Metallic Materials Development for Solid Oxide Fuel Cells

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Outline

1. Low CTE Nickel Base Alloys (J.Dunning)
   - Composition
   - Production of Strip
2. Modifications for Improved Oxidation Resistance (J. Dunning)
   - Nickel-Base and Ferritic Alloys
3. Balance of Plant (J. Hawk)

Low CTE Nickel Alloy Design Concepts

Oxidation Resistance and Low CTE

Oxidation Resistance: Chromia former required

Cr-Mn Spinel is conductive and minimizes Chrome evaporation

CTE vs. Oxidation Resistance: A balancing act

Chrome raises CTE while Mo and W lower CTE

Al, Ti and C also lower CTE

Fe and Co raise CTE

Alloy Design Concepts

- Formulation for CTE

$$\mathbf{CTE}=13.87 + 7.28\times10^{-2}[\mathbf{Cr}] - 7.96\times10^{-2}[\mathbf{W}] - 8.23\times10^{-2}[\mathbf{Mo}] - 1.83\times10^{-2}[\mathbf{Al}] - 1.63\times10^{-1}[\mathbf{Ti}]$$

R. Yamamoto et. al., in Materials for Adavanced Power Engineering – 2002, Proc. 7th Leige Conf. Sept 30-Oct 3, 2003, Energy and Technology Vol. 21.

- ThermoCalc software used to verify phases.
- Melted 28 different compositions

J-Series Ni-Cr-Mo Alloys

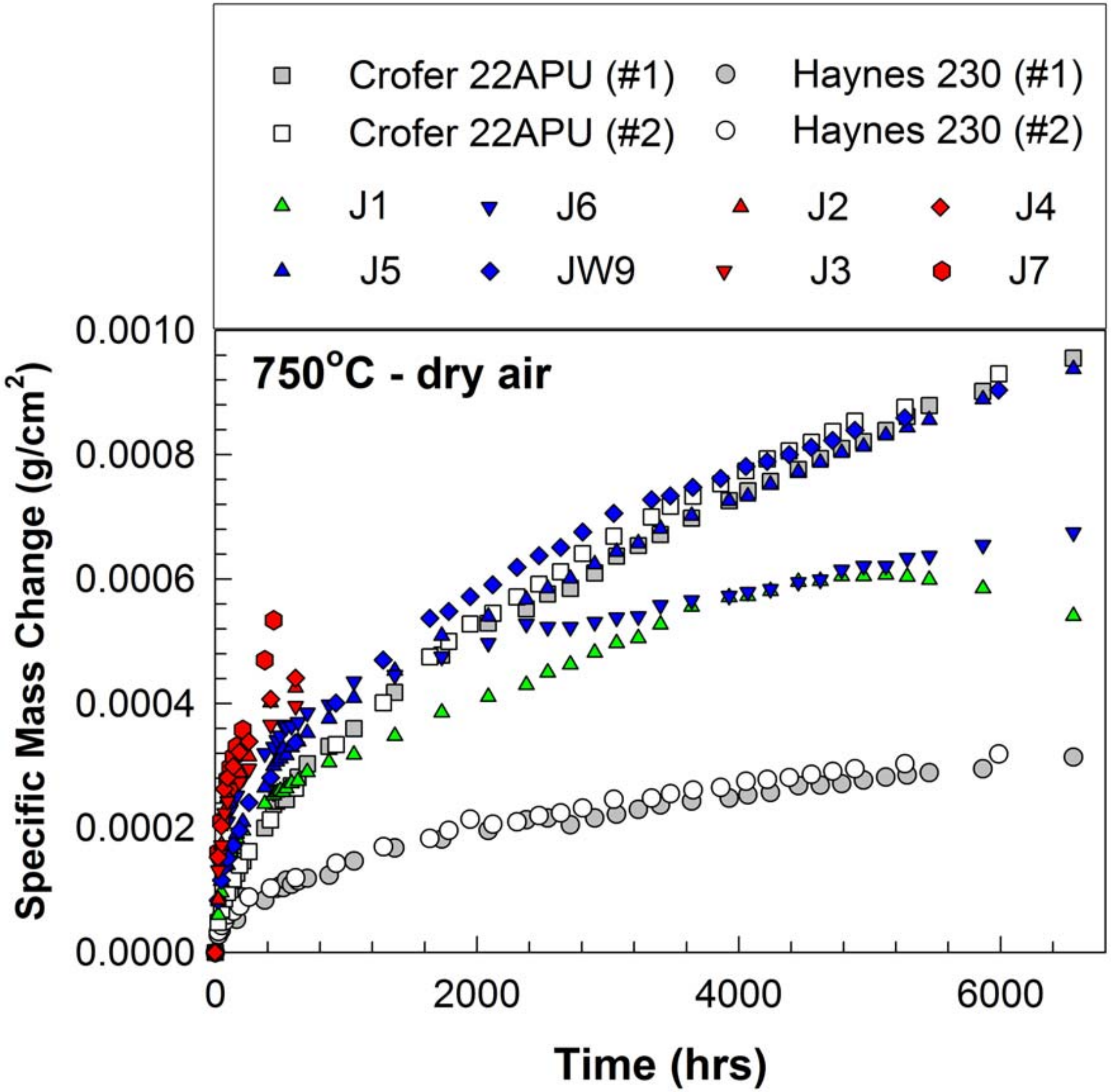
Nominal Composition (wt%)

