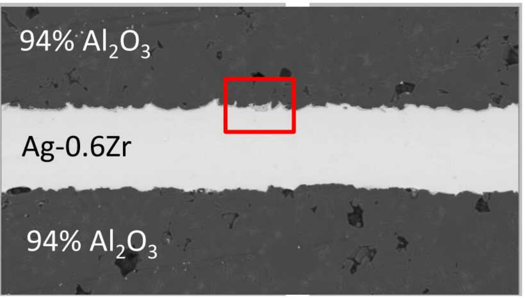
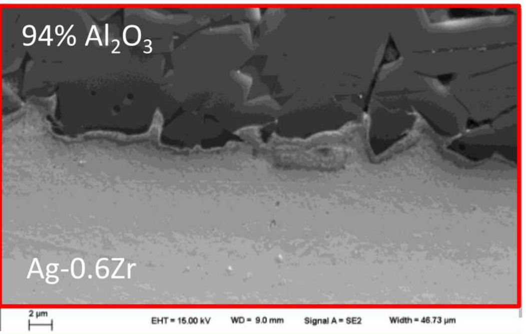
SAND2015-2994C

Single and double reaction layer formation using reduced active element containing brazing filler metals

IBSC 2015, International Brazing and Soldering Convention

April 19-22, 2015 Long Beach, CA





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Outline

Background:

- ***Brazing defined, metal-nonmetal braze considerations***
- ***Active brazing filler metals***

Thin-film active element additions & calculations

Test samples

- Results
- Analysis
- Discussion

Summary / Conclusions

Background: Brazing defined & nonmetal brazing considerations

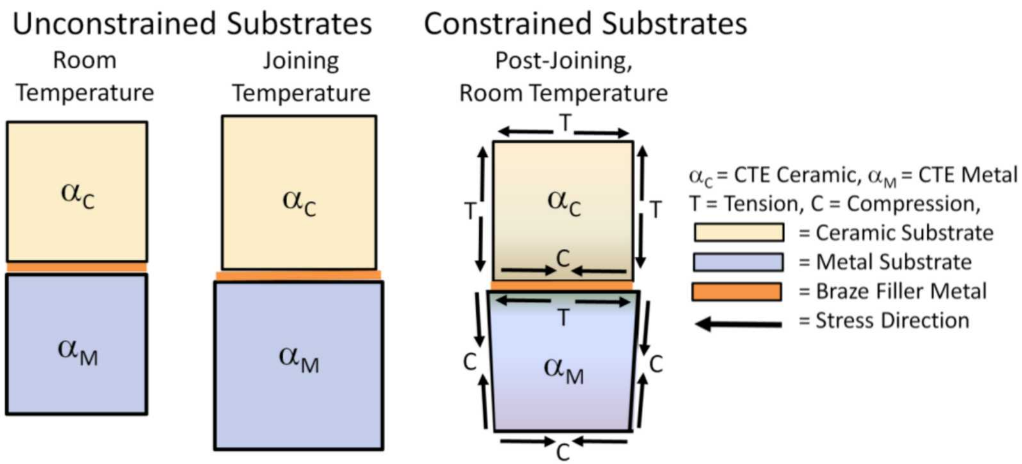
Brazing is a method of joining materials and typically meets three criteria:

- Takes place ≥ 450˚C
- Parent materials not melted
- Braze filler metal is drawn & held within the braze joint by capillary attraction.

Nonmetal brazing considerations:

- Brazing nonmetals to themselves or metals requires preplacement of the filler metal.
- Brazing to a nonmetals usually requires surface modification or the use of non-standard fillers.
- Coefficient of Thermal Expansion (CTE) mismatch is *especially important*.

CTE Metal > CTE Ceramic, ($\alpha_M > \alpha_C$)



Example: 94% - 97% Al_2O_3 brazed at ~1000C

Cu = 0.014”/1.0” mismatch
SS304 = 0.012”/1.0”
Kovar = 0.004”/1.0”
Niobium = 0.001”/1.0”
Mo = -0.002”/1.0”
W = -0.004”/1.0”

A 125mm (~5”) diameter assembly can have mismatch ranging from -0.020”- +0.060” (-0.5 - +1.5mm)

Advances in Brazing: Science, Technology and Applications (Woodhead Publishing Limited, 2013). Chapter 16, Metal-nonmetal brazing for electrical, packaging and structural applications. C.A. Walker, Sandia National Laboratories, USA, Page 500

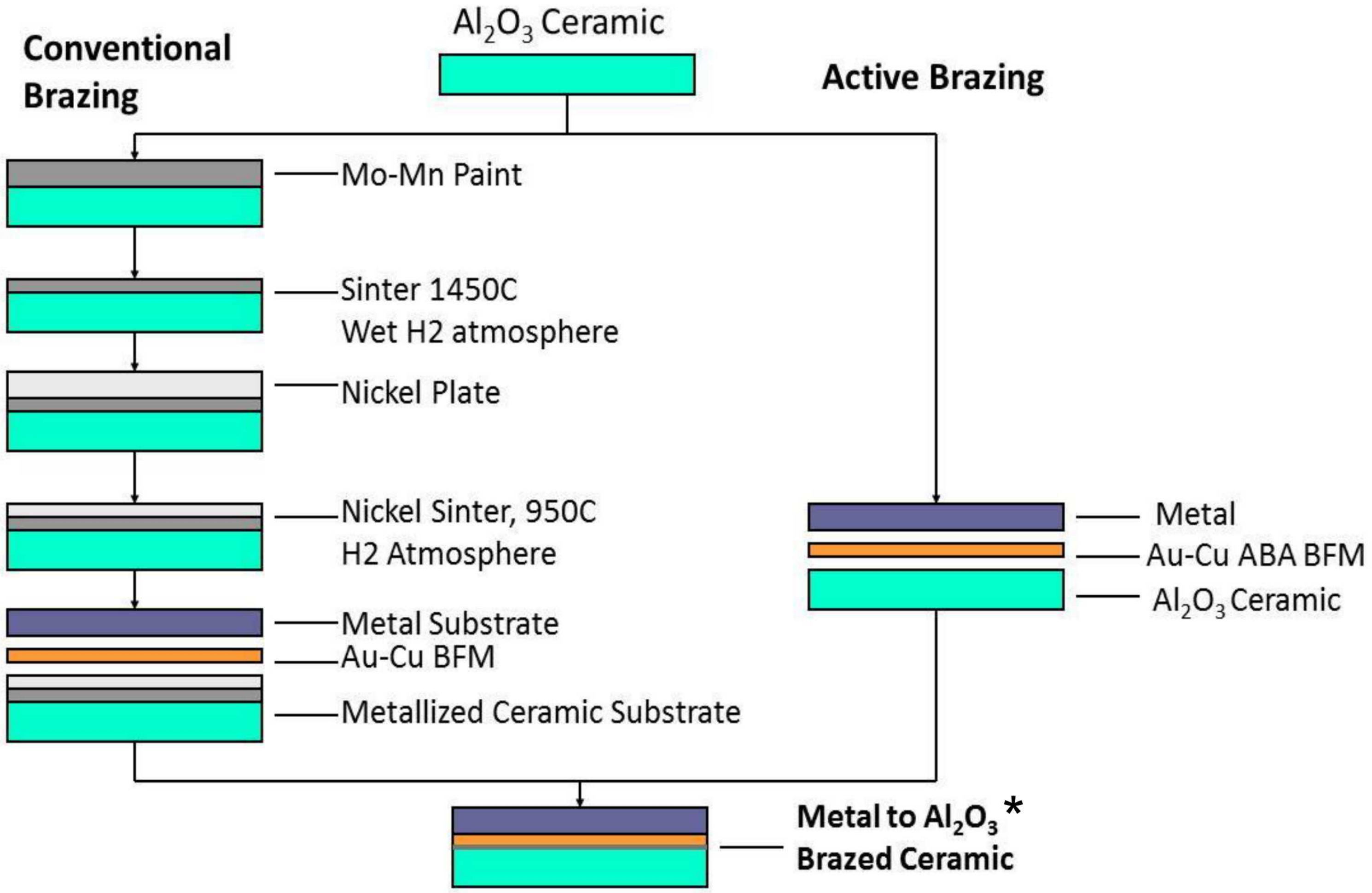
Active brazing filler metals

- Active brazing uses a filler metal that has been modified by the addition of a small amount (typically 1-2 wt. %) of a Group IVA element, such as: Ti, Zr, or Hf.
- These elements form strong oxides, stable at the liquidus temperature ranges of braze filler metals.
- Commercially available active filler metal compositions are limited and generic, resulting in a few standard compositions that must be made to work with many applications and materials systems.
- For this study, two commercially produced* active filler metals were used as a baseline: 98Ag-2Zr and 62Cu-35Au-2Ti-1Ni (weight percent).

* Morgan Technical Ceramics
Wesgo Metals
Hayward, CA

Why active braze?

