Corrosion and Erosion Resistant Features for High Pressure Supercritical Carbon Dioxide Heat Exchangers

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By

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For

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High Pressure Supercritical Carbon Dioxide Heat Exchanger Corrosion

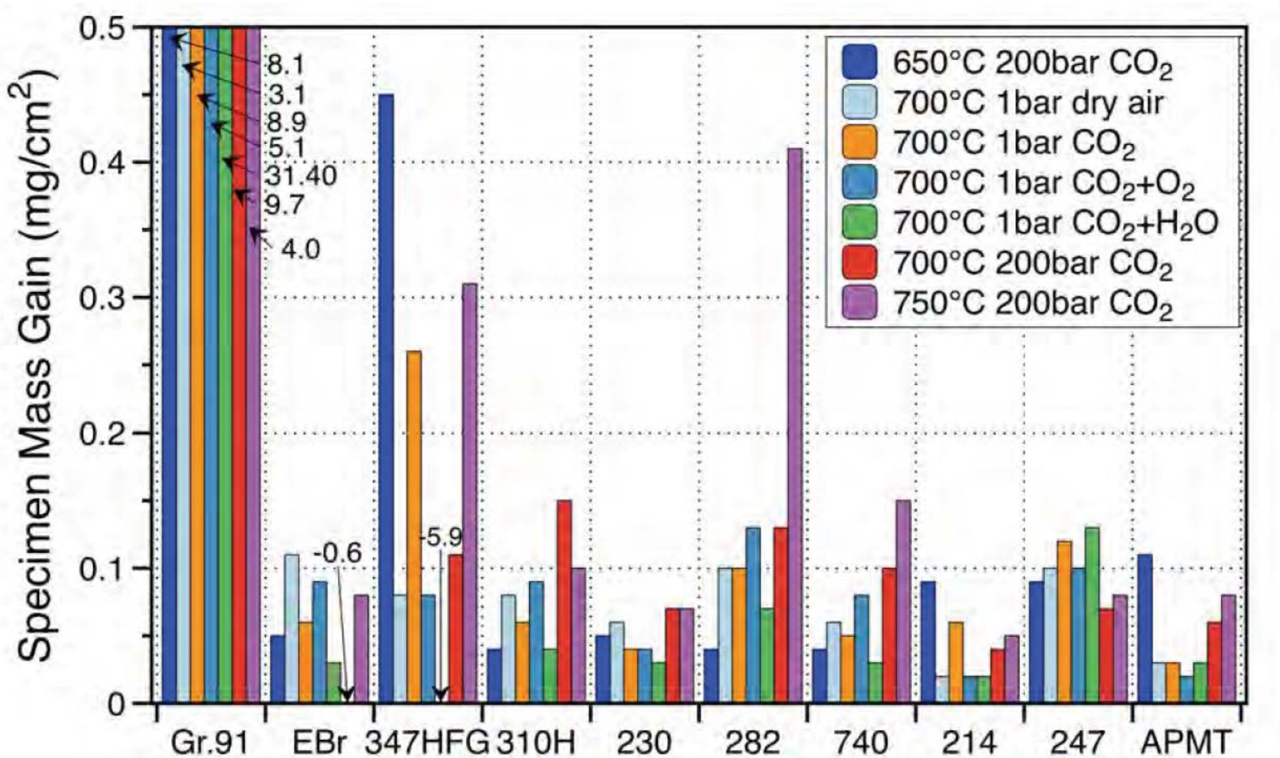
- ScCO2 power cycle recuperative heat exchanger capacities are massive, and are costly and subject to corrosion
- Use of nickel-based alloys help address corrosion, but alloys are expensive
- Additives that modify material surface properties can increase corrosion resistance at low cost
- Brazing used in bonding Altex heat exchanger components offers potential for surface modification for corrosion resistance

Project Objectives

- Formulate a braze compound and application method, called Load Assisted Braze-Corrosion Barrier (LAB-CB) process that has both high bonding strength and surface corrosion protection – a single material and process with two beneficial functions
- Test effectiveness of compound and process for joint strength and corrosion resistance
- Develop a LAB-CB braze compound corrosion resistance model that can support design of brazed heat exchangers
- Design, build and test a LAB-CB based heat exchanger

Altex with support by Vacuum Process Engineering

ORNL Weight Gain Test Results



- **Nickel based alloys with high Cr and Al have high corrosion resistance**
- **Si also forms oxide barriers to slow diffusion and thereby corrosion**

