



Materials Evaluation and Corrosion Test Needs for a Direct-Fired sCO₂ Oxy- Combustion Plant

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Presentation Overview



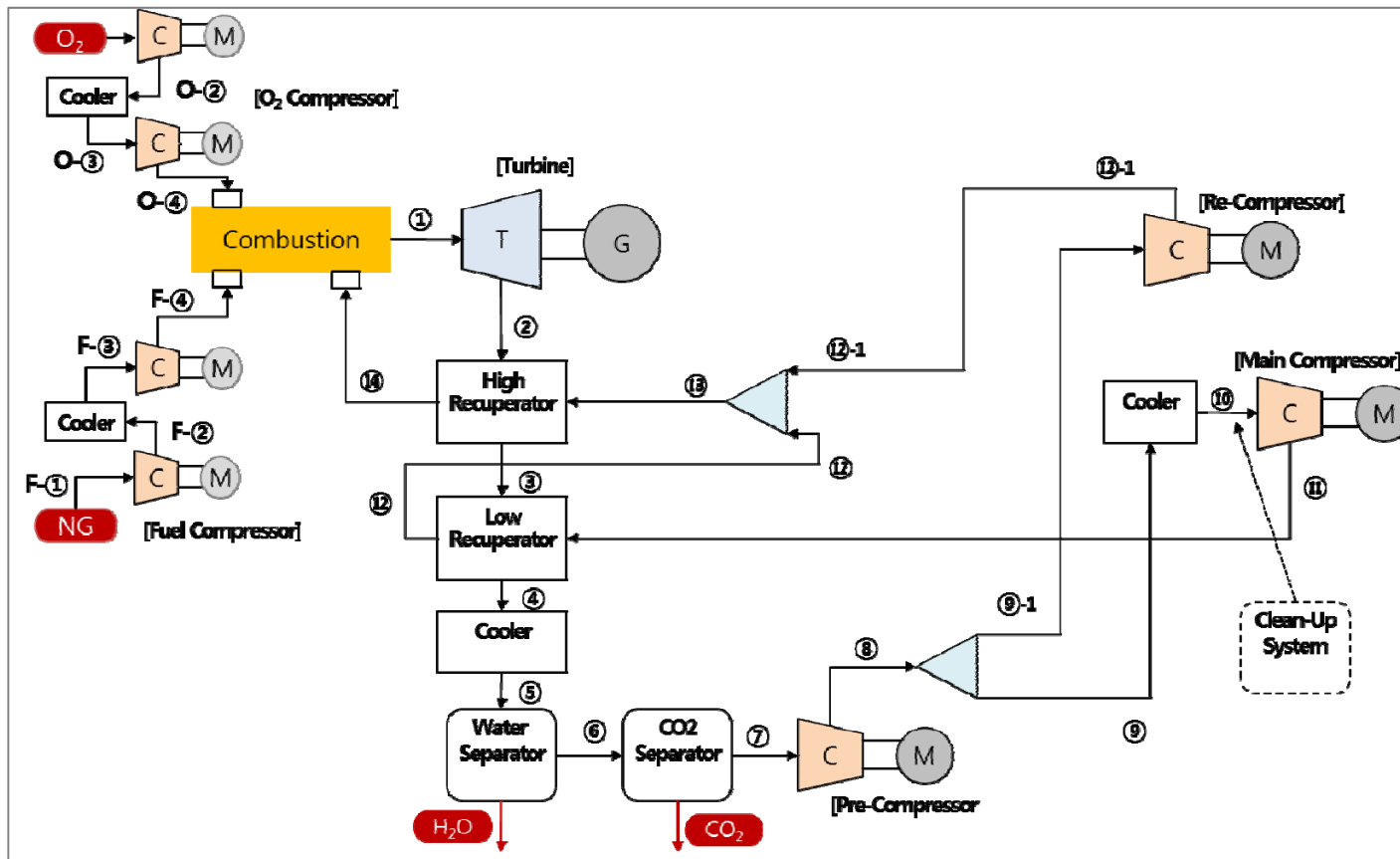
- Oxy-Combustion Application
- Overview of Materials
- Existing Test Data & Oxy-Combustion Variables of Interest
- Materials of Interest
 - 400 – 500 °C
 - 650 – 750 °C
- Future Test Needs and Recommendations

