



# Durable, Impermeable Brazes for Solid Oxide Fuel Cells

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# Outline

- Project and Team Introduction
- Accomplishments
- **Background and Motivation**
  - Benefits of Silver-Copper Brazes
  - Problems with Silver-Copper Brazes
- **Project Approach Summary**
- **Results and Discussions**
  - Simulations
  - Alloy Manufacture and Characterization
  - Braze Interface Engineering
  - Oxide Scale Manufacture and Characterization
  - Accelerated Testing
- **Future Work**

# Research Team

- **MSU:**

- Jason D. Nicholas                      PI, SOFC Expertise
- Yue Qi                                      PI, Computational Materials Science Expertise
- Thomas R. Bieler                      PI, Metallurgy Expertise
- Quan Zhou                                Graduate Student
- Tridip Das                                Graduate Student
- Yuxi Ma                                    Graduate Student
- Yang Kim                                 Undergraduate Student

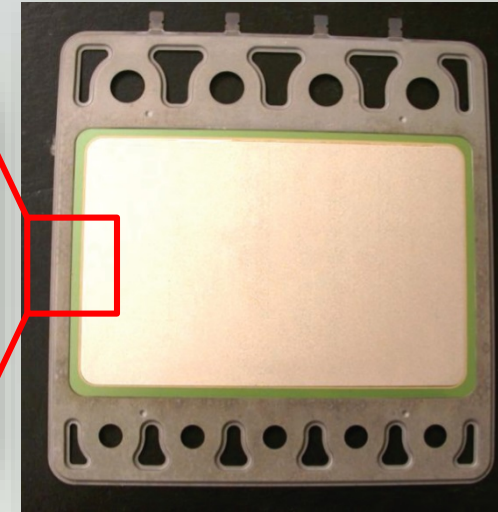
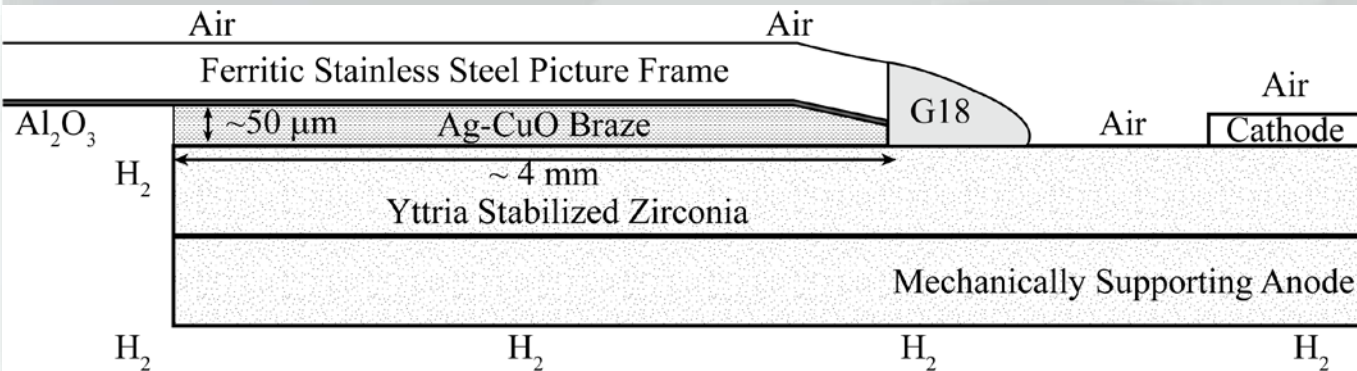
- **Delphi:**

- Rick Kerr (and his team ...)
- Stephanie Surface
- Bryan A. Gillispie

- **NETL**

- Joseph Stoffa

# State of the Art Delphi SOFC Joint Schematic



A. J. DeRose et. al. US 7855030 B2, Inhibitor for prevention of braze migration in solid oxide fuel cells

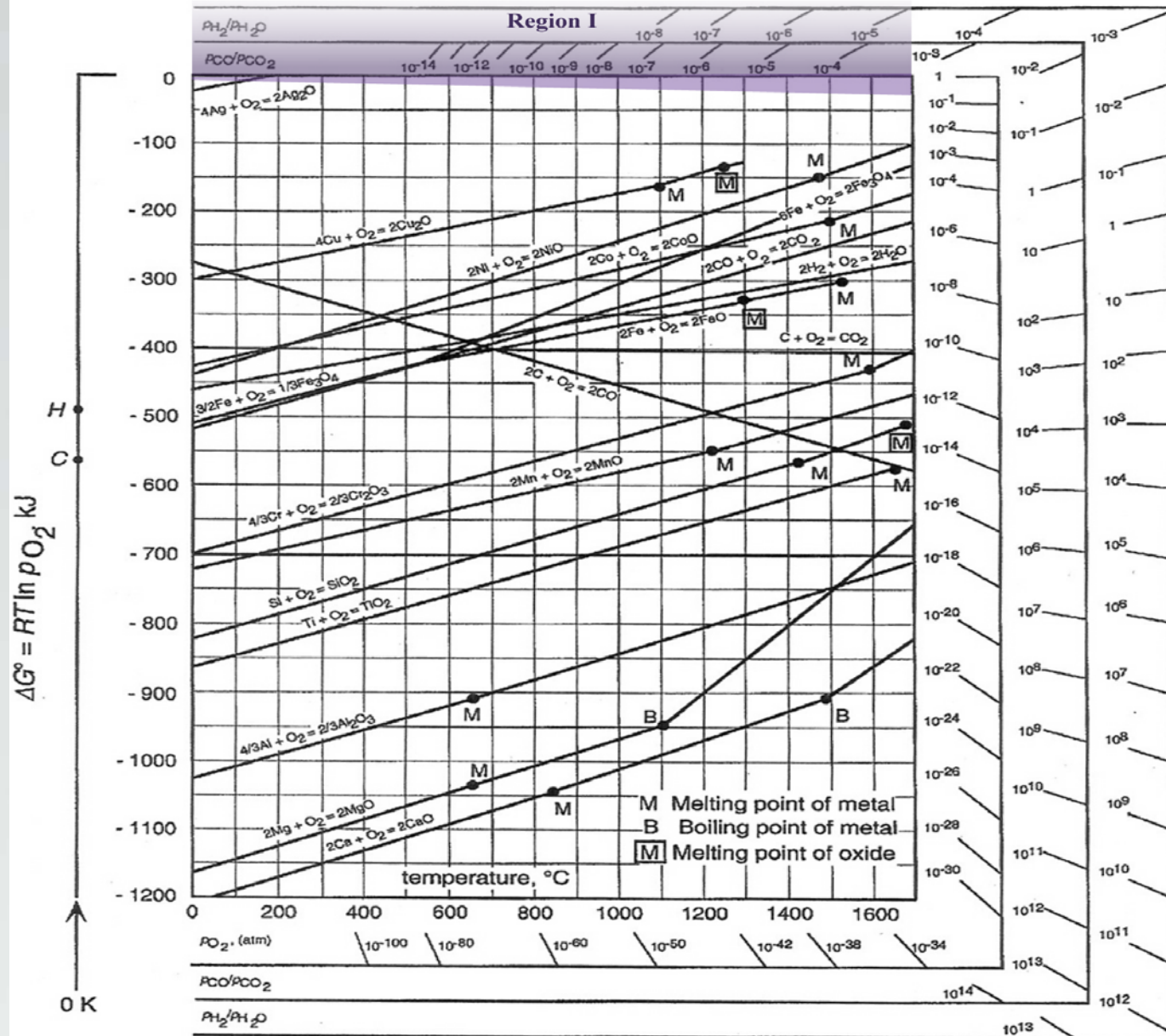
## Project Objectives

**Design and test new, SOFC-compatible, silver-free brazes forming durable, oxygen and hydrogen impermeable protective surface scales.**

