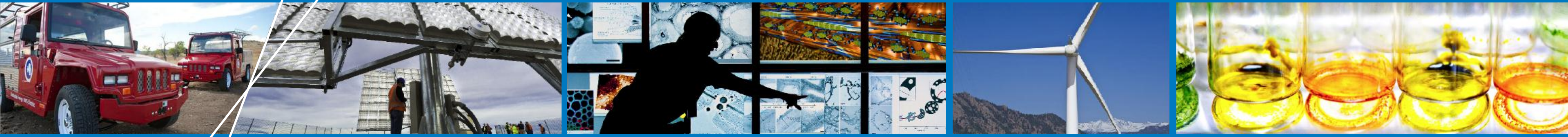
Degradation Mechanisms and Development of Protective Coatings for TES and HTF Containment Materials

October 2012 – September 2015



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Project Objectives

- Acquire understanding of fundamental degradation mechanisms of materials in molten salts, liquid aluminum alloys and supercritical CO_2 to design and evaluate potential coatings and/or surface modification techniques.

- Extend the lifetime of containment materials and thus reduce capital and maintenance costs.

- Develop and evaluate advanced protective coatings and surface modification techniques to achieve degradation rates lower than 30 µm/year, i.e., a material lifetime of 30 years.

Innovation

- Gain fundamental knowledge of degradation mechanisms in aggressive fluids at high temperatures.
- Develop protective coatings and working conditions for materials in contact with aggressive high temperature TES fluids and HTFs at the SunShot-relevant temperatures of 600 to 900°C.
- Develop coatings with low wettability by working fluids. Contact angles are measured at high temperatures under controlled atmospheres.

Technical Approach

- For molten salt corrosion, electrochemical techniques are employed to understand and control the hot corrosion mechanisms.
- Liquid aluminum alloys degradation are evaluated using immersion techniques.
- For supercritical CO_2 attack, autoclave and flow corrosion tests are used.
- First-principles molecular dynamics modeling is used to identify alloying elements that strengthen the grain boundaries and prevent metal embrittlement.
- Coatings are prepared and characterized for adhesion, wettability, and chemical qualitative analyses before degradation tests.

Project Tasks per Period

Phase 1 (FY13)

- Task 1.1: Identification and characterization of candidate protective coatings for particular molten salts and liquid metal alloys.
- Task 1.2: Electrochemical characterization of the substrate candidates.
- Task 1.3: Determine the effects of impurities in supercritical CO_2 on corrosion rates of different alloys (University of Wisconsin).

Phase 2 (FY14)

- Task 2.1: Electrochemical evaluation of coatings in molten salts.
- Task 2.2: Degradation evaluation of ceramic coatings in aluminum liquid metal alloys (LMA).
- Task 2.3: Study of surface treated materials and surface modification for performance improvement in s-CO_2 (University of Wisconsin).

Project Tasks per Period

Phase 3 (FY15)

- Task 3.1: Determination of re-deposition characteristics of Si coatings in the Al-Si eutectic alloy.
- Task 3.2: Fundamentals of degradation mechanisms of coated materials in aluminum liquid metal alloys (LMA).
- Task 3.3: Fundamentals of hot corrosion mechanisms of coated materials in molten salts.
- Task 3.4: Perform flow assisted corrosion tests and develop mechanistic corrosion model for alloys in s-CO2 in the presence of different impurities (University of Wisconsin).

Task 1.1: Methodology and Approach

- Selection of the fluids was performed using FactSage modeling, laboratory testing and results from previous work.

- Selection of the coating candidates was completed after evaluating current technologies applied to turbine blades and liquid aluminum containment materials.

- The wettability instrument was designed after evaluating current technologies.

- In the density-functional theory (DFT) simulations for liquid metal embrittlement, the total energies of grain boundaries (GBs) and GB-stabilized impurity phases were calculated.

Task 1.1: Results

Proposed fluids: Candidate molten salts and metal alloys have been prioritized in the following list for HTFs, and phase change material (PCM) for TES.

1. K_2CO_3 – 53.82 wt% Na_2CO_3 (PCM)
2. NaCl – 65.58 wt% LiCl (HTF)
3. Na_2CO_3 – 40.55 wt%NaCl (PCM)
4. Al–12.2 wt%Si (PCM for S-CO_2 system)
5. Al–51.42 wt%Mg (HTF)

Substrates to be evaluated in the electrochemical cell:

- High steel alloys, nickel superalloys and alumina forming alloys.