Oxy-Combustion Plant Application



- sCO₂ oxy-combustion cycles have potential for
 - High thermal and plant efficiencies
 - Reduced CO₂ emissions
- KEPCO Research Institute leading project to develop an oxy-combustion gas turbine power plant
 - Minimize development risk with maximum turbine inlet conditions of 750 °C and 300 bara.
 - Hanwha Power Systems (turbomachinery)
 - Southwest Research Institute (ox-combustor)
 - Other academic Institutions in Korea and U.S.

What's an Oxy-Combustion sCO₂ Cycle?



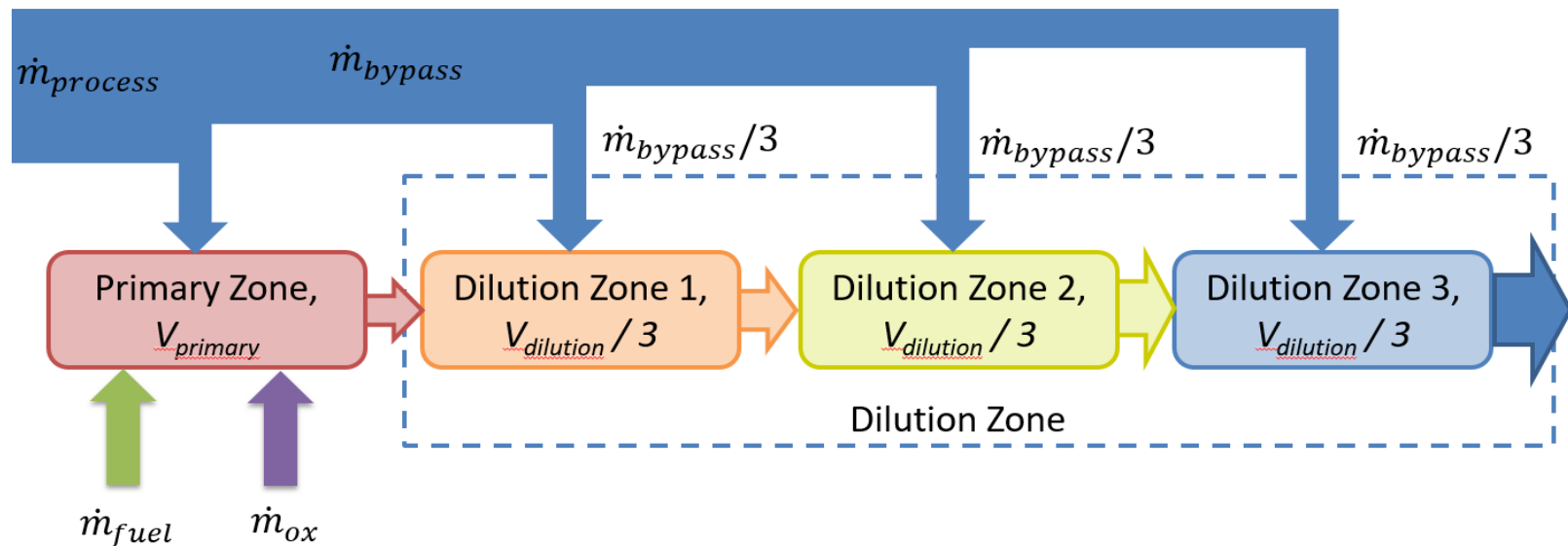
Closed Loop Composition is Affected by Air Separation, Combustion, and Cleanup

SCO₂ MATERIALS FOR OXY-COMBUSTION

Oxy-Combustor Material Needs



- Combustor pressure vessel at process temperature
- Injector, liner cooled by process but at higher temperatures, lower stress
 - 400 – 500 °C
- Two temperature ranges identified :
 - 650 – 750 °C



Why Focus on Corrosion?



