Durable, Impermeable Brazes for Solid Oxide Fuel Cells

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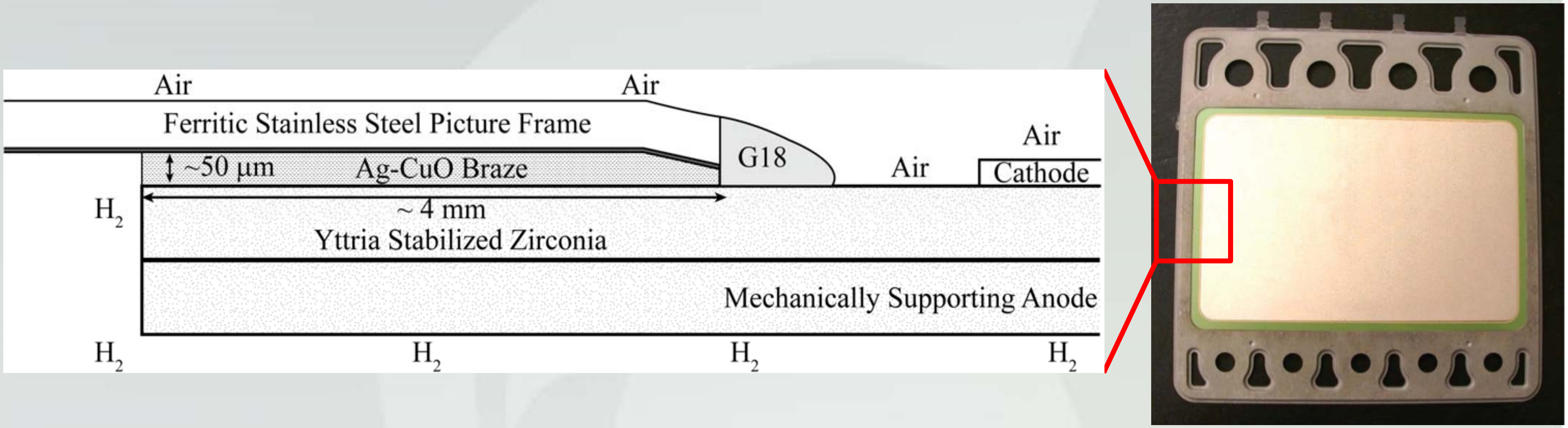
Research Team

- **MSU:**
  - Jason D. Nicholas — Lead PI, SOFC
  - Yue Qi — PI, Computational Materials Science
  - Thomas R. Bieler — PI, Metallurgy
  - Quan Zhou — Graduate Student (Ni-based Brazes)
  - Yuxi Ma — Graduate Student (Cu and Co-based Brazes)
  - Tridip Das — Graduate Student (Simulations)

- **Delphi:**
  - Rick Kerr (and his team …)
  - Stephanie Surface
  - Bryan A. Gillispie

- **NETL**
  - Joseph Stoffa

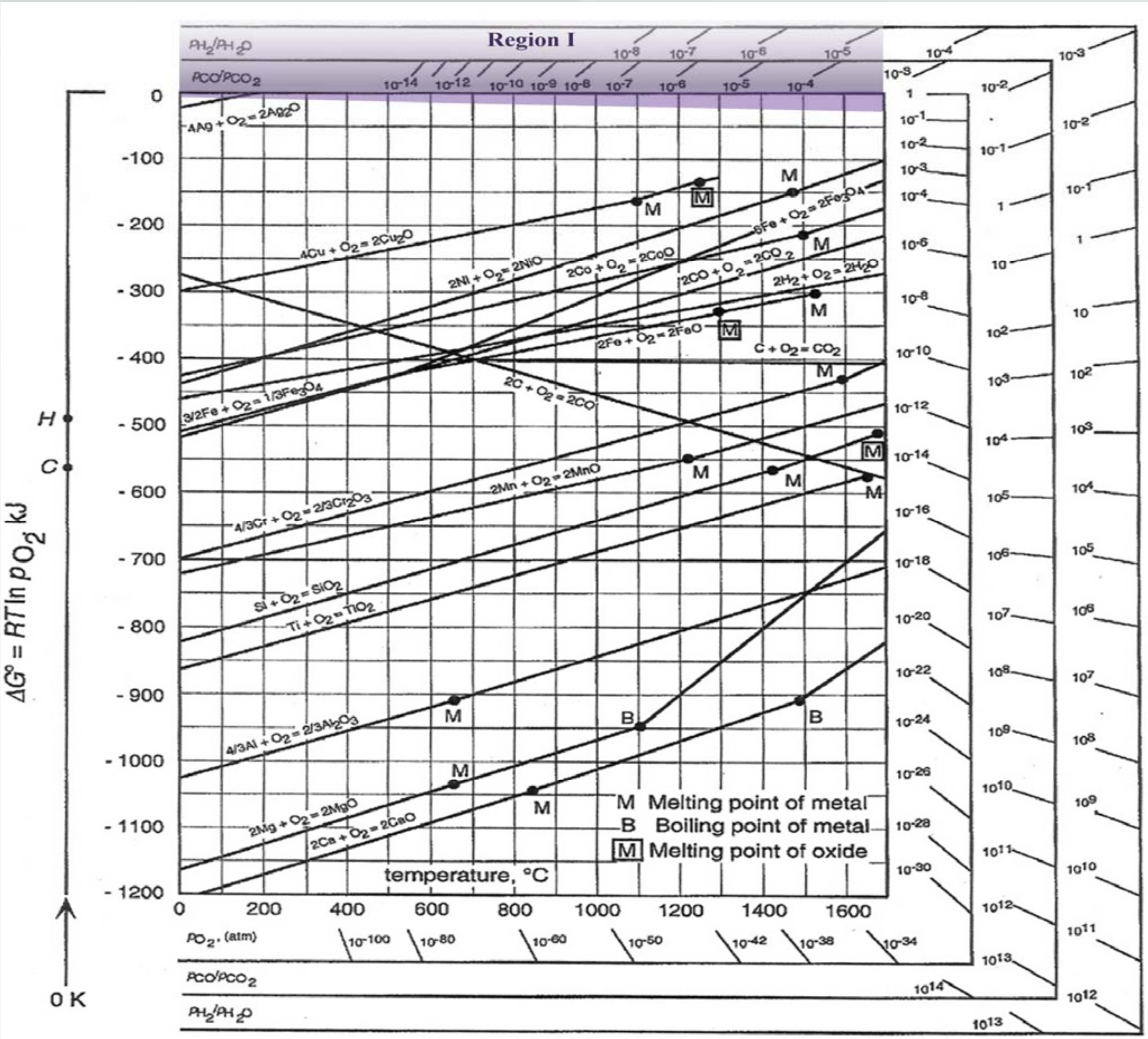
Metal Picture Frame Suspended SOFC Schematic



Project Objective:

Design and test new, SOFC-compatible, silver-free brazes with low oxygen and hydrogen permeability.

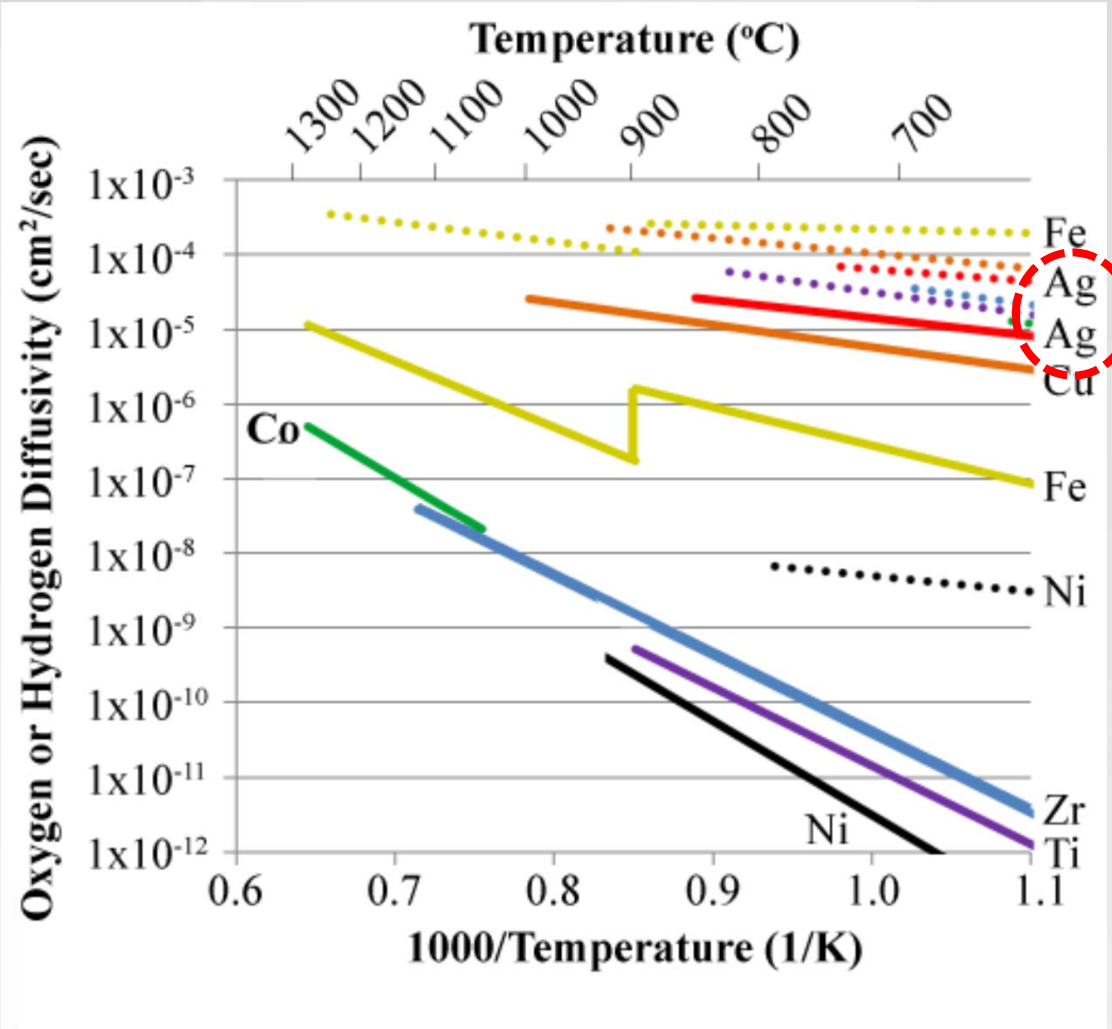
Ag-based Brazes Can be Fabricated in Air and Don’t Oxidize at High Temperatures



Metals in Region I (like Silver) Won’t Oxidize in Air

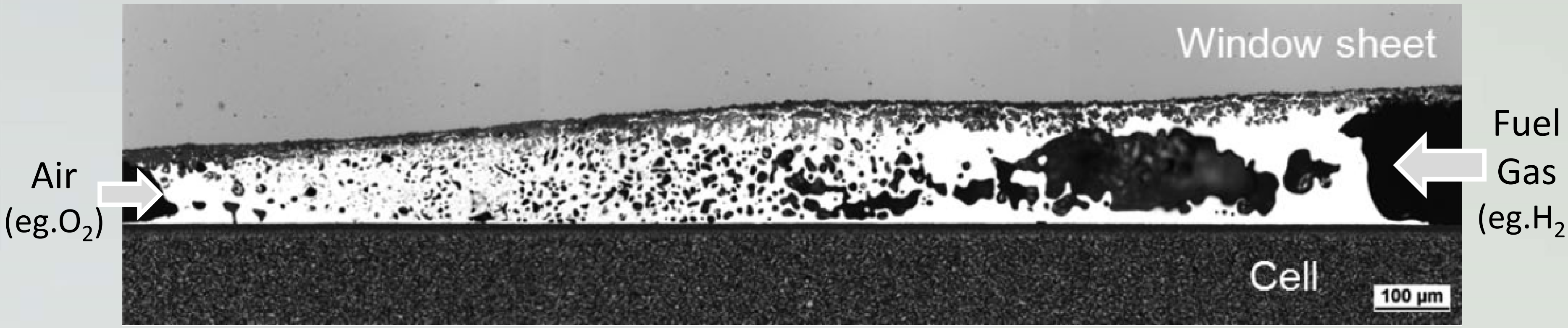
Ag+Cu brazes undergo reactive air brazing