Task 1.1: Results

Proposed coating design process:

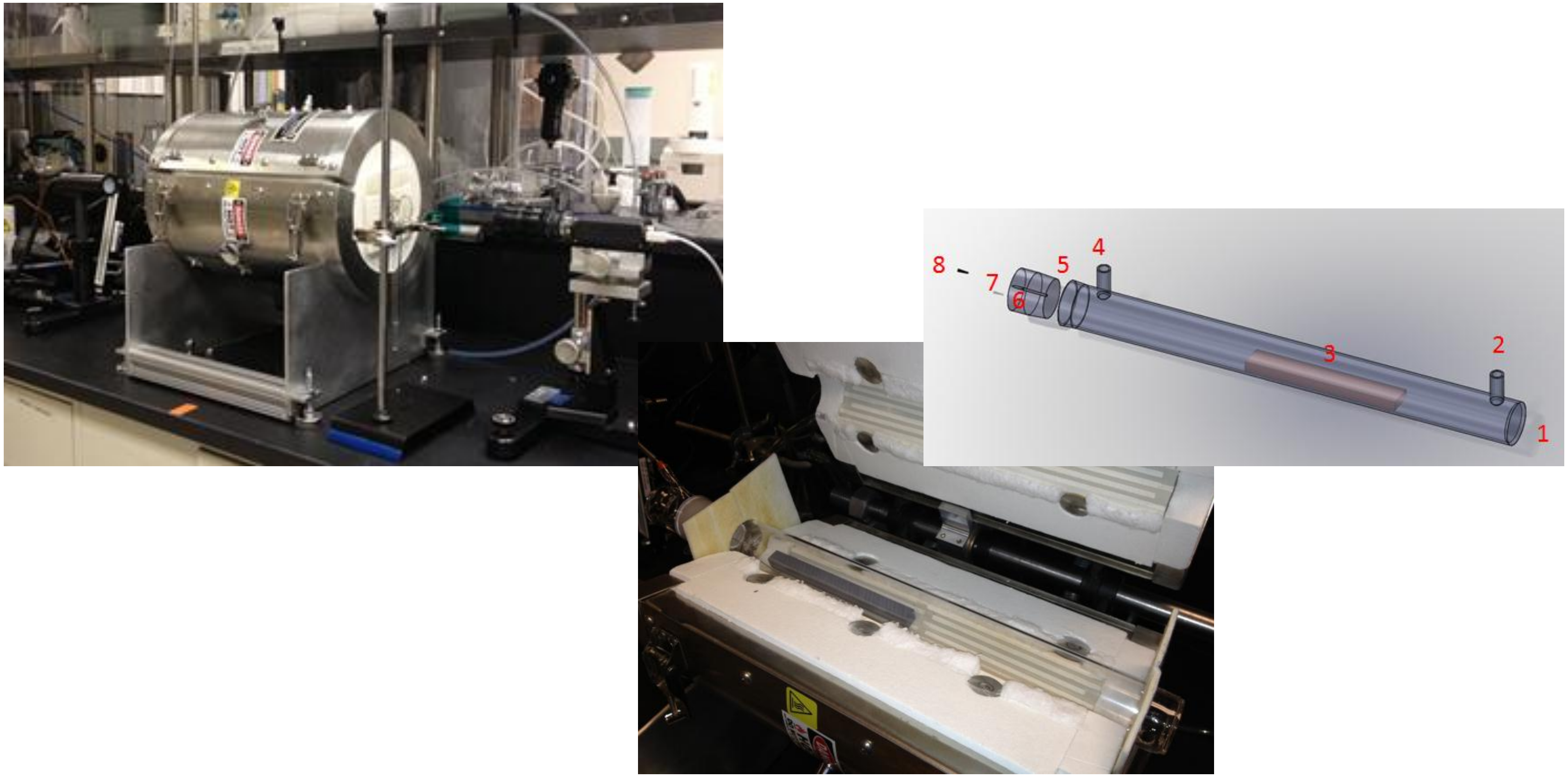
- A bond coat with similar composition to the substrate.
- Deposition of an outer layer of aluminum and controlled oxidation/annealing to form alumina.
- After step 2, deposition of alumina, aluminosilicate, or silica top coat .

Candidate coating deposition technologies:

- Sputtering, e-beam, and/or ion-beam assisted deposition will be used at NREL for preliminary coatings to evaluate adhesion and chemical qualitative behavior.
- For commercial applications - plasma spray and/or high-velocity oxy-fuel.