- **LAB-CB with Ni, Cr, Si, Al for both good bonding and corrosion**

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Base Materials Selection

Base Material	Application	Composition	Characteristics
316 Stainless Steel	Waste heat power system and lower temperature portion of high temperature system HEX	65.7 Fe, 12 Ni, 17 Cr, 2.5 Mo, 2 Mn, 0.75 Si, 0.045 P, 0.08 C, 0.03S, 0.1 N	Lower-cost structural material, but limited corrosion resistance at higher temperatures
Sanicro 25	Waste heat power system and lower temperature portion of high temperature system HEX	43 Fe, 25 Ni, 22.5 Cr, 0.5 Mn, 0.2 Si, 3.6 W, 1.5 Co, 3.0 Cu, Nb 0.5, .2 N	Lower-cost structural material, with better corrosion and creep resistance than 316 SS at higher temperatures
Haynes 282	High temperature portion of high temperature system HEX	0.2 Fe, 58 Ni, 19.3 Cr 1.4 Al, 8.3 Mo, 0.1 Mn, 0.06 Si, 10.3 Co, 2.2 Ti	Higher cost and stronger structural material that has good corrosion resistance at higher temperatures and higher creep resistance
Haynes 230	High temperature portion of high temperature system HEX	1.5 Fe, 60.5 Ni, 22.6 Cr, 0.3 Al, 1.4 Mo, 0.5 Mn, 0.4 Si, 12.3 W	Higher cost and stronger structural material that has good corrosion resistance at higher temperatures and is ASME code certified

High Nickel Content Braze Compositions

	Solidus [°C]	Liquidus [°C]	Diff	Cr	Si	Fe	Ni	P	B	C
BNi-1	977	1038	61	14	4	4.5	Bal		3.0	0.75
BNi-1a	970	1075	105	14	4.5	4.5	Bal		3.0	0.06 max
BNi-2	971	999	28	7	4.5		Bal	0.02	3.1	0.06 max
BNi-3	982	1038	56	0	4.5		Bal	0	3.1	0.06 max
BNi-5a	1052	1144	92	19	7.3	0	Bal	0	1.5	0.08
BNi-5b	1030	1126	96	15	7.3	0	Bal	0	1.4	0.06
BNi-6	877	877	0	0	0		Bal	11.0	0	
BNI-14	943	1071	128	22	6.5		Bal	4.5		
Amdry 105	990	1010	20	23	6.5	0	Bal	4.5	0	0
Amdry 108	1025	1055	30	23	6.5	15	Bal	4.5	0	0
Amdry 805	1075	1105	30	29	6.5	Bal	15	6.5	0	0
Nicrobraz 31 “BNi-14”	985			22	6.5	0	Bal	4.5	0	0
Nicrobraz 33	970	1045	75	29	6.5	0	Bal	6.0		
Nicrobraz 152	943	1024	81	30	4.0	0	Bal	6.0		
Niferobraz 9080				29.5	7	37.5	20	6.0	0	0

- **NB33 and NB152 high Cr and Si with potential corrosion resistance**
- **Amdry 386 has high Al content (14% Al, 21% Cr, 0.7% Si, 26% Co) and can be mixed with Amdry 105 to achieve a braze compound with needed aluminum content**

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High Nickel Content
Custom Braze Compositions

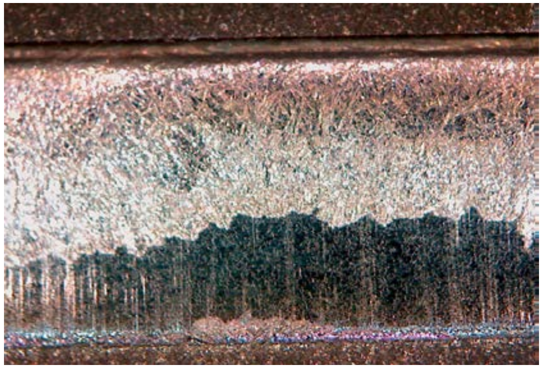
Mixture of Amdry 105 and Amdry 386 gives high Cr, Si and Al content braze