Alloy	Ni	Cr	Mo	Ti	Al	Mn	Y
J1	Bal	12	18	1.1	0.9	0	0
J2	Bal	10	22.5	3	0.1	0.5	0.1
J3	Bal	12.5	22.5	3	0.1	0.5	0.1
J4	Bal	15	22.5	3	0.1	0.5	0.1
J5	Bal	12.5	22.5	1	0.1	0.5	0.1
J6	Bal	12.5	27.7	0	0	0.5	0.1
J7	Bal	22	36.1	0	0	0.5	0.1

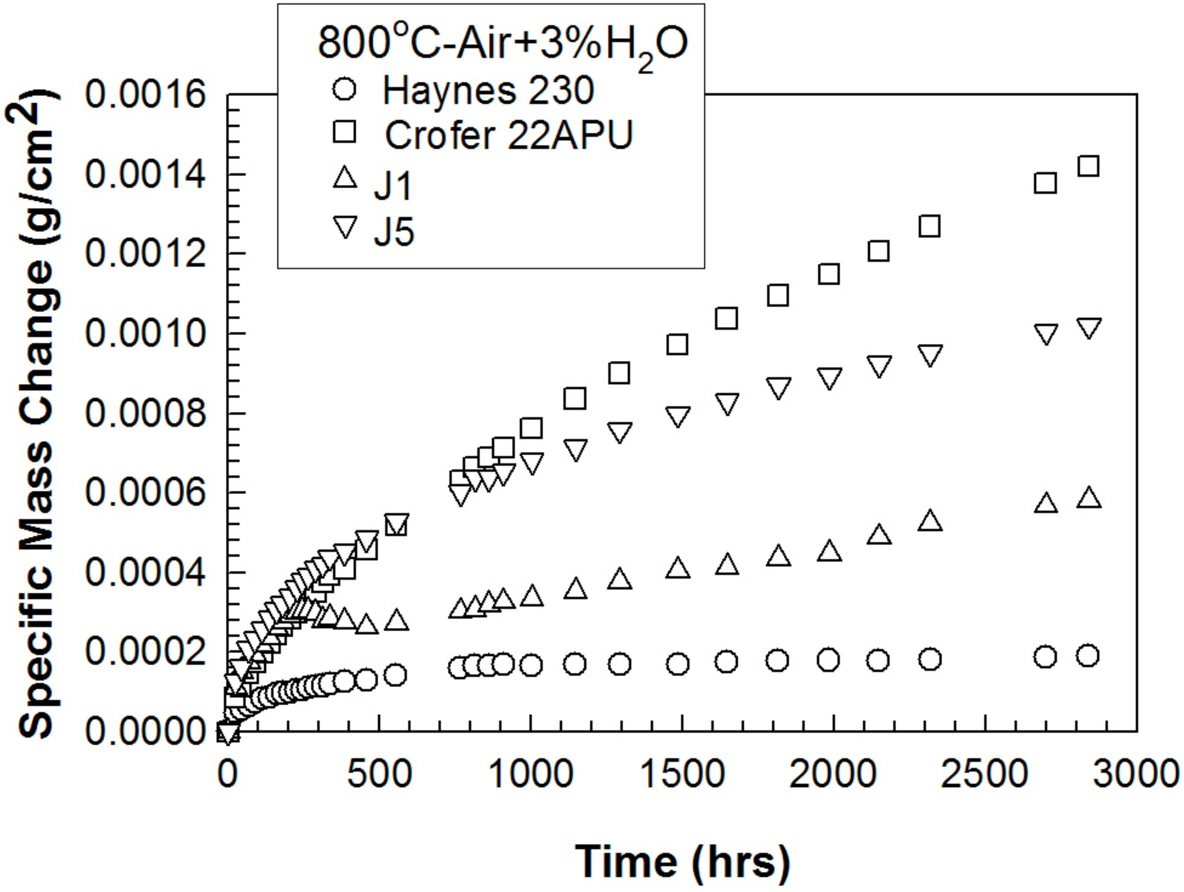
CTE-J series alloys

Alloy	Predicted (23-700^{o}C)	Measured (23-700^{o}C)	Measured (23-800^{o}C)	Measured (23-900^{o}C)
J1	13.06	12.9	13.6	14.4
J2	12.25	12.5	13.2	14.0
J3	12.44	12.3	13.4	14.3
J4	12.61	12.7	13.6	14.4
J5	**12.71**	**12.6**	**13.4**	**14.0**
J6	12.50	13.8	14.6	15.7
J7	12.50	11.2	11.9	12.5
Crofer	**----**	**11.0**	**11.9**	**12.6**
Haynes 230	**14.2**	**13.3**	**14.3**	**15.4**