Goniometer for contact angle measurements (wettability)

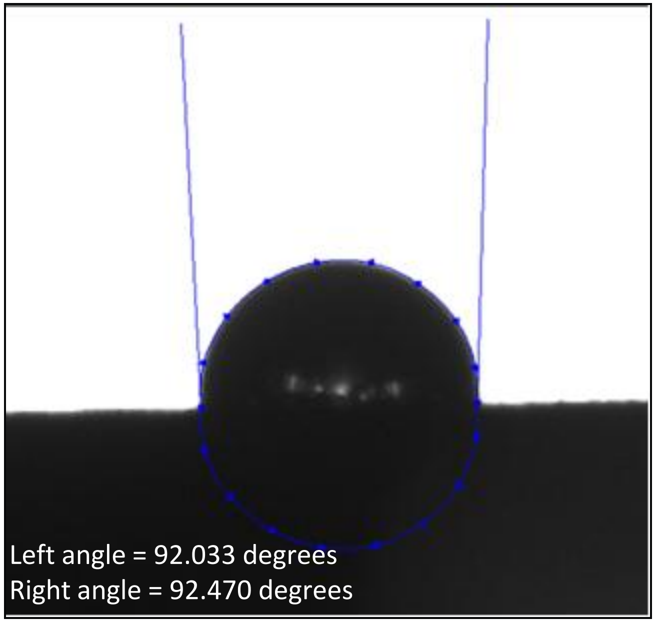
- 14” long split tubular furnace with air-tight quartz tube with inlet and outlet gas ports.



- Optics to give 13.5” working distance and 8.8mm x 6.5mm field of view (FOV).

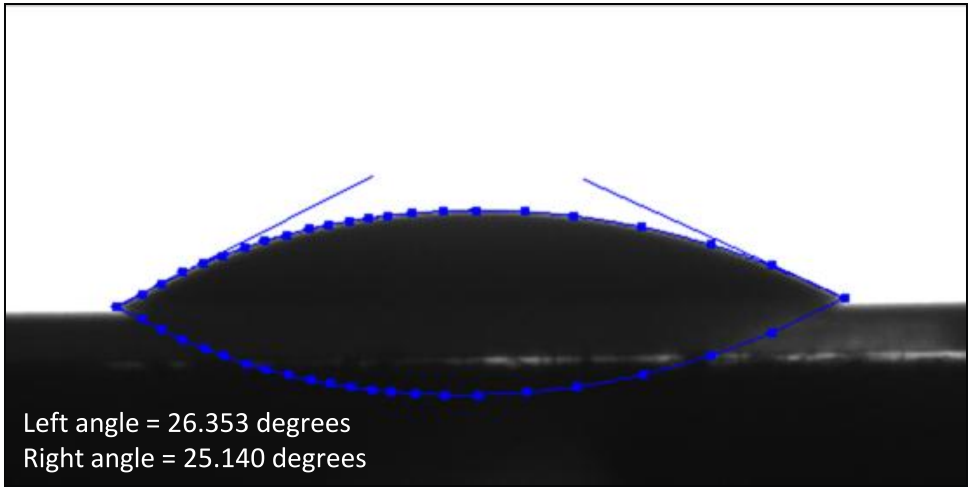
Goniometer for contact angle measurements (wettability)

- Images are processed using DropSnake software that utilizes the B-spline snake method [A. Stalder, *et al.* (2006). *Colloids and Surfaces A,* 286: 92].
- Instrument is being qualified using systems with known wettability to develop measurement protocols.



Left angle = 92.033 degrees
Right angle = 92.470 degrees

B_2O_3 on graphite, 500 °C, N_2 atmosphere.



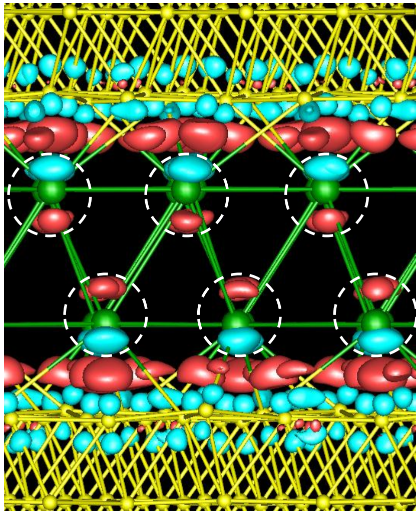
Left angle = 26.353 degrees
Right angle = 25.140 degrees

DI water on sapphire, room temperature, N_2 atmosphere.