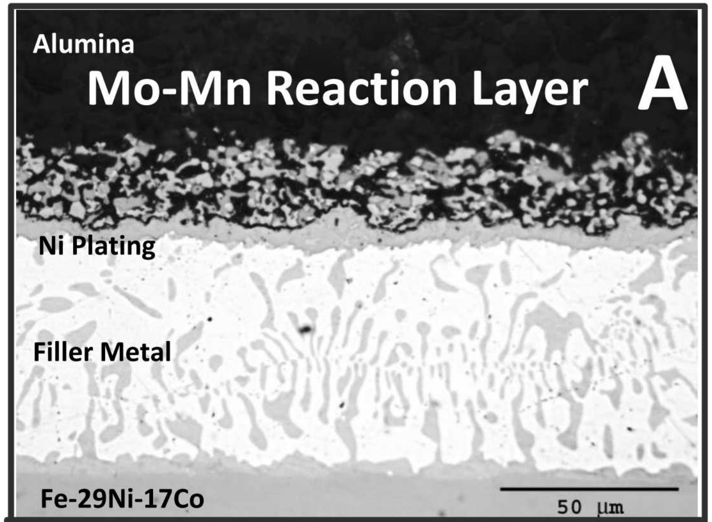
Conventional and active brazing comparison

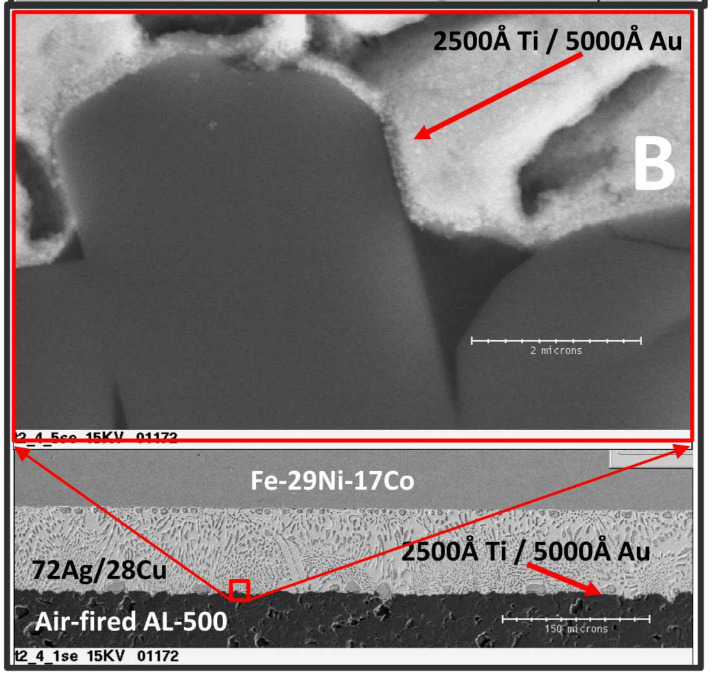


*Processes are similar for nonmetal-nonmetal brazing

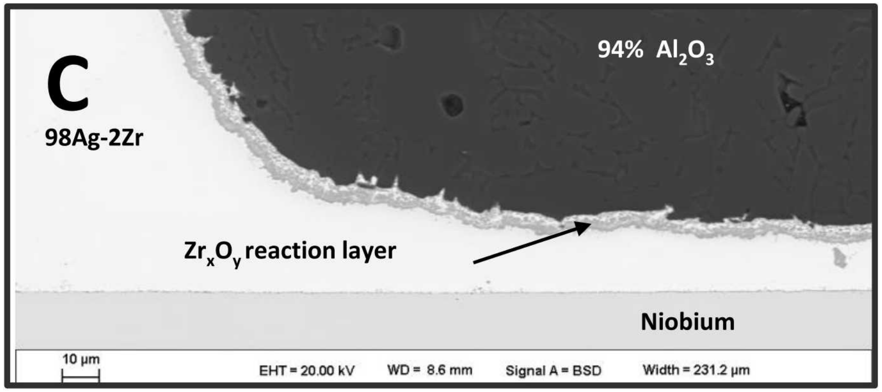
Adapted from AWS Brazing Handbook, 5th Edition, Page 463

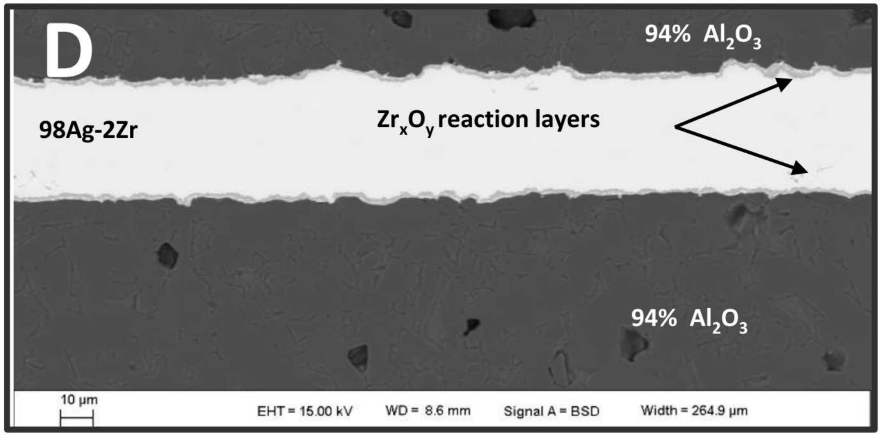
Conventional vs. Active brazed assemblies





A & B: 72Ag-28Cu, 810C - 3 min, dry H2





C & D: BSE images. 98Ag-2Zr at 985°C, 5 min vacuum atmosphere. C, 1 reaction layer, D, 2 reaction layers.

Note that the Zr has successfully migrated to the oxide ceramic surface(s) to allow the filler metal to wet/bond properly.

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Braze filler metal and sample materials preparation

Custom "active" filler metals:

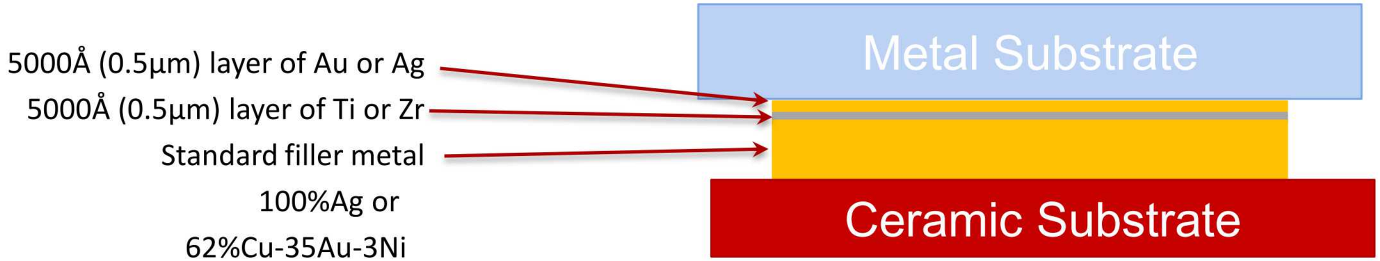
- Were fabricated by depositing a 5000Å (0.5µm) layers of either Ti & Au or Zr & Ag on standard filler metals.
- 5000Å thicknesses were chosen based on results from previous trials using similar thickness layers on bare ceramics.
- The sputter deposited thin-film layers on the filler metal were always positioned *toward the metal* faying surface when metal-ceramic samples were brazed to verify that the active element would diffuse through the liquid filler metal to form a proper reaction layer.

Ceramic substrates:

- Following the densification firing at the manufacturer the ceramic samples are ground to provide the required surface finish.
- Samples are solvent cleaned and air-fired (resintering/micro-crack healing step)

Metal substrates:

- Metal substrates used were stamped discs or washers made from commercially pure niobium or Kovar.
- Following solvent rinsing, the Nb samples were vacuum fired at 1450˚C , while the Kovar samples were hydrogen fired at 800˚C.



Active element sputtered thickness & equivalent weight %

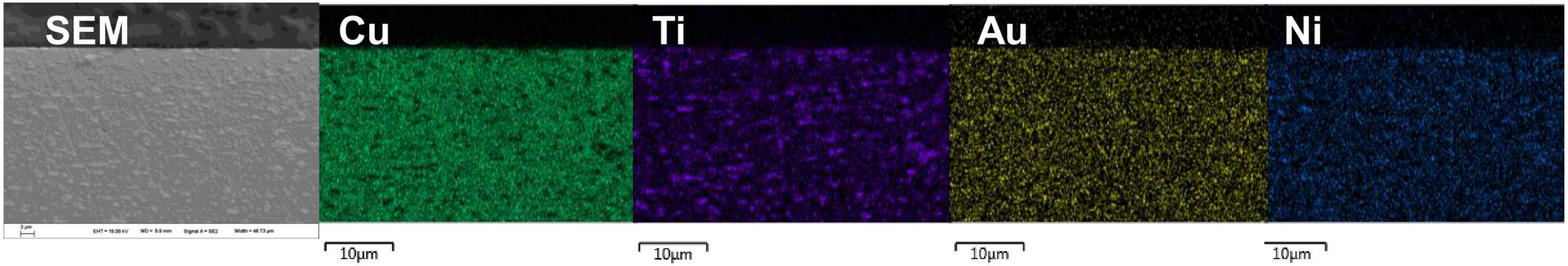
Brazing Filler Metal (BFM)	BFM Thickness µm, (in)	Weight percentage of active element	Sputtered layer equivalent, µm
A - Silver+0.625Zr	50.8 (0.002)	0.6	0.50
B - Silver+0.4Zr	76.2 (0.003)	0.4	0.50
C - BAu-3+0.35Ti	50.8 (0.002)	0.4	0.50
D - BAu-3+0.235Ti	76.2 (0.003)	0.2	0.50
E - 97Ag-1Cu-2Zr	50.8 (0.002)	2.0	1.61
F - 97Ag-1Cu-2Zr	76.2 (0.003)	2.0	2.41
G - Nicoro®+2%Ti	50.8 (0.002)	2.0	2.90
H - Nicoro®+2%Ti	76.2 (0.003)	2.0	4.35

Assumption: Sputtered layers are 100% dense.

