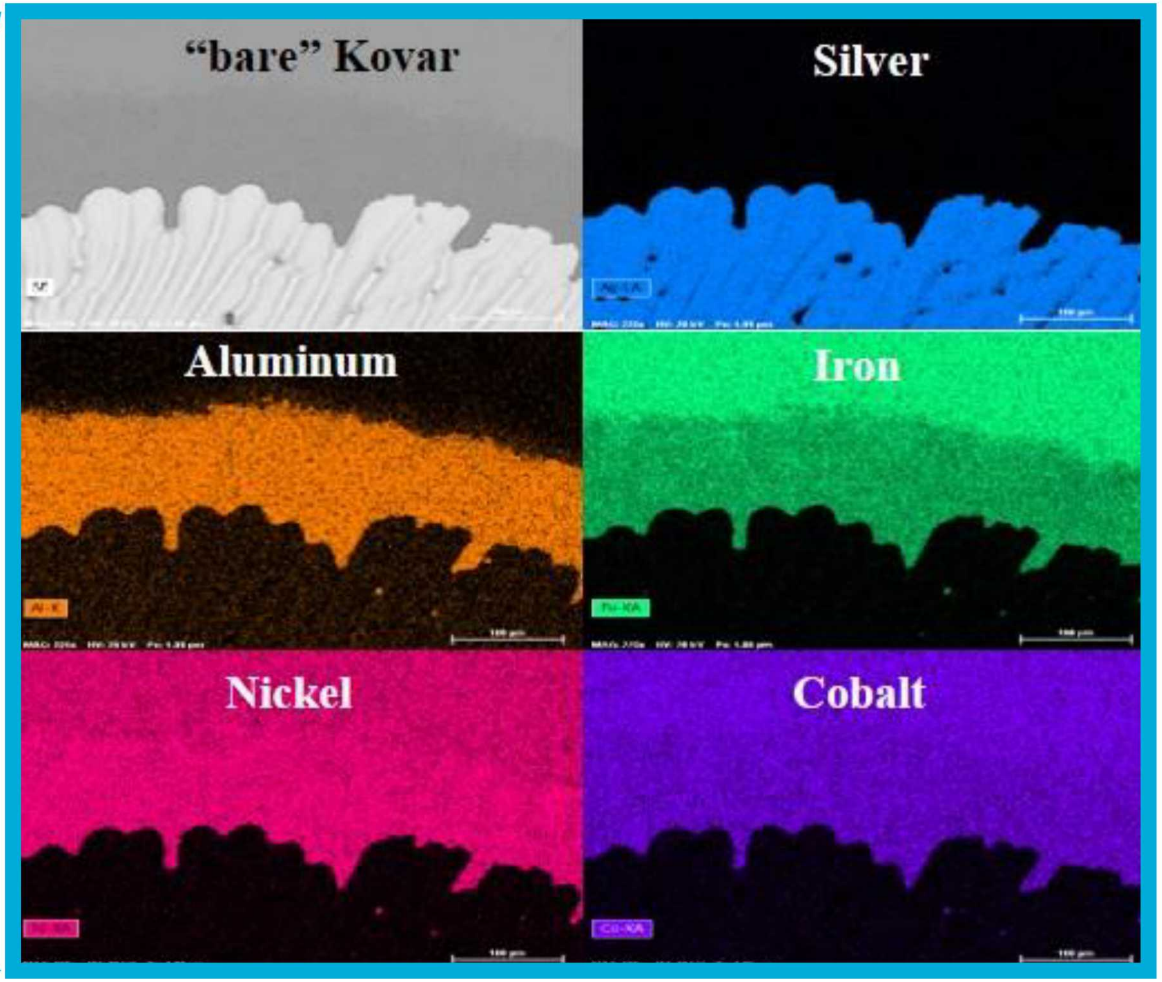
94ND10/Bare Kovar/94ND10 Tensile Button

Course of action taken: Atomic layer deposition (ALD) alumina, Al_2O_3

ALD alumina meets the following coating requirements:

- Thin (<20nm): less susceptible to CTE mismatch
- Coherent: high tensile strength
- Conformal: uniform coating across entire surface,
- Barrier: eliminate atomic Al in liquid filler metal