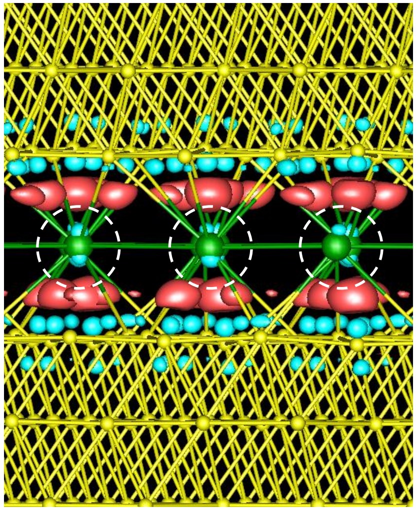
Molecular Dynamics Modeling of Metal Embrittlement

Microscopic origin of Bi bilayer phases stability

For the known system Bi-Ni, bismuth induces embrittlement in Ni grain boundaries (GB) because of the formation of Bi bilayer (BL) phases. The calculated bond strength of the Bi-Ni interfacial bonds for the bilayer was sufficiently larger than for the monolayer (ML).



Bismuth bilayer
Atomic dipoles at the Bi atoms due to Bi-Ni interaction



Bismuth monolayer
No atomic dipoles due to the symmetric Ni-Bi bond configuration

By forming the atomic dipoles at the Bi atoms, the Bi-Ni bond strength of the bilayer becomes enhanced by 24% as compared to that of the monolayer.

Modeling: Summary of Results to date

- Boron is being considered as an embrittlement preventing impurity in polycrystalline Ni.

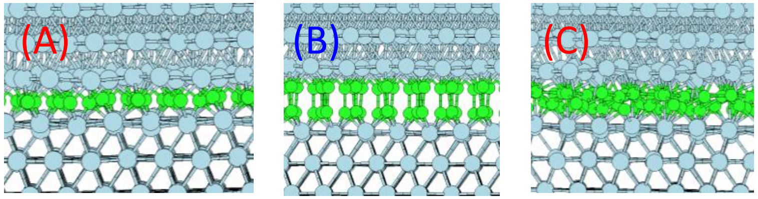
  - Boron atoms can be dissolved in the Ni matrix as substitution defect in nickel lattice positions ($B_{[Ni]}$) or as interstitial impurity atoms ($B_{[i]}$)
  - Calculations were performed on Ni twist GB with θ=21.8° and Ni tilt GB with Σ=5. The same trend was observed.
  - Formation energy of B impurities for $\mu_{Ni}=\mu_{Ni}$(bulk) and $\mu_B=\mu_B(B_{[i]}$ in Ni)

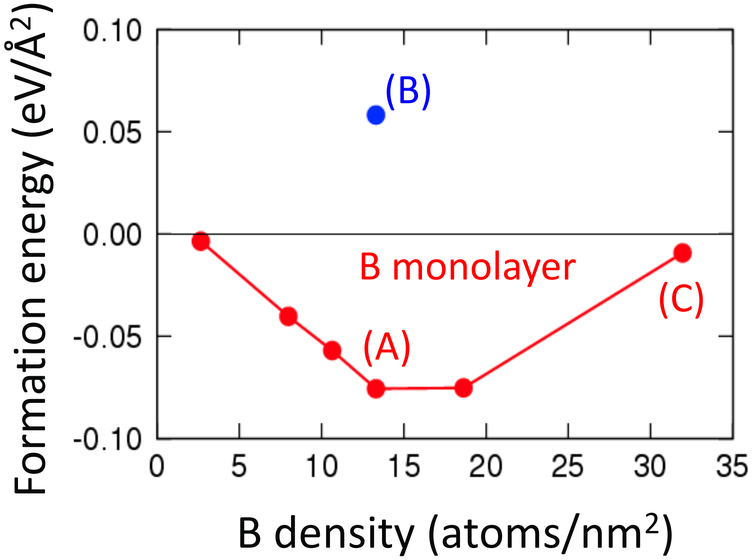
$B_{[Ni]}$(bulk): 0.53 eV
$B_{[Ni]}$(GB interface): 0.47 eV