Oxygen Diffusivities (Solid Lines) and Hydrogen Diffusivity (Dotted Lines) for Several Common Metals



C. Smithells, W. Gale, T. Totemeier. Smithells Metals Reference Book. 8th ed.

Standard Silver-Copper Brazes Have Durability Problems



- Type I Pores: Form During Manufacturing
- Type II Pores: Form at Braze Interface due to CuO Reduction
- Type III Pores: Form in Braze due to Water Pocket Formation

T. Bause, J. Malzbender et. al., Damage and Failure of Silver Based Ceramic/Metal Joints for SOFC Stacks,2013

Braze Alloy Design Criteria and Evaluation Methods

Design Parameter	Target Values	Justification	97.5Ag-2.5CuO Values
Solidus Temperature (T_S)	900°C $\leq T_s \leq$ 1015°C	So the braze is solid during SOFC operation & does not alter the microstructure of previously made layers	**912°C**
Linear Coefficient of Thermal Expansion (CTE)	7 ppm/K ≤25-750°C CTE≤ 16 ppm/K	To prevent surface oxide spallation. 25-750°C YSZ CTE=9 ppm/K [1]. 25-750°C 441 Steel CTE=12ppm/K [1].	*~21 ppm/K [2]* *Non-passivating, spallation/reduction prone CuO forms on the surface in air [3]*
Ductility	≥3%	So the braze can withstand YSZ-441 thermal expansion mismatch stress	**Sufficient [4], but unknown**
Vapor Pressure	750°C Vapor Pressure $<1\times10^{-8}$ torr	To ensure that volatilization does not degrade the braze or the protective oxide	*Ag 750°C Vapor Pressure in Air = 1×10^{-5} torr [5]*

1. J. W. Fergus, *Materials Science and Engineering A*, **397**, 271 (2005).
2. A. Laik, P. Mishra, K. Bhanumurthy, G. B. Kale and B. P. Kashyap, *Acta Materialia*, **61**, 126 (2013).
3. A. Kar, S. Mandal, S. Rathod and A. K. Ray, in *Brazing and Soldering: Proceedings of theThird International Brazing and Soldering Conference April 24-26, 2006, San Antonio, TX*, J. J. Stevens and K. Weil Editors, San Antonio, TX (2006).
4. R. Kerr, Michigan State University/Delphi Cell to Retainer Braze Discussion, in, J. Nicholas Editor, Fenton, MI (2014).
5. J. L. Margrave, *The Characterization of High-Temperature Vapors*, John Wiley & Sons, New York (1967).

Braze Interface Design Criteria and Evaluation Methods

Design Parameter	Target Values	Justification	97.5Ag-2.5CuO Values
Wetting Angle (θ)	$0^o \leq \theta \leq 45^o$	To ensure that the braze spreads through the joint during manufacturing	*45°[1]. Causes Type I pores to form in the braze*
Metallurgical Bonding with 441 Steel	Interdiffusion or new phase formation	To promote good wetting and the possibility of a strong joint.	**Interdiffusion**
Metallurgical Bonding with YSZ	Interdiffusion or new phase formation	To promote good wetting and the possibility of a strong joint.	**A Y-Cu-O phase[2, 3]**
Braze Joint Strength (σ_B)	$\sigma_B > 120$ MPa	So the braze can accommodate YSZ-441 CTE mismatch stress	**220 MPa[1]**

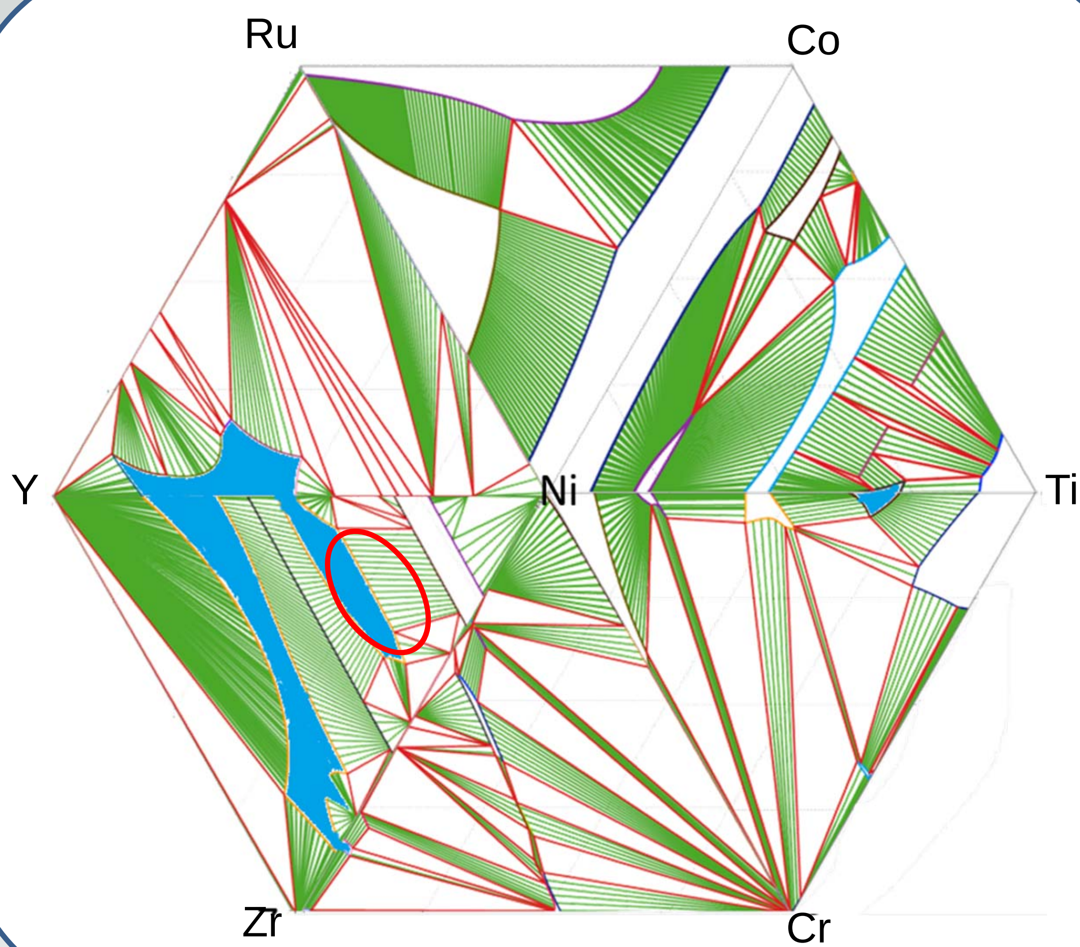
1. J. Y. Kim, J. S. Hardy and K. S. Weil, *Journal of the American Ceramic Society*, **88**, 2521 (2005).
2. J. L. Shi, T. S. Yen and H. Schubert, *Journal of Materials Science*, **32**, 1341 (1997).
3. J. C. Ruiz-Morales, J. Canales-Vazquez, D. Marrero-Lopez, J. Pena-Martinez, A. Tarancon, J. T. S. Irvine and P. Nunez, *Journal of Materials Chemistry*, **18**, 5072 (2008).

Brazed SOFC Design Criteria and Evaluation Methods

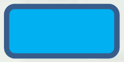
Design Parameter	Target Values	Justification	97.5Ag-2.5CuO Values
Oxygen and Hydrogen Conductivity (σ_{O_2}, σ_{H_2})	$\sigma_{O_2} < 1x10^{-8}$ S/cm $\sigma_{H_2} < 1x10^{-8}$ S/cm	If no surface oxide forms, the braze should have a low oxygen conductivity to prevent Type III pores. If a surface oxide forms, the oxide should have a low oxygen conductivity to prevent Type III pores and to ensure a ductile metal braze core remains.	**Ag stable above 160°C in air** [1] *σ_{O_2}=2x10^{-4} S/cm at 750°C [2] promoting Type III pores [3].*
Stability over 40,000 hours of SOFC Operation	Retention of all design parameter target values	To ensure reliable SOFC operation	*Does not last past 10,000 hours of SOFC operation [4]*

1. I. Barin and F. Sauert, *Thermochemical data of pure substances*, Weinheim, Federal Republic of Germany ; VCH, New York, NY, USA (1989).
2. R. A. Outlaw, S. N. Sankaran, G. B. Hoflund and M. R. Davidson, *Journal of Materials Research*, **3**, 1378 (1988).
3. J. Y. Kim, J. S. Hardy and S. Weil, *International Journal of Hydrogen Energy*, **32**, 3655 (2007).
4. R. Kerr, Michigan State University/Delphi Cell to Retainer Braze Discussion, in, J. Nicholas Editor, Fenton, MI (2014).

Sample Thermo-Calc Computed Ni-based Ternary phase diagram at 1000^{o}C

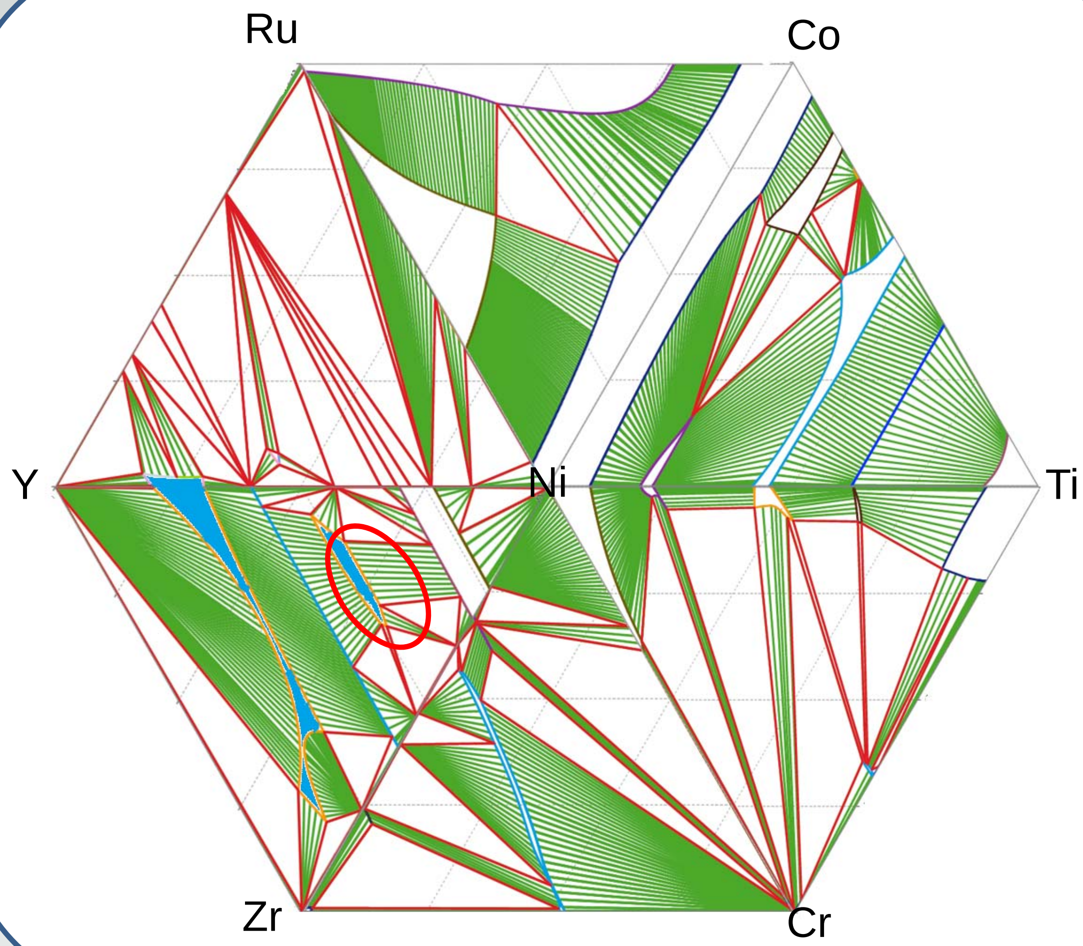


- Each corner of the hexagon is 100 mass % composition of the elements (mentioned at each corner).
- Centre of the hexagon represents 100% Ni



Shows the liquid phases.