- The **majority of metal alloys** will corrode.
- Corrosion affects **every industry**: Infrastructure, Utilities, Transportation, Production & Manufacturing, Government
- Engineering design usually increase corrosion issues.
- Corrosion is **expensive**: estimated between B\$575 (3.1% GDP) to T\$1.1 (6% GDP).

Materials Deterioration in sCO₂



- **Corrosion:**

- Reaction of metals with oxygen.
- Oxygen comes from: $\text{CO}_2 = 0.5 \text{ O}_2 + \text{CO}$.
- Growth of oxide film layer.

- **Carburization:**

- Cr reacts with C → chromium carbide.
- Carbon penetrate through grain boundary.
- Carburization leads to spallation of oxide films.

Materials of Interest



- 5 families of materials:
 - **MFSS: martensitic** stainless steels (10%-30% Cr) and **ferritic** stainless steels (12%-17% Cr with 0.15 – 0.63% C)
 - **ASS: austenitic** stainless steels (16 to 30% chromium and 2 to 20% nickel).
 - **Al SS: alumina oxide** austenitic **stainless steels**.
 - **CrNi: chromium nickel** alloys.
 - **AlNi: alumina oxide nickel** alloys.

Experimental Methods Summary



Method	Measure	Pros	Cons
Weight measurement	Oxide film growth	<ul style="list-style-type: none"> • Easy • Cheap 	<ul style="list-style-type: none"> • No carburization/corrosion product differentiation. • Spallation and material loss affect measurement.
Micro hardness	Carburization	Easy	Coupled with SEM/EDS to confirm carburization
SEM/EDS	Oxide film morphology and composition		
Tensile test	mechanical properties	Environmental effect on mechanical properties	Only after exposure
GENERAL			Lack of in-situ (HTHP problem)

Effect of Temperature



Temperature ↗ = worsen corrosion, increase carburization

Temperature (°C)	300	350	400	450	500	550	660	650	700	750	800	850	900
Type of alloy													
Martensitic & Ferritic	Green				Red								
Austenitic	Green								Red				
Alumina SS	Red											Green	
Chromium Ni	Green										Red		
Alumina Ni	Red											Green	

Based on combination of mass gain, oxide thickness, presence of crack, carburization, etc...:

Green: acceptable

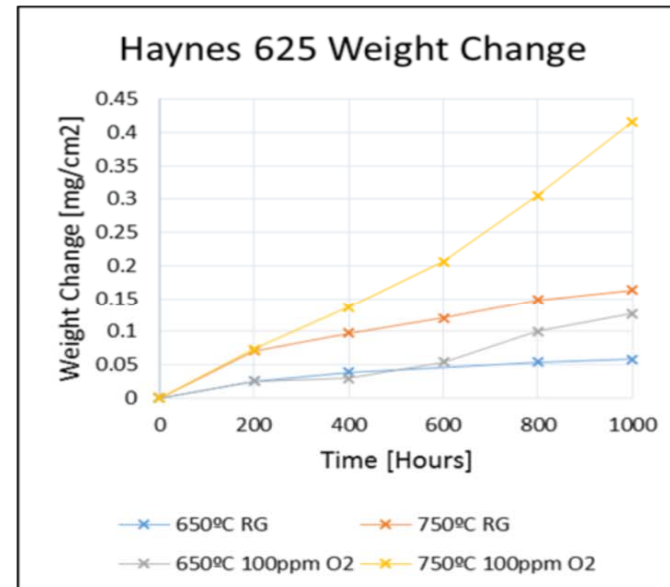
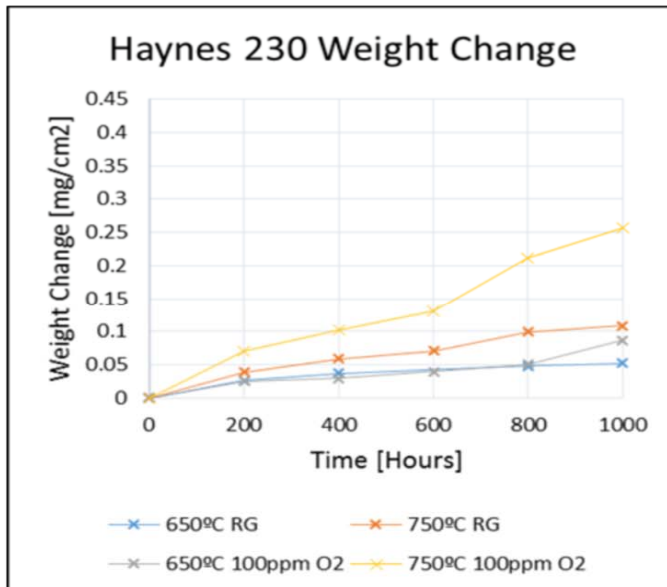
Red: avoid