$B_{[i]}$(bulk): 0 eV
$B_{[i]}$(GB interface): -0.19 eV

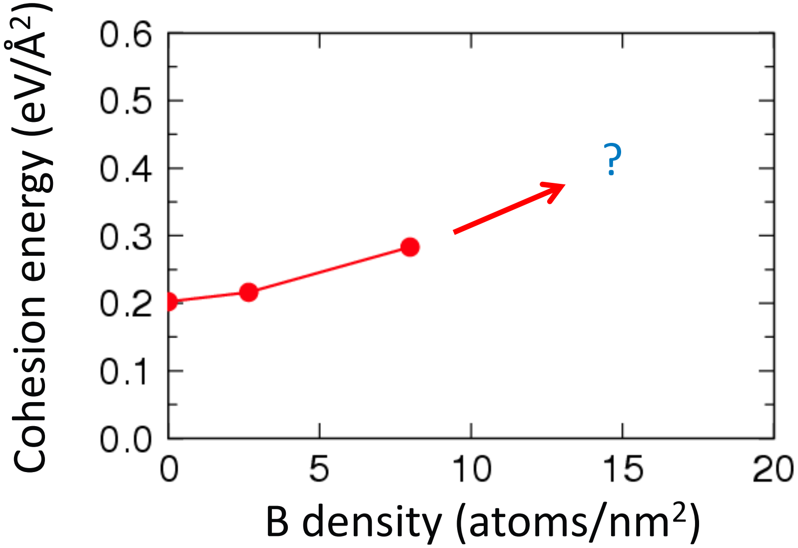
The B impurities in polycrystalline Ni exist as interstitial defects, which will be segregated into the GB region by annealing.

Modeling: Summary of Results to date



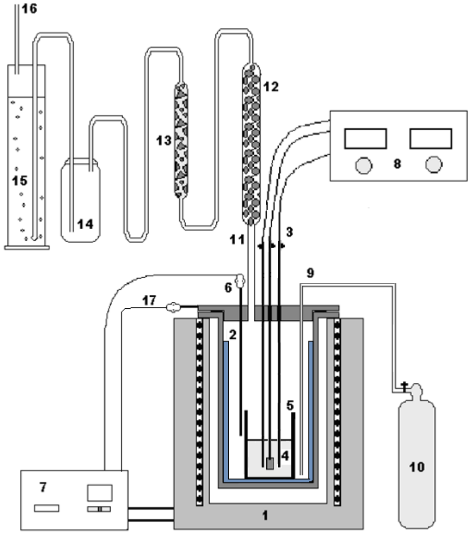


- Negative formation energy (i.e., $B_{(i)}$ segregation at GBs).
- B density at GB estimated to be around 15 atoms/nm².
- Positive formation energy for B bilayer phase (unstable).

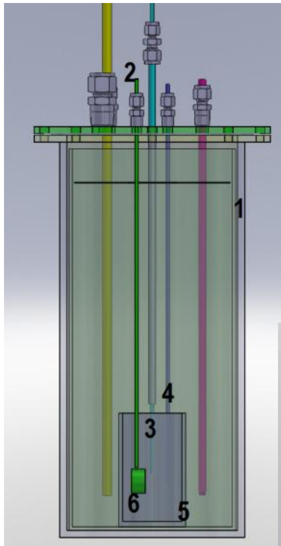


- B segregation significantly enhances the cohesion energy of Ni GBs.
- The improved adhesive property of Ni GBs will prevent the formation of impurity bilayer phases and associated GB embrittlement.

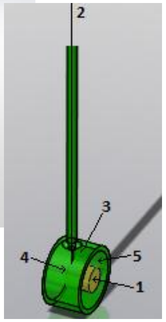
Task 1.2: Electrochemical characterization of the substrate candidates



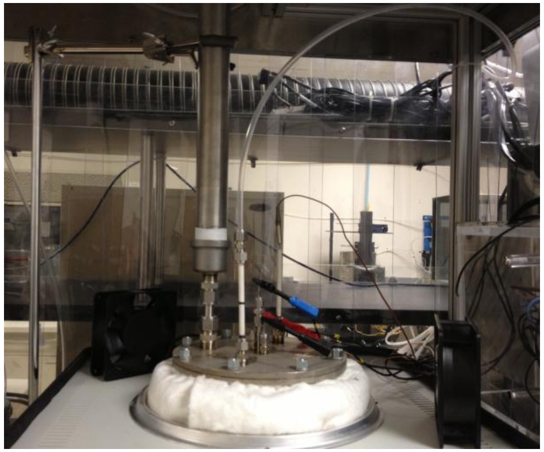
1: crucible furnace, **2**:silica liner, **3**: three-electrode arrangement, **4**: molten salt, **5**: alumina crucible, **6**: thermocouple, **7**: furnace controller with over-temperature control, **8**: potentiostat/power-supply, **9**: purge gas inlet, **10**: argon tank, **11**: off-gas outlet, **12**: chlorine compounds trap, **13**: water removal trap, **14**: water reflux trap, **15**: alkaline scrubber, **16**: exhaust gases, and **17**: thermocouple for overheating control