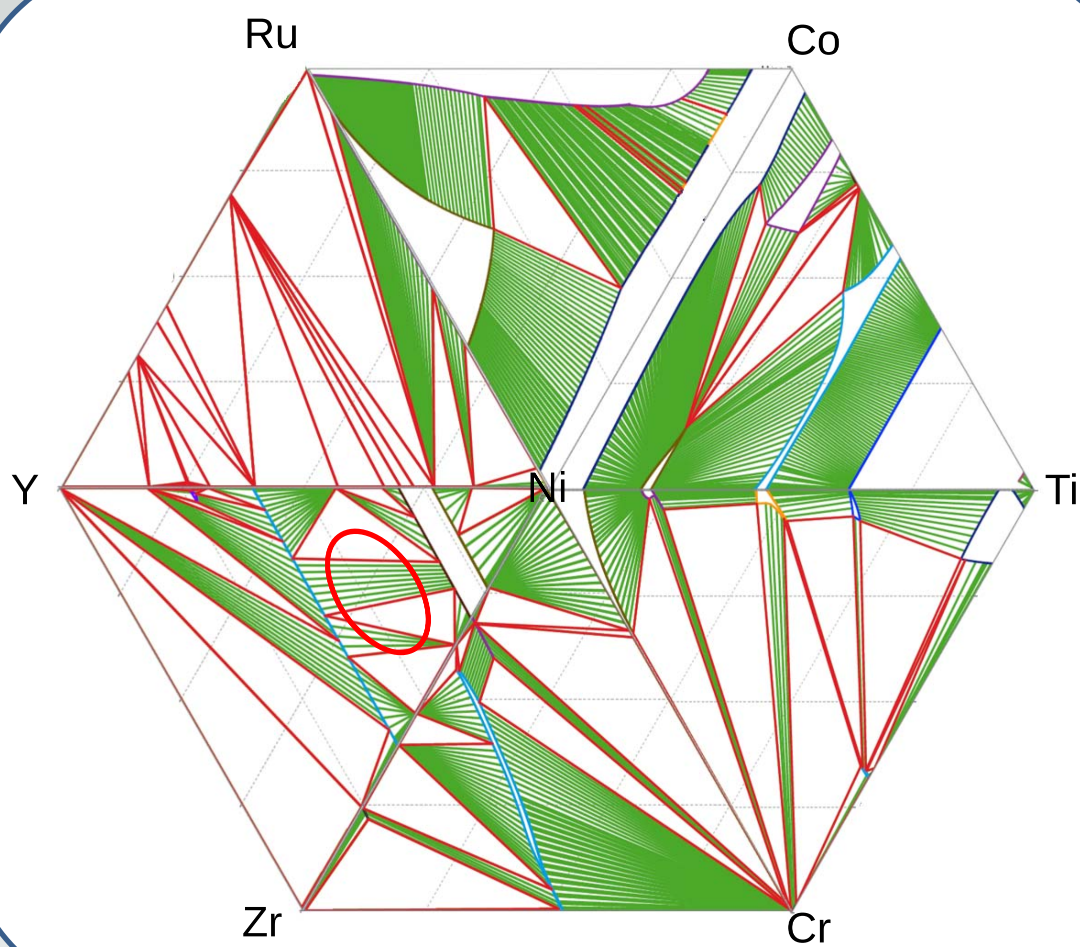
Sample Thermo-Calc Computed Ni-based Ternary phase diagram at 900ºC



- Each corner of the hexagon is 100 mass % composition of the elements (mentioned at each corner).
- Centre of the hexagon represents 100% Ni

Shows the liquid phases.

Sample Thermo-Calc Computed Ni-based Ternary phase diagram at 800ºC



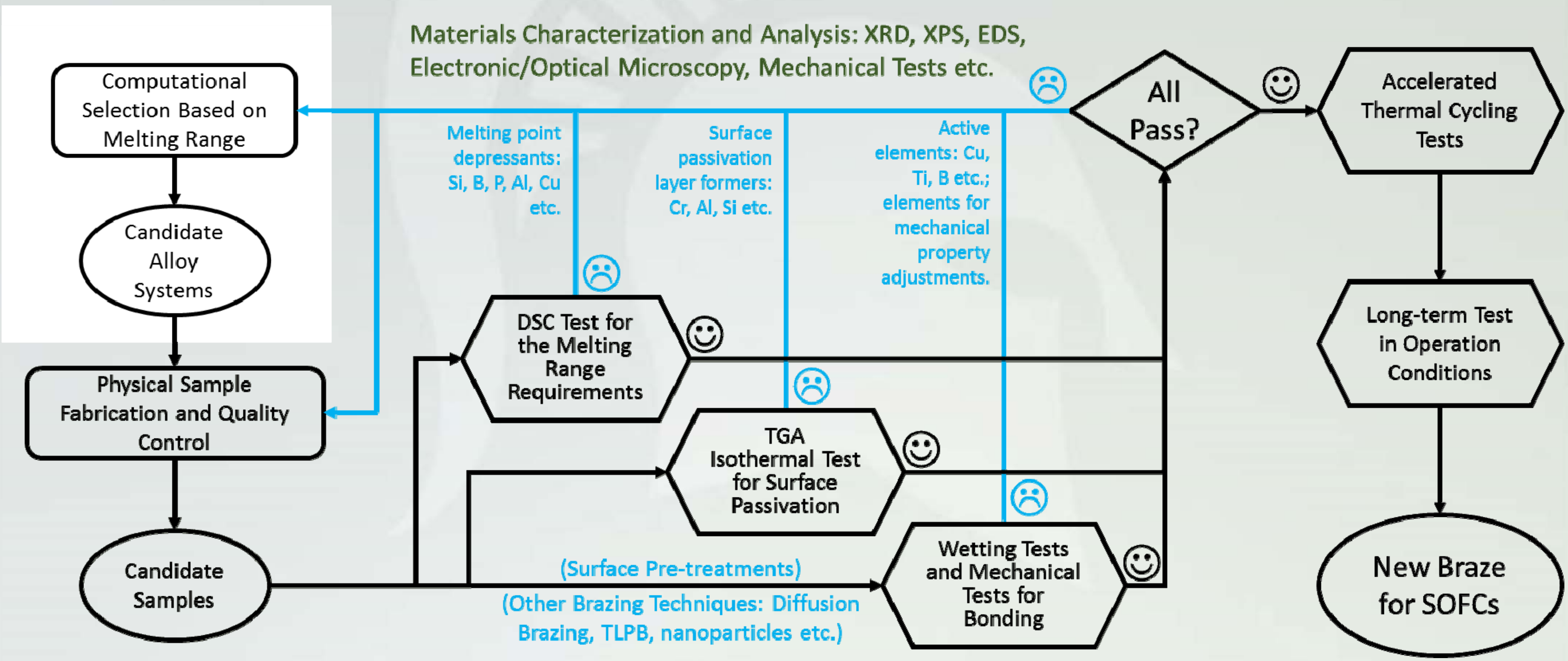
- Each corner of the hexagon is 100 mass % composition of the elements (mentioned at each corner).
- Centre of the hexagon represents 100% Ni

Outline

- **Background and Motivation**
  - Benefits of Silver-Copper Brazes
  - Problems with Silver-Copper Brazes
- **Methods**
- **Results and Discussions**
  - Simulations
  - Oxidation Behavior of Top Candidates
  - Wetting Test on Different Substrates
  - A Preliminary Transient Multilayer Braze System
- **Conclusions**

Computation Led New Alloy Design

- With the power of computation, hundreds of alloy systems can be effectively screened, providing initial candidates for further optimization;
- Various techniques, characterization methods and strategies will be applied to solve different problems.



Braze Samples were Prepared with Arc Melting

Prepare raw materials from 99.99% pure metals. (Cut, clean, weight)

Select the right getter material to secure the partial pressure of O_2 during melting.

Purge with Ar gas➔vacuum the chamber➔ melt the getters➔ melt the sample

Flip 5~10 times and re-melt

Diameter: ~0.5’’

Cut with high-speed diamond saw.

Outline

- **Background and Motivation**
  - Benefits of Silver-Copper Brazes
  - Problems with Silver-Copper Brazes
- **Methods**
- **Results and Discussions**
  - Simulations
  - Oxidation Behavior
  - Wetting Tests
  - A Preliminary Transient Multilayer Braze System
- **Conclusions**

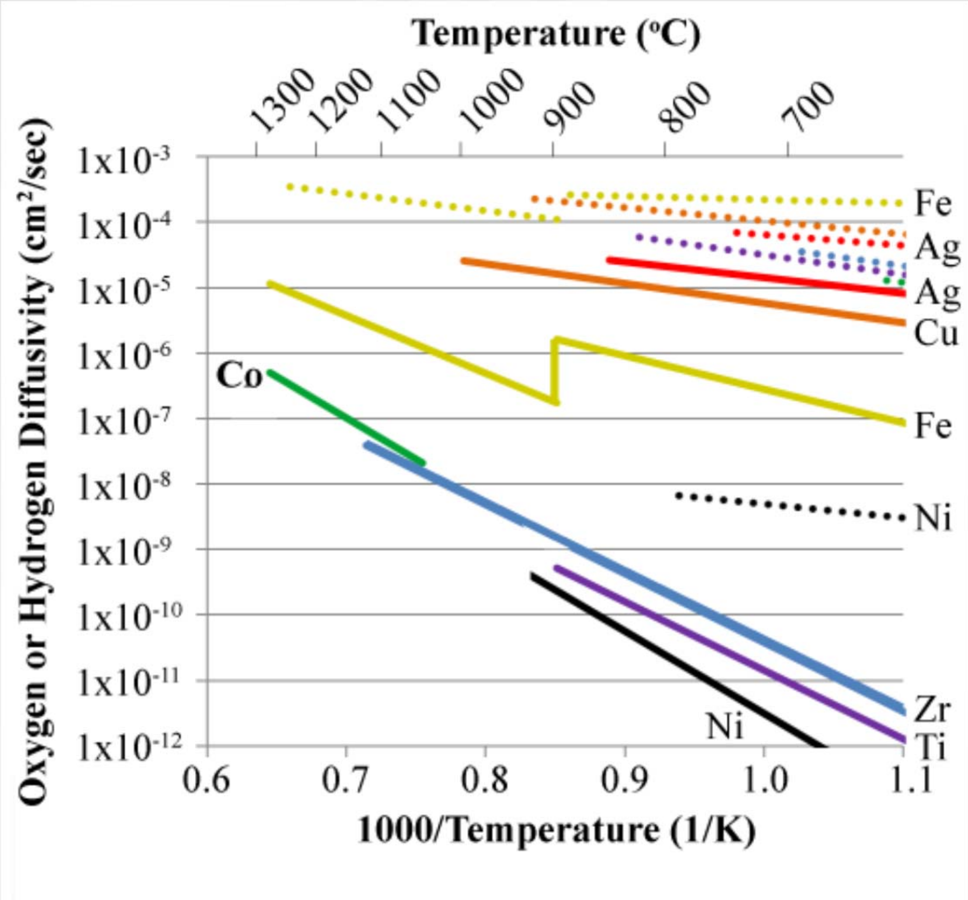
Major Alloy Constituent Element Selection