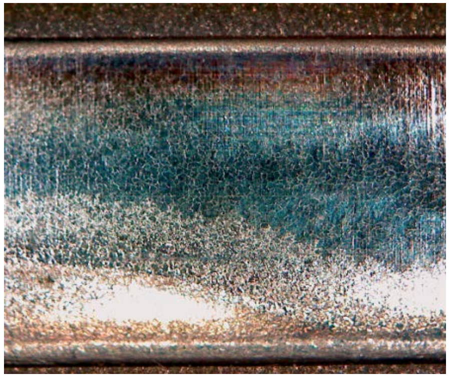
Compound 1		Compound 2		Ni	Cr	Co	Si	Al	Y	P	Fe	Hf	Melt Supp.	Corr. Prot.
	%		%	%	%	%	%	%	%	%	%	%	%	%
Amdry 105	90%	Amdry 386	10%	64.16	22.4	2.2	5.44	1.2	0.05	4.5	0	0.05	9.94	29.04
Amdry 105	80%	Amdry 386	20%	62.32	21.8	4.4	4.88	2.4	0.1	4	0	0.1	8.88	29.08
Amdry 105	70%	Amdry 386	30%	60.48	21.2	6.6	4.32	3.6	0.15	3.5	0	0.15	7.82	29.12
Amdry 105	60%	Amdry 386	40%	58.64	20.6	8.8	3.76	4.8	0.2	3	0	0.2	6.76	29.16

- **Cr >20.6%, Si>3.76%, Al >1.2% with total corrosion barrier components similar for mixes**
- **Melt temperature suppressants (Si, P) decrease as Al content increases – total spans low to upper range of braze compounds**

Braze Compound Spreadability

Braze migration from joint application not adequate for complete coverage and must braze coat all components for acceptable coverage of surface





Peel Type Joints

Butt Type Joints

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Braze Application to Washers and Coupons

Several braze compound application methods have been successfully applied for forming strong joints

Braze alloy application methods	Notes/Comments
Roller	Can be used to apply custom powder slurries to non-uniform surfaces
Spray	Can be used to apply custom powder slurries to non-uniform surfaces.
Wet chemistry (electroplating)	Electroless plating of nickel-phos is widely available, and has been used on other Altex HEX's. Custom alloy plating may be possible, or plating/coating of multiple layers.
Transfer tape	Used in earlier tests with good results. Custom alloy formulations possible. Possible issues with scaling up process.
Foil	Unclear as to what custom formulations are possible
Paste	Probably applied via spray or roller
Silk screen	Can apply a slurry over large surfaces, or specific patterns
PVD coating	May be used to apply silicon and chrome only to nickel plated layer. Not a good fit for thick films (> a few microns)

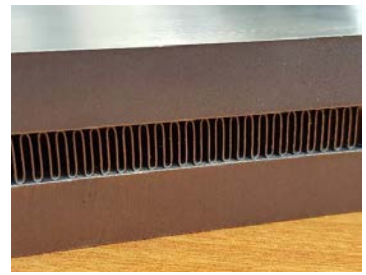
Low cost spray application selected for LAB-CB to completely cover surface

Bonding and Corrosion Test Coupons

Braze compound coated washers used in corrosion tests with heat exchanger structure coupons used to determine braze bond strength

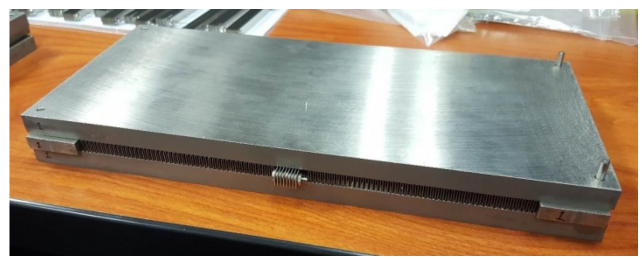
SS 316 Stainless Steel

Haynes 282



316 SS

316 SS



316 SS

HR 282

Heat Exchanger Structure Coupons

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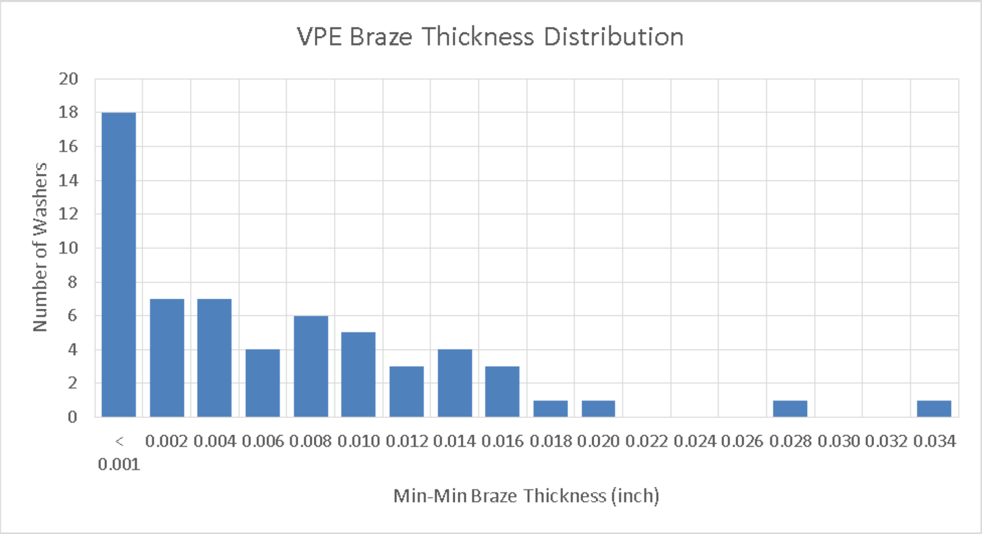
Spray Application of Braze to Washer Coupons