- **1**: stainless steel chamber with silica lining;
- **2**: working electrode (sample) electrical connector;
- **3**: platinum reference electrode;
- **4**: platinum counter electrode;
- **5**: alumina crucible;
- **6**: encapsulated working electrode;
- **7**: radiation shield



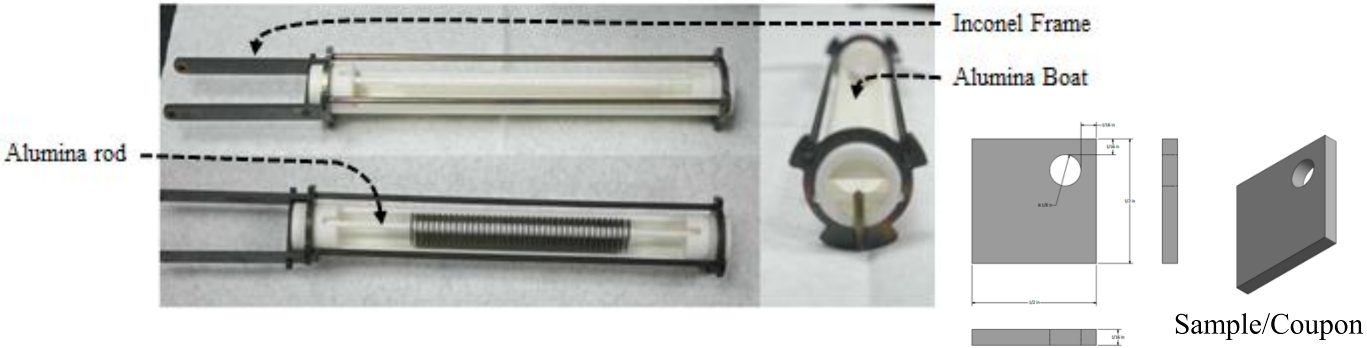
- **1**: Coated Sample (disk 8 mm dia. x 8 mm height)
- **2**: Wire for electrical connection
- **3**: Quartz for encapsulation
- **4**: Wire spot welded to the back of disk/coupon
- **5**: High temperature ceramic cement

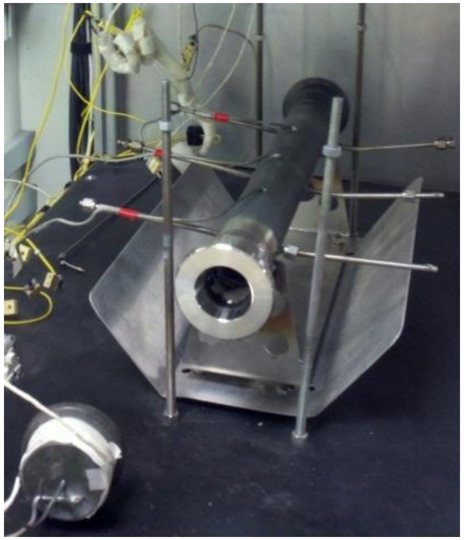


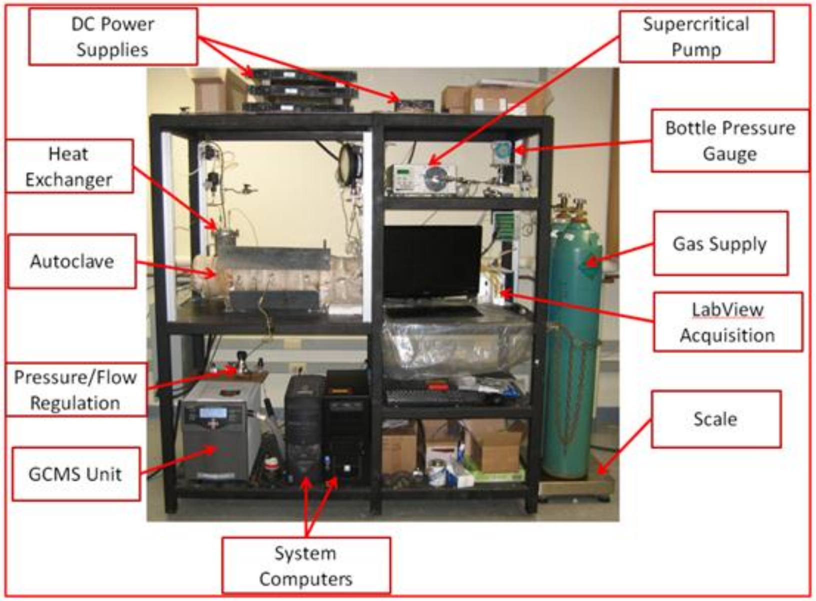
Energy Systems Integration Facility (ESIF)