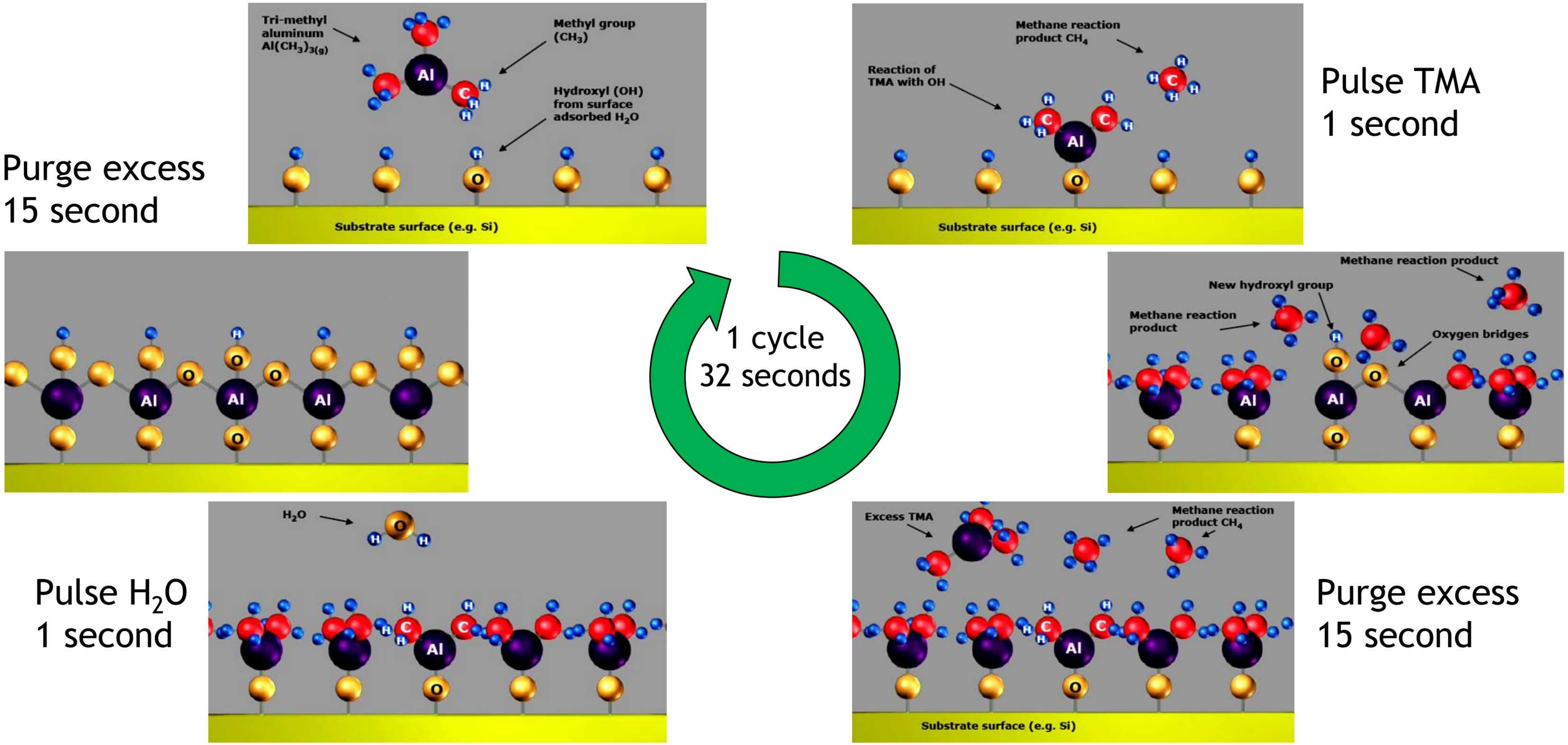




Understanding the Run-out Behavior of a Ag-Cu-Zr Braze Alloy When Used to Join Alumina to an Fe-Ni-Co Alloy, Vianco, P.T., et. al, IBSC 2015

Course of action taken: Atomic layer deposition (ALD) alumina

ALD cycle for Al_2O_3 deposition

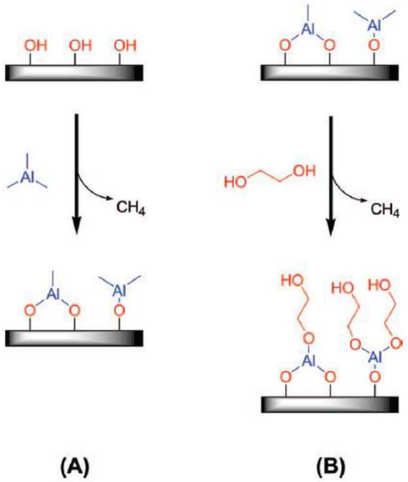


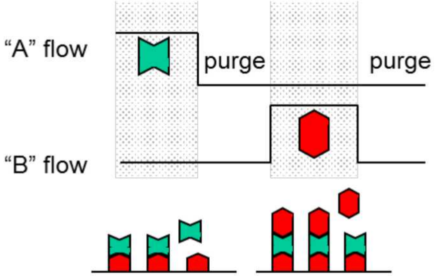
Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. http://www.cambridgenanotech.com/

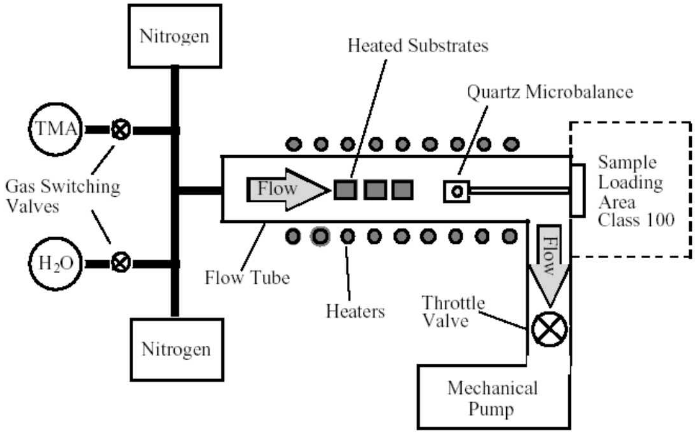
Groner, M.D., et.al, Low-Temperature Al2O3 Atomic Layer Deposition. Chemistry of Materials 2004.

ALD Al_2O_3 Sequential Reagent Exposures and Surface Limited Reactions

ALD Alumina

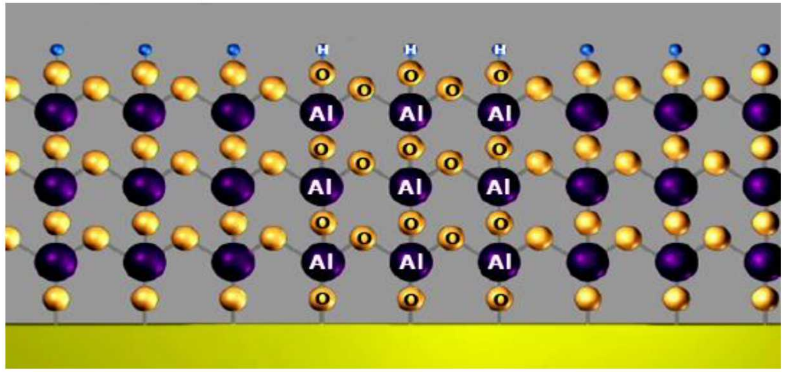






"A"	"B"	film
$Al(CH3)_3$ - TMA	H_2O	Al_2O_3

"Highly Conformal Coatings with Exquisite Control of Film Thickness"



ALD Al_2O_3 film after 3 cycles

Al_2O_3 CVD - reaction:

$$2Al(CH_3)_3(g) + 3H_2O(g) \rightarrow Al_2O_3(s) + 6CH_4(g)$$

ALD Al_2O_3 half-reactions: (200°C ~ 1.1 Å/cycle)

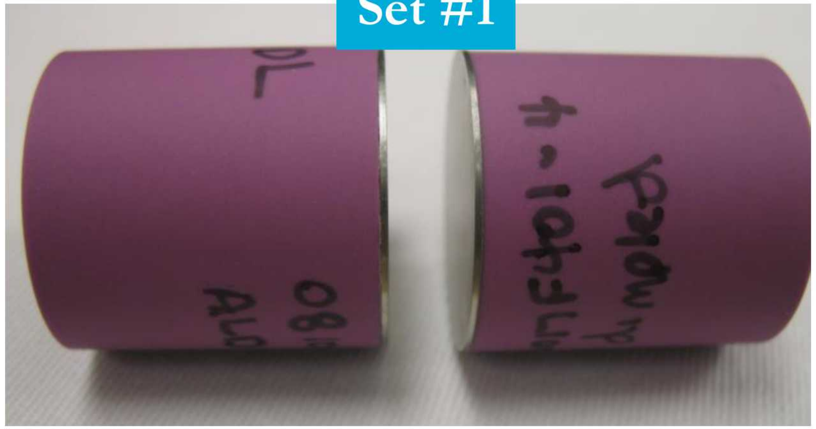
$$Al(CH_3)_3(g) + Al\text{-}OH^* \rightarrow Al\text{-}OAl(CH_3)_2^* + CH_4(g)$$

$$2H_2O(g) + \text{-}Al(CH_3)_2^* \rightarrow \text{-}Al(OH)_2^* + 2CH_4(g)$$

Goeke, R.S., et.al, Eliminating Excess Flow during Active Brazing through Surface Preparation with ALD, AVS 64th International Symposium 2017
Groner, M.D., et.al, Low-Temperature Al2O3 Atomic Layer Deposition. Chemistry of Materials 2004