Here, all elements from the Periodic Table were considered but after dropping elements for the following reasons

Elements Dropped	Consideration
Noble gases (He, Ne, Ar etc.)	Hardly any bonding with metals to form alloys
Pm (Z:61) , Po and higher atomic number elements (Z>83)	Braze should not be radioactive
Alkali metals, Halogens and Chalcogens	Reactive with air and water, hard to mix with metal,
Bi and Lanthanide group	Braze should not have good conductivity for oxygen and hydrogen ions
Alkaline earth metals and semiconducting elements	Braze should not have high vapor pressure ($\geq$ 0.1 Torr) at 750 ^{0}C
Cd, Pb, Tl	Elements should not be toxic
Re, Pd, Ru, Pt, Au, Os, Ir, Sc and Rh	Elements should not to too expensive

25 elements remained: (B, C, Mg, Al, Si, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Nb, Mo, In, Sn, Ta, W, Ti, Y, Zr, Hf, Ag)

Here Ni (due to Low Hydrogen and Oxygen Diffusivity), Co (due to Low Hydrogen and Oxygen diffusivity), and Cu (due It's Good Wetting with YSZ) Were Chosen as Ternary Braze Base Elements



C. Smithells, W. Gale, T. Totemeier. Smithells Metals Reference Book. 8th ed.

Computations Revealed 19 Nickel-Containing Ternary Systems with at Least 1 Composition with $T_{solidus}$>900ºC & $T_{liquidus}$<1000ºC

Ni-based Ternary Alloy Calculations
Database: TCNI7 and TCSLD2

Ni	B	C	Mg	Al	Si	V	Cr	Mn	Fe	Co	Cu	Zn	Ga	Nb	Mo	In	Sn	Ta	W	Ti	Y	Zr	Hf
B																							
C	Ni-B-C																						
Mg	Ni-B-Mg	Ni-C-Mg																					
AL	Ni-B-AL	Ni-C-AL	Ni-Mg-AL																				
Si	Ni-B-Si	Ni-C-Si	Ni-Mg-Si	Ni-Al-Si																			
V	Ni-B-V	Ni-C-V	Ni-Mg-V	Ni-Al-V	Ni-Si-V																		
Cr	Ni-B-Cr	Ni-C-Cr	Ni-Mg-Cr	Ni-Al-Cr	Ni-Si-Cr	Ni-V-Cr																	
Mn	Ni-B-Mn	Ni-C-Mn	Ni-Mg-Mn	Ni-Al-Mn	Ni-Si-Mn	Ni-V-Mn	Ni-Cr-Mn																
Fe	Ni-B-Fe	Ni-C-Fe	Ni-Mg-Fe	Ni-Al-Fe	Ni-Si-Fe	Ni-V-Fe	Ni-Cr-Fe	Ni-Mn-Fe															
Co	Ni-B-Co	Ni-C-Co	Ni-Mg-Co	Ni-Al-Co	Ni-Si-Co	Ni-V-Co	Ni-Cr-Co	Ni-Mn-Co	Ni-Fe-Co														
Cu	Ni-B-Cu	Ni-C-Cu	Ni-Mg-Cu	Ni-Al-Cu	Ni-Si-Cu	Ni-V-Cu	Ni-Cr-Cu	Ni-Mn-Cu	Ni-Fe-Cu	Ni-Co-Cu													
Zn	Ni-B-Zn	Ni-C-Zn	Ni-Mg-Zn	Ni-Al-Zn	Ni-Si-Zn	Ni-V-Zn	Ni-Cr-Zn	Ni-Mn-Zn	Ni-Fe-Zn	Ni-Co-Zn	Ni-Cu-Zn												
Ga	Ni-B-Ga	Ni-C-Ga	Ni-Mg-Ga	Ni-Al-Ga	Ni-Si-Ga	Ni-V-Ga	Ni-Cr-Ga	Ni-Mn-Ga	Ni-Fe-Ga	Ni-Co-Ga	Ni-Cu-Ga	Ni-Zn-Ga											
Nb	Ni-B-Nb	Ni-C-Nb	Ni-Mg-Nb	Ni-Al-Nb	Ni-Si-Nb	Ni-V-Nb	Ni-Cr-Nb	Ni-Mn-Nb	Ni-Fe-Nb	Ni-Co-Nb	Ni-Cu-Nb	Ni-Zn-Nb	Ni-Ga-Nb										
Mo	Ni-B-Mo	Ni-C-Mo	Ni-Mg-Mo	Ni-Al-Mo	Ni-Si-Mo	Ni-V-Mo	Ni-Cr-Mo	Ni-Mn-Mo	Ni-Fe-Mo	Ni-Co-Mo	Ni-Cu-Mo	Ni-Zn-Mo	Ni-Ga-Mo	Ni-Nb-Mo									
In	Ni-B-In	Ni-C-In	Ni-Mg-In	Ni-Al-In	Ni-Si-In	Ni-V-In	Ni-Cr-In	Ni-Mn-In	Ni-Fe-In	Ni-Co-In	Ni-Cu-In	Ni-Zn-In	Ni-Ga-In	Ni-Nb-In	Ni-Mo-In								
Sn	Ni-B-Sn	Ni-C-Sn	Ni-Mg-Sn	Ni-Al-Sn	Ni-Si-Sn	Ni-V-Sn	Ni-Cr-Sn	Ni-Mn-Sn	Ni-Fe-Sn	Ni-Co-Sn	Ni-Cu-Sn	Ni-Zn-Sn	Ni-Ga-Sn	Ni-Nb-Sn	Ni-Mo-Sn	Ni-In-Sn							
Ta	Ni-B-Ta	Ni-C-Ta	Ni-Mg-Ta	Ni-Al-Ta	Ni-Si-Ta	Ni-V-Ta	Ni-Cr-Ta	Ni-Mn-Ta	Ni-Fe-Ta	Ni-Co-Ta	Ni-Cu-Ta	Ni-Zn-Ta	Ni-Ga-Ta	Ni-Nb-Ta	Ni-Mo-Ta	Ni-In-Ta	Ni-Sn-Ta						
W	Ni-B-W	Ni-C-W	Ni-Mg-W	Ni-Al-W	Ni-Si-W	Ni-V-W	Ni-Cr-W	Ni-Mn-W	Ni-Fe-W	Ni-Co-W	Ni-Cu-W	Ni-Zn-W	Ni-Ga-W	Ni-Nb-W	Ni-Mo-W	Ni-In-W	Ni-Sn-W	Ni-Ta-W					
Ti	Ni-B-Ti	Ni-C-Ti	Ni-Mg-Ti	Ni-Al-Ti	Ni-Si-Ti	Ni-V-Ti	Ni-Cr-Ti	Ni-Mn-Ti	Ni-Fe-Ti	Ni-Co-Ti	Ni-Cu-Ti	Ni-Zn-Ti	Ni-Ga-Ti	Ni-Nb-Ti	Ni-Mo-Ti	Ni-In-Ti	Ni-Sn-Ti	Ni-Ta-Ti	Ni-W-Ti				
Y	Ni-B-Y	Ni-C-Y	Ni-Mg-Y	Ni-Al-Y	Ni-Si-Y	Ni-V-Y	Ni-Cr-Y	Ni-Mn-Y	Ni-Fe-Y	Ni-Co-Y	Ni-Cu-Y	Ni-Zn-Y	Ni-Ga-Y	Ni-Nb-Y	Ni-Mo-Y	Ni-In-Y	Ni-Sn-Y	Ni-Ta-Y	Ni-W-Y	Ni-Ti-Y			
Zr	Ni-B-Zr	Ni-C-Zr	Ni-Mg-Zr	Ni-Al-Zr	Ni-Si-Zr	Ni-V-Zr	Ni-Cr-Zr	Ni-Mn-Zr	Ni-Fe-Zr	Ni-Co-Zr	Ni-Cu-Zr	Ni-Zn-Zr	Ni-Ga-Zr	Ni-Nb-Zr	Ni-Mo-Zr	Ni-In-Zr	Ni-Sn-Zr	Ni-Ta-Zr	Ni-W-Zr	Ni-Ti-Zr	Ni-Y-Zr		
Hf	Ni-B-Hf	Ni-C-Hf	Ni-Mg-Hf	Ni-Al-Hf	Ni-Si-Hf	Ni-V-Hf	Ni-Cr-Hf	Ni-Mn-Hf	Ni-Fe-Hf	Ni-Co-Hf	Ni-Cu-Hf	Ni-Zn-Hf	Ni-Ga-Hf	Ni-Nb-Hf	Ni-Mo-Hf	Ni-In-Hf	Ni-Sn-Hf	Ni-Ta-Hf	Ni-W-Hf	Ni-Ti-Hf	Ni-Y-Hf	Ni-Zr-Hf	
Ag	Ni-B-Ag	Ni-C-Ag	Ni-Mg-Ag	Ni-Al-Ag	Ni-Si-Ag	Ni-V-Ag	Ni-Cr-Ag	Ni-Mn-Ag	Ni-Fe-Ag	Ni-Co-Ag	Ni-Cu-Ag	Ni-Zn-Ag	Ni-Ga-Ag	Ni-Nb-Ag	Ni-Mo-Ag	Ni-In-Ag	Ni-Sn-Ag	Ni-Ta-Ag	Ni-W-Ag	Ni-Ti-Ag	Ni-Y-Ag	Ni-Zr-Ag	Ni-Hf-Ag

Disqualified for lacking liquidus regions at or below 1000˚C

Disqualified for lacking solidus regions at or below 900˚C

Systems with alloys that were liquid or liquid + solid at or below 1000˚C and solid below 900˚C

No Thermocalc data available

Computations Revealed 31 Cobalt-Containing Ternary Systems with at Least 1 Composition with $T_{solidus}$>900ºC & $T_{liquidus}$<1000ºC