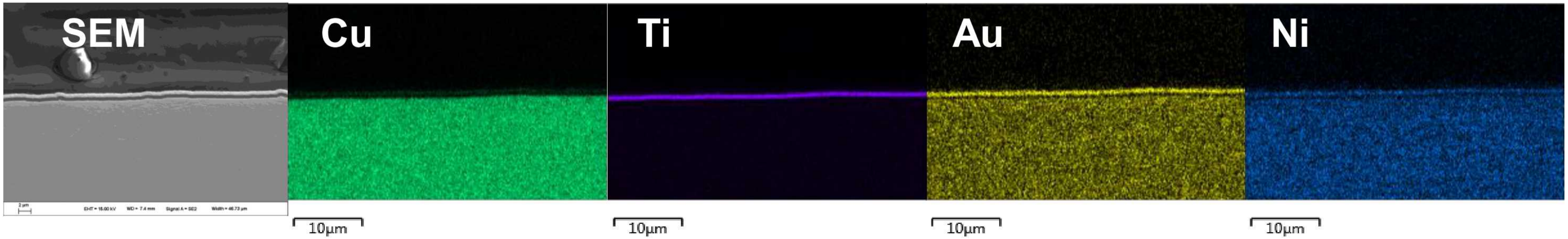
Commercially fabricated* and verses custom fabricated active braze filler metal

SEM & EDS maps of Au-based filler metals (as-received/fabricated)

Commercially fabricated 62Cu-35Au-2Ti-1Ni (weight percent)



Custom fabricated Nicoro®+5kÅ Ti & 5kÅ Au filler metal

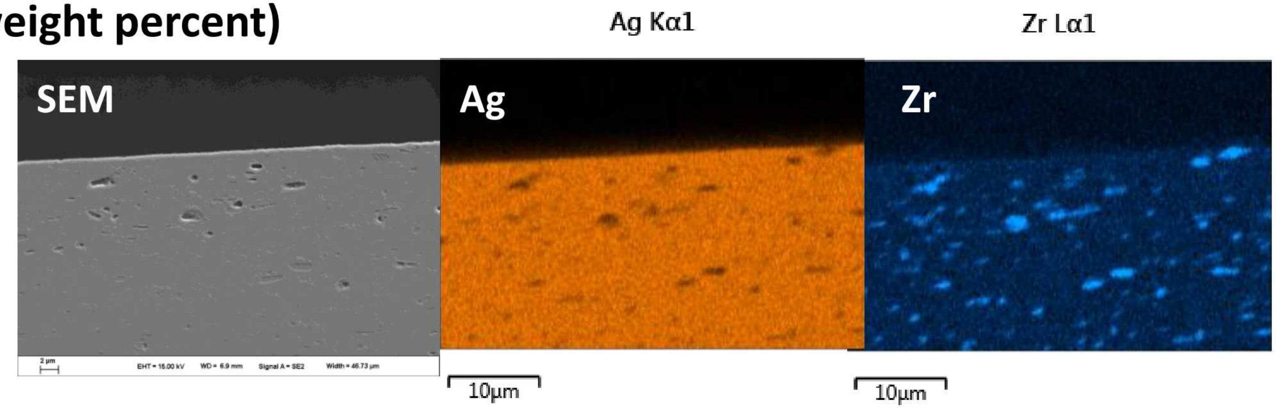


* Morgan Technical Ceramics
Wesgo Metals
Hayward, CA

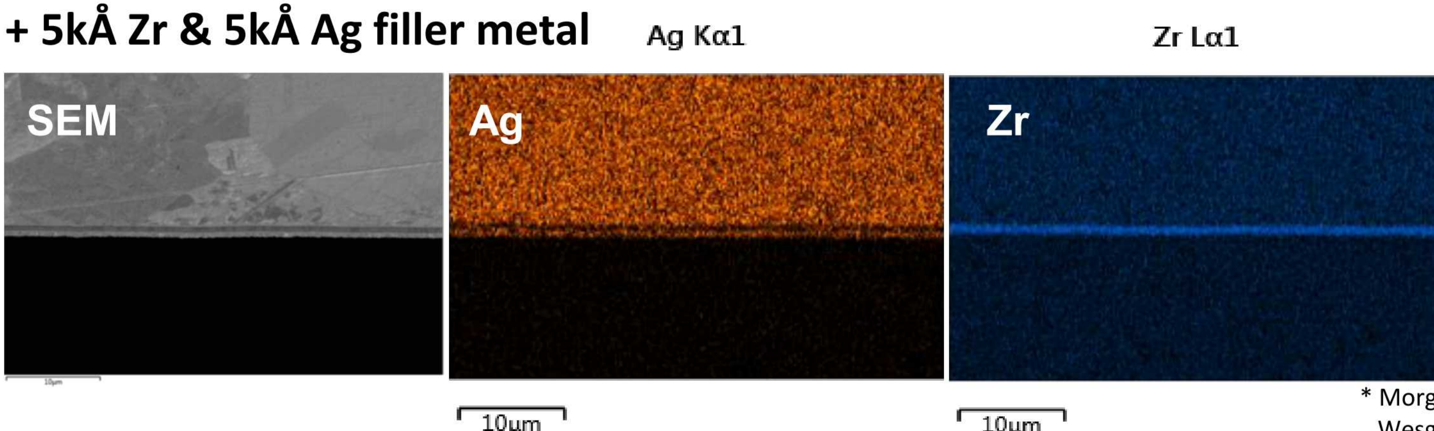
Commercially fabricated* and verses custom fabricated active braze filler metal

SEM & EDS maps of Ag-based filler metals (as-received/fabricated)

98Ag-2Zr (weight percent)



100%Ag + 5kÅ Zr & 5kÅ Ag filler metal



* Morgan Technical Ceramics
Wesgo Metals
Hayward, CA

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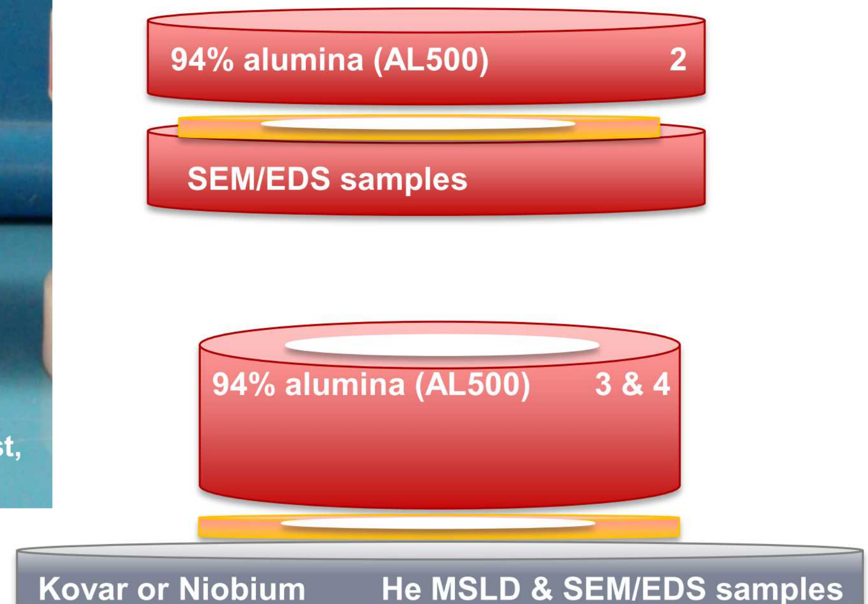

Summary / Conclusions

Metal-Ceramic sample results

1-reaction layer: *Nb or Kovar to Al-500*

Filler Metal ID	Interlayer	BFM thickness (mils)	Pass %	Average Tensile Stress (psi)	Notes:	Ceramic Firing
A	Kovar	2	100	n/a	99.375Ag-0.625Zr: 5kÅ Zr/5kÅ Ag on Ag foil.	1575˚C-2 hrs, air
B	Kovar	3	100	n/a	99.6Ag-0.4Zr: 5kÅ Zr/5kÅ Ag on Ag foil.	1575˚C-2 hrs, air
C	Niobium	2	100	n/a	Nicoro®+0.35%Ti: 5kÅ Ti/5kÅ Au on Nicoro® foil.	1575˚C-2 hrs, air
D	Niobium	3	100	n/a	Nicoro®+0.235%Ti: 5kÅ Ti/5kÅ Au on Nicoro® foil.	1575˚C-2 hrs, air
E	Kovar	2	100	n/a	98Ag-2Zr, Standard ABA BFM.	1575˚C-2 hrs, air
F	Kovar	3	100	n/a	98Ag-2Zr, Standard ABA BFM.	1575˚C-2 hrs, air
G	Niobium	2	100	n/a	Nicoro®+2%Ti, Standard ABA BFM	1575˚C-2 hrs, air
H	Niobium	3	100	n/a	Nicoro®+2%Ti, Standard ABA BFM	1575˚C-2 hrs, air

Ceramic-metal samples:

- All samples were hermetic (leak rates <5E-12 atm-cc/sec).
- No tensile testing done.
- Samples cross-sectioned and analyzed (SEM/EDS)

2-reaction layer ASTM-F19 tensile button results (*94ND10* Ceramic-Ceramic)

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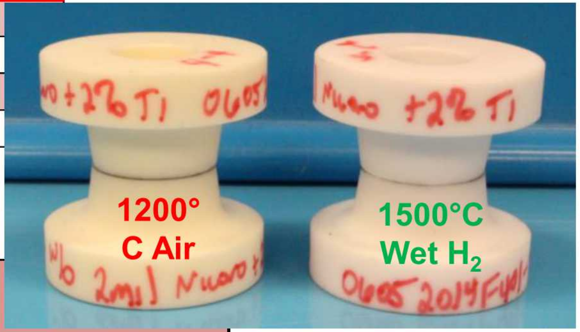
Filler Metal ID	Interlayer	BFM thickness (mils)	Pass*/ Total	Average Tensile Stress (psi)	Notes:
A	None	2	0/4	3323	99.375Ag-0.625Zr: 5kÅ Zr/5kÅ Ag on Ag foil.
B	None	3	0/4	1077	99.6Ag-0.4Zr: 5kÅ Zr/5kÅ Ag on Ag foil.
C	None	2	0/4	4368	Nicoro®+0.35%Ti: 5kÅ Ti/5kÅ Au on Nicoro® foil.
D	None	3	0/4	3320	Nicoro®+0.235%Ti: 5kÅ Ti/5kÅ Au on Nicoro® foil.
E	None	2	1/4	4137	98Ag-2Zr, Standard ABA BFM.
F	None	3	2/4	10619	98Ag-2Zr, Standard ABA BFM.
G	**None**	**2**	**0/4**	**8752**	**Nicoro®+2%Ti, Standard ABA BFM**
H	**None**	**3**	**2/4**	**12041**	**Nicoro®+2%Ti, Standard ABA BFM**

Standard ABA filler metal joint tensile strengths are much less than typically observed: 14-24 ksi (95-165Mpa), and not consistently hermetic .