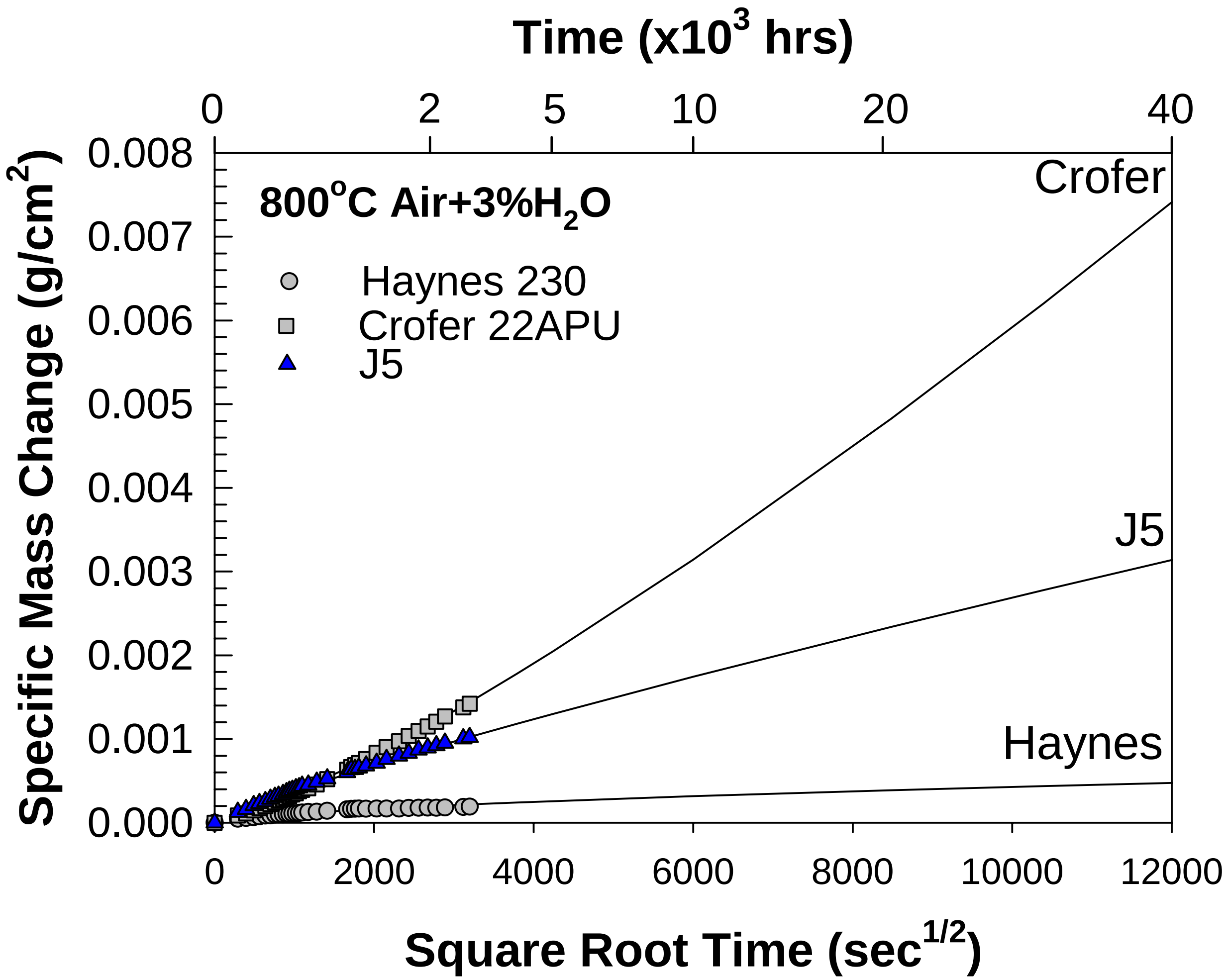
750ºC Oxidation



800ºC Oxidation

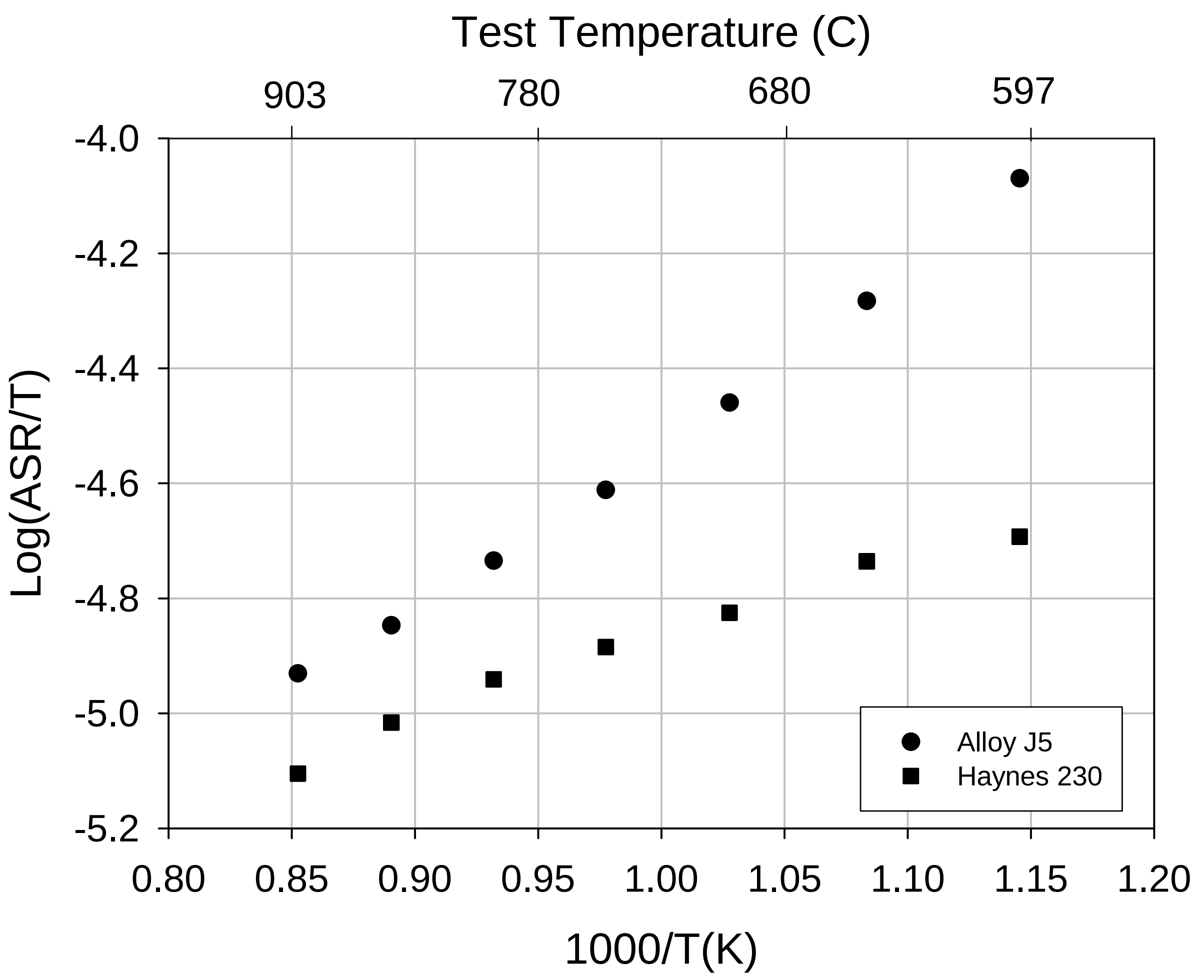


40,000 hr Extrapolated Behavior