Can produce range of braze layer thicknesses by spray application



- **By setting spray pressure, distance, timing and number of passes, .002” or .004” layer braze thicknesses can be consistently produced**
- **While washer face layer thicknesses are consistent, sharp outer edges “pin” layer on washer coupons**

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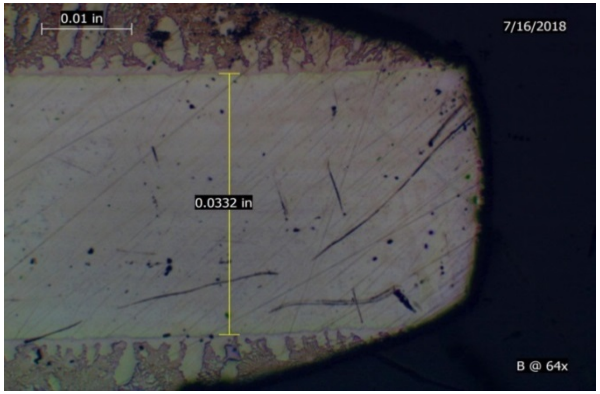
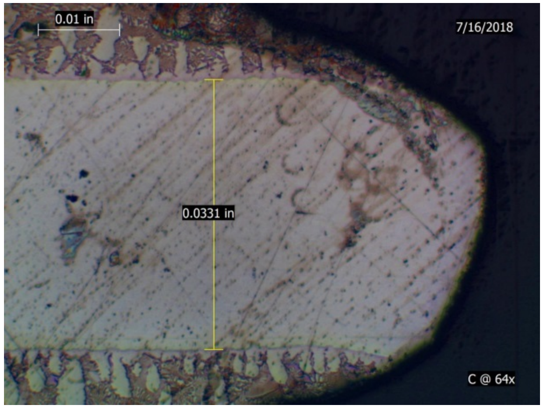
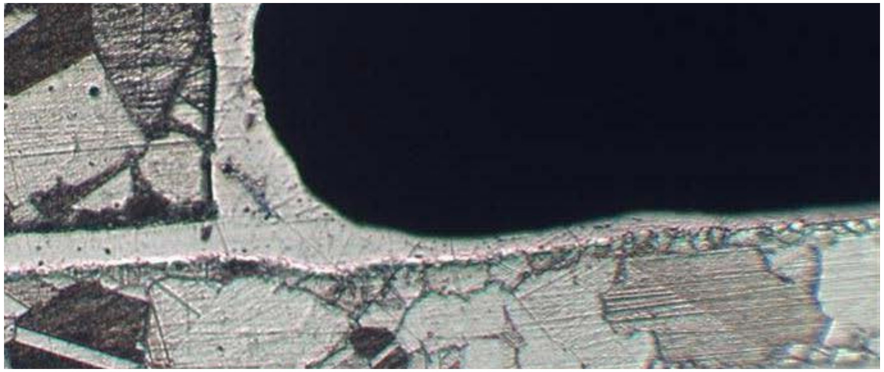
Edge Coating Effects for Test Coupons and HEX Components

Sharp outer edges on coupons reduce braze layer thickness at edges while inner edges on HEX components increase layer thickness at corners





- **Coupons with sharp outer edges have "pinning" of layers at the edges**
- **Coupons with rounded outer edges have better coverage**



- **Heat exchanger components have inner edges with braze squeezed out of joints to create fillets to more fully cover edges and surfaces**

Braze Wettability and Spreadability

NB33 braze wettability and spreadability is an indicator of braze migration, base material coverage and adherence

- **Sanicro (top) – 96% spread,**
- **HR230 (bottom left) – 114%,**
- **HR 282 (bottom middle) – 64%**
- **316 SS (bottom right) – 160%**