Experimental Plan – 3 sample sets

Set #1



Set #2 & Set #3

	Ceramic Substrates		Kovar Discs & Interlayers			
Experiment Set	Material	Resintering Atmosphere	Bare	Bare with Dimples	ALD Al_2O_3 Coating Thicknesses	Dimples & ALD Al_2O_3 Coating Thicknesses
1	Diamonite	Wet H2	Y	Y	10nm	10nm
2	Diamonite	Wet H2	Y	Y	5nm, 10nm, 20nm	5nm, 10nm, 20nm
3	94ND10	Wet H2 or Air	Y	Y	1nm, 5nm, 10nm, 20nm	1nm, 5nm, 10nm, 20nm

Table 1. Materials and Input variables for Proposed Experiments

Experimental Plan: Sample preparation and fixturing

Cleaning

94% alumina ceramic substrates

3-step solvent cleaning: 1) vapor degrease in Lenium-ES solvent; 2) acetone rinse; 3) IPOH rinse

Wet, 28°C dew point, hydrogen resintering at 1500°C – 60 min, or air-firing at 1575° - 120 minutes.

Kovar discs and interlayers

3-step solvent cleaning

Pickling acid etch process (deionized water/hydrochloric acid)

Bright-dip (acetic/nitric/hydrochloric acid solution)

Rinse in deionized water.

Braze filler metal preforms (50μm thick Ag-1Cu-2Zr)

3-step solvent cleaning

Fixturing:

Cylinders and Kovar discs for Experiment 1 were assembled into laser-machined alumina ceramic fixtures

Standard ASTM F-19 tensile button fixturing was used for the tensile button assemblies.

A mass providing ~30g/cm^2 (200g/in^2) of joint preload force was positioned onto each fixtured assembly.

Experimental Plan: Performing the braze

Furnace Loading:

Two "dummy" assemblies with TCs monitored the brazing process temperatures.
The samples were uniformly distributed in the furnace hot-zone.

Performing the braze

All samples were brazed in an oil-free, top-loading, cryogenic-pumped, high-vacuum furnace. A NIST-traceable ionization gauge verified that the proper pressure, ~7E-05 - 1E-04Pa (5E-07 - 1E-06 Torr) were achieved and maintained during the brazing cycle.

The furnace brazing temperature cycle used was as follows:

15˚C/min ramp from ambient to 925˚C, soak 15 minutes;
10˚C/min from 925˚C/ to 985˚C, soak 5 minutes;
25˚C/min from 985˚C to 925˚C, soak 0 minutes;
Furnace cool (uncontrolled) to ambient.

Experiment – 1: Braze "flush mount" Kovar discs to one end of Diamonite cylinders

Input variables:

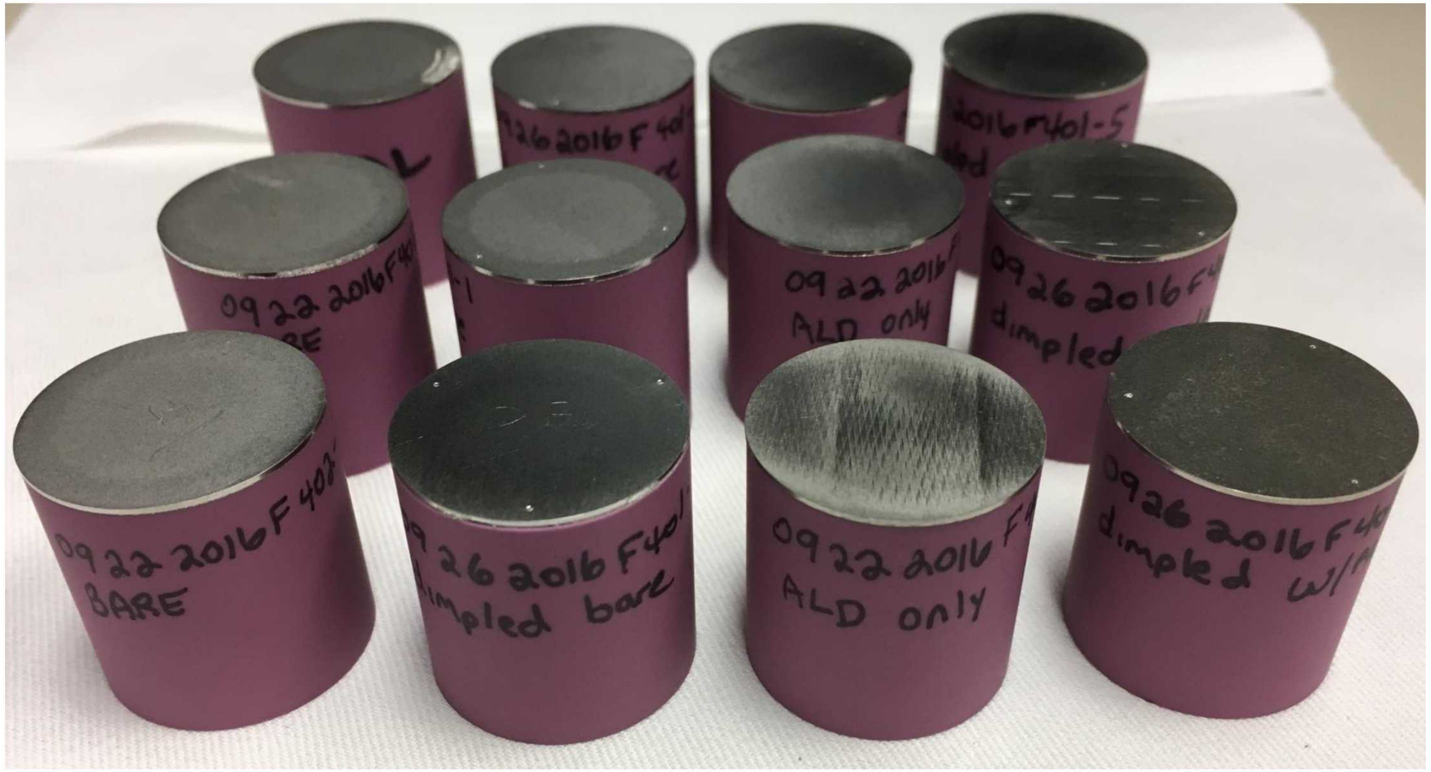
- Dimpled[1] or undimpled Kovar
- bare Kovar or 10nm thick ALD Al_2O_3

Observed/Measured responses:

- Runout/excess flow[2]
- Joint hermeticity[3]

Sample Quantity:

- 4 unique combinations, 3 replicates each



Active-brazed Diamonite cylinders to flush-mount Kovar flanges

1-3 dimples are formed 120° apart on the substrates, target dimple heights are 25µm - 38µm (0.001" – 0.0015").
2-filler metal on inner or outer surfaces and edges of the Kovar alloy beyond the joint proper that can be observed without magnification.
3- defined as having total helium leak rates ≤5E-13 Pa-M^3s^{-1} (≤5E-12 atm-cm^3s^{-1})

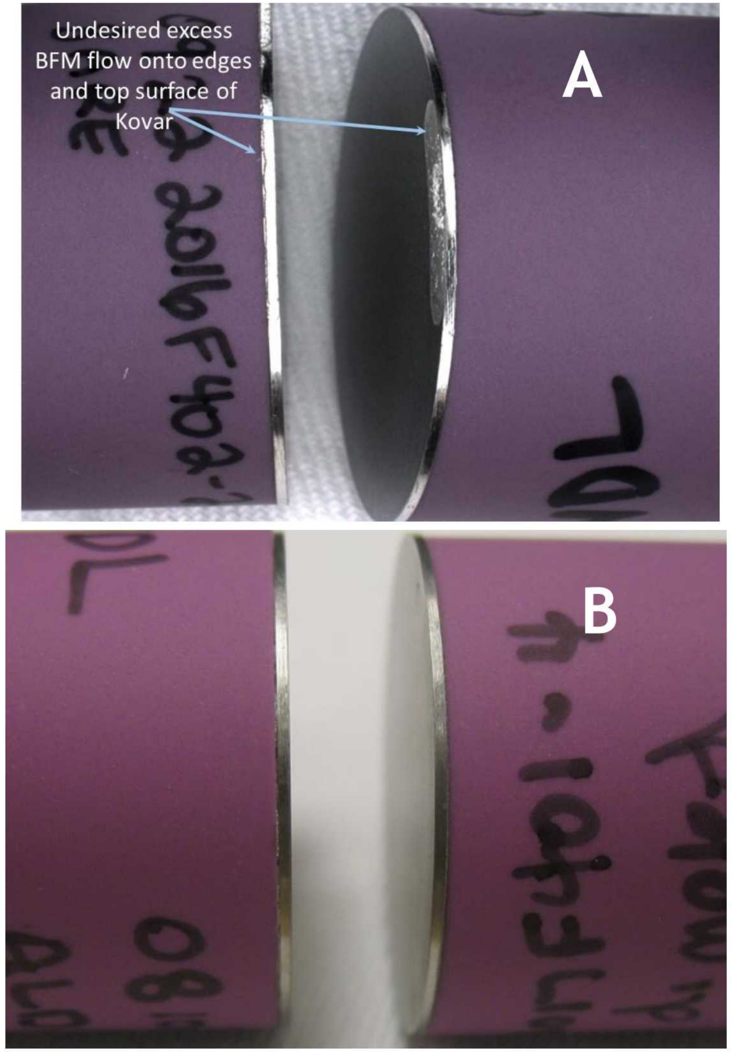
Experiment 1: Braze "flush mount" Kovar discs to one end of Diamonite cylinders - **Results**

Runout/excess flow:

- Diamonite/Bare Kovar: 1/3 pass
- Diamonite/Dimpled bare Kovar: 2/3 pass
- Diamonite/10nm ALD Al_2O_3 undimpled Kovar: 3/3 pass
- Diamonite/10nm ALD Al_2O_3 dimpled Kovar: 3/3 pass

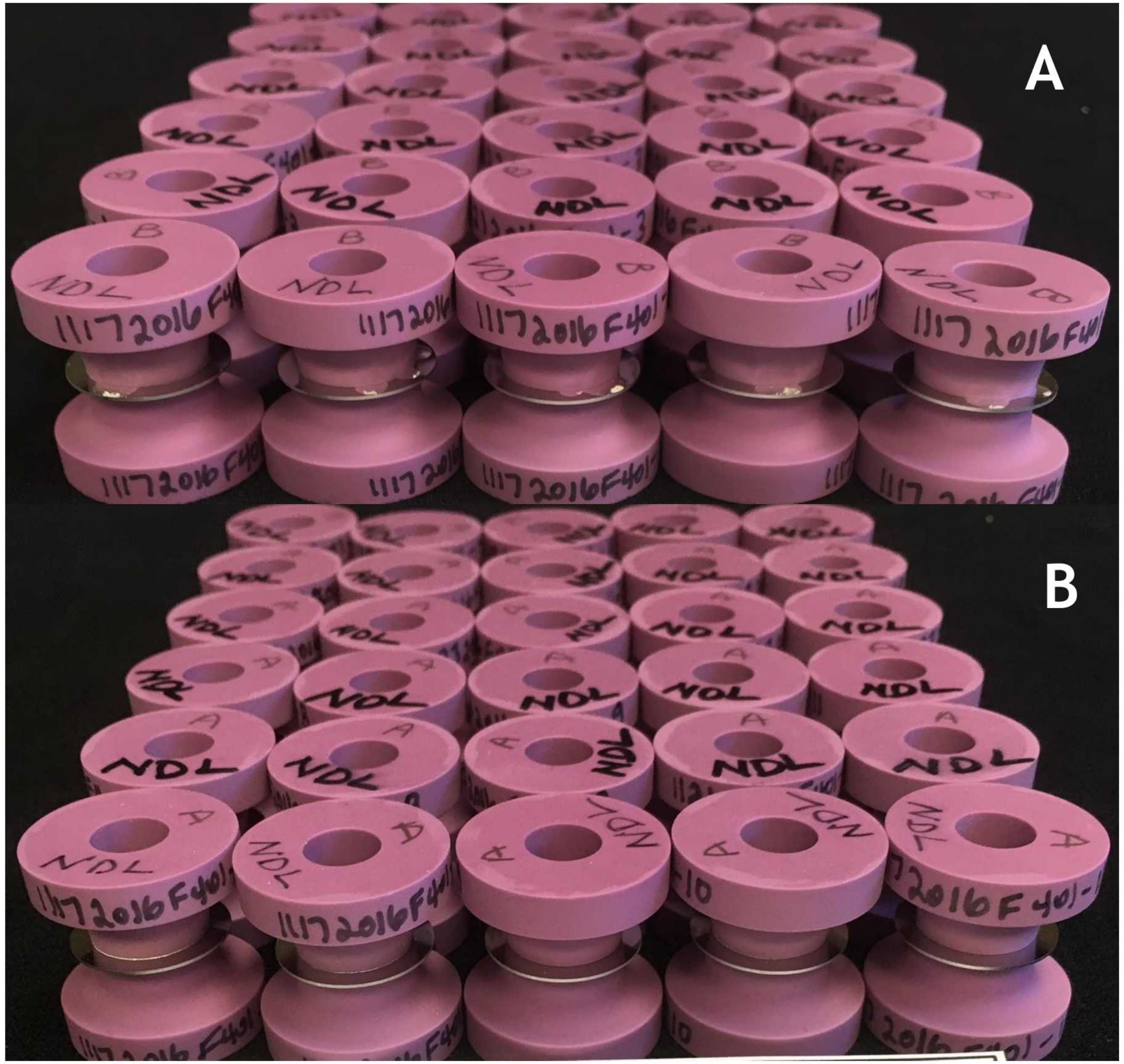
Hermeticity:

- 12/12 samples (100%) had no detectable leaks (NDL).