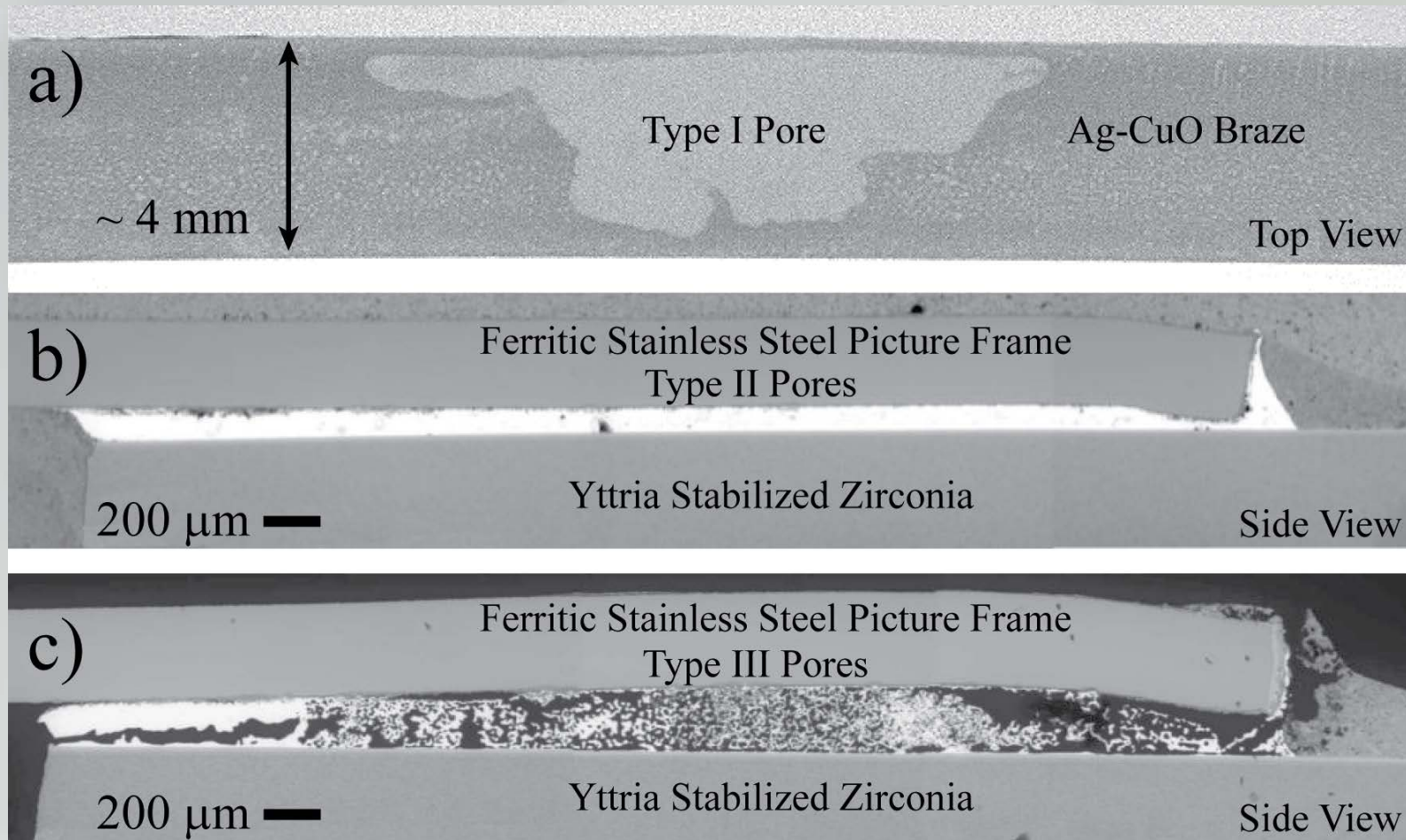
## Accomplishments

- Systematic computational evaluation of all ternary combinations of acceptable elements in the periodic table identified some surprising alloys that melt between 900 and 1000°C , such as those containing refractory metals such as Nb and Ta ( $T_m$  for Nb = 2469°C,  $T_m$  for Ta = 3020°C)
- A new, computationally identified Ta-Ni-Si alloy was shown to have oxidation resistance superior to that BNi2 (one of the most oxidation resistant commercially available Ni superalloys).
- The Ellingham diagrams proved to be a reliable guide for identifying surface-forming oxides.