- **NB 33 braze shows good wettability and spreadability on all base materials**

Braze Wettability and Spreadability

Braze wettability and spreadability for NB 152 is good for all base materials

- **Sanicro 25 (top) – 88% spread,**
- **HR230 (bottom left) – 106%,**
- **316 SS (bottom middle) – 172%**
- **HR 282 (bottom right) – 59%**

- **NB152 shows good wettability and spreadability on all base materials**

Braze Wettability and Spreadability

Wettability and spreadability of Amdry 105/Amdry 386 mixtures increases as Amdry 386 and aluminum content decreases

3.6% Al
6% spread

2.4% Al
46% spread

1.2% Al
54% spread

Aluminum content may be limited to less than 3% due to reduced wettability and spreadability

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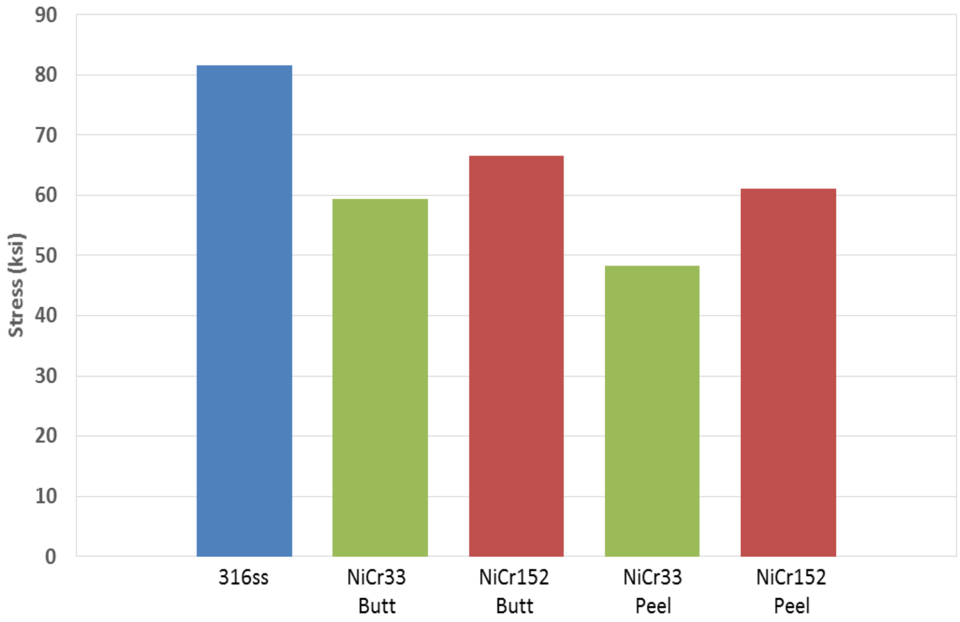
LAB-CB Joint Strength Results

LAB-CB joint strength is very good, particularly at operating conditions

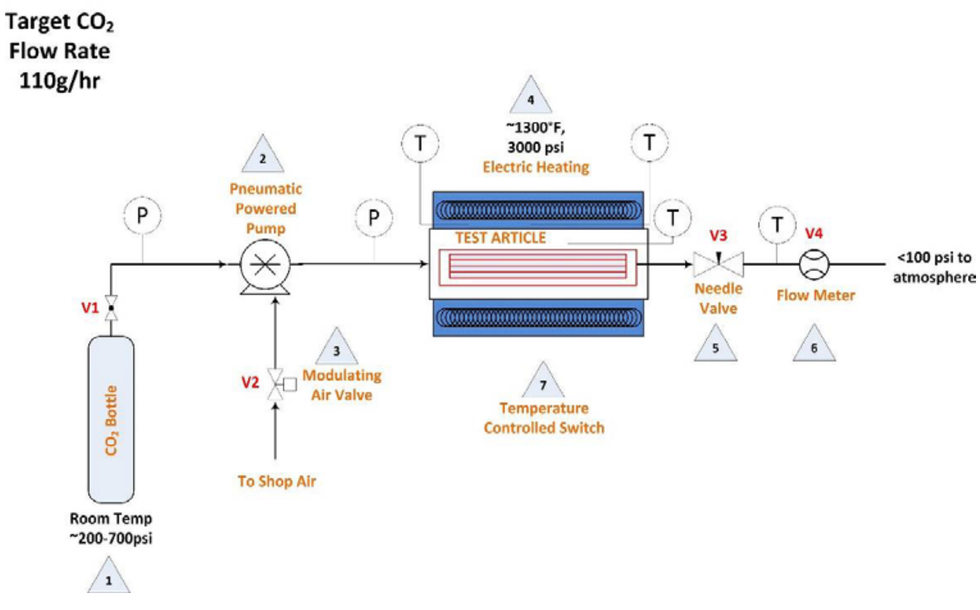


- NB 33 and NB152 braze with 316SS creates high strength butt joints at room temperature
- Up to 83% of 316SS strength
- Peel joints have lower strength than butt joints