Excess braze filler metal flow (A) on flush-mount Kovar flanges brazed to Diamonite Cylinders

Experiment 2, Braze Diamonite ASTM F19 Tensile Buttons to Oversized Kovar interlayers



Diamonite tensile button assemblies. A: Uncoated Kovar (30/30 with excess flow); B: 10nm ALD Al_2O_3 coated Kovar (0/30 with excess flow).

Input variables:

- Dimpled or undimpled Kovar
- bare Kovar or ALD Al_2O_3 (5nm, 10nm & 20nm)

Observed/Measured responses:

- Runout/excess flow (results shown, right)
- Joint hermeticity
- Tensile strength[1]

Sample Quantity:

- 4 unique combinations, 3 replicates each

1-MTS test frame, displacement rate of 5.1E-05m-s^{-1} (0.002in-s^{-1})

Experiment 2, Braze Diamonite ASTM F19 Tensile Buttons to Oversized Kovar interlayers – **Excess Flow & Hermeticity Results**

Runout/excess flow:

- Undimpled bare Kovar: 0/30 pass
- Dimpled bare Kovar: 0/5 pass
- 5nm ALD Al_2O_3 undimpled: 30/30 pass
- 10nm ALD Al_2O_3 undimpled: 30/30 pass
- 20nm ALD Al_2O_3 undimpled: 30/30 pass
- 5nm ALD Al_2O_3 dimpled: 5/5 pass
- 10nm ALD Al_2O_3 dimpled: 5/5 pass
- 20nm ALD Al_2O_3 dimpled: 5/5 pass

Atmosphere / Dimples	Bare Kovar	5nm ALD Al_2O_3	10nm ALD Al_2O_3	20nm ALD Al_2O_3
Wet H2 / no dimples	(0/30)	(30/30)	(30/30)	(30/30)
Wet H2 / dimples	(0/5)	(5/5)	(5/5)	(5/5)

Table 2. Diamonite/Kovar/Diamonite Brazed Tensile Button Excess Filler Metal Flow Results

Hermeticity:

- 139/140 samples had no detectable leaks (NDL).
- 1 sample having a 5nm ALD Al_2O_3 coating failed

Atmosphere / Dimples	Bare Kovar	5nm ALD Al_2O_3	10nm ALD Al_2O_3	20nm ALD Al_2O_3
Wet H2 / no dimples	(30/30)	(29/30)	(30/30)	(30/30)
Wet H2 / dimples	(5/5)	(5/5)	(5/5)	(5/5)

Table 3. Diamonite/Kovar/Diamonite Brazed Tensile Button Helium Leak Check Results

Experiment 2, Braze Diamonite ASTM F19 Tensile Buttons to Oversized Kovar interlayers – **Tensile Test Results**

Tensile strengths

Shown

- Undimpled bare Kovar:
- Dimpled bare Kovar:
- 10nm ALD Al_2O_3 undimpled Kovar:
- 10nm ALD Al_2O_3 dimpled Kovar

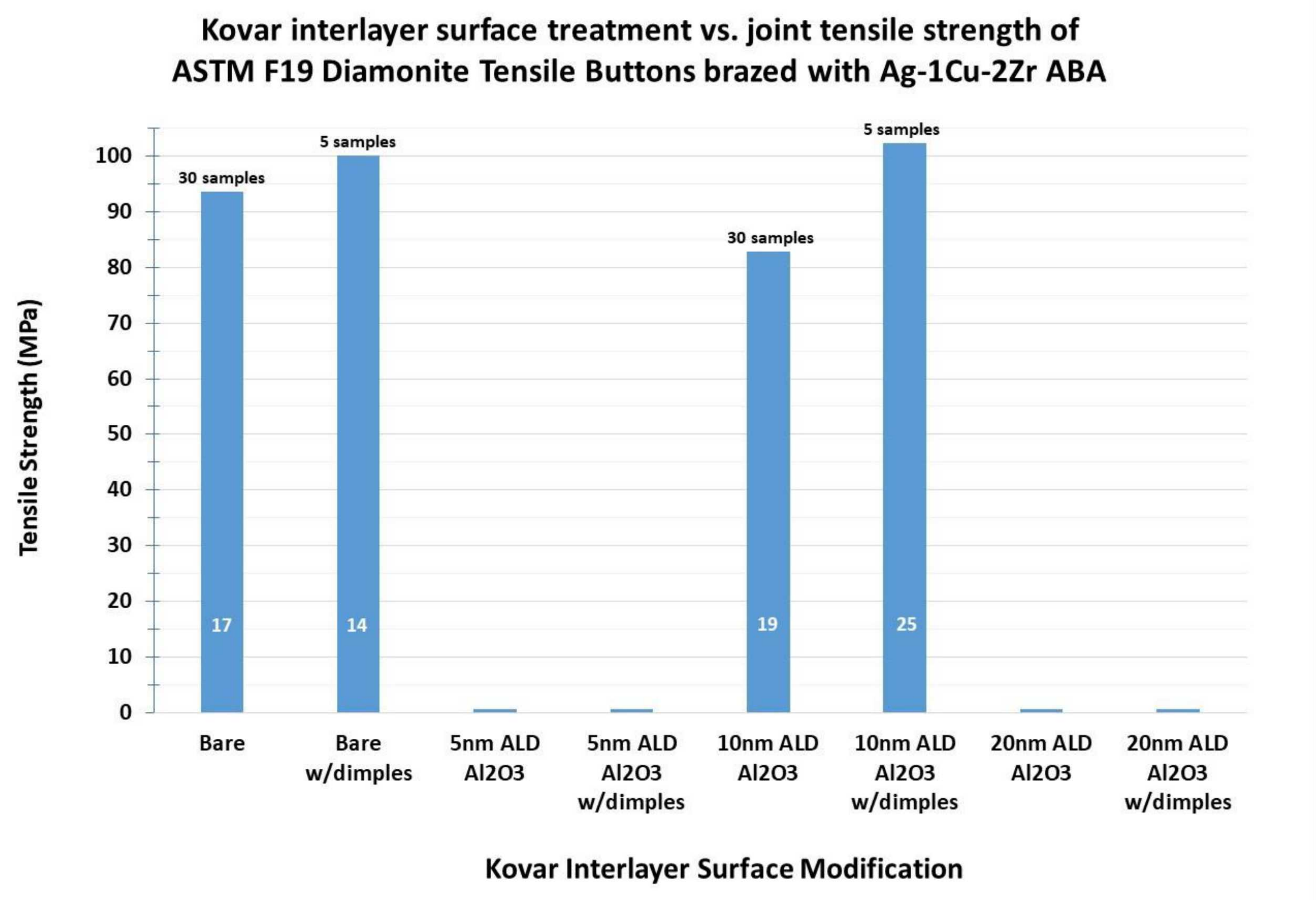
Not Shown*

- 5nm ALD Al_2O_3 undimpled Kovar:
- 5nm ALD Al_2O_3 dimpled Kovar
- 20nm ALD Al_2O_3 undimpled Kovar:
- 20nm ALD Al_2O_3 dimpled Kovar