Co-based Ternary Alloy Calculations
Database: TCIN7 and TCSLD2

Co	B	C	Mg	Al	Si	V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Nb	Mo	In	Sn	Ta	W	Ti	Y	Zr	Hf	Ag
B																								
C	Co-B-C																							
Mg	Co-B-Mg	Co-C-Mg																						
Al	Co-B-Al	Co-C-Al	Co-Mg-Al																					
Si	Co-B-Si	Co-C-Si	Co-Mg-Si	Co-Al-Si																				
V	Co-B-V	Co-C-V	Co-Mg-V	Co-Al-V	Co-Si-V																			
Cr	Co-B-Cr	Co-C-Cr	Co-Mg-Cr	Co-Al-Cr	Co-Si-Cr	Co-V-Cr																		
Mn	Co-B-Mn	Co-C-Mn	Co-Mg-Mn	Co-Al-Mn	Co-Si-Mn	Co-V-Mn	Co-Cr-Mn																	
Fe	Co-B-Fe	Co-C-Fe	Co-Mg-Fe	Co-Al-Fe	Co-Si-Fe	Co-V-Fe	Co-Cr-Fe	Co-Mn-Fe																
Ni	Co-B-Ni	Co-C-Ni	Co-Mg-Ni	Co-Al-Ni	Co-Si-Ni	Co-V-Ni	Co-Cr-Ni	Co-Mn-Ni	Co-Fe-Ni															
Cu	Co-B-Cu	Co-C-Cu	Co-Mg-Cu	Co-Al-Cu	Co-Si-Cu	Co-V-Cu	Co-Cr-Cu	Co-Mn-Cu	Co-Fe-Cu	Co-Ni-Cu														
Zn	Co-B-Zn	Co-C-Zn	Co-Mg-Zn	Co-Al-Zn	Co-Si-Zn	Co-V-Zn	Co-Cr-Zn	Co-Mn-Zn	Co-Fe-Zn	Co-Ni-Zn	Co-Cu-Zn													
Ga	Co-B-Ga	Co-C-Ga	Co-Mg-Ga	Co-Al-Ga	Co-Si-Ga	Co-V-Ga	Co-Cr-Ga	Co-Mn-Ga	Co-Fe-Ga	Co-Ni-Ga	Co-Cu-Ga	Co-Zn-Ga												
Nb	Co-B-Nb	Co-C-Nb	Co-Mg-Nb	Co-Al-Nb	Co-Si-Nb	Co-V-Nb	Co-Cr-Nb	Co-Mn-Nb	Co-Fe-Nb	Co-Ni-Nb	Co-Cu-Nb	Co-Zn-Nb	Co-Ga-Nb											
Mo	Co-B-Mo	Co-C-Mo	Co-Mg-Mo	Co-Al-Mo	Co-Si-Mo	Co-V-Mo	Co-Cr-Mo	Co-Mn-Mo	Co-Fe-Mo	Co-Ni-Mo	Co-Cu-Mo	Co-Zn-Mo	Co-Ga-Mo	Co-Nb-Mo										
In	Co-B-In	Co-C-In	Co-Mg-In	Co-Al-In	Co-Si-In	Co-V-In	Co-Cr-In	Co-Mn-In	Co-Fe-In	Co-Ni-In	Co-Cu-In	Co-Zn-In	Co-Ga-In	Co-Nb-In	Co-Mo-In									
Sn	Co-B-Sn	Co-C-Sn	Co-Mg-Sn	Co-Al-Sn	Co-Si-Sn	Co-V-Sn	Co-Cr-Sn	Co-Mn-Sn	Co-Fe-Sn	Co-Ni-Sn	Co-Cu-Sn	Co-Zn-Sn	Co-Ga-Sn	Co-Nb-Sn	Co-Mo-Sn	Co-In-Sn								
Ta	Co-B-Ta	Co-C-Ta	Co-Mg-Ta	Co-Al-Ta	Co-Si-Ta	Co-V-Ta	Co-Cr-Ta	Co-Mn-Ta	Co-Fe-Ta	Co-Ni-Ta	Co-Cu-Ta	Co-Zn-Ta	Co-Ga-Ta	Co-Nb-Ta	Co-Mo-Ta	Co-In-Ta	Co-Sn-Ta							
W	Co-B-W	Co-C-W	Co-Mg-W	Co-Al-W	Co-Si-W	Co-V-W	Co-Cr-W	Co-Mn-W	Co-Fe-W	Co-Ni-W	Co-Cu-W	Co-Zn-W	Co-Ga-W	Co-Nb-W	Co-Mo-W	Co-In-W	Co-Sn-W	Co-Ta-W						
Ti	Co-B-Ti	Co-C-Ti	Co-Mg-Ti	Co-Al-Ti	Co-Si-Ti	Co-V-Ti	Co-Cr-Ti	Co-Mn-Ti	Co-Fe-Ti	Co-Ni-Ti	Co-Cu-Ti	Co-Zn-Ti	Co-Ga-Ti	Co-Nb-Ti	Co-Mo-Ti	Co-In-Ti	Co-Sn-Ti	Co-Ta-Ti	Co-W-Ti					
Y	Co-B-Y	Co-C-Y	Co-Mg-Y	Co-Al-Y	Co-Si-Y	Co-V-Y	Co-Cr-Y	Co-Mn-Y	Co-Fe-Y	Co-Ni-Y	Co-Cu-Y	Co-Zn-Y	Co-Ga-Y	Co-Nb-Y	Co-Mo-Y	Co-In-Y	Co-Sn-Y	Co-Ta-Y	Co-W-Y	Co-Ti-Y				
Zr	Co-B-Zr	Co-C-Zr	Co-Mg-Zr	Co-Al-Zr	Co-Si-Zr	Co-V-Zr	Co-Cr-Zr	Co-Mn-Zr	Co-Fe-Zr	Co-Ni-Zr	Co-Cu-Zr	Co-Zn-Zr	Co-Ga-Zr	Co-Nb-Zr	Co-Mo-Zr	Co-In-Zr	Co-Sn-Zr	Co-Ta-Zr	Co-W-Zr	Co-Ti-Zr	Co-Y-Zr			
Hf	Co-B-Hf	Co-C-Hf	Co-Mg-Hf	Co-Al-Hf	Co-Si-Hf	Co-V-Hf	Co-Cr-Hf	Co-Mn-Hf	Co-Fe-Hf	Co-Ni-Hf	Co-Cu-Hf	Co-Zn-Hf	Co-Ga-Hf	Co-Nb-Hf	Co-Mo-Hf	Co-In-Hf	Co-Sn-Hf	Co-Ta-Hf	Co-W-Hf	Co-Ti-Hf	Co-Y-Hf	Co-Zr-Hf		
Ag	Co-B-Ag	Co-C-Ag	Co-Mg-Ag	Co-Al-Ag	Co-Si-Ag	Co-V-Ag	Co-Cr-Ag	Co-Mn-Ag	Co-Fe-Ag	Co-Ni-Ag	Co-Cu-Ag	Co-Zn-Ag	Co-Ga-Ag	Co-Nb-Ag	Co-Mo-Ag	Co-In-Ag	Co-Sn-Ag	Co-Ta-Ag	Co-W-Ag	Co-Ti-Ag	Co-Y-Ag	Co-Zr-Ag	Co-Hf-Ag	

No liquid phase present in the phase diagram below 1000 °C
There exists some specific composition zone, which completely solidifies from liquid phase, between temperature window of 900 and 1000 °C
The composition of liquid zone at 1000 °C, remains liquid or solid+liquid below 900 °C
Not available in database

- Disqualified for lacking liquidus regions at or below 1000˚C
- Disqualified for lacking solidus regions at or below 900˚C
- Systems with alloys that were liquid or liquid + solid at or below 1000˚C and solid below 900˚C
- No Thermocalc data available

Computations Revealed 64 Copper-Containing Ternary Systems with at Least 1 Composition with $T_{solidus}$>900ºC & $T_{liquidus}$<1000ºC

Cu-based Ternary Alloy Calculations
Database: TTTI3 and TCSLD2

Cu	B	C	Mg	Al	Si	V	Cr	Mn	Fe	Co	Ni	Zn	Nb	Mo	In	Sn	Ta	Ti	Zr	Ag
B																				
C	Cu-B-C																			
Mg	Cu-B-Mg	Cu-C-Mg																		
Al	Cu-B-Al	Cu-C-Al	Cu-Mg-Al																	
Si	Cu-B-Si	Cu-C-Si	Cu-Mg-Si	Cu-Al-Si																
V	Cu-B-V	Cu-C-V	Cu-Mg-V	Cu-Al-V	Cu-Si-V															
Cr	Cu-B-Cr	Cu-C-Cr	Cu-Mg-Cr	Cu-Al-Cr	Cu-Si-Cr	Cu-V-Cr														
Mn	Cu-B-Mn	Cu-C-Mn	Cu-Mg-Mn	Cu-Al-Mn	Cu-Si-Mn	Cu-V-Mn	Cu-Cr-Mn													
Fe	Cu-B-Fe	Cu-C-Fe	Cu-Mg-Fe	Cu-Al-Fe	Cu-Si-Fe	Cu-V-Fe	Cu-Cr-Fe	Cu-Mn-Fe												
Co	Cu-B-Co	Cu-C-Co	Cu-Mg-Co	Cu-Al-Co	Cu-Si-Co	Cu-V-Co	Cu-Cr-Co	Cu-Mn-Co	Cu-Fe-Co											
Ni	Cu-B-Ni	Cu-C-Ni	Cu-Mg-Ni	Cu-Al-Ni	Cu-Si-Ni	Cu-V-Ni	Cu-Cr-Ni	Cu-Mn-Ni	Cu-Fe-Ni	Cu-Co-Ni										
Zn	Cu-B-Zn	Cu-C-Zn	Cu-Mg-Zn	Cu-Al-Zn	Cu-Si-Zn	Cu-V-Zn	Cu-Cr-Zn	Cu-Mn-Zn	Cu-Fe-Zn	Cu-Co-Zn	Cu-Ni-Zn									
Nb	Cu-B-Nb	Cu-C-Nb	Cu-Mg-Nb	Cu-Al-Nb	Cu-Si-Nb	Cu-V-Nb	Cu-Cr-Nb	Cu-Mn-Nb	Cu-Fe-Nb	Cu-Co-Nb	Cu-Ni-Nb	Cu-Zn-Nb								
Mo	Cu-B-Mo	Cu-C-Mo	Cu-Mg-Mo	Cu-Al-Mo	Cu-Si-Mo	Cu-V-Mo	Cu-Cr-Mo	Cu-Mn-Mo	Cu-Fe-Mo	Cu-Co-Mo	Cu-Ni-Mo	Cu-Zn-Mo	Cu-Nb-Mo							
In	Cu-B-In	Cu-C-In	Cu-Mg-In	Cu-Al-In	Cu-Si-In	Cu-V-In	Cu-Cr-In	Cu-Mn-In	Cu-Fe-In	Cu-Co-In	Cu-Ni-In	Cu-Zn-In	Cu-Nb-In	Cu-Mo-In						
Sn	Cu-B-Sn	Cu-C-Sn	Cu-Mg-Sn	Cu-Al-Sn	Cu-Si-Sn	Cu-V-Sn	Cu-Cr-Sn	Cu-Mn-Sn	Cu-Fe-Sn	Cu-Co-Sn	Cu-Ni-Sn	Cu-Zn-Sn	Cu-Nb-Sn	Cu-Mo-Sn	Cu-In-Sn					
Ta	Cu-B-Ta	Cu-C-Ta	Cu-Mg-Ta	Cu-Al-Ta	Cu-Si-Ta	Cu-V-Ta	Cu-Cr-Ta	Cu-Mn-Ta	Cu-Fe-Ta	Cu-Co-Ta	Cu-Ni-Ta	Cu-Zn-Ta	Cu-Nb-Ta	Cu-Mo-Ta	Cu-In-Ta	Cu-Sn-Ta				
Ti	Cu-B-Ti	Cu-C-Ti	Cu-Mg-Ti	Cu-Al-Ti	Cu-Si-Ti	Cu-V-Ti	Cu-Cr-Ti	Cu-Mn-Ti	Cu-Fe-Ti	Cu-Co-Ti	Cu-Ni-Ti	Cu-Zn-Ti	Cu-Nb-Ti	Cu-Mo-Ti	Cu-In-Ti	Cu-Sn-Ti	Cu-Ta-Ti			
Zr	Cu-B-Zr	Cu-C-Zr	Cu-Mg-Zr	Cu-Al-Zr	Cu-Si-Zr	Cu-V-Zr	Cu-Cr-Zr	Cu-Mn-Zr	Cu-Fe-Zr	Cu-Co-Zr	Cu-Ni-Zr	Cu-Zn-Zr	Cu-Nb-Zr	Cu-Mo-Zr	Cu-In-Zr	Cu-Sn-Zr	Cu-Ta-Zr	Cu-Ti-Zr		
Ag	Cu-B-Ag	Cu-C-Ag	Cu-Mg-Ag	Cu-Al-Ag	Cu-Si-Ag	Cu-V-Ag	Cu-Cr-Ag	Cu-Mn-Ag	Cu-Fe-Ag	Cu-Co-Ag	Cu-Ni-Ag	Cu-Zn-Ag	Cu-Nb-Ag	Cu-Mo-Ag	Cu-In-Ag	Cu-Sn-Ag	Cu-Ta-Ag	Cu-Ti-Ag	Cu-Zr-Ag	