Alumina alloys are not good at low temperature because the alumina oxide does not form fast enough.

Contamination of sCO₂ with O₂



- Contamination with O₂, water, and combination of both.
 - O₂: may be beneficial or detrimental.
 - Water: accelerates corrosion.
 - Combination: accelerates corrosion.

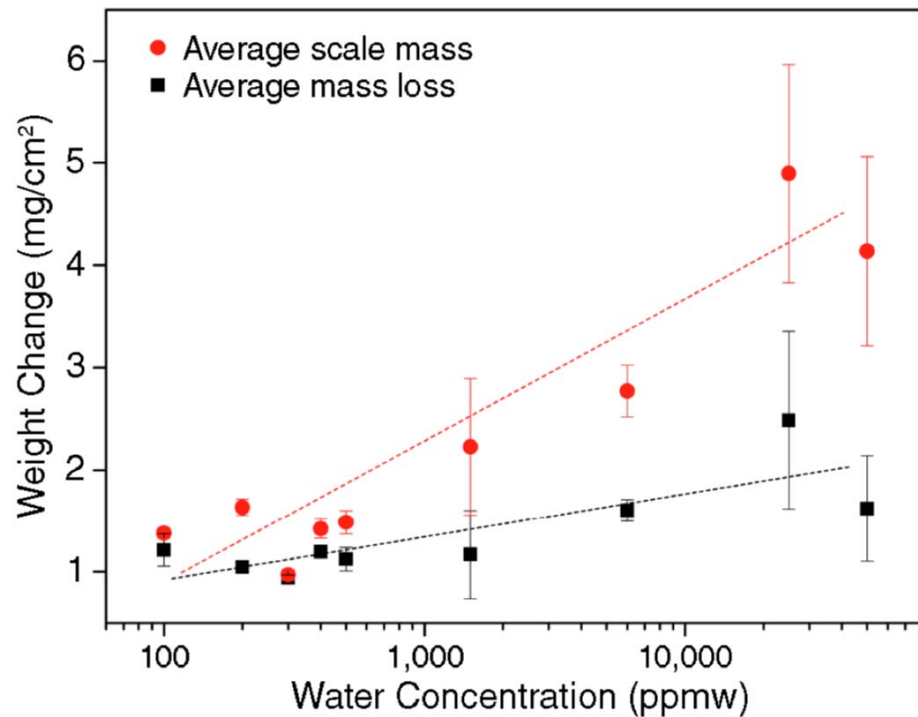


sCO₂ MA Mahaffey, J., et al., 5th Symposium on sCO₂ Power Cycles, , 2016, Paper #114.

Contamination of sCO₂ with H₂O



- Contamination with water accelerates corrosion.
- Impact of water on weight change in sCO₂ at 8 MPa, 40°C.



Coating



- Thermal barrier coating (TBC) for corrosion protection:
 - Diffusion bond coatings (Pt diffusion or simple or Pt-modified aluminide) with commercially vapor-deposited yttria-stabilized zirconia (YSZ) top coatings.
 - High velocity oxygen fuel (HVOF) sprayed MCrAlYHfSi bond coatings with air-plasma sprayed YSZ top coatings.
- Data only at higher temperature (1150°C): failure after 2260 1 hr cycles.
- CO₂ and/or air contamination reduces the time to failure.
- Intrinsic damages: oxide growth, internal stresses leading to cracking and failure.
- Extrinsic damages: erosion, local damages due to impact or particles melting, diffusing, and hardening the top coat leading to potential failure.