Trends

- Slightly higher strengths for dimpled Kovar samples

*Issues with samples/furnace



Diamonite/Kovar/Diamonite Brazed Tensile Button Average Tensile Strengths

Experiment 3, Braze ASTM F19 94ND10 Tensile Buttons to Oversized Kovar interlayers

Input variables:

- Dimpled or undimpled Kovar
- bare Kovar or ALD Al_2O_3

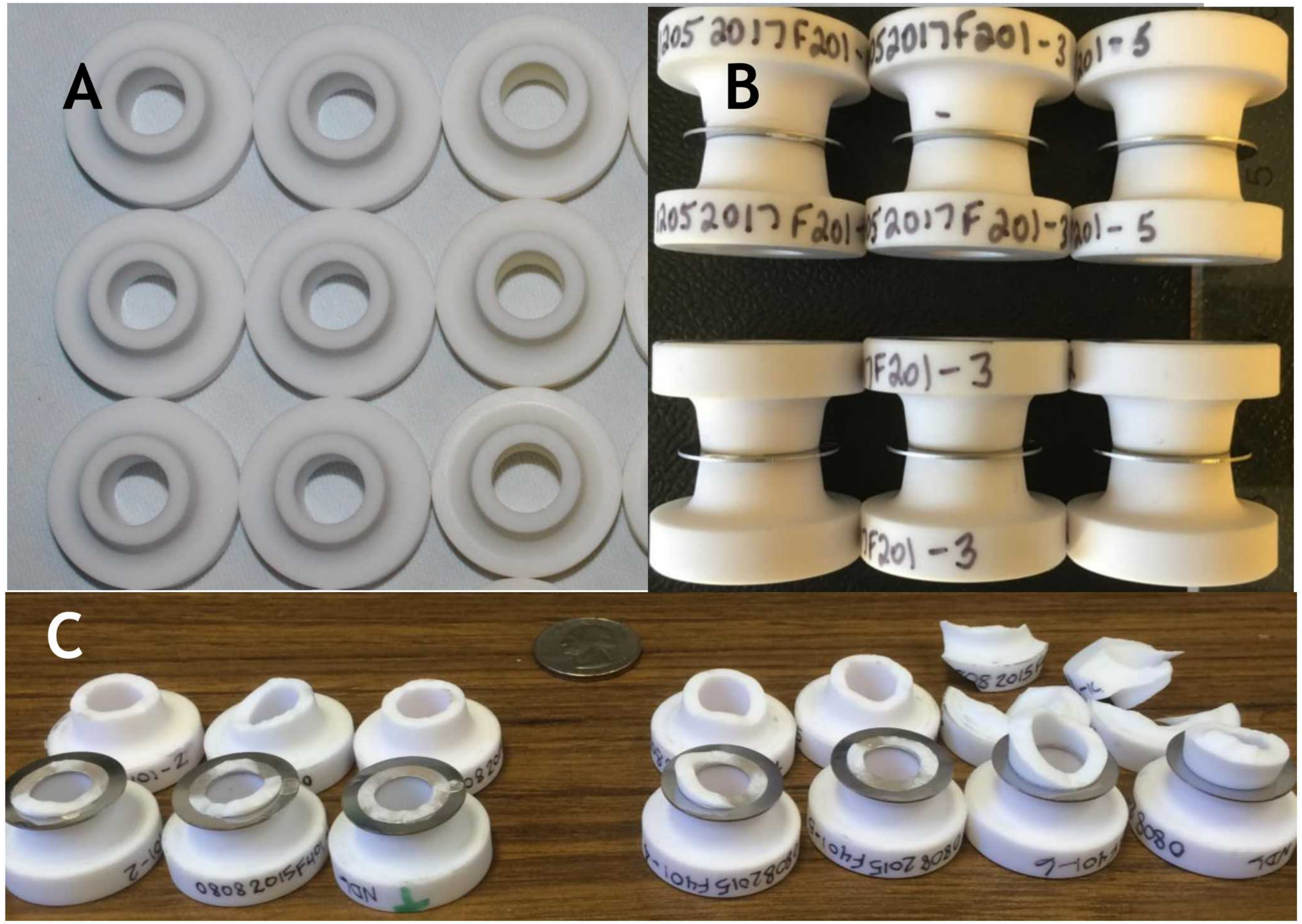
  (1nm, 5nm, 10nm & 20nm)

Observed/Measured responses:

- Runout/excess flow (results shown, right)
- Joint hermeticity
- Tensile strength

Sample Quantity:

- 4 unique combinations, 3 replicates each



94ND10 ASTM F19 tensile buttons after resintering (A), brazing (B), and post tensile-testing (C).

Experiment 3, Braze 94ND10 ASTM F19 Tensile Buttons to Oversized Kovar interlayers – **Excess Flow & Hermeticity Results**

Runout/excess flow trends

- Kovar: Dimpled outperformed undimpled
- ALD Al_2O_3 coatings: ≥5nm 100% pass
- Resintering atmosphere: behaved similarly
- 11/13 "failing" samples had runout on both sides

Atmosphere / Dimples	Bare	1nm	5nm	10nm	20nm
Wet H2 / no dimples	(3/3)	(1/3)	(0/3)	(0/3)	(0/3)
Wet H2 / dimples	(0/3)	(2/3)	(0/3)	(0/3)	--
Air-fired/ no dimples	(3/3)	(1/3)	(0/3)	(0/3)	(0/3)
Air-fired / dimples	(0/3)	(3/3)	(0/3)	(0/3)	--

Table 4. 94ND10/Kovar/94ND10 Brazed Tensile Button Excess Filler Metal Flow Results

Hermeticity Results/Trends:

- 48/54 samples passed the helium leak testing
- The 6 failing samples all used dimpled Kovar
- No trend observed for bare vs. coated Kovar
- No trends observed for resintering atmosphere
- It is believed that the dimples heights exceeded the tolerance for the filler metal thickness used.