No liquid phase present in the phase diagram below 1000 °C

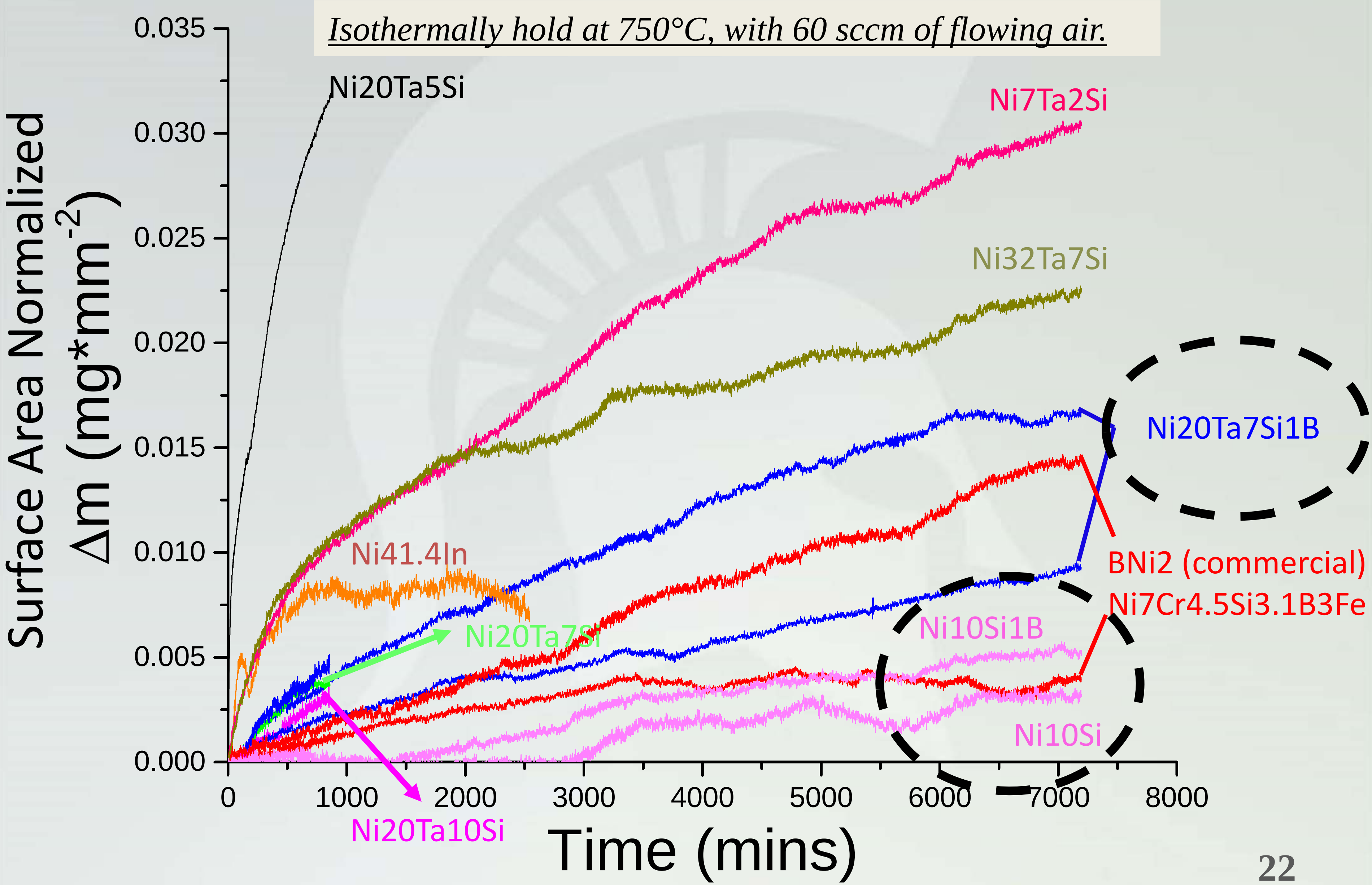
There exists some specific composition zone, which completely solidifies from liquid phase, between temperature window of 900 and 1000 °C

The composition of liquid zone at 1000 °C, remains liquid or solid+liquid below 900 °C

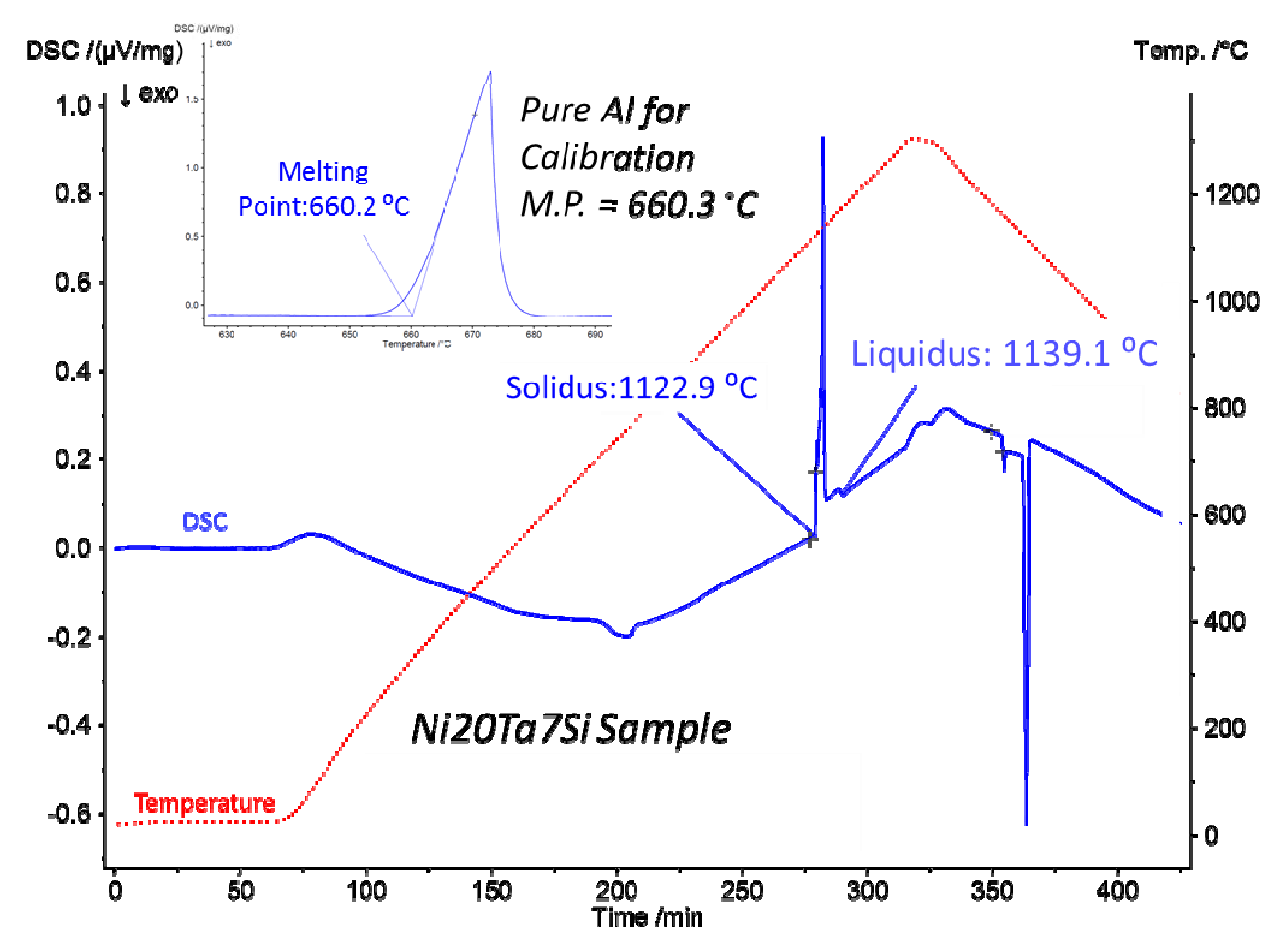
Not available in database

- Disqualified for lacking liquidus regions at or below 1000˚C
- Disqualified for lacking solidus regions at or below 900˚C
- Systems with alloys that were liquid or liquid + solid at or below 1000˚C and solid below 900˚C
- No Thermocalc data available

Ni-10Si(B) Showed Excellent Oxidation Resistance



Sample DSC Melting Point Determination Curve



Ni-Si (Ta, B) is a Promising System

Alloy Composition	48 hr 750°C Oxidation Resistance in Air	Solidus Temperature	Liquidus Temperature
$Ni_{88.5}Si_{4.5}Cr_{7.0}\underline{\mathbf{B_{3.1}}}Fe_{3.0}$ (Commercial BNi2 Containing Iron)	Excellent	Excellent	Excellent
$Ni_{75}Si_{5.0}Ta_{20}$	Poor	Too High (1132.1)	Too High (1138.0)
$Ni_{73}Si_{7.0}Ta_{20}$	Good	Too High (1122.9)	Too High (1139.1)
$Ni_{72}Si_{7.0}Ta_{20}\underline{\mathbf{B_{1}}}$	Good	Good (1057.6)	Good (1068.0)
$Ni_{70}Si_{7.0}Ta_{20}\underline{\mathbf{B_{3}}}$	Good	Good (1059.6)	Good (1086.8)
$Ni_{70}Si_{10.0}Ta_{20}$	Excellent	Too High (1124.1)	Too High (1162.9)
$Ni_{60}Si_{7.0}Ta_{32}\underline{\mathbf{B_{1}}}$	Good	Good (1059.3)	Good (1070.1)
$Ni_{61}Si_{7.0}Ta_{32}$	Marginal	Too High (1125.4)	Too High (1146.1)
$Ni_{61}Si_{7.0}Ta_{25}$		Too High (1124.5)	Too High (1137.9)
$Ni_{83}Si_{7.0}Ta_{10}$		Too High (1127.4)	Too High (1140.3)
$Ni_{82}Ta_{10}Si_{7}\underline{\mathbf{B_{1}}}$		Good (1033.7)	Good (1074.3)
$Ni_{90}Si_{10}$	Excellent	Too High (1126.5)	Too High (1222.5)
$Ni_{89}Si_{10}\underline{\mathbf{B_{1}}}$	Excellent	Good (992.0)	Good (1032.8)

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$Ni_{90}Si_{10}$	Excellent	Too High (1126.5)	Too High (1222.5)
$Ni_{89}Si_{10}\mathbf{B_1}$	Excellent	Good (992.0)	Good (1032.8)

- B addition (1wt.%, nominal) will significantly suppress the melting range of Ni-Si(Ta) alloys by ~100°C.