ASR

700C/100h/Dry Air



Measurements by: C. Johnson, NETL

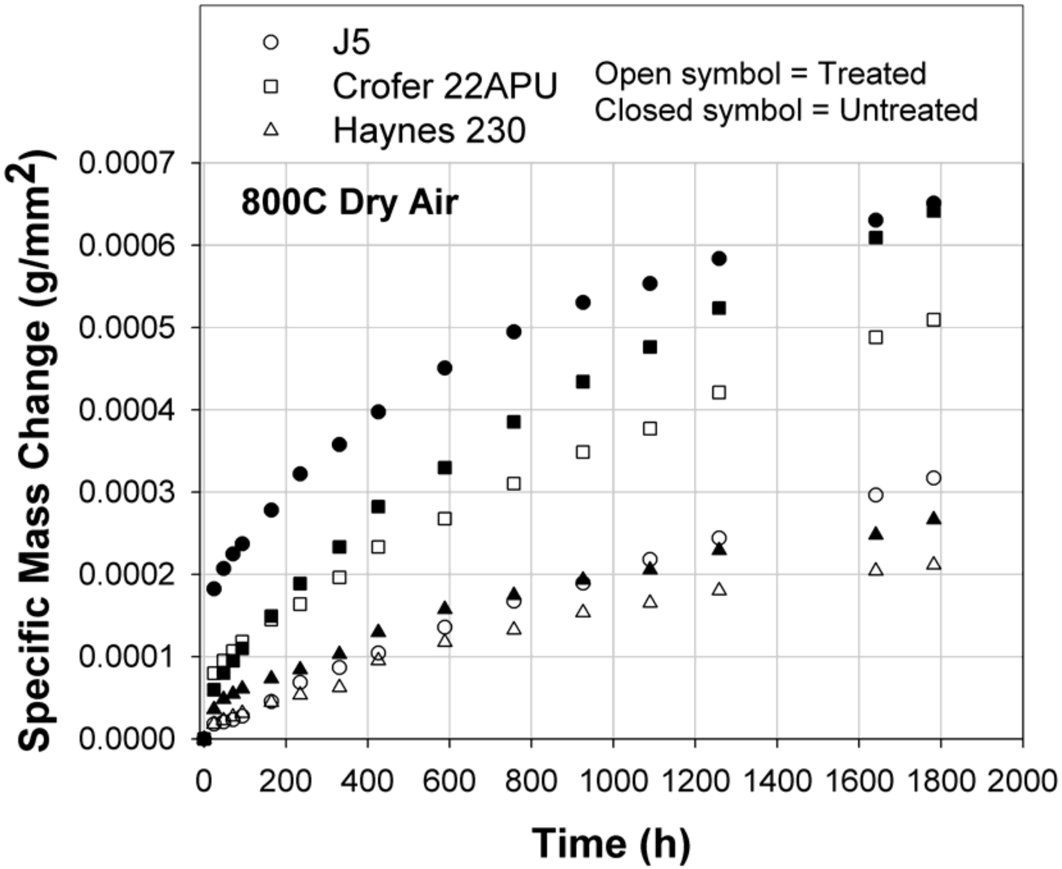
Modifications for Improved Oxidation Resistance