Task 1.3: Effect of Gas Purity on S-CO_2 Corrosion (University of Wisconsin-Madison)

Autoclave corrosion testing at 650°C, 20 MPa in pure (research), industrial and bone grade S-CO_2.







Task 1.3: Summary of Results to date

- All candidate alloys tested at 650°C and 20 MPa using industrial grade CO_2 showed lower levels of weight gain compared to research grade CO_2.
  - Some impurities could be acting as slight corrosion inhibitors.
- SEM and optical imaging analyses are being performed to evaluate the morphology and chemical elements of the oxidation layer.
- Since it is likely that any plant operation would use industrial grade gas, results seem promising.

Measured weight gains (mg/cm^2) after 200 hours in S-CO_2 at 650°C and 20 MPa (Average ± Uncertainty at 95% Confidence).

Test #	Gas Purity	Temp (ºC)	Pressure (MPa)	Exposure Time (hrs)	**Mat'l 1** 347SS	**Mat'l 2** IN800H	**Mat'l 3** AFA-OC6	**Mat'l 4** 316L	**Mat'l 5** Haynes 230
1	Research Grade CO_2 (99.9998%)	650	20	200	0.072 ± 0.005	0.101 ± 0.010	0.096 ± 0.012	-	-
2	Industrial Grade CO_2 (99.85%)	650	20	200	0.051 ± 0.017	0.079 ± 0.010	0.011 ± 0.033	0.127 ± 0.022	0.024 ± 0.008

Barriers and Mitigation in Phase I

- **Deposition of crystalline alpha (α) alumina (Al_2O_3) top coat.**
  - Mitigation: Preliminary tests will be performed to define deposition conditions of $\alpha\text{–}Al_2O_3$ or annealing conditions to transform deposited coating.
- **S-CO_2 corrosion for short durations does not give much indication of weight change.**
  - Mitigation: Investigate oxidation layer with SEM and optical techniques. Oxidation layers are pretty thin with these alloys which is a good indication that they will work.
- **It may be difficult to determine which species of impurity is mitigating S-CO_2 corrosion.**
  - Mitigation: If there are changes in the oxide layer this might give some clues.

Future Work

- Qualify hot corrosion electrochemical system and calibrate reference electrode for a specific molten salt system.
- Conduct electrochemical testing on four bare substrates (310SS, 347SS, 800H and Inconel 625) and conduct metallographic characterization of substrates before and after molten salt interaction.
- Design and construct chemical cell for liquid alloys degradation studies.
- Synthesize candidate ceramic and/or metallic coatings and perform exploratory down selection of coatings based on adhesion and chemical qualitative tests.
- Identify the role of H_2O, CO, O_2, and hydrocarbon impurities on corrosion. Investigate the effect of different water concentrations and the role of other impurities (identified by Sandia National Laboratories) on the corrosion by S-CO_2.