Ni-Si (Ta, B) is a Promising System

Alloy Composition	48 hr 750°C Oxidation Resistance in Air	Solidus Temperature	Liquidus Temperature
$Ni_{88.5}Si_{4.5}Cr_{7.0}\mathbf{B_{3.1}}Fe_{3.0}$ (Commercial BNi2 Containing Iron)	Excellent	Excellent	Excellent
$Ni_{75}Si_{5.0}Ta_{20}$	Poor	Too High (1132.1)	Too High (1138.0)
$Ni_{73}Si_{7.0}Ta_{20}$	Good	Too High (1122.9)	Too High (1139.1)
$Ni_{72}Si_{7.0}Ta_{20}\mathbf{B_{1}}$	Good	Good (1057.6)	Good (1068.0)
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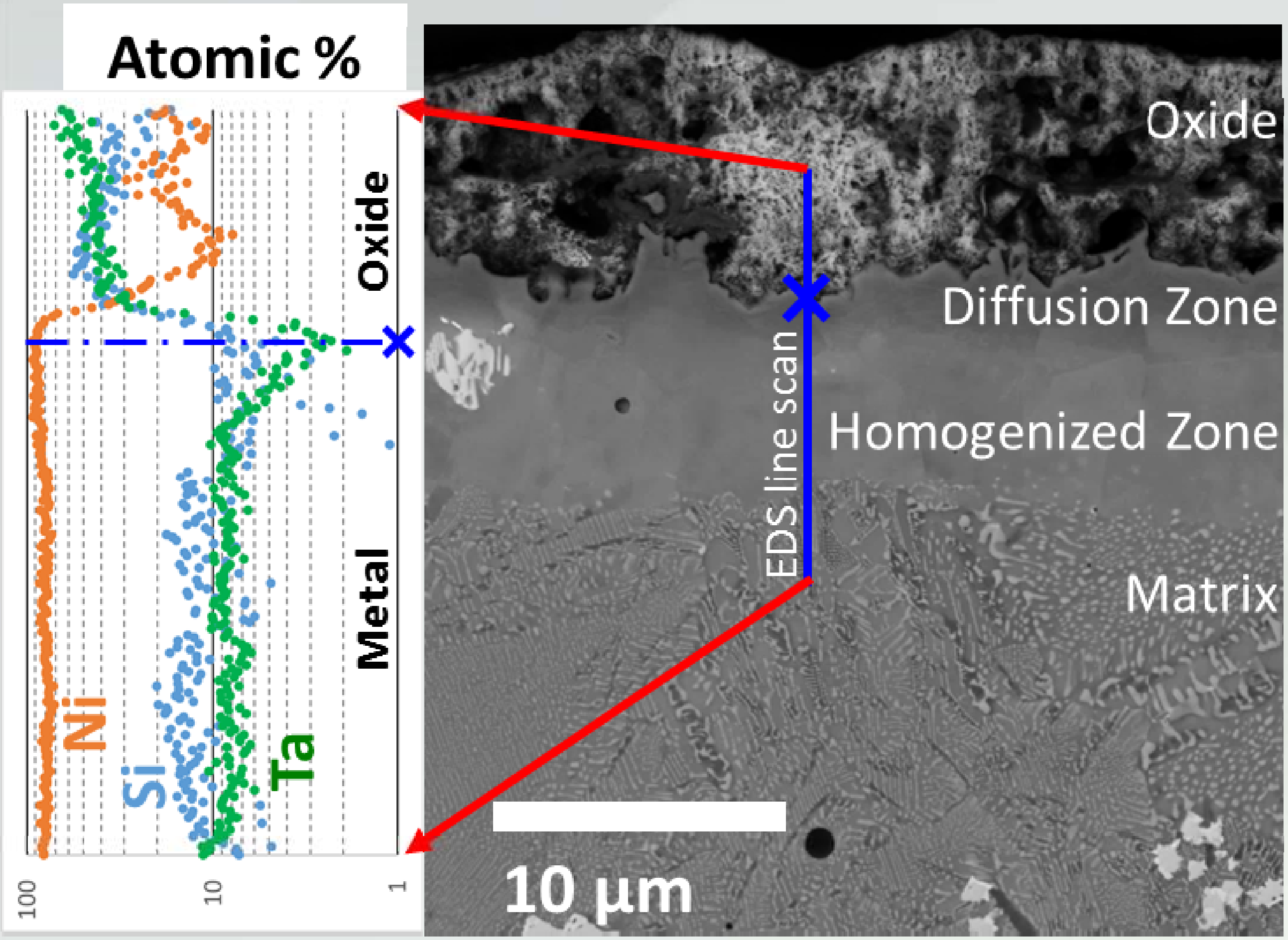
- B addition (1wt.%, nominal) will significantly suppress the melting range of Ni-Si(Ta) alloys by ~100°C.
- Adding Ta into the Ni-Si system will reduce the liquidus temperature by ~60°C.

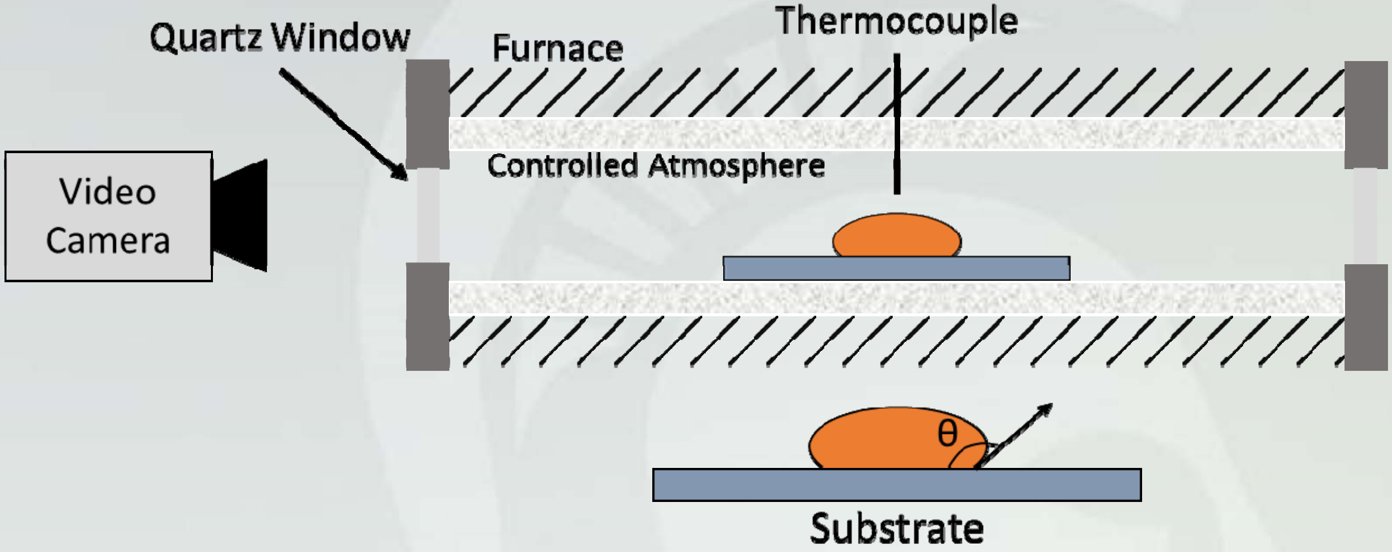
New Oxidation Mechanism can Provide a Different Angle in Alloy Design



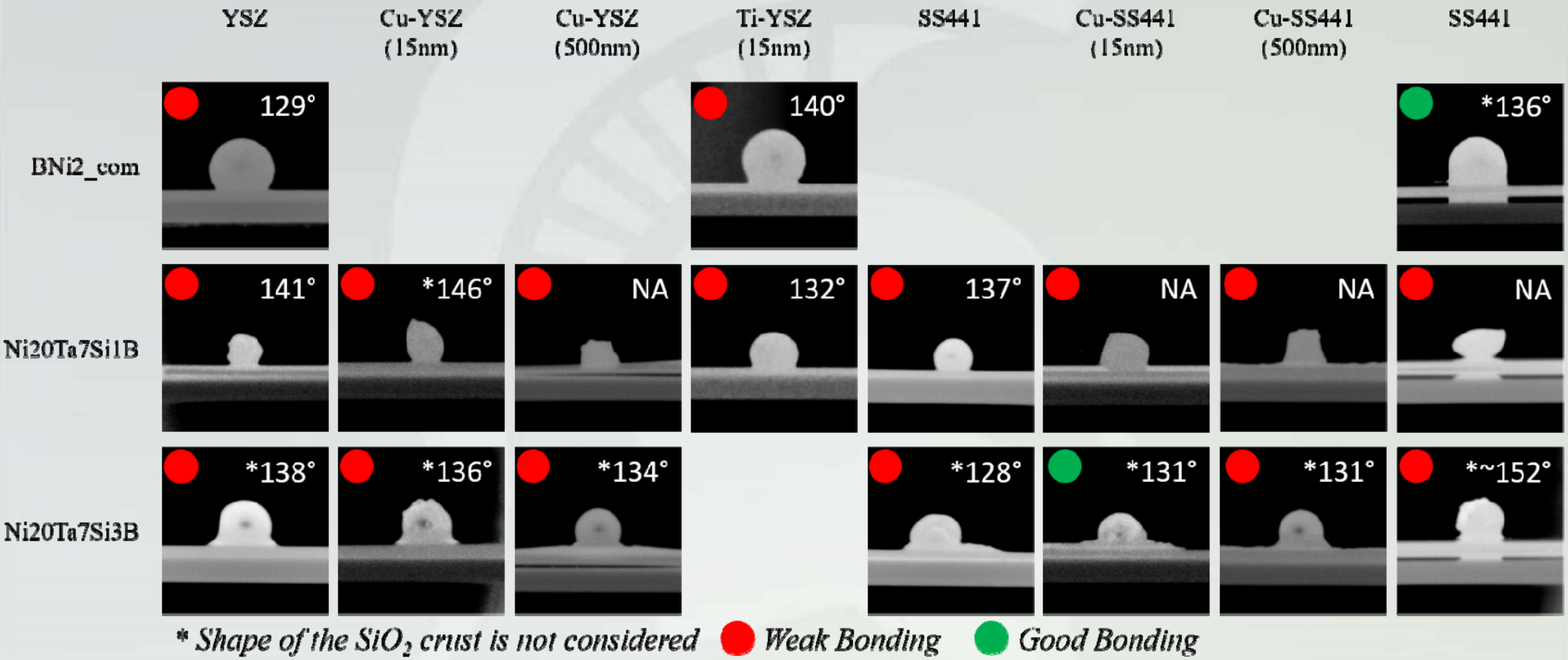
BSE image of the cross-section of an oxidized Ni20Ta7Si1B sample (192hrs / flowing air / 750°C) and atomic percentages of different elements from an EDS line scan.

- Although Ta addition seems to decrease the oxidation resistance, a different oxidation mechanism was observed.
- As shown in the EDS data, the “reaction layer” consists of a homogenized zone and a diffusion zone where Ta (and Si) diffuses toward the surface.
- Diffusion of Ta in the “reaction layer” might be the controlling process for the oxidation mechanism.