Filler Metal ID	Interlayer	BFM thickness (mils)	Pass / Total	Average Tensile Stress (psi)	Notes:	Ceramic Firing
A	None	2	0/4	3323	99.375Ag-0.625Zr: 5kÅ Zr/5kÅ Ag on Ag foil.	1200˚C-Air
B	None	3	0/4	1077	99.6Ag-0.4Zr: 5kÅ Zr/5kÅ Ag on Ag foil.	1200˚C-Air
C	None	2	0/4	4368	Nicoro®+0.35%Ti: 5kÅ Ti/5kÅ Au on Nicoro® foil.	1200˚C-Air
D	None	3	0/4	3320	Nicoro®+0.235%Ti: 5kÅ Ti/5kÅ Au on Nicoro® foil.	1200˚C-Air
E	None	2	1/4	4137	98Ag-2Zr, Standard ABA BFM.	1200˚C-Air
F	None	3	2/4	10619	98Ag-2Zr, Standard ABA BFM.	1200˚C-Air
G	None	2	**0/2**	**11396**	Nicoro®+2%Ti, Standard ABA BFM	**1500˚C-Wet H2**
G	None	2	**0/2**	**6108**	**Nicoro®+2%Ti, Standard ABA BFM**	1200˚C-Air
H	None	3	**2/2**	**13664**	Nicoro®+2%Ti, Standard ABA BFM	**1500˚C-Wet H2**
H	None	3	**0/2**	**10437**	**Nicoro®+2%Ti, Standard ABA BFM**	1200˚C-Air

Discovered most of the ceramic samples were inadvertently fired in air at 1200˚C (lower strength), not 1575˚C. A few samples were fired in wet hydrogen at 1500˚C. (higher strength)

MTS crosshead speed = 8.38E-03 mm/sec)

***Pass = Helium leak rates <5E-12 atm-cc/sec (5E-13 Pa-M³/s)**

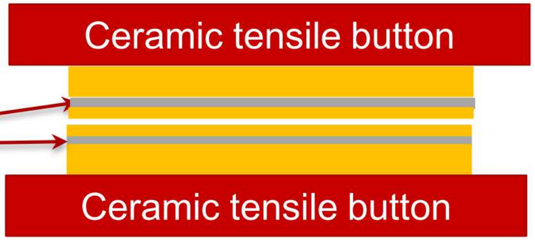
Atmosphere & Temperature Effects

2-reaction layer (2nd-group) ASTM-F19 tensile button results *(94ND10-wet H2 fired)*

Filler Metal ID	Interlayer	BFM thickness (mils)	Pass / Total	Average Tensile Stress (psi)	Notes:	Ceramic Firing
A	None	2	0/2	7893	99.375Ag-0.625Zr: 5kÅ Zr/5kÅ Ag on Ag foil.	1500˚C-Wet H2
B	None	3	0/2	3442	99.6Ag-0.4Zr: 5kÅ Zr/5kÅ Ag on Ag foil.	1500˚C-Wet H2
E	None	2	TBD	TBD	98Ag-2Zr, Standard ABA BFM.	1500˚C-Wet H2
F	None	3	TBD	TBD	98Ag-2Zr, Standard ABA BFM.	1500˚C-Wet H2
C	None	2	1/2	10694	Nicoro®+0.35%Ti: 5kÅ Ti/5kÅ Au on Nicoro® foil.	1500˚C-Wet H2
D	None	3	2/2	8816	Nicoro®+0.235%Ti: 5kÅ Ti/5kÅ Au on Nicoro® foil.	1500˚C-Wet H2
G	None	2	4/4	12801	Nicoro®+2%Ti, Standard ABA BFM	1500˚C-Wet H2
H	None	3	4/4	9860	Nicoro®+2%Ti, Standard ABA BFM	1500˚C-Wet H2
I	None	3	2/2	14580	Nicoro®+1%Ti, Standard ABA BFM	1500˚C-Wet H2
J	None	3	2/2	10313	Nicoro®+1%Ti, Standard ABA BFM	1500˚C-Wet H2
K	None	3	2/2	17927	Nicoro®+0.33%Ti, Standard ABA BFM	1500˚C-Wet H2
L	None	2	2/2	14119	Nicoro®+0.5%Ti, Standard ABA BFM	1500˚C-Wet H2
M	None	2	2/2	14110	Nicoro®+0.67%Ti, Standard ABA BFM	1500˚C-Wet H2

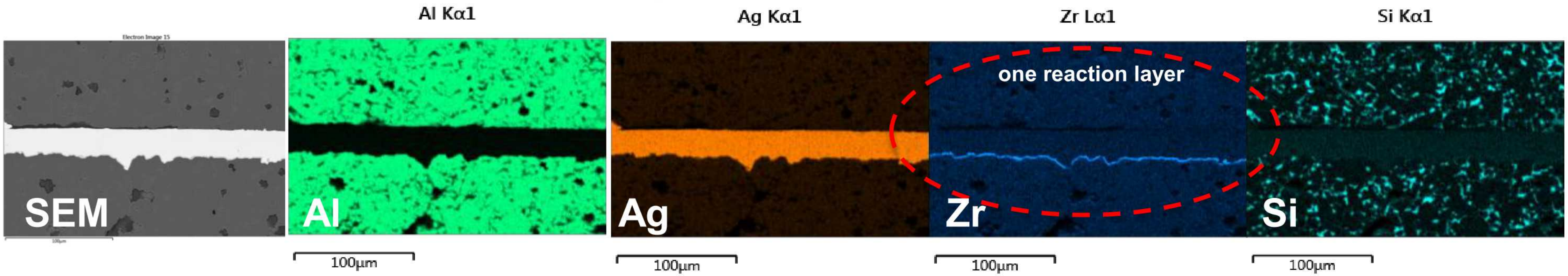
- **Improvement was observed for wet H2 fired ceramics used with Ti-containing braze material.**
- **No improvement noticed for Ag-Zr samples. “Standard” samples still remain to be completed.**
- **Filler metals I - M were prepared as before except sputtered layers were positioned toward each other as shown.**

2nd-Group, I-M
7200Å (0.72µm) - 14400Å (1.44µm)
layers of Ti only (no Ag-Zr samples made)



Sample B – 99.6%Ag – 0.4%Zr, 75µm thick

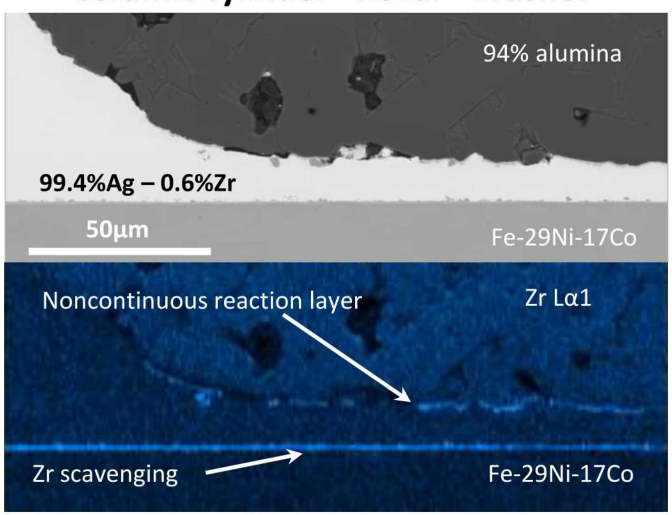
2 reaction layer ceramic-ceramic discs



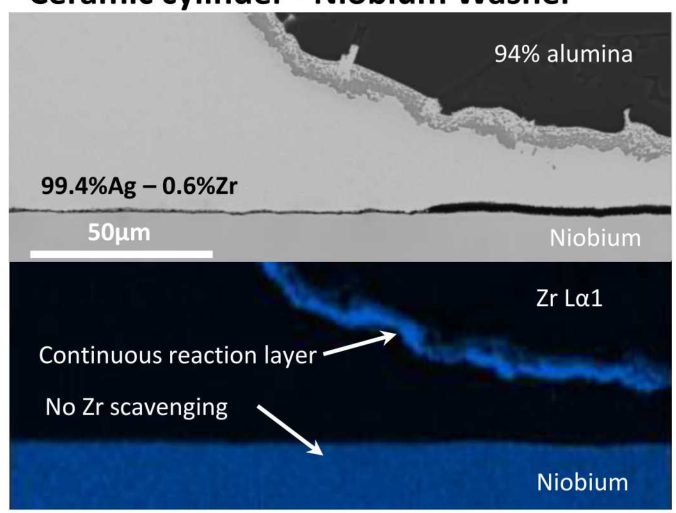
AK & AN – 99.375%Ag – 0.625%Zr, 50µm thick