Chosen Materials – 400-500°C Combustor Inlet & Pressure Vessel



Trade Name	UNS	Standard Specification	Notes	Max Temperature Limit [°C] (BPV Code Section)	Allowable Stress at 500°C [MPa]
Gr91	K90901	ASTM A387 Grade 91 Class 2	Reference. Most commonly tested MFSS.	649 (VIII-2)	204
800H	N08800	ASTM B407		816 (VIII-2)	138
310	S31000	ASTM A965		816 (VIII-2)	116
347H/347HF G	S34709	ASTM A965		816 (VIII-2)	125

Alternative Materials – 400-500°C Combustor Inlet & Pressure Vessel



Trade Name	UNS	Standard Specification	Max Temperature Limit [°C] (BPV Code Section)	Allowable Stress at 500°C [MPa]
625	N06625	ASTM B443	593 (I) or 649 (VIII-1)	192
HK40	J94204	ASTM A351	-	-
HK50	J94224	ASTM A297	-	-
310HCbN/HR3C	S31042	ASTM A959	732 (I)	117-158
NF709	S31025	ASTM A213	-	-
HR120	N08120	ASTM B515	899 (VIII-1)	113-153

Chosen Materials – 650-750°C Combustor Exit & Liner



Trade Name	UNS	Standard Specs	Max Temperature Limit [°C] (BPV Code Section)	Allowable Stress at 500°C [MPa]	Yield Strength at 750-760°C [MPa]	Creep Rupture Strength at 750°C [MPa] (hr)
740H	N07740	ASTM B983	800 (I)	84.1	596	200 (10k)
282	N07208	ASTM B637-12	800 (est.)	105 (est.)	612	186 (10k)
230	N06230	ASTM B572-06	982 (VIII-1)	50.8	323	91-98 (10k)

Alternative Materials – 650-750°C Combustor Exit & Liner

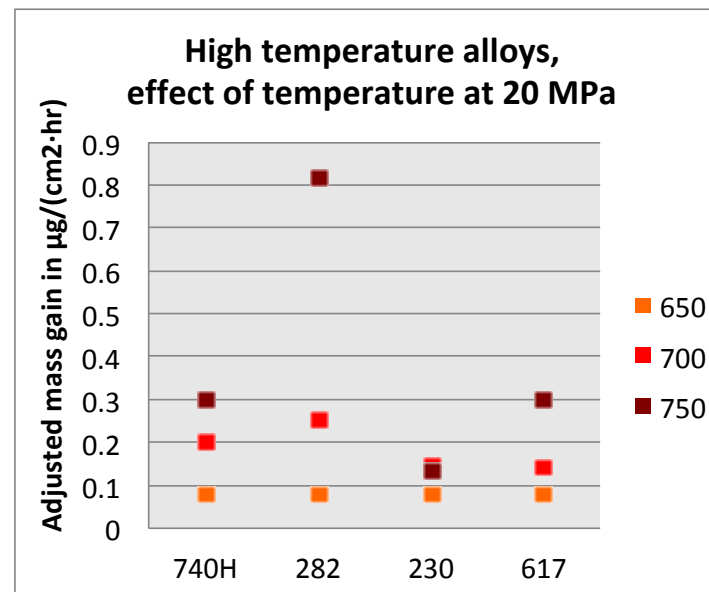
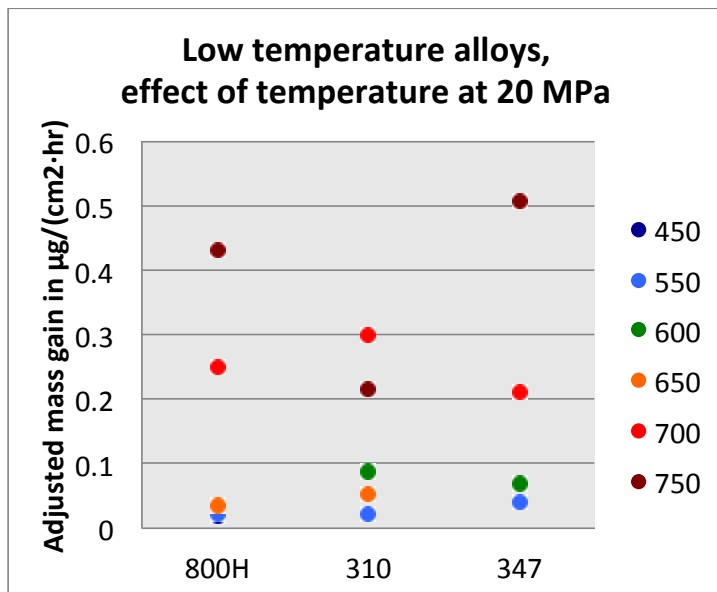