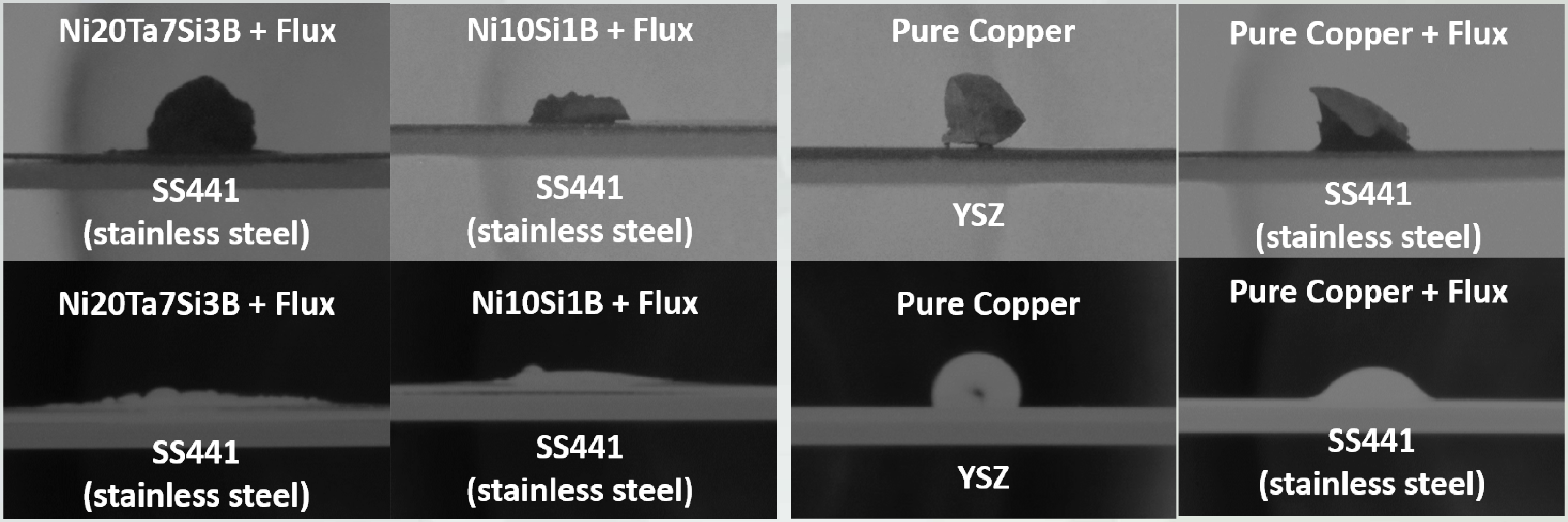
In situ Braze Wetting Measurement Setup



Without Flux, Ni-based Brazes Do Not Wet Coated Stainless Steel or YSZ



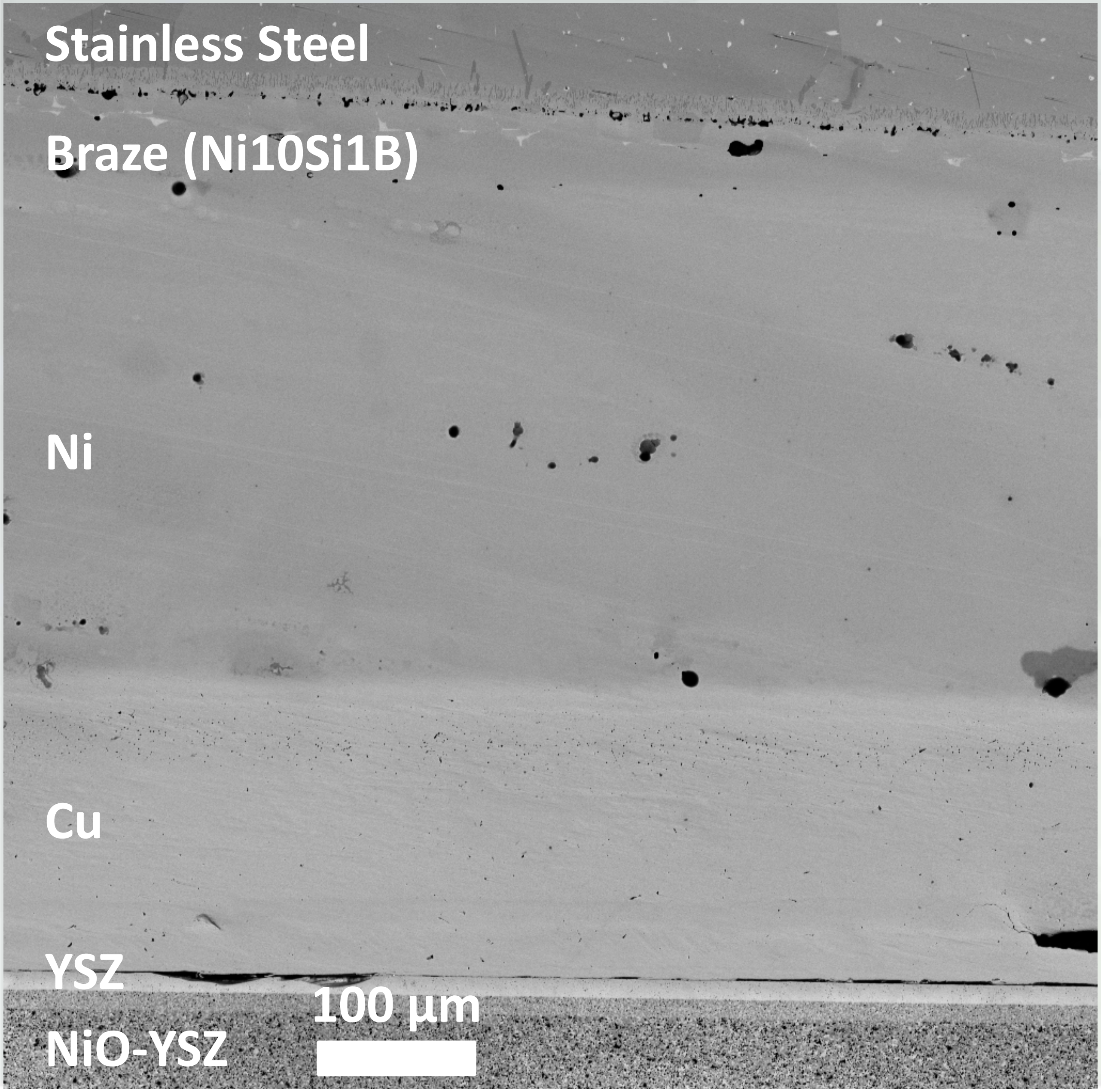
With Flux, Ni-based Brazes Wet Coated Stainless Steel or YSZ



A Preliminary Transient Multilayer Braze System

- A prototype multilayered braze joint was produced.
- Ni-Si(B) braze + Flux were applied to join the stainless steel; pure copper was used to join the YSZ.
- Sufficient interdiffusion occurred near the braze/SS interface to ensure good bonding.
- Pure nickel in the middle stopped Cr, Fe from diffusing into the YSZ interface.
- Biggest concern is the bonding near the YSZ.

A Preliminary Transient Multilayer Braze System



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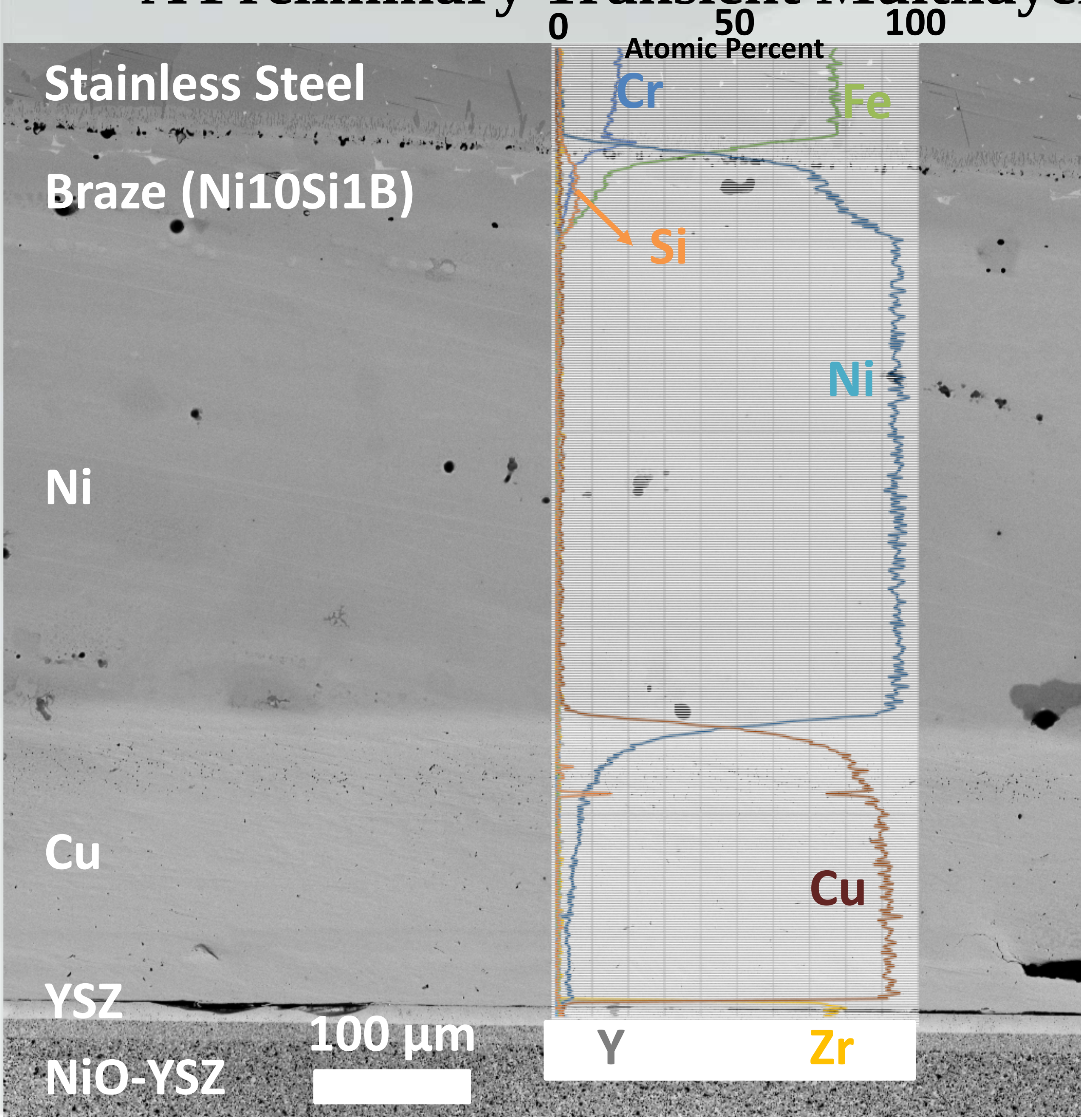

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- Pure nickel in the middle stopped Cr, Fe from diffusing into the YSZ interface.
- Biggest concern is the bonding near the YSZ.

Conclusions

- A Cr-free, Ni-10Si(1B) braze showed ***excellent oxidation resistance*** that is better than the commercial BNi2 braze.

- Ta reduces the liquidus temperature of the Ni-Si system by ~60°C and changes the ***oxidation mechanism***, which might provide passivation.

- A ***transient multilayer brazing system*** was explored, and a joint was successfully produced.

- Besides its application in SOFCs, the Ni-Si (Ta, B) system provides ***a new family*** of brazes for general applications.

- A systematic computation-experiment combined approach was established to ***search for, fabricate, and characterize new braze candidates*** for SOFC application.