1-reaction layer metal-ceramic assembly

Ceramic cylinder - Kovar® Washer

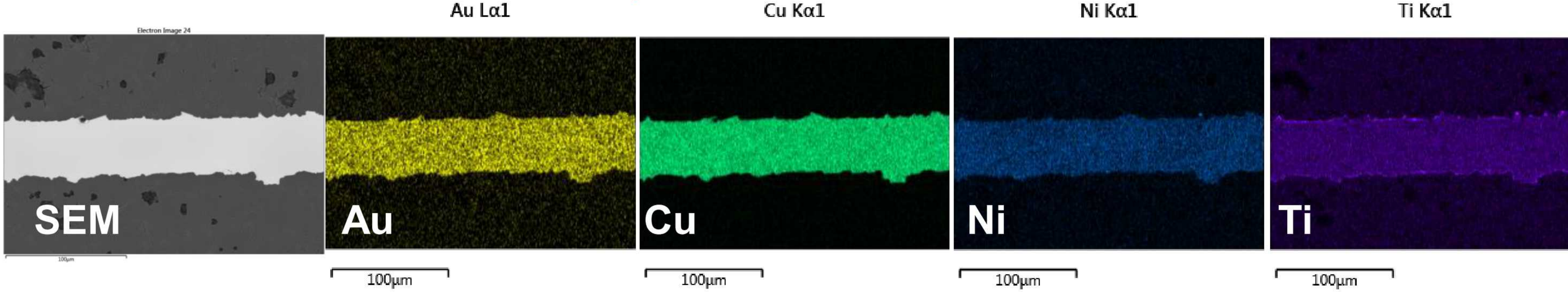


Ceramic cylinder - Niobium Washer



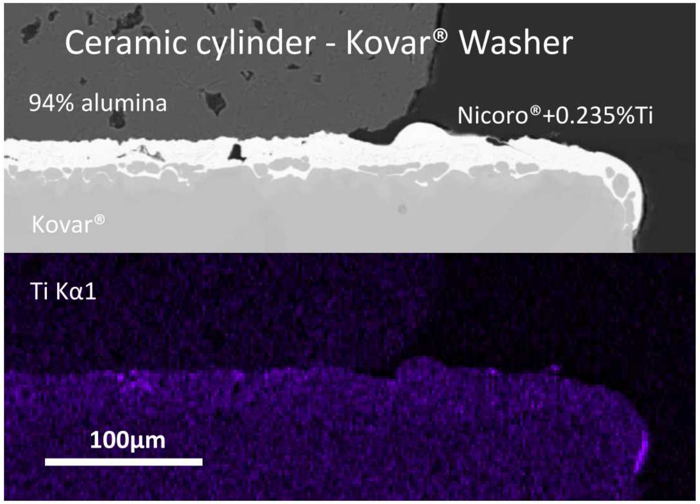
Sample C – Nicoro®+0.35%Ti, 50µm thick

2-reaction layer ceramic-ceramic discs



DK & DN – Nicoro®+ 0.235%Ti, 75µm thick

1-reaction layer metal-ceramic assembly



TB-F5: 98Ag-2Zr, Standard ABA,75µm thick

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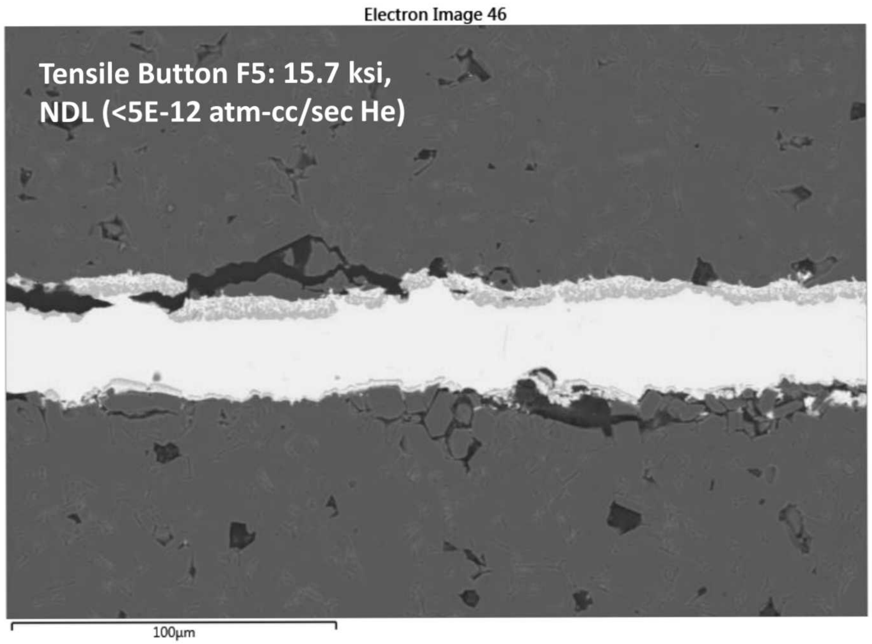
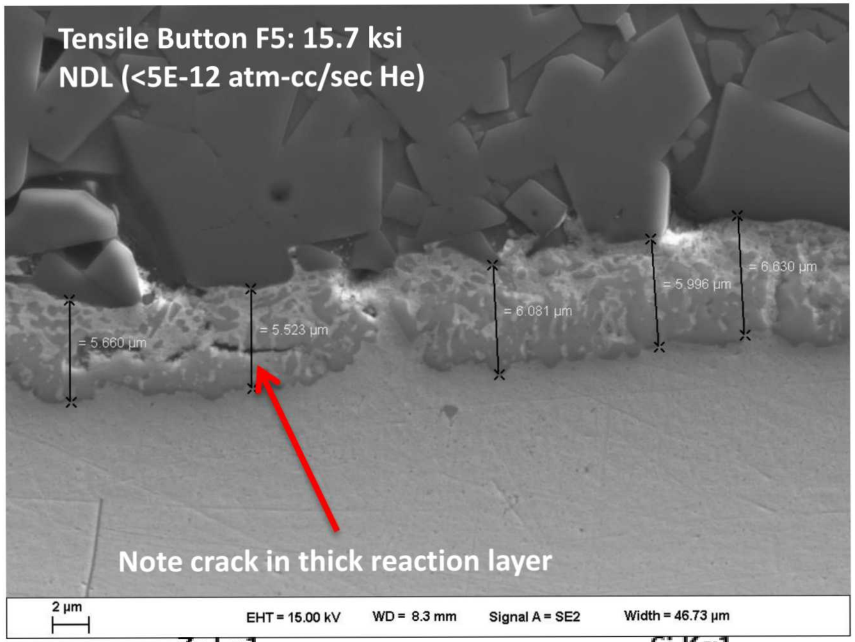
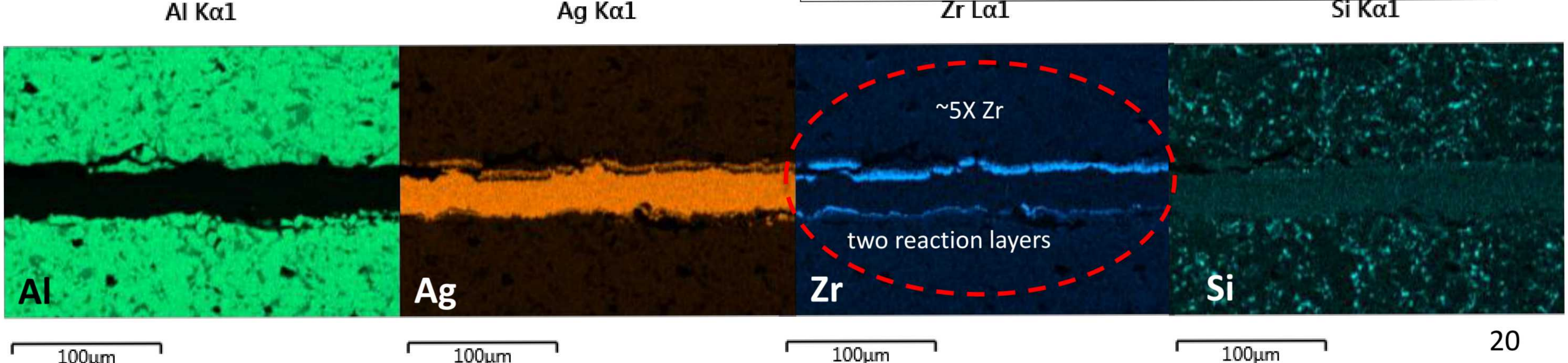
2-reaction layer ASTM F-19 Tensile Buttons