- At 910C NB 33 butt joints have 101% of 316SS tensile strength

Original Corrosion Test Apparatus

High pressure (200 bar) tube furnace with ScCO2 flow and temperatures up to 750C



Washer Coupons on Support Rod

Enhanced Capability Corrosion Test Apparatus

Further corrosion testing in new higher capacity test system

- Testing of over 80 samples possible
- 200 bar pressure and 750 C maximum temperature
- Results will be used to support model

Washer Corrosion Sample Appearance

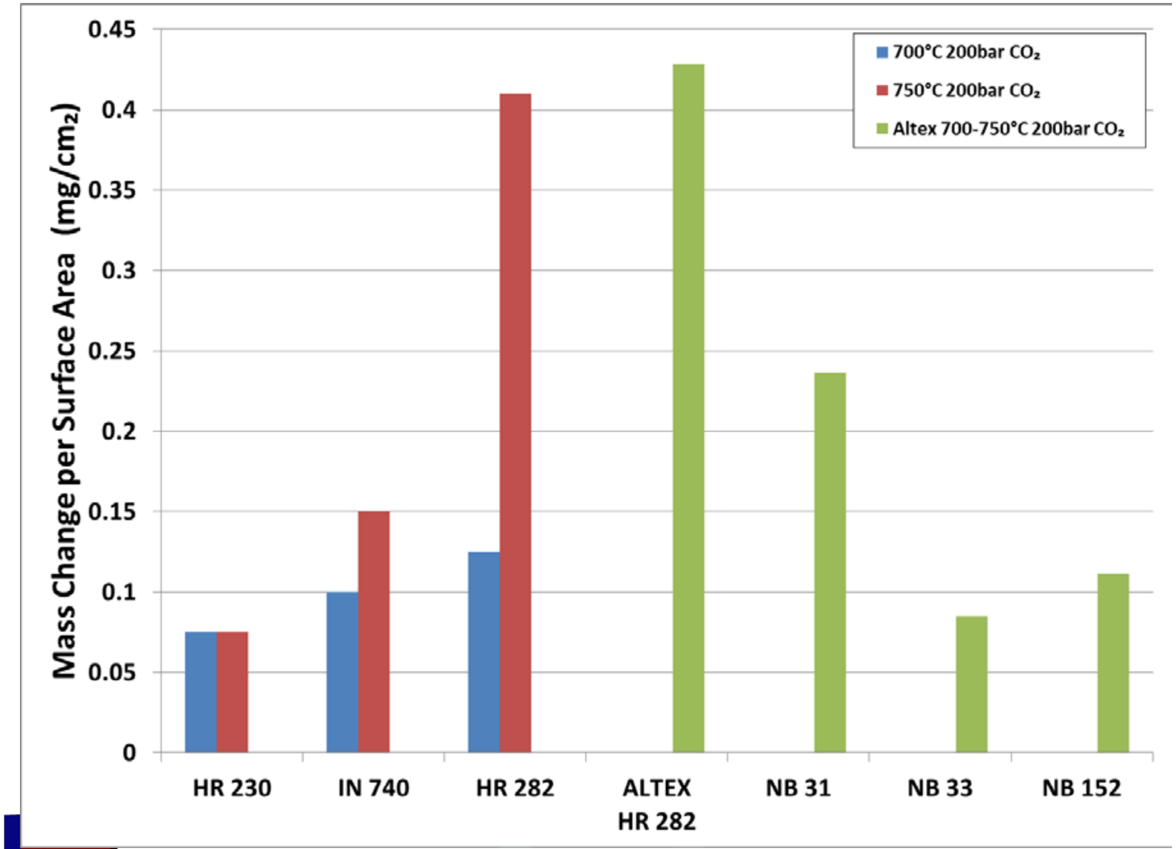
Typical high nickel alloy and stainless steel corrosion appearance