# Only **Metals** in Region I Won't Oxidize in Air

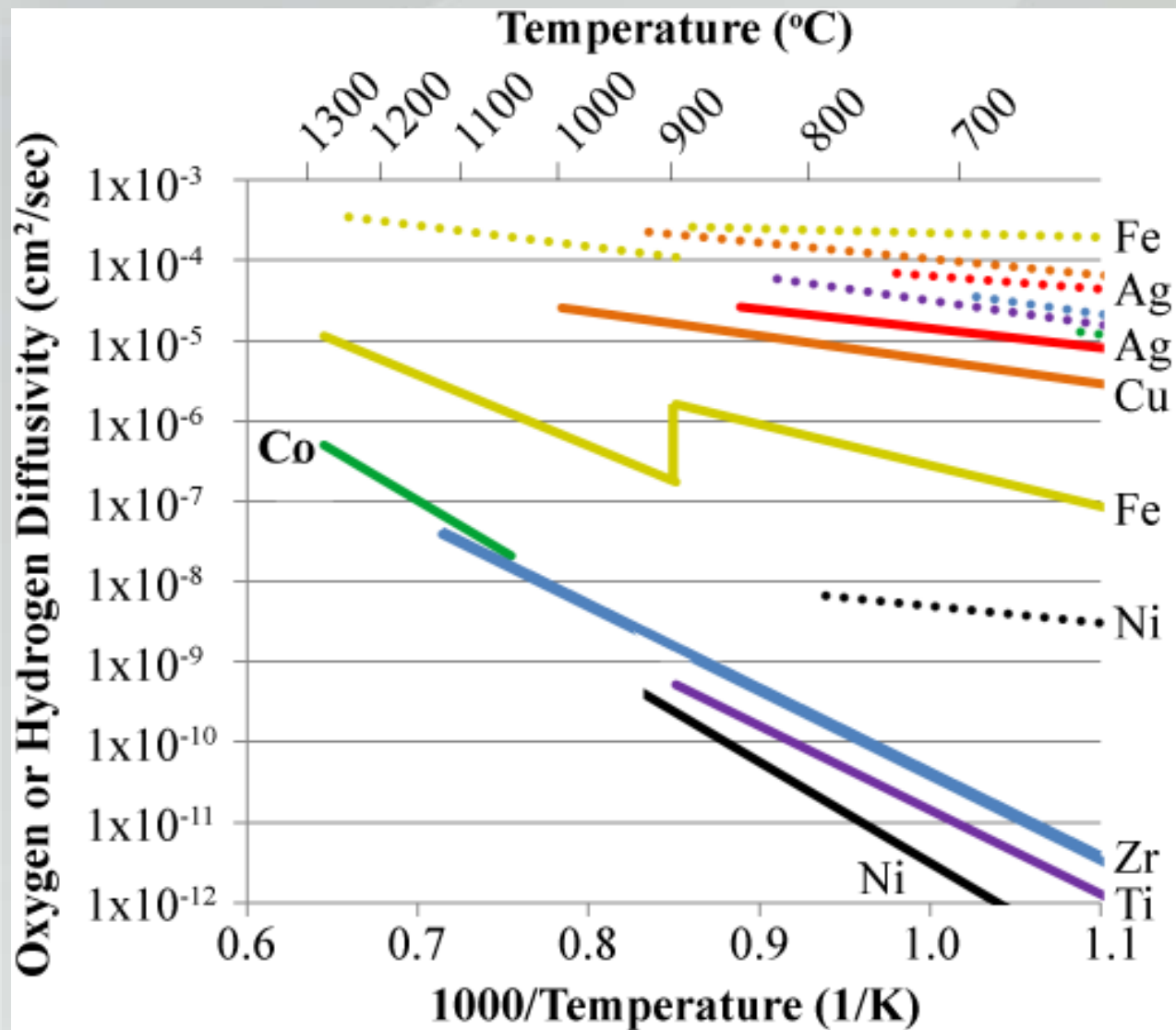


# Delphi 97.5%Ag-2.5%Cu Braze Degradation



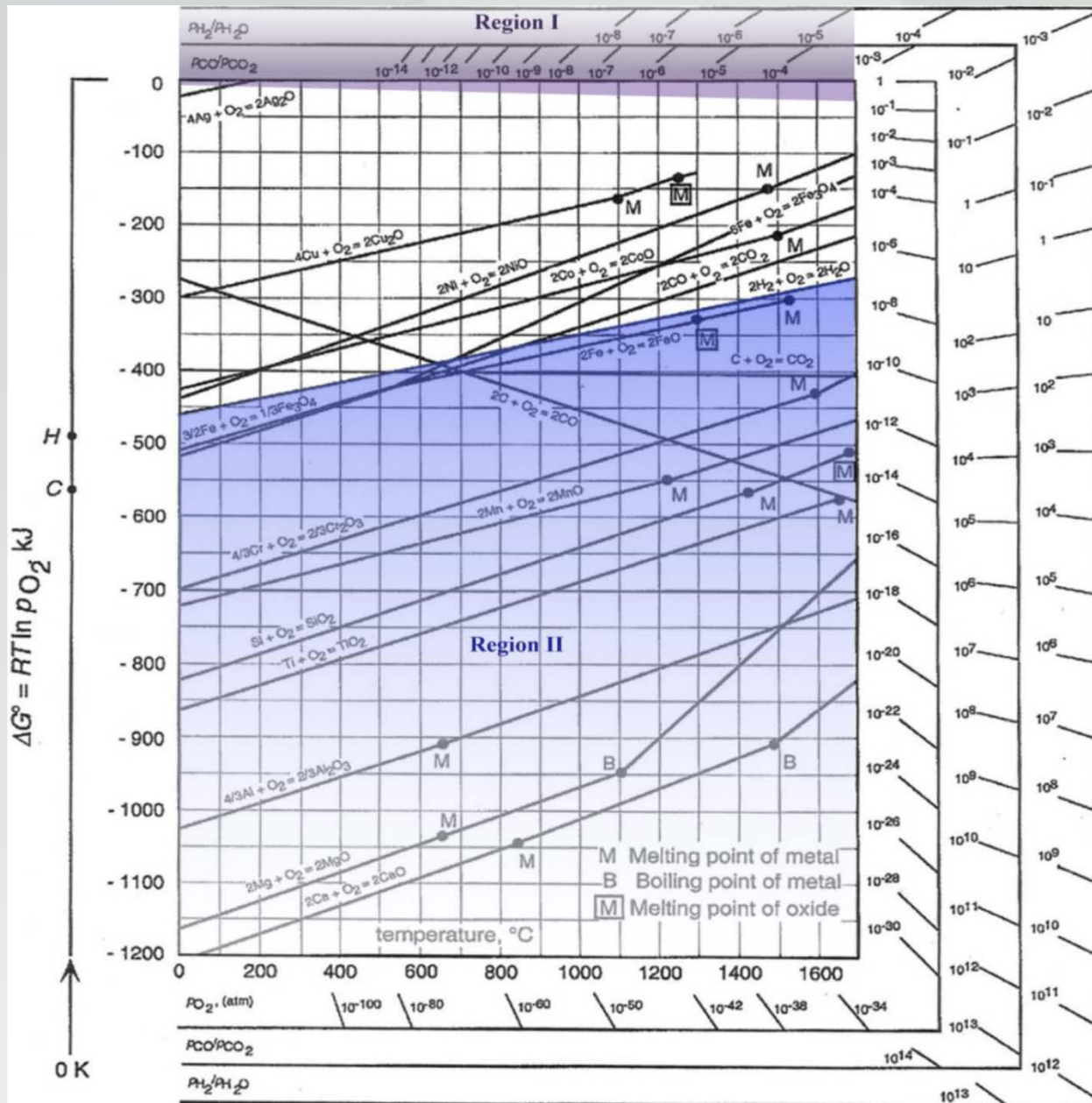
- Type I Pores: Form During Manufacturing
- Type II Pores: Form at Braze Interface due to CuO Reduction
- Type III Pores: Form in Braze due to Water Pocket Formation

# Oxygen (Solid) & Hydrogen (Dashed) Diffusivities in Common Metals





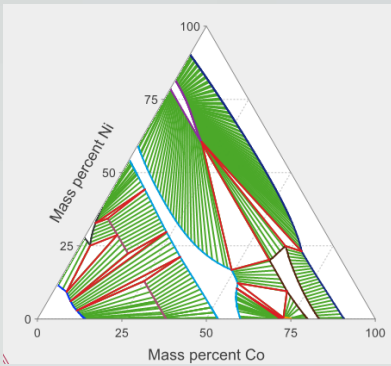
# Only Metals in Region II Form Oxide Scales Stable in H<sub>2</sub>



# Project Approach Summary

## I: Computationally Guided Alloy Composition Search/Design

### Phase Diagram Calculations



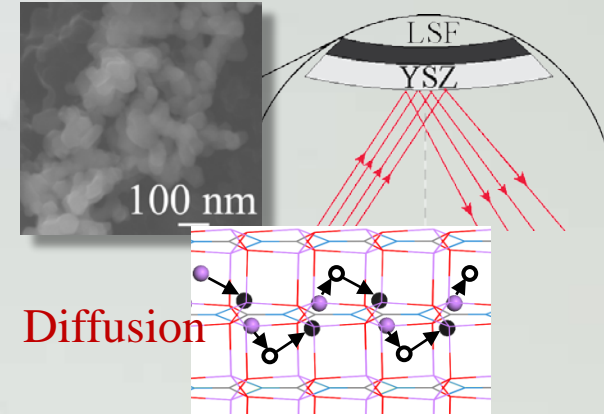
Identify composition with manufacturing compatible liquidus temperature