Trade Name	UNS	Standard Specs	Max Temperature Limit [°C] (BPV Code Section)	Allowable Stress at 500°C [MPa]	Yield Strength at 750-760°C [MPa]	Creep Rupture Strength at 750°C [MPa] (hr)
Waspaloy	N07001	ASTM B637	-	-	706	290 (1k)
Udimet 720	N07720	n/a	-	-	770	480 (1k)
Rene 41	N07041	SAE AS7469B	-	-	938	276 (1k)
617	N06617	ASTM B167	982 (VIII-1)	50.4	872	140 (1k)
MA 754	N07754	n/a	-	-	275	-
Hastelloy X	N06002	ASTM B572-06	482 (VIII-2)	-	218	107 (1k)

Proposed Materials: Existing Data in sCO₂, constant pressure.



- Data adjust to mass gain in $\mu\text{g}/(\text{cm}^2\cdot\text{hr})$ because not all tests are the same duration.
- Increase in mass gain with increase in temperature at 20 MPa.



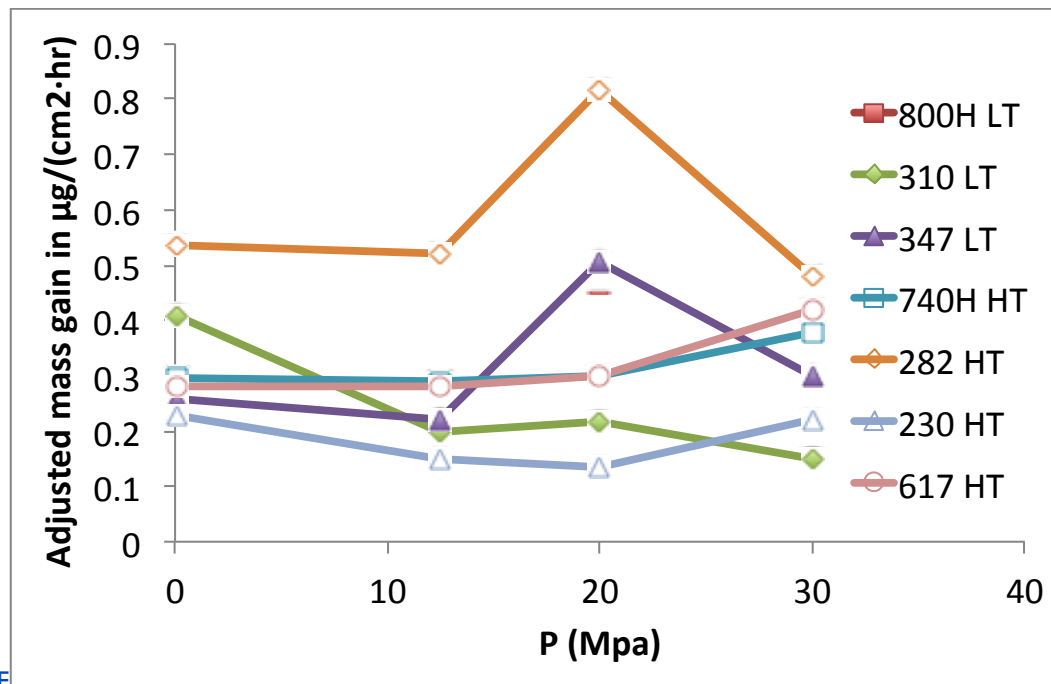
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 Pint, B.A., Keiser, J.R., 4th Symposium on sCO₂ Power Cycles, , 2014, Paper #61
 Pint, B.A., Keiser, J.R., JOM, 11, 2015
 Pint, B.A., et al., NACE Paper C2016-7747
 Pint, B.A., et al. 5th Symposium on sCO₂ Power Cycles, , 2016, Paper #56.