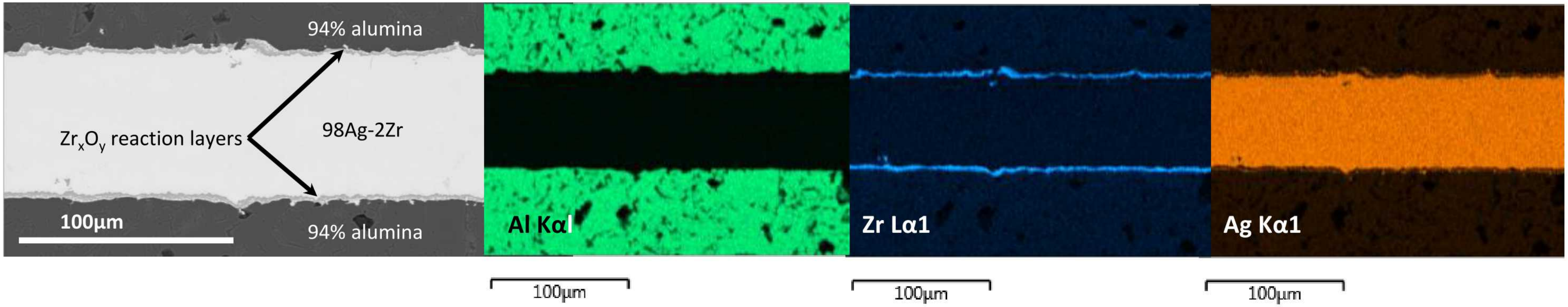






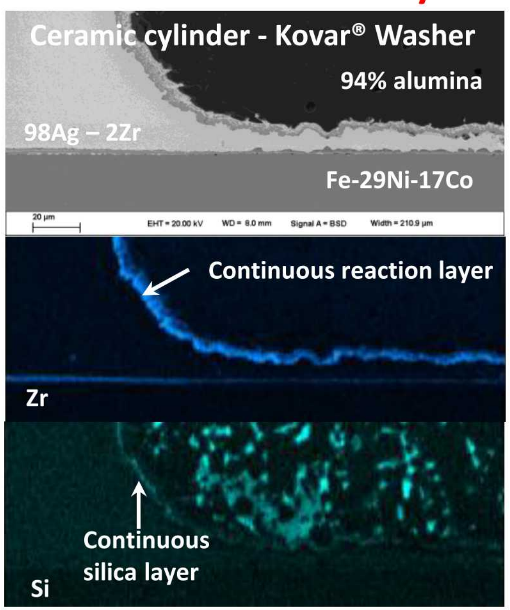
Sample E: 98Ag-2Zr, 50μm thick

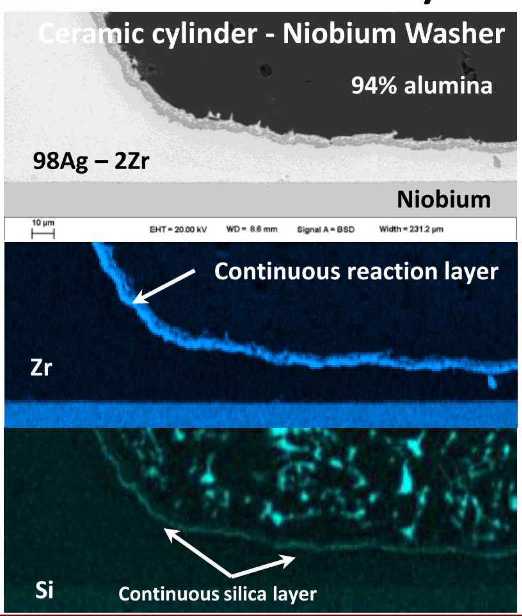
2-reaction layer ceramic-ceramic discs



EK & EN – 98 Ag + 2Zr, 50μm thick

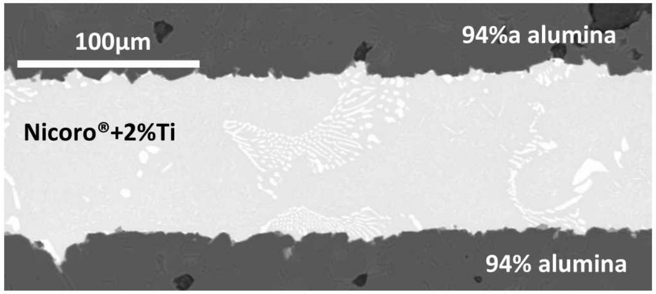
1-reaction layer metal-ceramic assembly

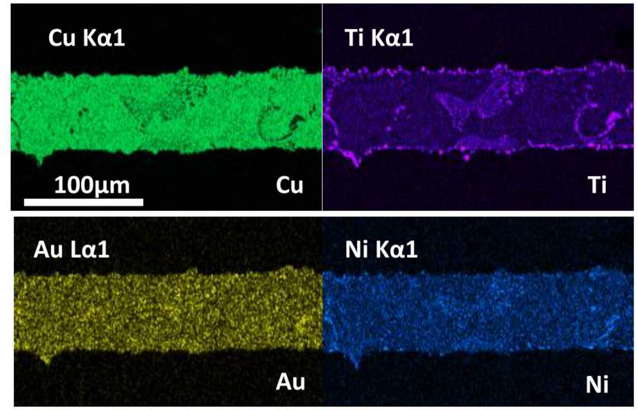




Sample G –Nicoro®+ 2%Ti, 50µm thick

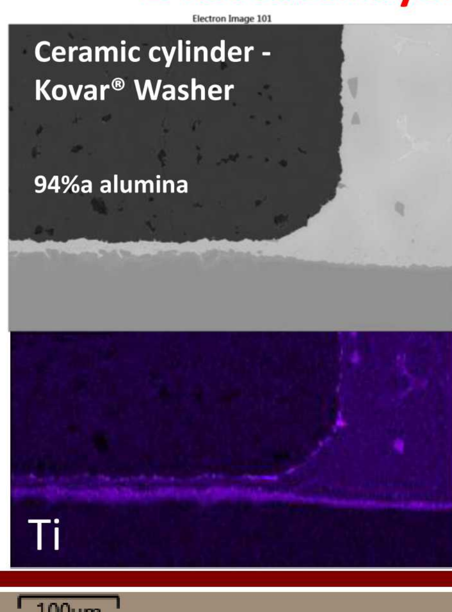
2 reaction layers, Ceramic-Ceramic Discs