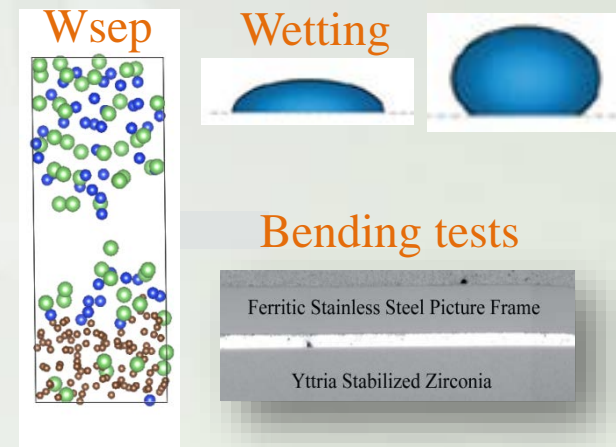
Identify composition forming chemical stable CTE-compatible oxides



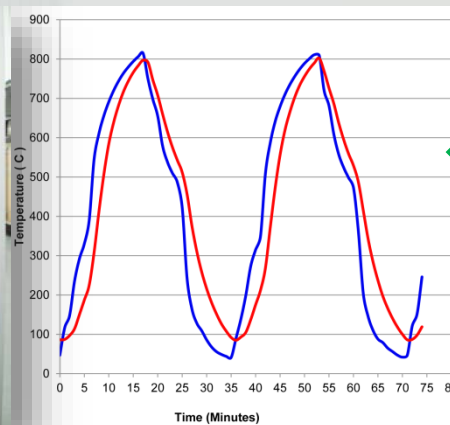
## II: Oxide Passivation



## III: Braze Interface Engineering



## IV: Braze Performance under Accelerated SOFC Operating Conditions



## Results and Discussions

- Computationally, rational design of alloy compositions
- Experimentally, forming and testing the promising alloy compositions
  - Focus so far
    - Liquidus temperature
    - Solidus temperature
    - Oxidation resistance --- Passivation property

# Brazing Element Selection Criteria

- ✓ Elements tend to form solid solutions or solid phase compounds.
  - Noble gases are dropped
- ✓ Should not be radioactive.
  - Polonium onwards (atomic number  $> 83$ ) elements are dropped
- ✓ Elements should not react to form undesired phases, like brittle phase, liquid or vapor phase.
  - Alkali metals, Halogens and Chalcogens are dropped.
- ✓ Should not be a good conductor of oxygen or hydrogen ions.
  - Polarizable Lanthanide group is dropped along with Bi.
- ✓ Elements should not have high vapor pressure ( $\geq 0.1$  Torr) at  $750^{\circ}\text{C}$ 
  - Alkaline earth metals and semiconducting elements are not considered except Mg as it can form passivating oxide layer with Al and O.
- ✓ Should not be banned element due to toxicity (by REACH-ECHA or US-EPA)
  - Cd, Pb, Tl
- ✓ Should not be in vapor or liquid state at braze operating condition
  - Ga
- ✓ Should not be of high cost ( $\geq \sim \$50/\text{gm}$  w.r.t Ag  $\sim \$3/\text{gm}$ )\*
  - Re, Pd, Ru, Pt, Au, Os, Ir, Sc, Rh are dropped

Elements List I (13): Ni, Al, Co, Cr, In, Mn, Mo, Nb, Si, Sn, Ta, W, Zn

Elements List II (25): 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

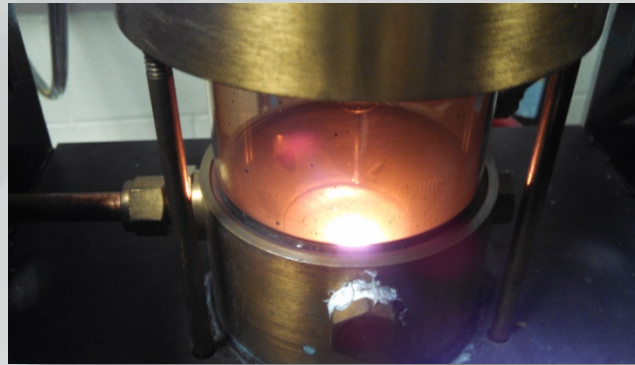
# Criteria Used for Braze Alloy Base Composition From CALPHAD Calculations

- CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) approach implemented in Thermocalc® was used.

Database	Description
TCNI7	Ni based alloys and superalloy solutions database
TCOX5	Thermo-Calc Software Metal Oxide solutions database
TCSLD2	TCS solder alloy solutions database
TTTI3	Titanium based database (didn't purchase)
PURE5	Scientific Group Thermochemical Europe Pure Elements database
PSUB	TCS public substances database
PBIN	TCS public binary alloys database
PKP	Kaufman binary alloys database

- Binary and ternary phase diagram was computed to identify alloy compositions with
  - the liquidus temperature of the braze below 1000°C (maximum 1050°C)
  - the solidus temperature of the braze above 900°C (minimum 850°C)

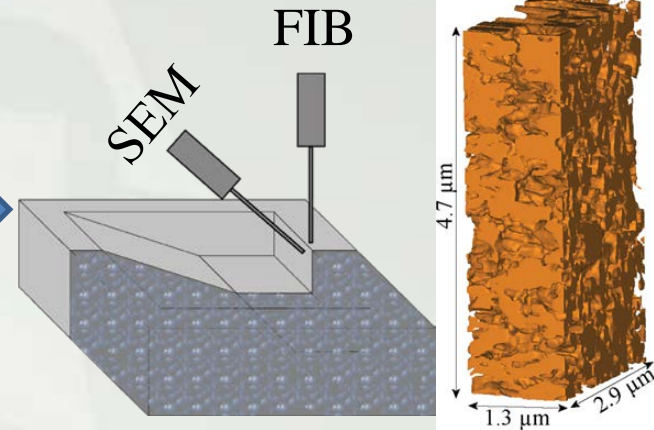
# Alloy Manufacturing and Characterization