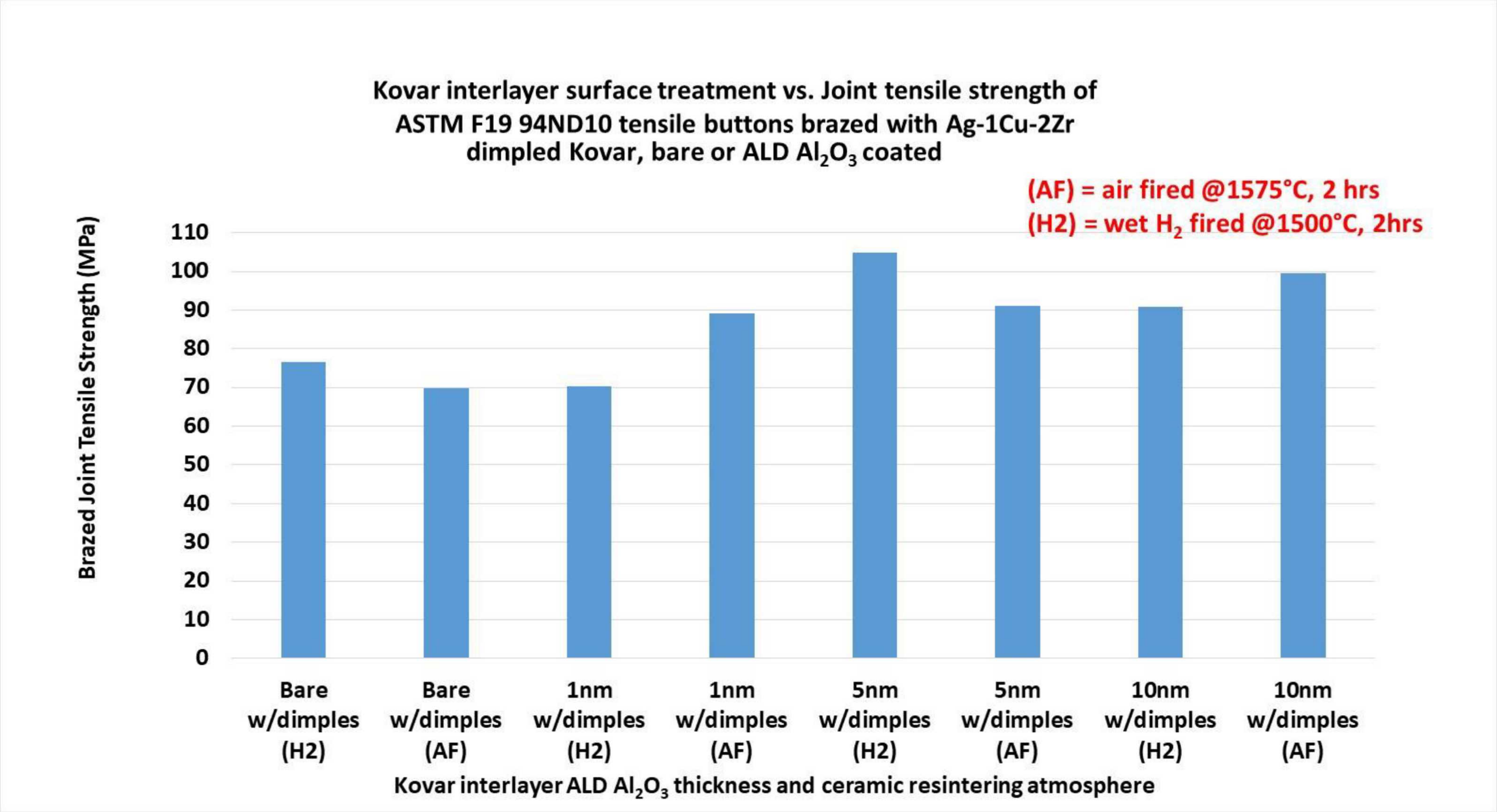
Atmosphere / Dimples	Bare Kovar	1nm ALD Al_2O_3	5nm ALD Al_2O_3	10nm ALD Al_2O_3	20nm ALD Al_2O_3
Wet H2 / no dimples	(3/3)	(3/3)	(3/3)	(3/3)	(3/3)
Wet H2 / dimples	(1/3)	(3/3)	(2/3)	(2/3)	--
Air-fired/ no dimples	(3/3)	(3/3)	(3/3)	(3/3)	(3/3)
Air-fired/ dimples	(1/3)	(3/3)	(3/3)	(3/3)	--

Table 5. 94ND10/Kovar/94ND10 Brazed Tensile Button Helium Leak Check Results

Experiment 3, Braze 94ND10 ASTM F19 Tensile Buttons to Oversized Kovar interlayers – **Tensile Test Results**

Trend:

Slight increase in strength for ALD Al_2O_3 coated Kovar samples versus bare Kovar samples