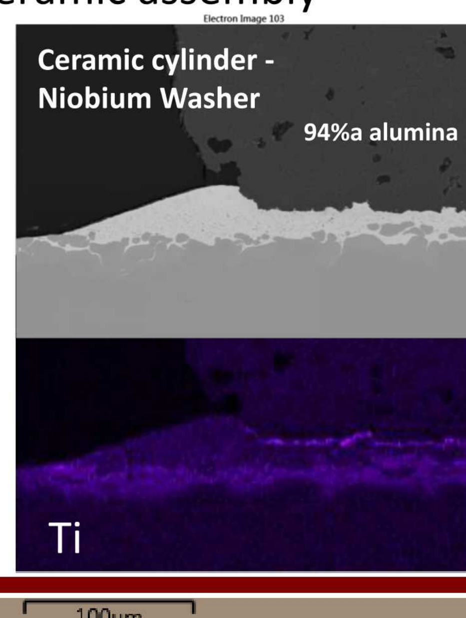




GK & GN –Nicoro®+ 2%Ti, 50µm thick

1-reaction layer metal-ceramic assembly





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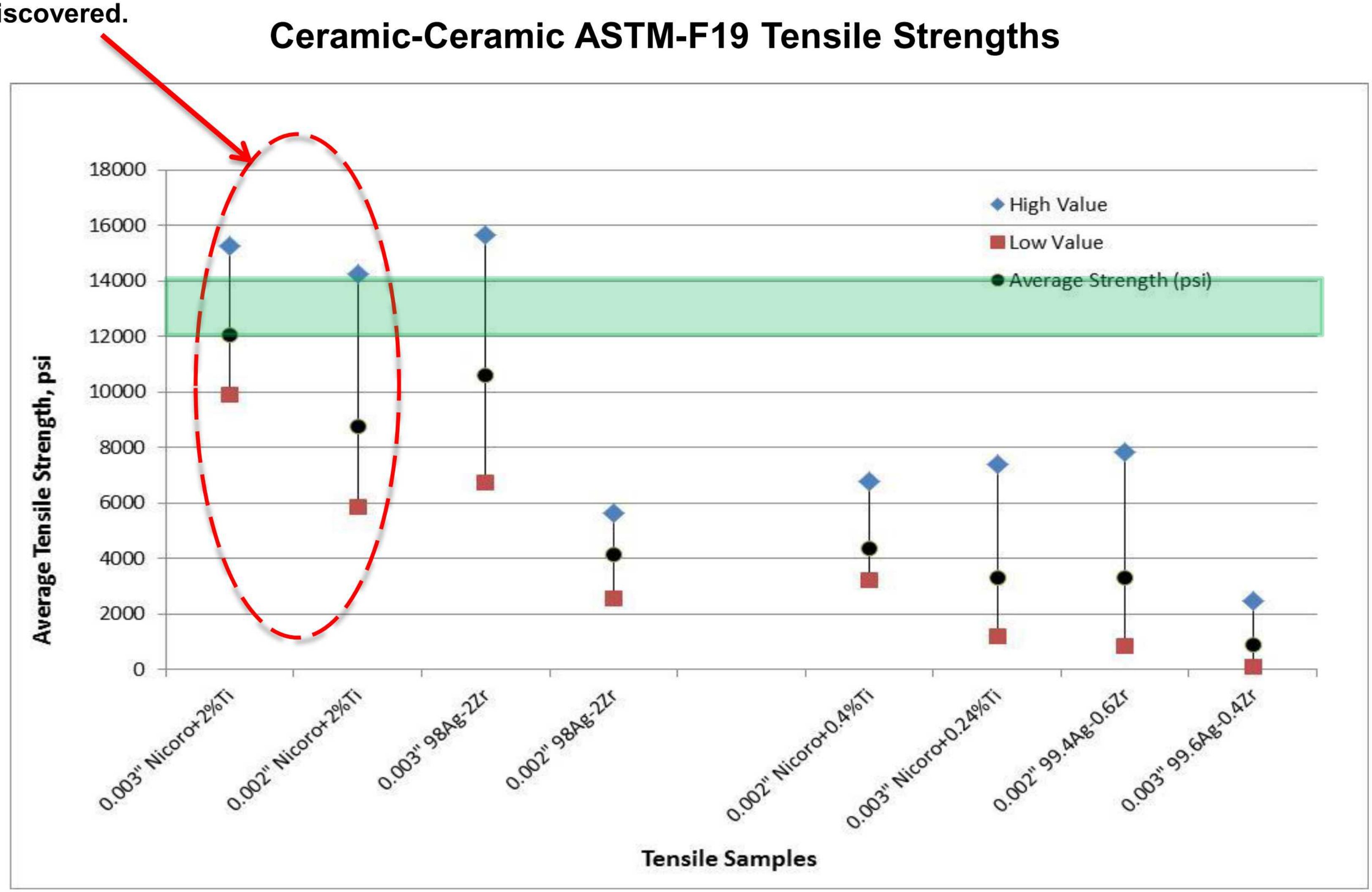
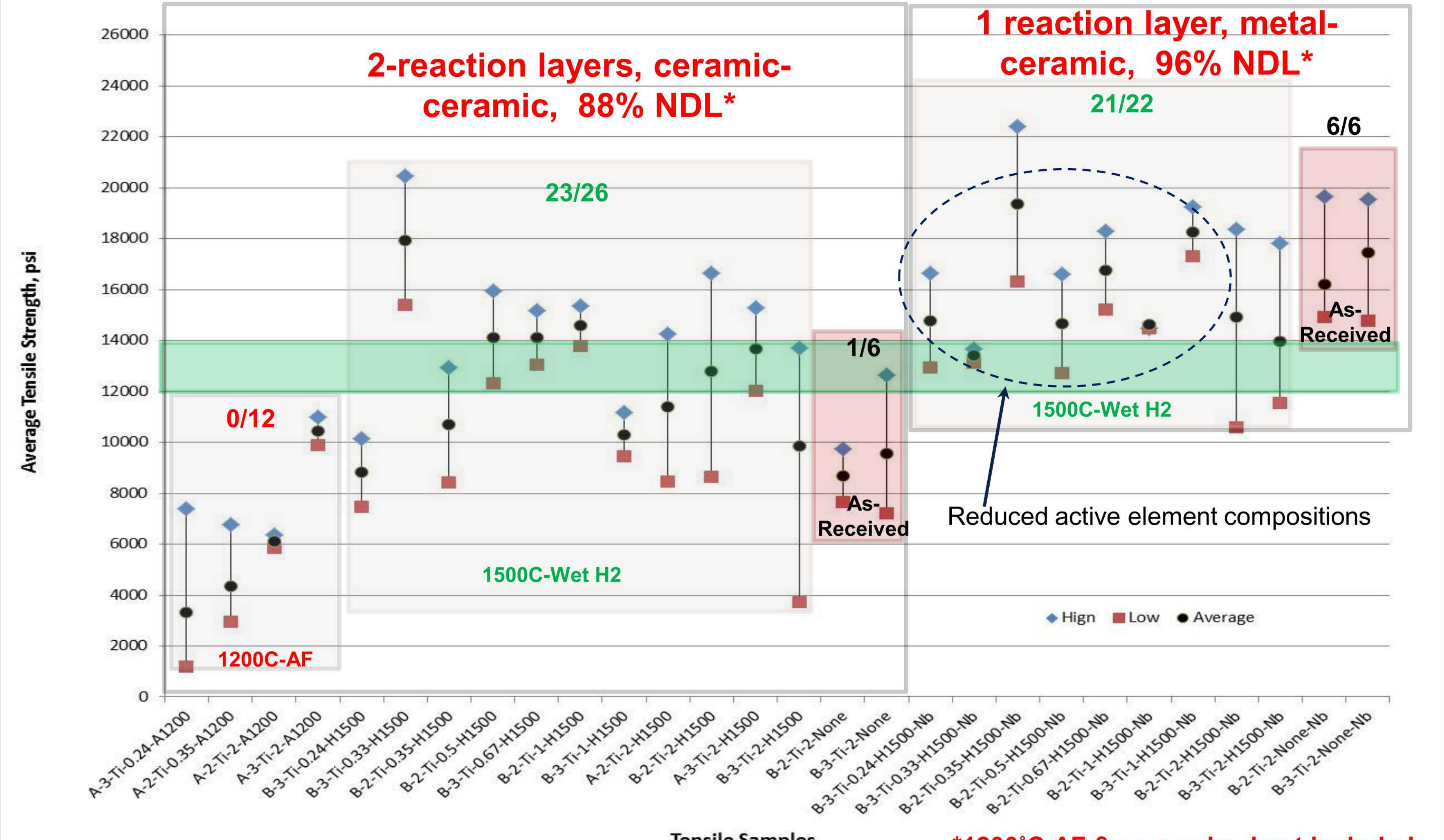
Different resintering atmospheres & temperatures within the groups discovered.



Tensile strengths of Nicoro®+Ti variants

ASTM F-19 Tensile Buttons



*1200˚C-AF & as-received not included

Conclusions

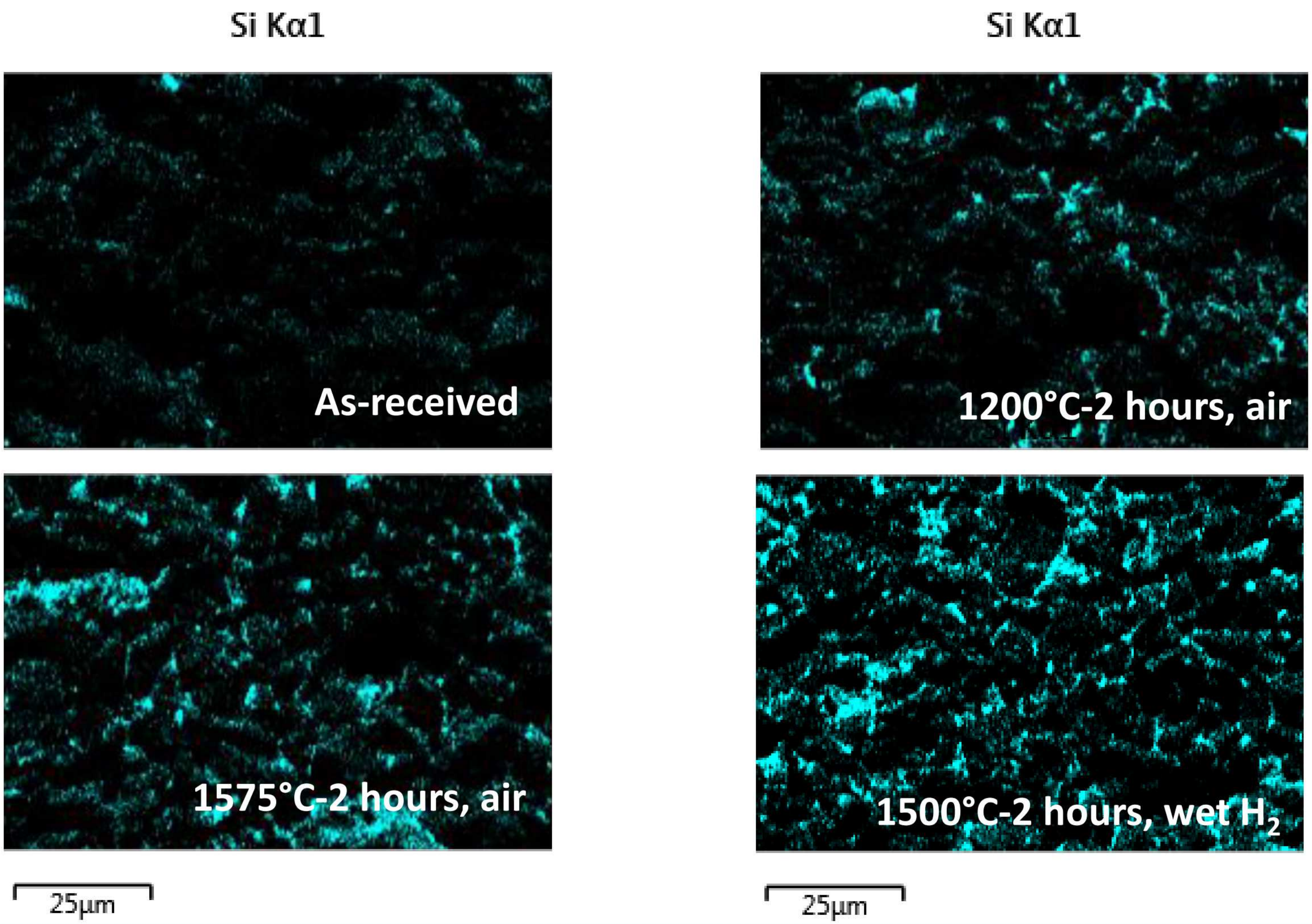
- This study confirmed the feasibility of producing active brazing filler metals capable of producing strong, hermetically sealed ceramic-ceramic and metal-ceramic brazed assemblies.
- Work was focused on producing filler metals having significantly lower active element additions (0.235 – 1.0 weight percent) than those typically commercially available.
- The in-house fabricated active filler metals generally performed better (created a more continuous reaction layers, had greater percentages hermetic, had higher average tensile strengths) when they were used in single reaction layer samples than for two-reaction layer systems: i.e. metal-ceramic joints were more robust than ceramic-ceramic joints.
- Future effort focus:
    1) Fine-tune the amount of active element required to create reliable, robust brazed assemblies for one and two-reaction layer systems.
    2) Investigate further/characterize ceramic firing conditions (air and wet hydrogen) necessary properly prepare alumina ceramic substrates for future active brazing applications.