99.99% Pure Metals    Arc Melting Multicomponent Metals    44%Ni-44%Ti-12%Co



Dilatometry Testing

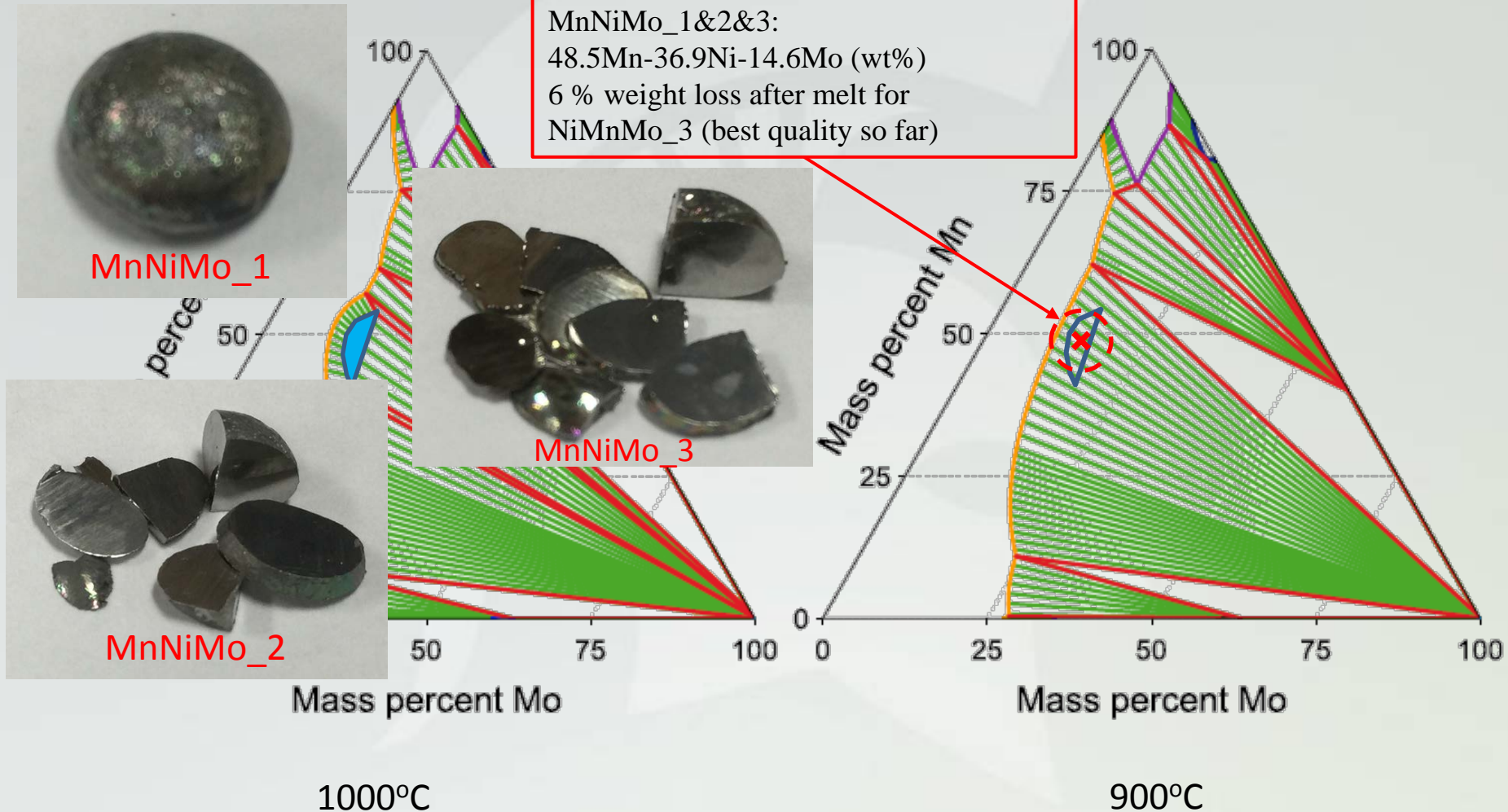



TGA-DSC Testing



Wetting Studies, XPS, etc.

# Thermo-Calc (TCNI7) Computed Ni-Mn-Mo Ternary Phase Diagram



 Shows the liquid phase.

# List of Possible Binary Alloys from Selected Elements

Elements selected (13): Ni, Al, Co, Cr, In, Mn, Mo, Nb, Si, Sn, Ta, W, Zn

Possible binary alloys from above list:  $^{13}C_2 = 78$

	Ni	Al	Co	Cr	In	Mn	Mo	Nb	Si	Sn	Ta	W	Zn											
Ni		All phases are selected from database for Binary alloy calculations.																						
Al	Ni-Al																							
Co	Ni-Co													Al-Co										
Cr	Ni-Cr													Al-Cr	Co-Cr									
In	Ni-In													Al-In	Co-In	Cr-In								
Mn	Ni-Mn													Al-Mn	Co-Mn	Cr-Mn	In-Mn							
Mo	Ni-Mo													Al-Mo	Co-Mo	Cr-Mo	In-Mo	Mn-Mo						
Nb	Ni-Nb													Al-Nb	Co-Nb	Cr-Nb	In-Nb	Mn-Nb	Mo-Nb					
Si	Ni-Si													Al-Si	Co-Si	Cr-Si	In-Si	Mn-Si	Mo-Si	Nb-Si				
Sn	Ni-Sn													Al-Sn	Co-Sn	Cr-Sn	In-Sn	Mn-Sn	Mo-Sn	Nb-Sn	Si-Sn			
Ta	Ni-Ta													Al-Ta	Co-Ta	Cr-Ta	In-Ta	Mn-Ta	Mo-Ta	Nb-Ta	Si-Ta	Sn-Ta		
W	Ni-W													Al-W	Co-W	Cr-W	In-W	Mn-W	Mo-W	Nb-W	Si-W	Sn-W	Ta-W	
Zn	Ni-Zn													Al-Zn	Co-Zn	Cr-Zn	In-Zn	Mn-Zn	Mo-Zn	Nb-Zn	Si-Zn	Sn-Zn	Ta-Zn	W-Zn

	Liquid phase or coexists with solid below 900 C at 1 atm
	NO liquid phase below 1000C
	Not available in database
	Liquid to solid phase transition between 1000 and 900C

Ni-In, Ni-Si, Ni-Zn and Co-Zn have eutectic reaction in binary phase diagram



# List of Possible Ni-containing Ternary Alloys from Selected Elements

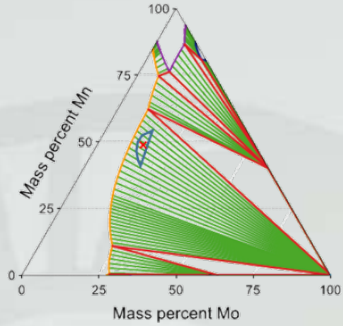
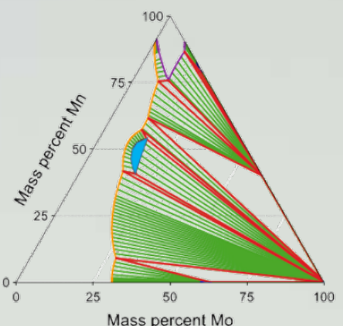
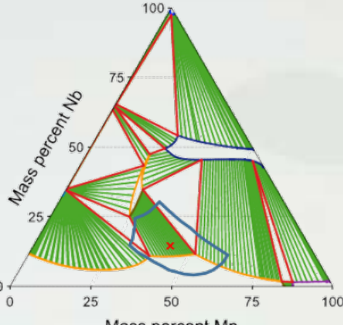
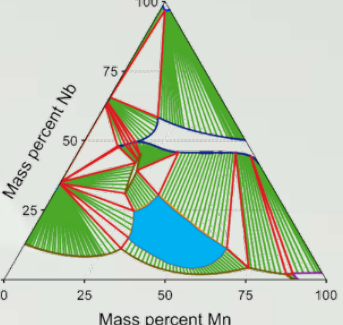
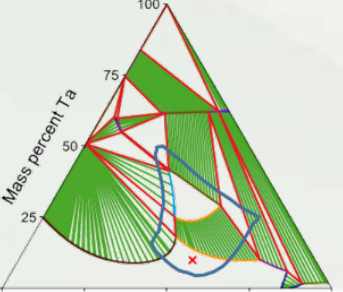
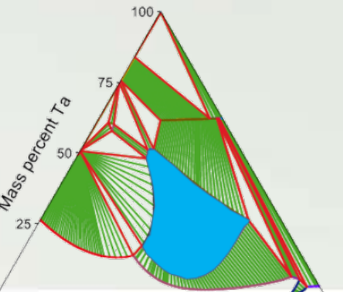
Elements selected (13): **Ni**, Al, Co, Cr, In, Mn, Mo, Nb, Si, Sn, Ta, W, Zn