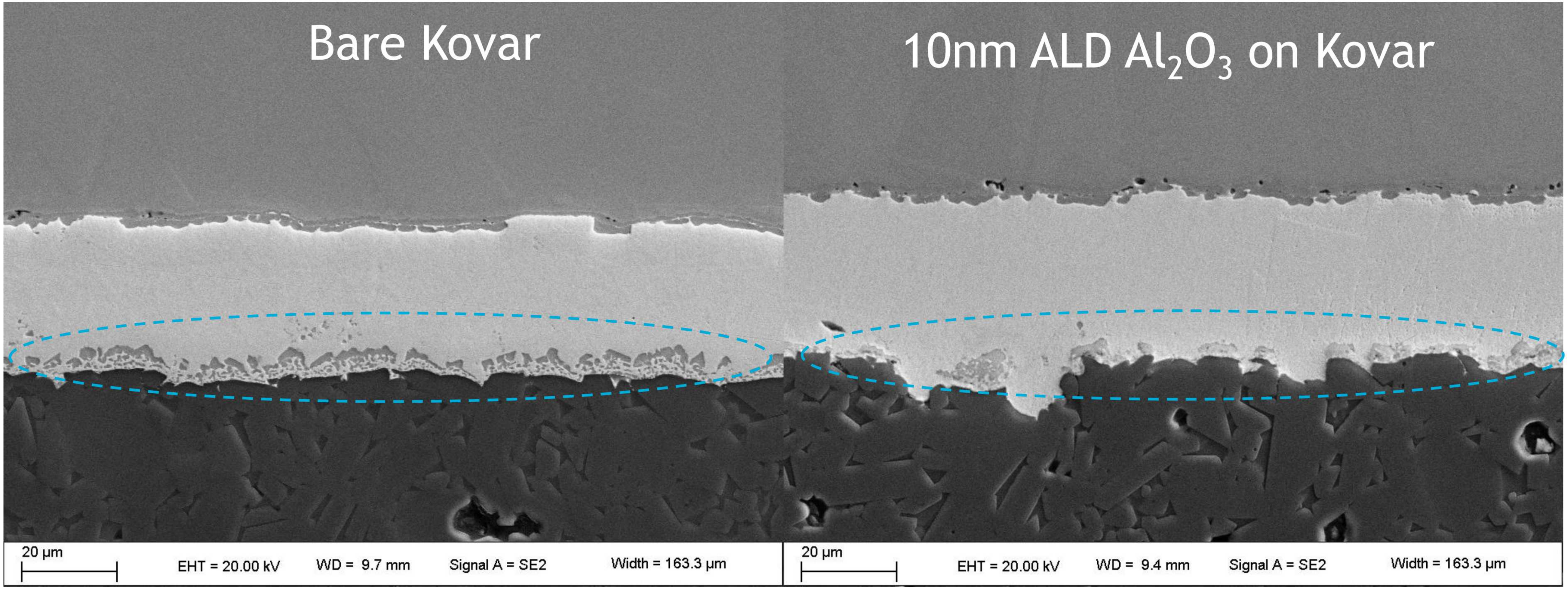


(3 samples/condition)

Figure 9. 94ND10/Kovar/94ND10 Brazed Tensile Button Average Tensile Strengths

Results and Discussion

No visible differences between ALD Al_2O_3 Kovar and bare Kovar observed on µm scale.

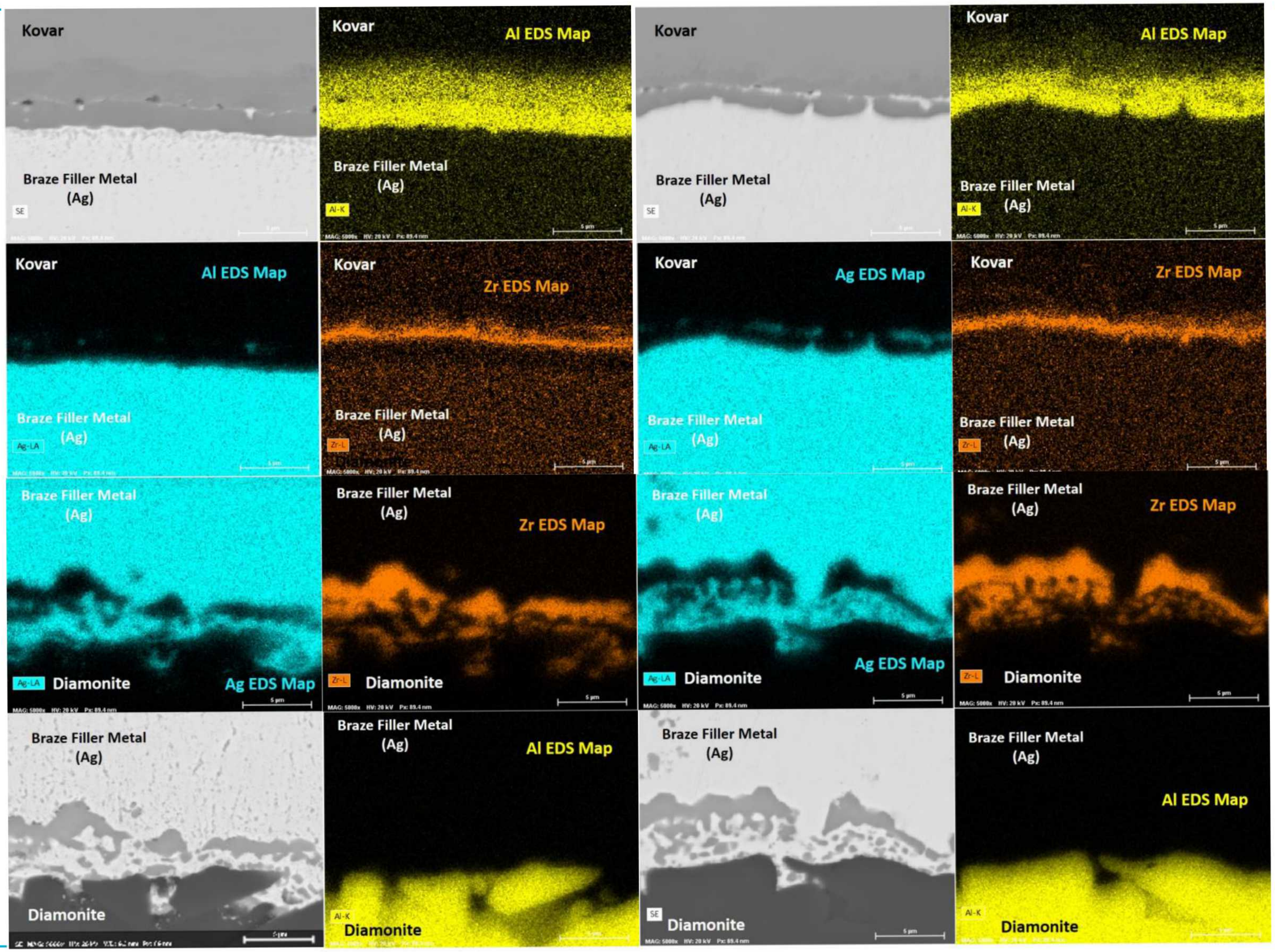


Zr reaction phase at visible near ceramic interface

Results and Discussion

No visible differences between ALD Al_2O_3 Kovar and bare Kovar observed on µm scale.

Diamonite and 10nm ALD Al_2O_3 Kovar SEM Image and EDS Maps



Diamonite and bare Kovar SEM Image and EDS Maps

Discussion & Conclusions

Effectiveness of ALD Al_2O_3 coatings with respect to:

Runout Prevention: For all three experiments, ALD Al_2O_3 coatings ≥5nm were successful 100% of the time (276/276 metal-ceramic brazements) in preventing excessive filler metal runout. Conversely, 82% of the samples having no coating or Al_2O_3 coatings ≤1nm failed the runout criteria (82/100 samples).

Hermeticity: The active filler metal Ag-1Cu-2Zr is a proven performer with respect to creating hermetic seals, whether or not a coating is utilized. As was reported in experiment #1, 12/12 seals were hermetic; 279/280 seals were hermetic for experiment #2 samples; and 101/108 hermetic brazements for the experiment #3 samples. Of the 7 total failures, 6 occurred in incorrectly dimpled substrates. The remaining failure occurred in a sample having 5nm ALD Al_2O_3 coating.

Tensile Strength: In general the strengths are very similar for samples brazed with bare Kovar or ALD Al_2O_3 coated Kovar. Samples brazed using Diamonite alumina were slightly weaker when coated while those brazed using 94ND10 alumina were slightly stronger.

Future Work:

Future efforts will pursue analyzing other active braze filler metals as well as other ALD oxide coatings to determine their effectiveness.