Thanks much!

Appendix / Additional slides

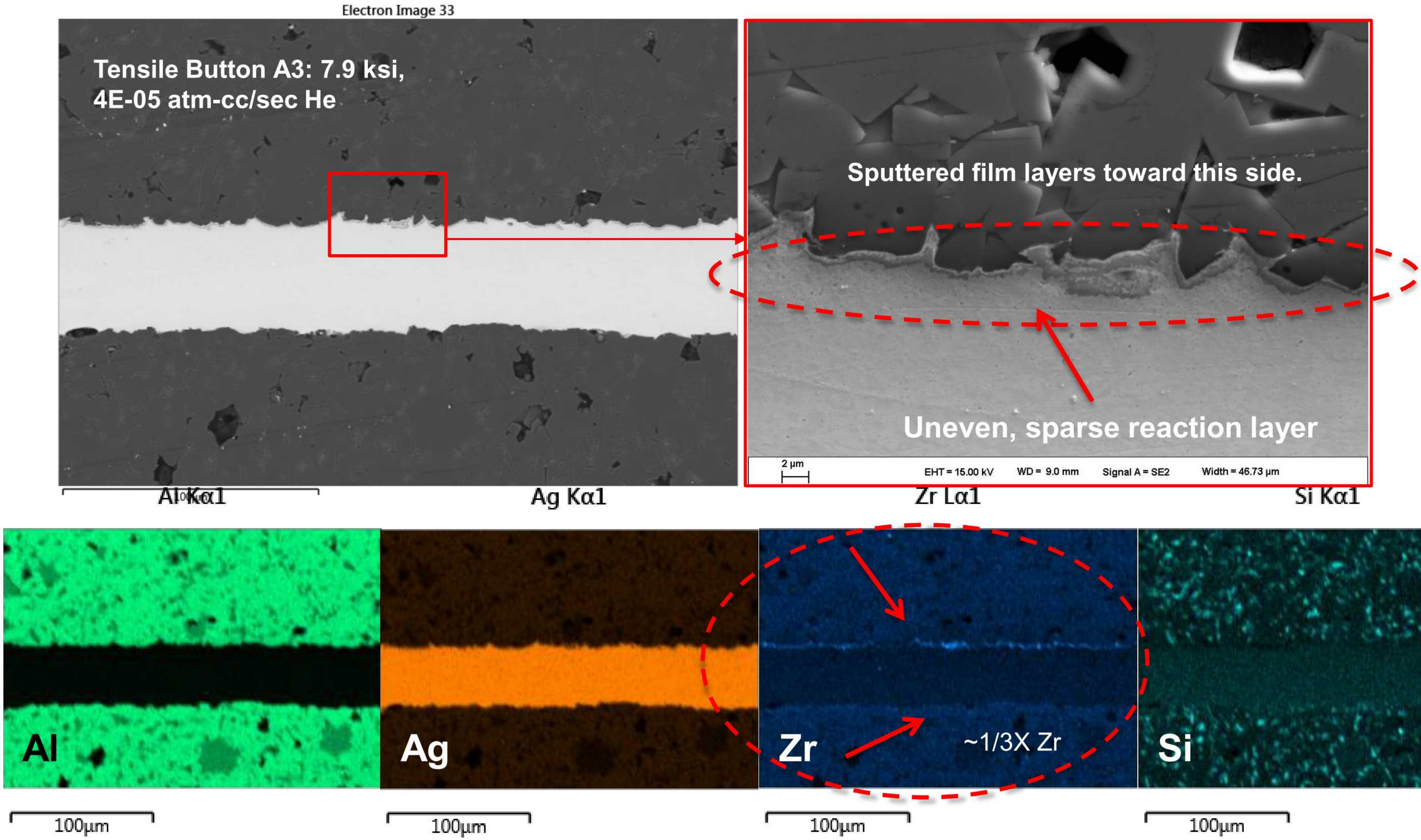
Discussion

Ceramic Firing Differences: EDS Si spectra comparison



TB-A3: 99.375Ag-0.625Zr, 50µm Ag foil

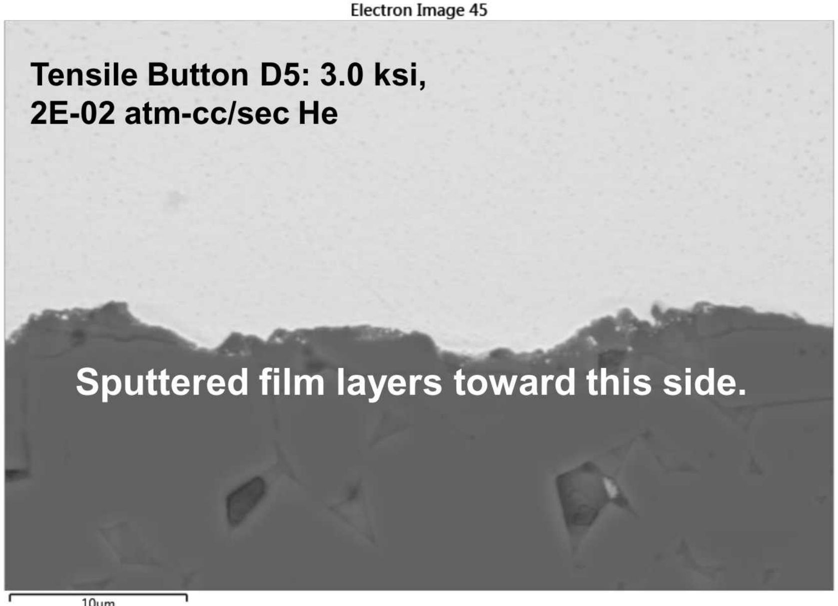
2-reaction layer ASTM F-19 Tensile Buttons

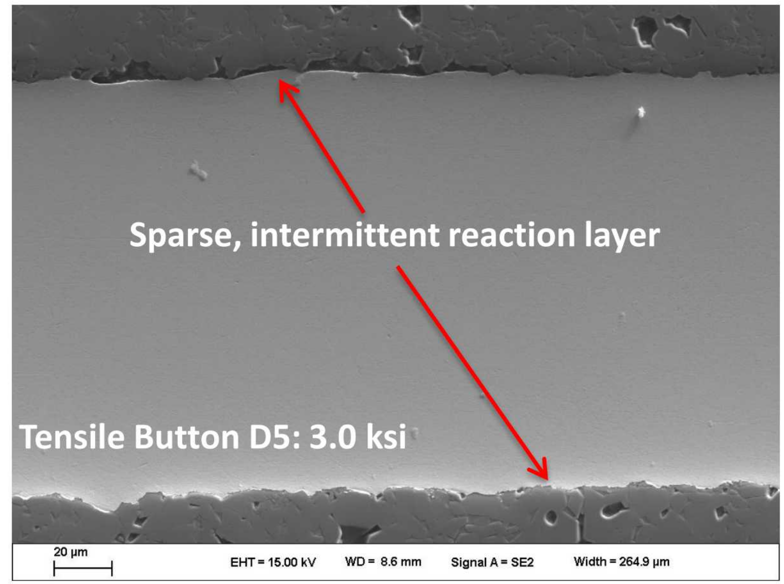


TB-D5 - Nicoro®+ 0.235%Ti, 75µm thick

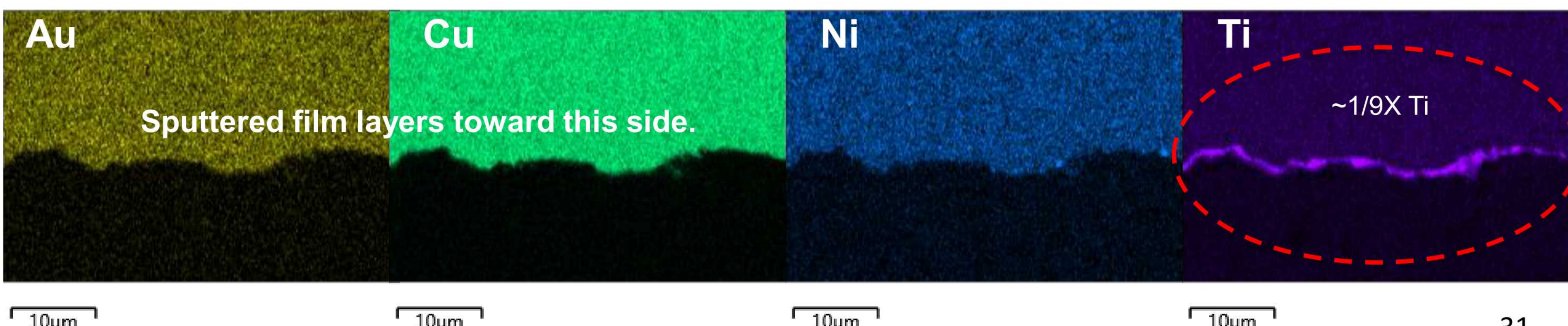
2-reaction layer ASTM F-19 Tensile Buttons

Electron Image 45





Au Lα1 Cu Kα1 Ni Kα1 Ti Kα1



TB-H5: Nicoro®+2%Ti, 75µm thick

2-reaction layers ASTM F-19 Tensile Buttons

Electron Image 55