- Ferritic Steels
- Nickel Alloys

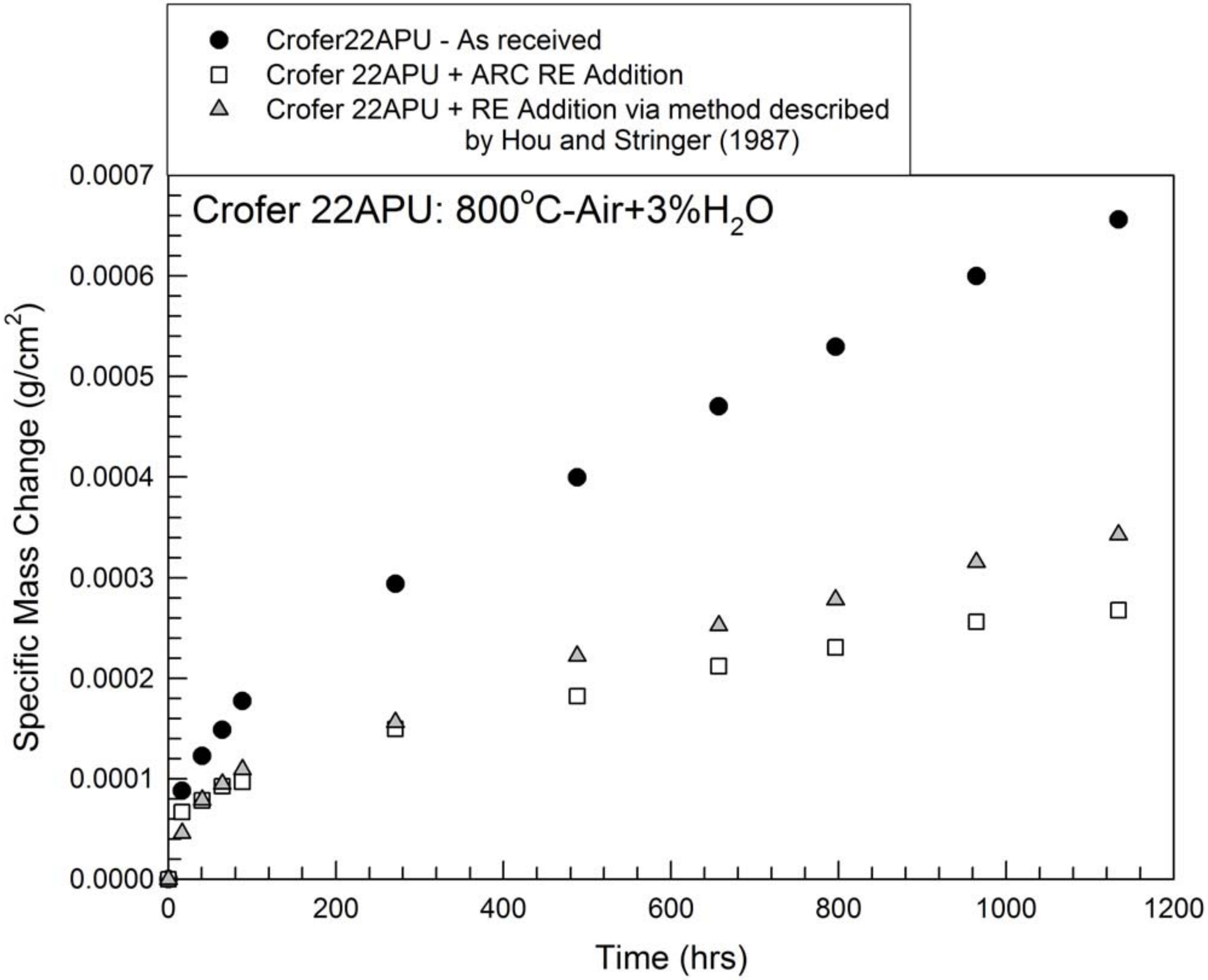
Reactive Element Additions

- Minor additions of rare earth (Ce, La, Y, etc.) improve oxidation resistance.
- Developed method for enhancing rare earth element (RE) content of alloys (patent application filed).
- Comparing with other treatments, such as method described by Hou and Stringer (1987).

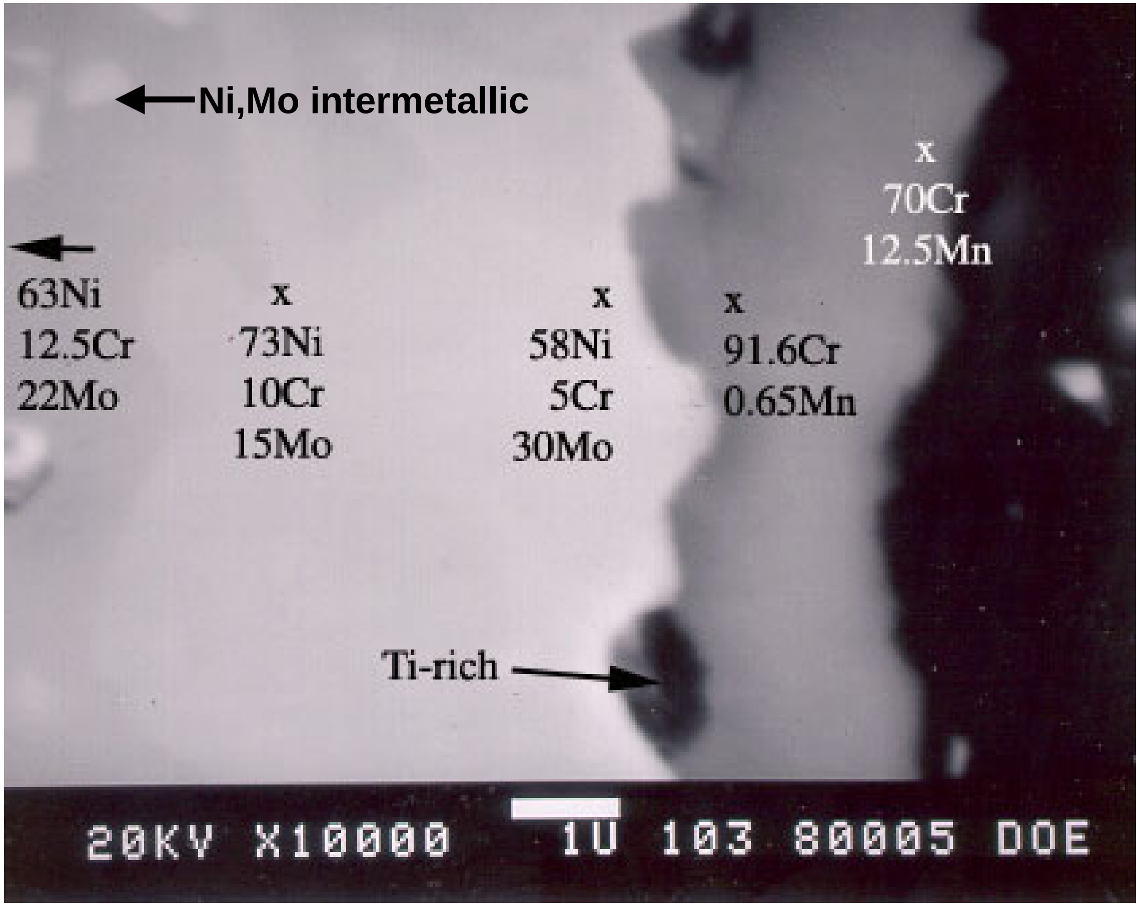
Treatment to Enhance Oxidation Resistance Via RE Additions