Proposed Materials: Existing Data in sCO₂, constant temperature.



- No visible trend of mass gain with increase in pressure at 750C.
- High temperature materials had lower mass gain than low temperature materials.



References:

- Mahaffey, J., et al.**, 5th Symposium on sCO₂ Power Cycles, , 2016, Paper #114.
- Pint, B.A., Keiser, J.R.**, 4th Symposium on sCO₂ Power Cycles, , 2014, Paper #61
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Test Plan – Variables of Interest

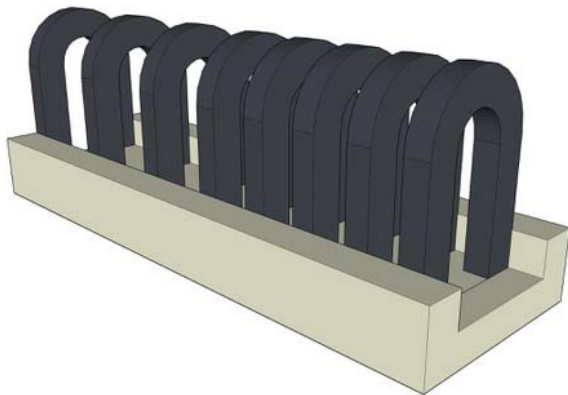


- Temperature: low (combustor inlet) and high (high temperature)
- Pressure: high pressure based on design
- Contamination (O_2 , H_2O): CO_2 , H_2O , and O_2 mixture matching predicted composition at combustor inlet (low temperature) and exit (high temperature).
- Welding: potential negative impact on the corrosion behavior of chromium-containing alloys

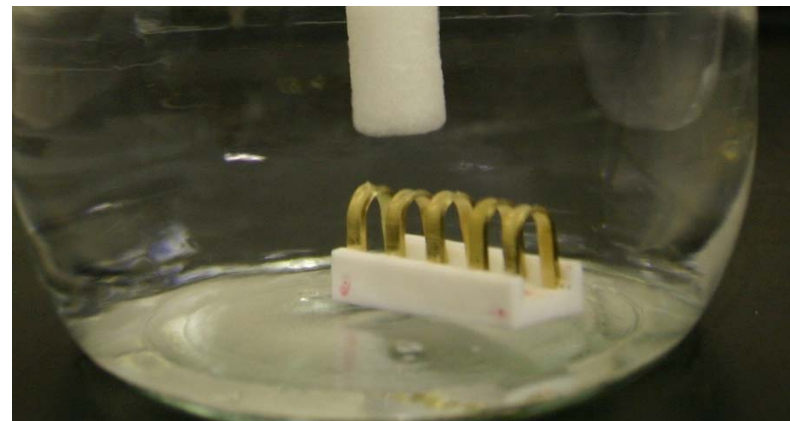
Test Plan – Variables of Interest



- Stress corrosion cracking: corrosion combined with stress can lead to early mechanical failure.
- Galvanic corrosion: corrosion may worsen when dissimilar materials are in contact.
- Coating: testing bare and coating materials vapor deposited YSZ, and air-plasma sprayed YSZ.



SCO2 MATE



Test Plan



- The recommended tests in O₂/H₂O/CO₂ are:
 - High Temp Weight Gain with Tensile Test
 - High Temp C-Ring/U bend
 - Low Temp Weight Gain with Tensile Test
 - High Temp Welding
 - Low Temp C-Ring/U bend
 - Micro hardness
- Statistic: 5 specimens for each test.
- Combine all low temperature and all high temperature.