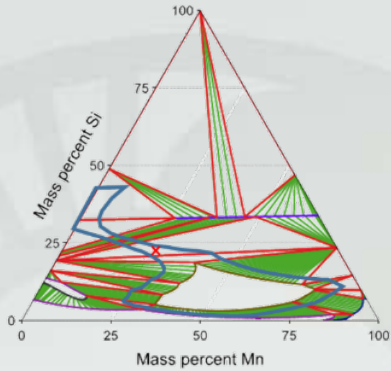
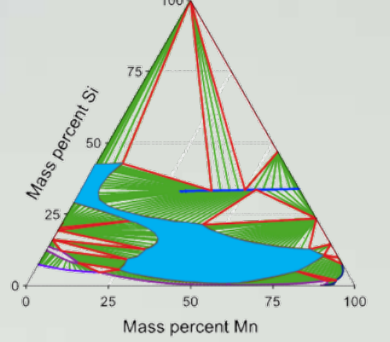
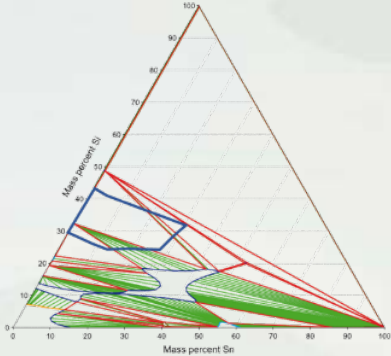
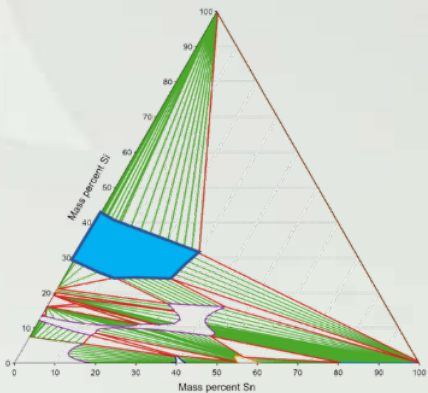
Possible ternary alloys from above list with Ni base:  $^{12}C_2 = 66$

Ni	Al	Co	Cr	In	Mn	Mo	Nb	Si	Sn	Ta	W	Zn
Al												
Co	Ni-Al-Co											
Cr	Ni-Al-Cr	Ni-Co-Cr										
In	Ni-Al-In	Ni-Co-In	Ni-Cr-In									
Mn	Ni-Al-Mn	Ni-Co-Mn	Ni-Cr-Mn	Ni-In-Mn								
Mo	Ni-Al-Mo	Ni-Co-Mo	Ni-Cr-Mo	Ni-In-Mo	Ni-Mn-Mo							
Nb	Ni-Al-Nb	Ni-Co-Nb	Ni-Cr-Nb	Ni-In-Nb	Ni-Mn-Nb	Ni-Mo-Nb						
Si	Ni-Al-Si	Ni-Co-Si	Ni-Cr-Si	Ni-In-Si	Ni-Mn-Si	Ni-Mo-Si	Ni-Nb-Si					
Sn	Ni-Al-Sn	Ni-Co-Sn	Ni-Cr-Sn	Ni-In-Sn	Ni-Mn-Sn	Ni-Mo-Sn	Ni-Nb-Sn	Ni-Si-Sn				
Ta	Ni-Al-Ta	Ni-Co-Ta	Ni-Cr-Ta	Ni-In-Ta	Ni-Mn-Ta	Ni-Mo-Ta	Ni-Nb-Ta	Ni-Si-Ta	Ni-Sn-Ta			
W	Ni-Al-W	Ni-Co-W	Ni-Cr-W	Ni-In-W	Ni-Mn-W	Ni-Mo-W	Ni-Nb-W	Ni-Si-W	Ni-Sn-W	Ni-Ta-W		
Zn	Ni-Al-Zn	Ni-Co-Zn	Ni-Cr-Zn	Ni-In-Zn	Ni-Mn-Zn	Ni-Mo-Zn	Ni-Nb-Zn	Ni-Si-Zn	Ni-Sn-Zn	Ni-Ta-Zn	Ni-W-Zn	
	Liquid phase or coexists with solid below 900 C at 1 atm											
	NO liquid phase below 1000C											
	Not available in database											
	Liquid to solid phase transition between 1015 and 900C											

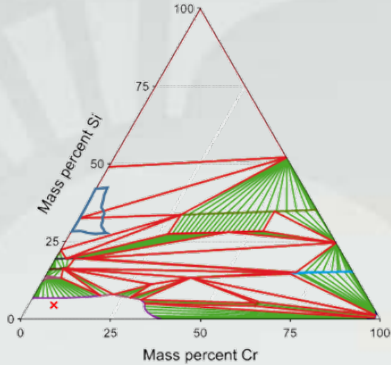
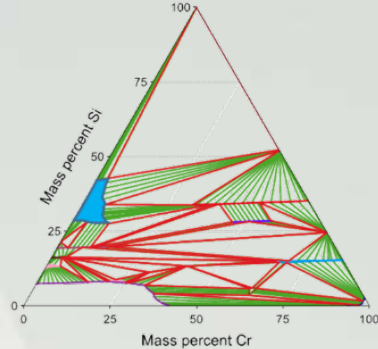
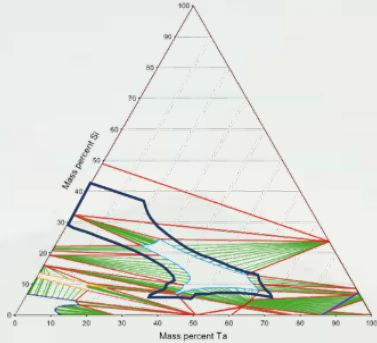
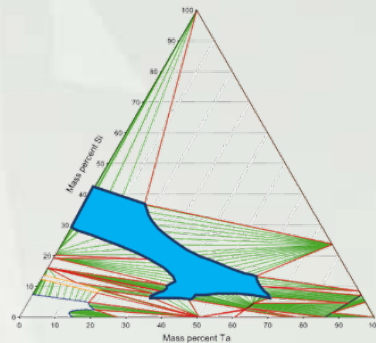
The 7 alloys systems can be further categorized into two systems:

**NiSi(Cr,Sn,Ta,Mn)** & **NiMn(Mo,Nb,Ta,Si)**

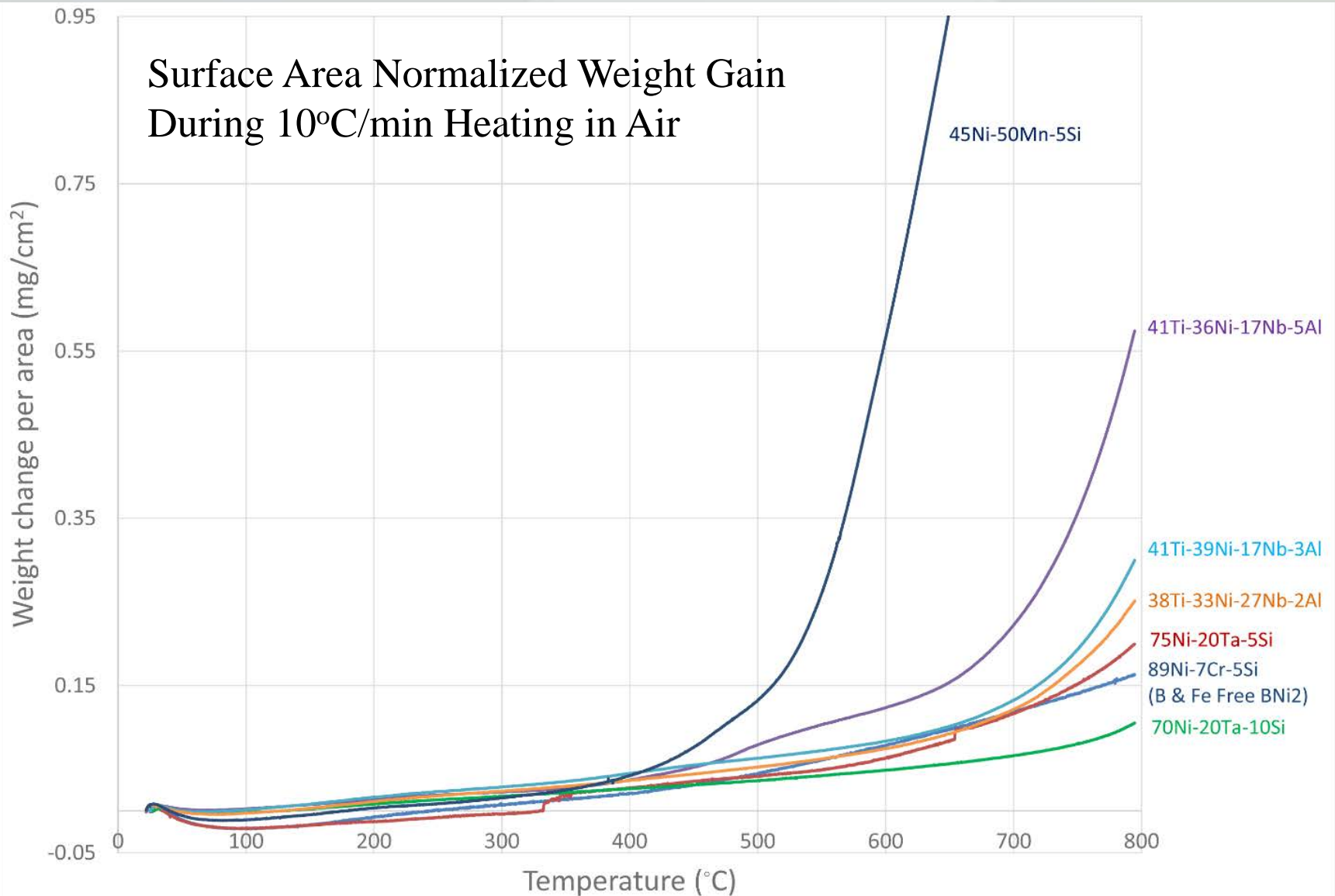
Tested Compositions	Characterization Results	900°C Ternary Phase Diagram	1000°C Ternary Phase Diagram
49Mn36Ni-15Mo	<ul style="list-style-type: none"> <li>Poor Oxidation Resistance</li> </ul>	<p>Ni-Mn-Mo</p> 	<p>Ni-Mn-Mo</p> 
41Ni-43Mn-15Nb	<ul style="list-style-type: none"> <li>Poor Oxidation Resistance</li> </ul>	<p>Ni-Mn-Nb</p> 	<p>Ni-Mn-Nb</p> 
37Ni-52Mn-11Ta	<ul style="list-style-type: none"> <li>Poor Oxidation Resistance</li> </ul>	<p>Ni-Mn-Ta</p> 	<p>Ni-Mn-Ta</p> 

Tested Compositions	Characterization Results	900°C Ternary Phase Diagram	1000°C Ternary Phase Diagram
45Ni-50Mn-5Si	<ul style="list-style-type: none"> <li>Poor Oxidation Resistance</li> <li>Brittle</li> </ul>	<p data-bbox="987 222 1164 262">Ni-Mn-Si</p> 	<p data-bbox="1476 222 1653 262">Ni-Mn-Si</p> 
52Ni-26Mn-22Si	<ul style="list-style-type: none"> <li>So Brittle it Disintegrated During Fabrication</li> </ul>	<p data-bbox="993 762 1159 802">Ni-Sn-Si</p> 	<p data-bbox="1481 762 1647 802">Ni-Sn-Si</p> 
<p data-bbox="123 762 788 996">Untested because the high (&gt;25%) Si content required to produce alloys with desirable melting properties suggest that these alloys are likely brittle due to silicide formation</p>			

# Promising systems to pursue

Tested Compositions	Characterization Results	900°C Ternary Phase Diagram	1000°C Ternary Phase Diagram
<p>89Ni-7Cr-5Si (Fe-Free &amp; B-Free BNi2)</p> <p>BNi2:14.0-Cr, 4.0-Si, 3.1-B, 0.02-P, 78.88-Ni</p>	<ul style="list-style-type: none"> <li>Excellent Oxidation Resistance</li> <li>Ductile</li> </ul>	<p>Ni-Cr-Si</p> 	<p>Ni-Cr-Si</p> 
<p>75Ni-20Ta-5Si</p>	<ul style="list-style-type: none"> <li>Good Oxidation Resistance</li> <li>Ductile</li> </ul>	<p>Ni-Ta-Si</p> 	<p>Ni-Ta-Si</p> 
<p>Possible Optimal Composition</p>			
<p>70Ni-20Ta-10Si</p>	<ul style="list-style-type: none"> <li>Excellent Oxidation Resistance</li> <li>Brittle</li> </ul>		

# Ta-Ni-Si An Oxidation Resistance Superior to BNi2



## Conclusion and Accomplishments

- Systematic computational evaluation of all ternary combinations of acceptable elements in the periodic table identified some surprising alloys that melt between 900 and 1000°C , such as those containing refractory metals such as Nb and Ta ( $T_m$  for Nb = 2469°C,  $T_m$  for Ta = 3020°C)
- A new, computationally identified Ta-Ni-Si alloy was shown to have oxidation resistance superior to that BNi2 (one of the most oxidation resistant commercially available Ni superalloys).
- The Ellingham diagrams proved to be a reliable guide for identifying surface-forming oxides.

### On going

- 25x25 combinations have been tested, more alloys systems and compositions will be tested.

# Braze Alloy Design Criteria and Evaluation Methods

Design Parameter	Target Values	Justification	97.5Ag-2.5CuO Values
Liquidus Temperature ( $T_L$ )	900°C $\leq T_L \leq$ 1015°C	So the braze is solid during SOFC operation & does not alter the microstructure of previously made layers	<b>912°C</b>
Linear Coefficient of Thermal Expansion (CTE)	7 ppm/K $\leq 25-750^\circ\text{C}$ CTE $\leq$ 16 ppm/K	To prevent surface oxide spallation. 25-750°C YSZ CTE=9 ppm/K [11]. 25-750°C 441 Steel CTE=12ppm/K [11].	<i>~21 ppm/K [12]</i> <i>Non-passivating, spallation-prone CuO forms on the surface in air [13]</i>
Ductility	$\geq 3\%$	So the braze can withstand YSZ-441 thermal expansion mismatch stress	<b>Sufficient [18], but unknown</b>
Vapor Pressure	750°C Vapor Pressure $< 1 \times 10^{-8}$ torr	To ensure that volatilization does not degrade the braze or the protective oxide	<i>Ag 750°C Vapor Pressure in Air = <math>1 \times 10^{-5}</math> torr [19]</i>