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NREL_Gomez_A

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Other Contributors
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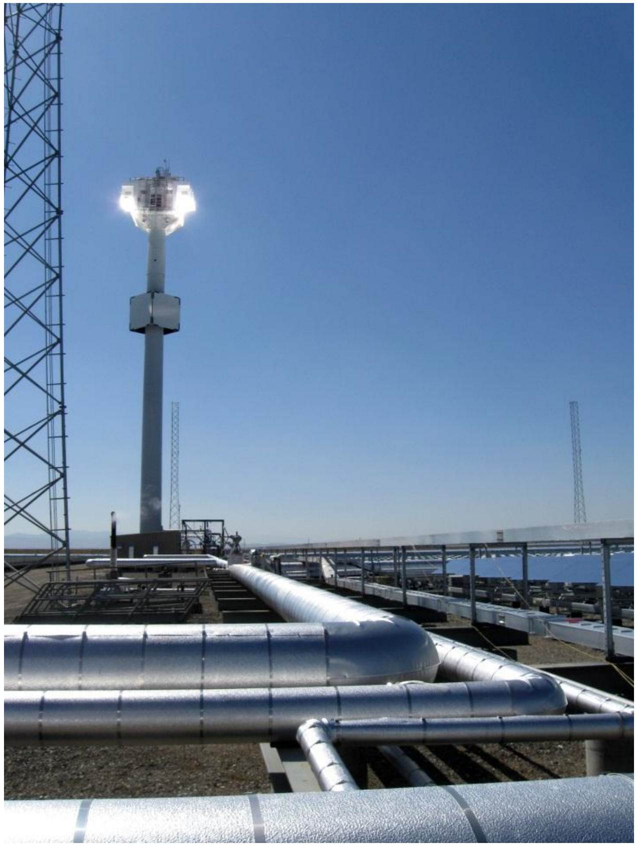
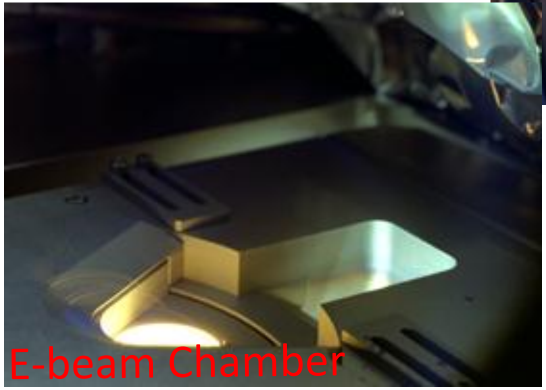


eSolar Sierra SunTower power tower plant.
Source: NREL

Supportive Slides

Coating Deposition at NREL

- Aluminum preliminary trials are being performed in the “three-chamber” deposition system.
- Thermal oxidation and annealing of Al at high temperatures is being evaluated to produce alumina.
- Deposition process for crystalline alumina is under study.
- The “five-chamber” system is being installed to perform depositions of metallic bond coat and alumina top coat.



Impurities of Interest for the Modeling Effort

Representative Alloy	Principal Alloy Element	Low-Concentration Alloy Elements	Common Impurities	Embrittlement Causing Impurities	Embrittlement Preventing Impurities	Representative Elements for Modeling LME
IN625	Ni	Co, Mo, Nb, Ti, Al, C, Mn, Si	S, P	S, P	B	Ni matrix with Bi, B, S, P, and Bi-B impurities
IN800H	Ni	Ti, Al, C, Mn, Si	S, P, Cu	S, P	B	
310SS	Fe	C, Mn, Si	S, P, Sn	S, P, Sn	B	Fe matrix with B, S, P, and Sn impurities
347SS	Fe	C, Mn, Si, Nb	S, P, Sn, Cu	S, P, Sn	B	
AFA-OC6	Fe	C, Mn, Si, P, S, Nb, Cu, Mo, W, Ti, V, N, B	S, P, N, Cu	S, P	B	

Task 1.3: Test Matrix

Task	347SS	800H	AFA-OC6	# of samples
1.3.1	Industrial grade CO_2 max impurity levels	Industrial grade CO_2 max impurity levels	Industrial grade CO_2 max impurity levels	9
1.3.1	Bone Dry CO_2 max impurity levels	Bone Dry CO_2 max impurity levels	Bone Dry CO_2 max impurity levels	9
1.3.1	Research Grade max impurity levels	Research Grade max impurity levels	Research Grade max impurity levels	9
1.3.1	RG w 50ppm H_2O	RG w 50ppm H_2O	RG w 50ppm H_2O	9
1.3.1	RG w 75ppm H_2O	RG w 75ppm H_2O	RG w 75ppm H_2O	9
1.3.1	RG w 100ppm H_2O	RG w 100ppm H_2O	RG w 100ppm H_2O	9
1.3.1	RG w 1000ppm H_2O	RG w 1000ppm H_2O	RG w 1000ppm H_2O	9
1.3.2	SNL impurity level test	SNL impurity level test	SNl impurity level test	9
1.3.2	SNL specific impurity at 50% level	SNL specific impurity at 50% level	SNL specific impurity at 50% level	9
1.3.2	SNL specific impurity at 150% or solubility limit	SNL specific impurity at 150% or solubility limit	SNL specific impurity at 150% or solubility limit	9
2.3.1	Yttrium coating			3
2.3.1	Alumina coating			3
2.3.2	Grain refinement with shot peening			3
3.4.1	Flow testing with base alloy			3
3.4.1	Flow testing with best performing surface treatment			3