- Modest surface corrosion with nickel alloy and braze coated coupons

- Major surface corrosion and scaling and flaking with 316 SS

Braze Coated 316 SS Washer Coupon and High Nickel Alloy Corrosion Comparison

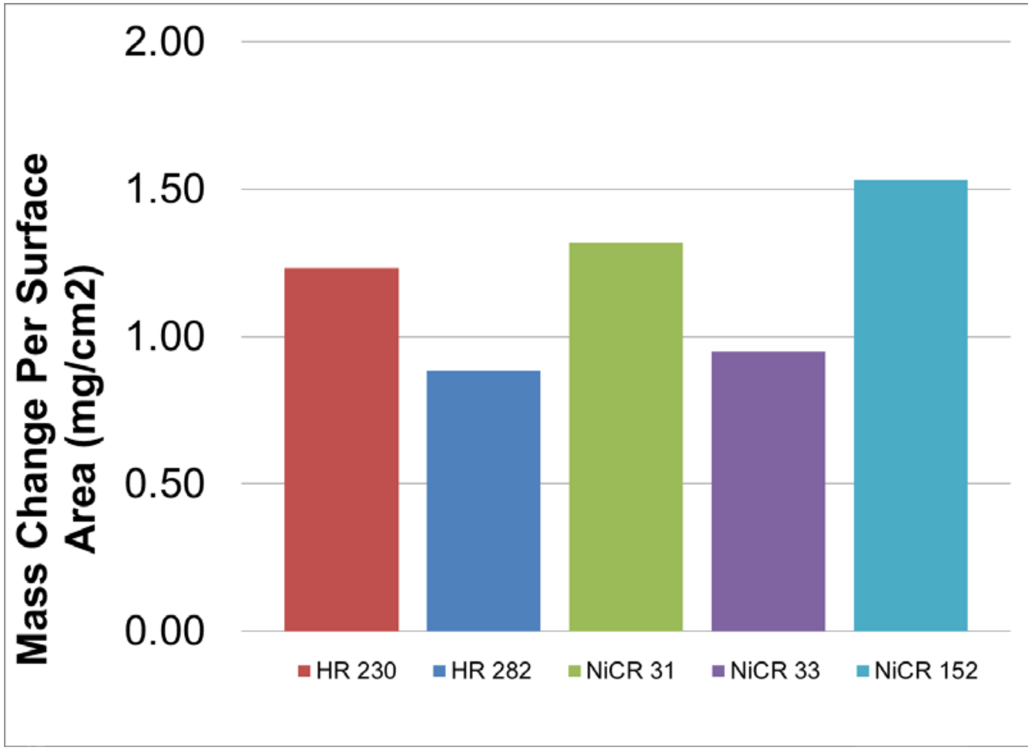
Corrosion resistance of braze coated 316 SS washer coupons as good as high nickel alloy results



- Lowest Cr (19.3%) HR 282 has lowest corrosion resistance
- Lowest Cr (22%) NB31 coated 316SShas the lowest corrosion resistance
- Braze compounds have higher Cr contents (up to 28%) and much higher Si contents (up to 1000%) than high nickel alloys
- LAB-CB has good corrosion resistance and strength

Braze Coated 316 SS Washer Coupon and High Nickel Alloy Corrosion Comparison

Braze coated 316SS as good as high nickel alloy corrosion resistance at 925C



- **Much higher temperature drives order of magnitude higher corrosion rates**
- **NB33 braze with high Cr gives best corrosion resistance at lower and high temperature**
- **HR 282 with high Al is more resistant than HR230**

- **Braze coated 316SS has similar corrosion resistance to high nickel alloys at ultra high temperature**

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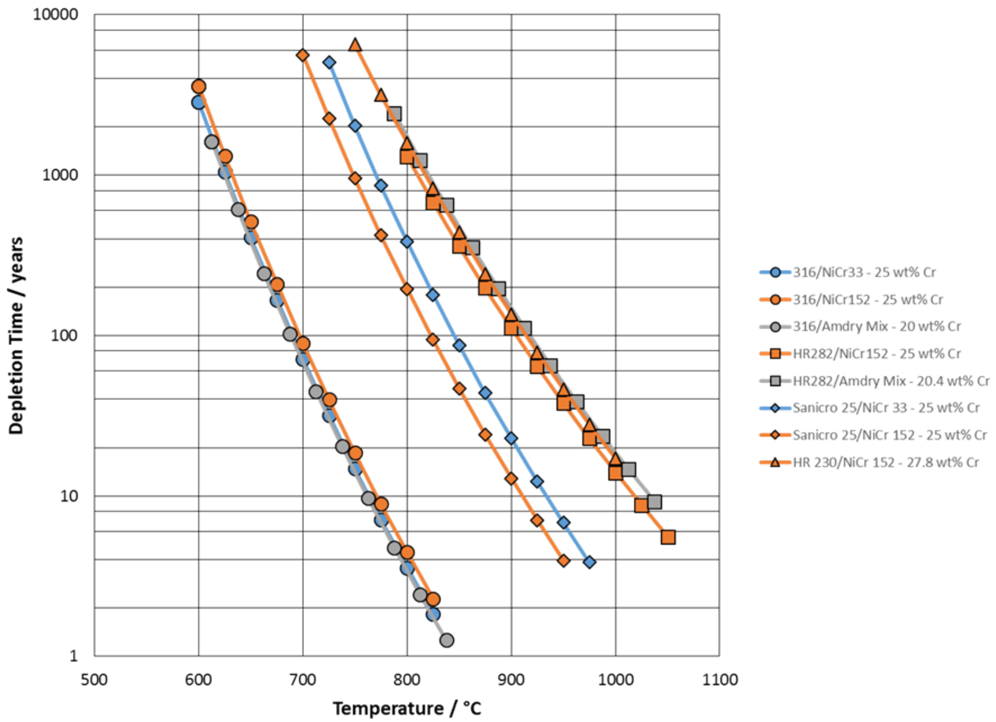
Long-Term Integrity of Corrosion Resistant Layer