# Braze Interface Design Criteria and Evaluation Methods

Design Parameter	Target Values	Justification	97.5Ag-2.5CuO Values
Wetting Angle ( $\theta$ )	$0^\circ \leq \theta \leq 30^\circ$	To ensure that the braze spreads through the joint during manufacturing	<i>45°[14]. Causes Type I pores to form in the braze</i>
Metallurgical Bonding with Al <sub>2</sub> O <sub>3</sub>	Interdiffusion or new phase formation	To promote good, active brazing with the Al <sub>2</sub> O <sub>3</sub> coating on the ferritic stainless steel	<b>CuAl<sub>2</sub>O<sub>4</sub>[15] or CuAlO<sub>2</sub> [14]</b>
Metallurgical Bonding with YSZ	Interdiffusion or new phase formation	To promote good, active brazing with the YSZ	<b>Interdiffusion or a Y-Cu-O phase [16, 17]</b>
Braze Joint Strength ( $\sigma_B$ )	$\sigma_B > 120$ MPa	So the braze can accommodate YSZ-441 CTE mismatch stress	<b>220 MPa [14]</b>



# Braze Oxide Design Criteria and Evaluation Methods

Design Parameter	Target Values	Justification	97.5Ag-2.5CuO Values
Alloy Oxygen and Hydrogen Conductivities ( $\sigma_{O_2}, \sigma_{H_2}$ )	$\sigma_{O_2} < 1 \times 10^{-8}$ S/cm $\sigma_{H_2} < 1 \times 10^{-8}$ S/cm	If no surface oxide forms, the braze should have a low oxygen conductivity to prevent Type III pores.	<b>Ag stable above 160°C in air [20]</b>  $\sigma_{O_2} = 2 \times 10^{-4}$ S/cm at 750°C [8] promoting Type III pores [10].
Braze Oxide Oxygen and Hydrogen Surface Exchange Coefficients ( $k_{O_2}, k_{H_2}$ )	$k_{O_2} < 1 \times 10^{-8}$ cm/sec $k_{H_2} < 1 \times 10^{-8}$ cm/sec	If a surface oxide forms, the oxide should have a low oxygen surface exchange coefficient to prevent Type III pores and to ensure a ductile metal braze core remains.	<i>Only a reducible CuO scale is present above ~150°C</i>
Stability over 40,000 hours of SOFC Operation	Retention of all design parameter target values	To ensure reliable SOFC operation	<i>Does not last past 10,000 hours of SOFC operation [18]</i>

# Project Timeline

		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12																									
Item	Item Description	months	Oct-14	Nov-14	Dec-14	Jan-15	Feb-15	Mar-15	Apr-15	May-15	Jun-15	Jul-15	Aug-15	Sep-15	Oct-15	Nov-15	Dec-15	Jan-16	Feb-16	Mar-16	Apr-16	May-16	Jun-16	Jul-16	Aug-16	Sep-16	Oct-16	Nov-16	Dec-16	Jan-17	Feb-17	Mar-17	Apr-17	May-17	Jun-17	Jul-17	Aug-17	Sep-17
<b>Task 1.0</b>	Project Management and Planning	36	Project Management and Planning																																			
<b>Phase I</b>	<b>Computationally Guided Alloy Composition Search/Design</b>	30	Phase I																																			
Objective 1	Identify new brazes with manufacturing-compatible liquidus temperatures	9	Engineer Liquidus Temperature																																			
Task 1.1	Compute nickel alloy phase diagrams to identify new eutectic compositions	9	Bieler/Qi																																			
Task 1.2	Compute nickel alloy-oxygen phase diagrams to identify surface oxide layers	9	Bieler/Qi																																			
Task 1.3	Compute alloy-oxygen phase diagrams in other systems	9	Bieler/Qi																																			
Task 1.4	Produce alloy samples	30	Bieler/Nicholas																																			
Task 1.5	Measure braze liquidus temperatures	6	Bieler																																			
Objective 2	Identify those Brazes Forming Chemically-stable, CTE-compatible Surface Oxides	6	Engineer Surface Oxide Stability																																			
Task 2.1	Produce braze oxide samples	6	Nicholas																																			
Task 2.2	Measure braze and braze oxide CTE in air and hydrogen	6	Nicholas																																			
Task 2.3	Confirm braze oxide stability in air, hydrogen, and wet hydrogen	6	Nicholas																																			
* Milestone 1 *	Calculate promising nickel alloy-oxygen phase diagrams	1	*																																			
* Milestone 2 *	Calculate other eutectic phase diagrams	1	*																																			
Decision Point 1	GO/NO-GO decision on whether to use Ni or an alternative braze base	1	*																																			
<b>Phase II</b>	<b>Braze Interface Engineering</b>	15	Phase II																																			
Objective 3	Produce Brazes with Appropriate Wetting Angles	12	Engineer Wetting																																			
Task 3.1	Measure and promote alloy interface wetting	12	Bieler/Qi																																			
Objective 4	Produce Brazes with Strong Interfacial Bonds, High Joint Strength, Sufficient Ductility	12	Engineer Joint Strength																																			
Task 4.1	Characterize and identify any interfacial compounds that form during brazing	12	Bieler/Nicholas																																			
Task 4.2	Compute interface phase formation	15	Qi																																			
Task 4.3	Measure braze interface strengths	12	Bieler																																			
Task 4.4	Measure braze high-temperature ductility	12	Bieler																																			
Task 4.5	Compute the effect alloy addition on work of adhesion and interface strength	12	Qi																																			
* Milestone 3 *	Measure the physical properties, microstructures, and interface strengths of promising alloys identified in Phase I	1	*																																			
* Milestone 4 *	Send promising , high-risk samples to Delphi for manufacturing compatibility testing	1	*																																			
Decision Point 2	GO/NO-GO decision on new base alloy system or continue with minor alloy additions	1	*																																			
<b>Phase III</b>	<b>Oxide Scale Passivation</b>	12	Phase III																																			
Objective 5	Produce brazes with Low-Vapor Pressure Protective Scales	12	Engineer Protective Scales																																			
Task 5.1	Measure pre-oxidized braze weight gains at elevated temperature	6	Nicholas																																			
Task 5.2	Measure oxide scale oxygen and hydrogen conductivities	12	Nicholas																																			
Task 5.3	Compute braze system oxygen and hydrogen conductivities	12	Qi																																			
Task 5.4	Model oxide scale growth rates	6	Qi/Nicholas																																			
* Milestone 5 *	Measure surface scale passivation ability	1	*																																			
* Milestone 6 *	Send promising , low-risk samples to Delphi for manufacturing compatibility testing	1	*																																			
<b>Phase IV</b>	<b>Braze Performance under Accelerated SOFC Operating Conditions</b>	15	Phase IV																																			
Objective 6	Produce brazes suitable for 40,000 hours of SOFC Operation at 750C	15	Manufacturing & Accelerated Testing																																			
Task 6.1	Perform coupon level rapid thermal cycling tests	12	Delphi																																			
Task 6.2	Perform stack level SOFC electrochemical tests	6	Delphi																																			
Task 6.3	Perform Failure Analysis and Final Braze Composition Optimization	9	Nicholas/Bieler																																			
* Milestone 7 *	Identify the specific braze compositions and processing conditions necessary to produce a reliable SOFC braze	1	*																																			

**Questions?**

**Thanks for your Attention!**