Crofer 22APU

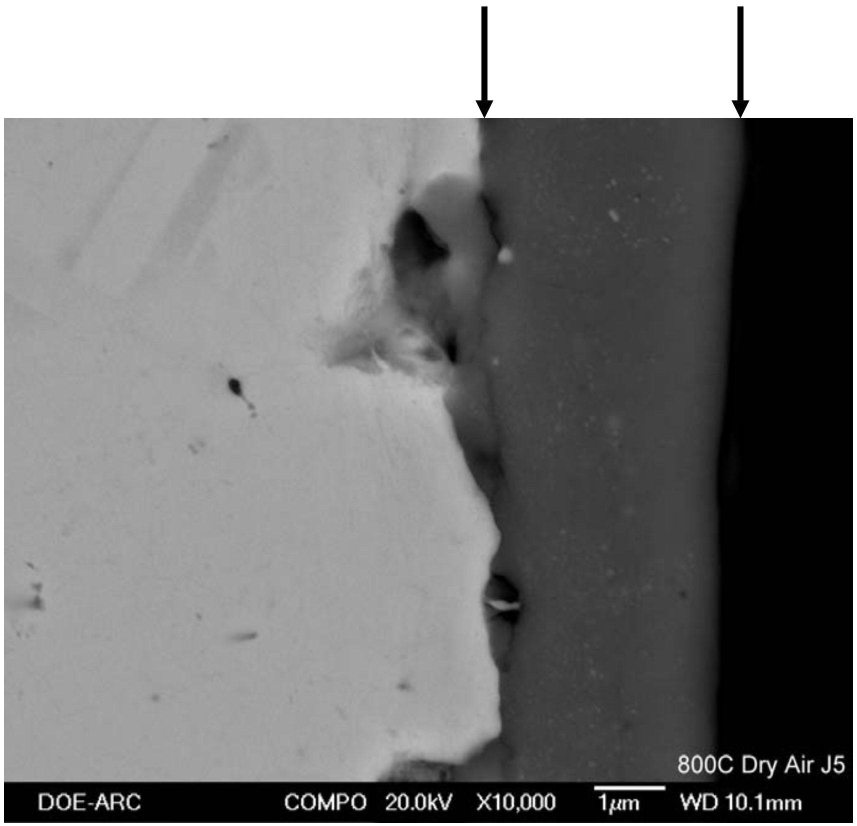


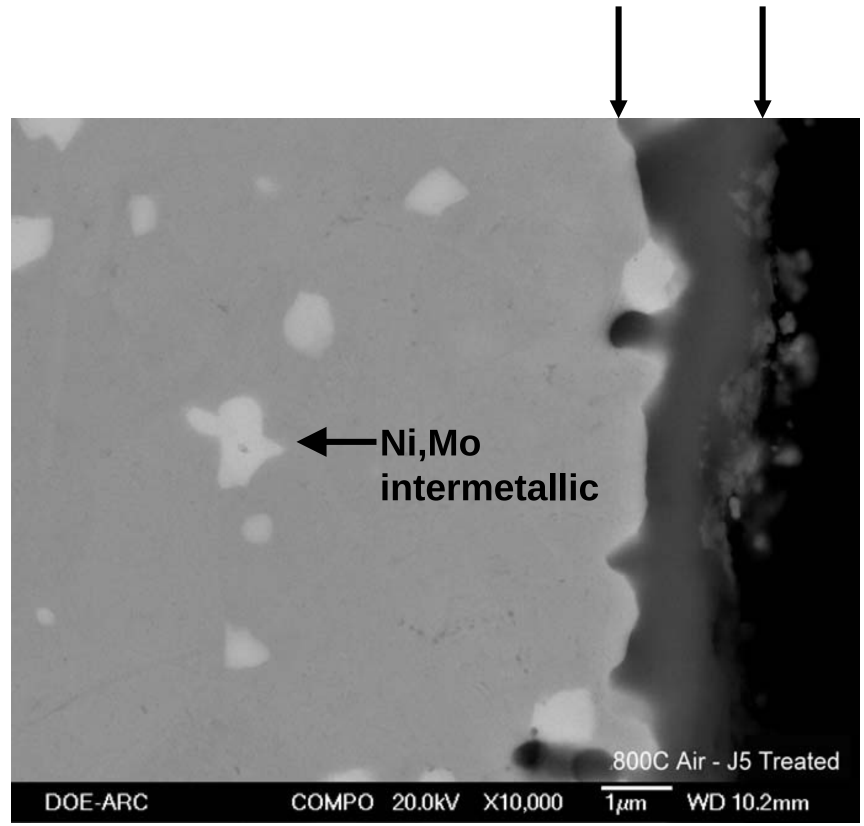
Oxide Scale: Alloy J5
500hr - 800^{o}C dry air