Long-term diffusion of layer components into base material could impact layer corrosion resistance



At operating temperatures of interest chrome depletion from layer takes over a hundred years

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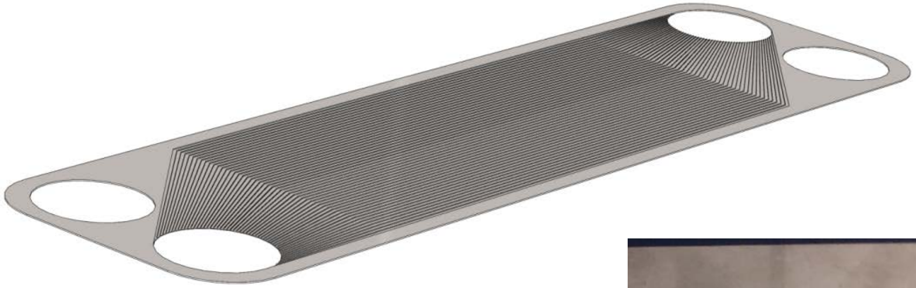
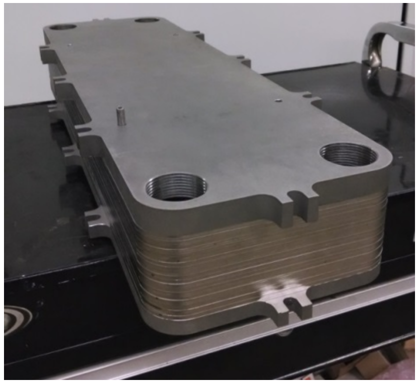
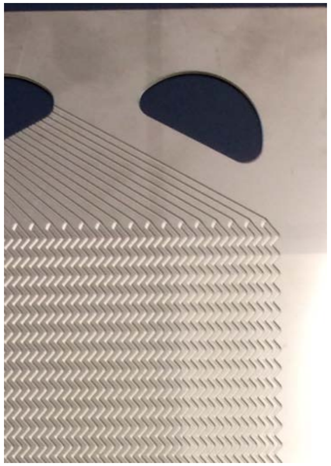
Heat Exchanger Design

LAB-CB bonded and corrosion resistant HEX design







- HEX components configured for easy and complete coating of LAB-CB compound
- VPEI-PCHE plates with etched HEX channels with channel dimensions that account for coating thickness
- Inner edges for creating LAB-CB fillets between parts and full coating of surface for maximum corrosion resistance as well as good bonding

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Summary Conclusions

- Selected braze compounds have multiple oxide barrier formers (Cr oxides, Si oxides) that modify base material (eg. 316SS) surface characteristics to enhance HEX corrosion resistance as well as form good joints
- Aluminum can be added to selected braze compounds to further enhance corrosion resistance
- LAB-CB has shown good results to date:

1. Wettabilty and spreadability tests show that four out of the five braze compounds have good joint and layer adherence potential, with 3.6% Al braze compound with less potential
2. Butt joint strength is up to 83% of 316SS base material strength at room temperature and exceeds 316SS base material strength at 910C – demonstrates good adherence at conditions of interest
3. Corrosion resistance with braze coated 316SS base material is similar to high Ni alloy resistance at both 750C and 925C and 200bar – order of magnitude better resistance than uncoated 316SS
4. Heat exchanger designed for good compatibility with LAB-CB to maximize strength, corrosion resistance and performance at the lowest cost