Oxide Scale: Alloy J5

1800 hrs - 800°C dry air





As polished

+ ARC Treated

Alloy J5: Strip Production

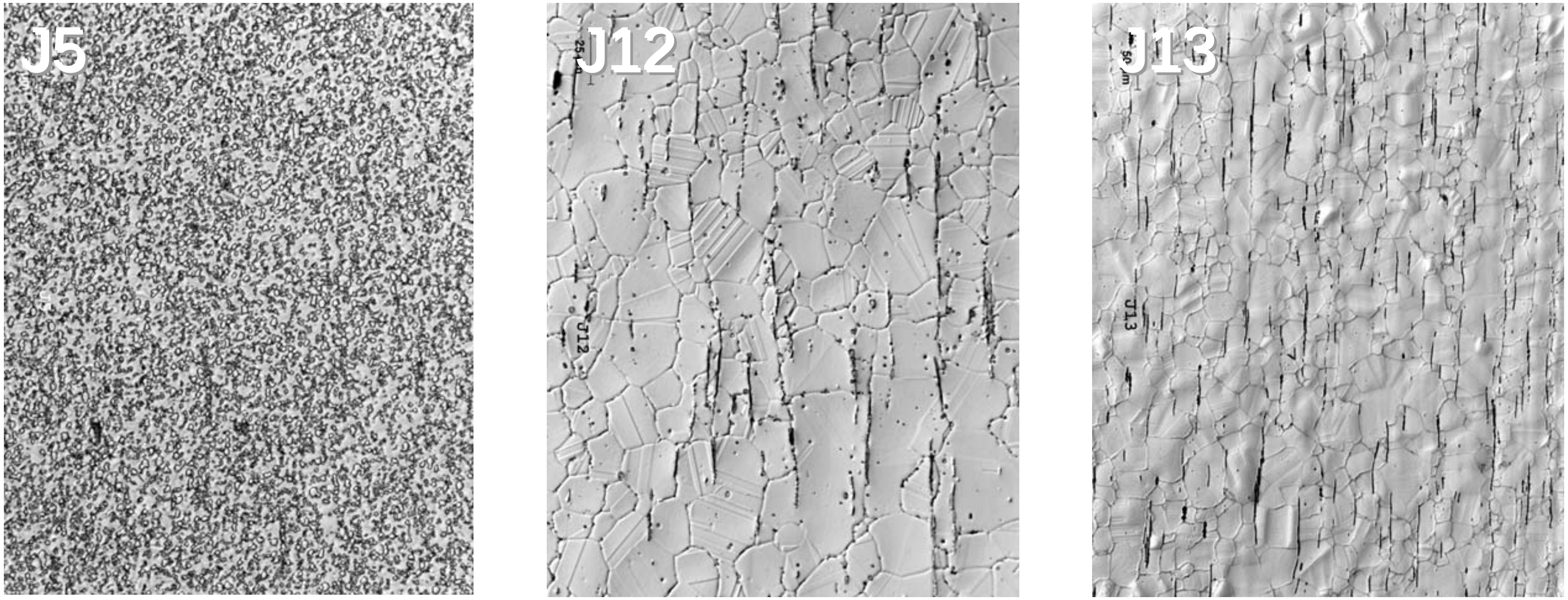
A length of 4” wide x 0.020” thick Alloy J5 prepared by cold rolling

Alloy J5 Strip and Treated J5 Strip

- PNNL (J. Stevenson and G. Yang)
  - Sent for testing
- GE (J. Guan, GE-Energy Systems and K. Browall, GE-GR&D)
  - In process of delivering material
- Requests for material from:
  - Versa Power Systems (Canada)
  - Korean Advanced Institute of Science and Technology (Korea)
  - Ikerlan Technical Research Center (Spain)
- ***Will send sample of J5 to any SECA participant or US entity for evaluation***

Contact: J. Dunning: dunning@alrc.doe.gov
(541) 967-5885

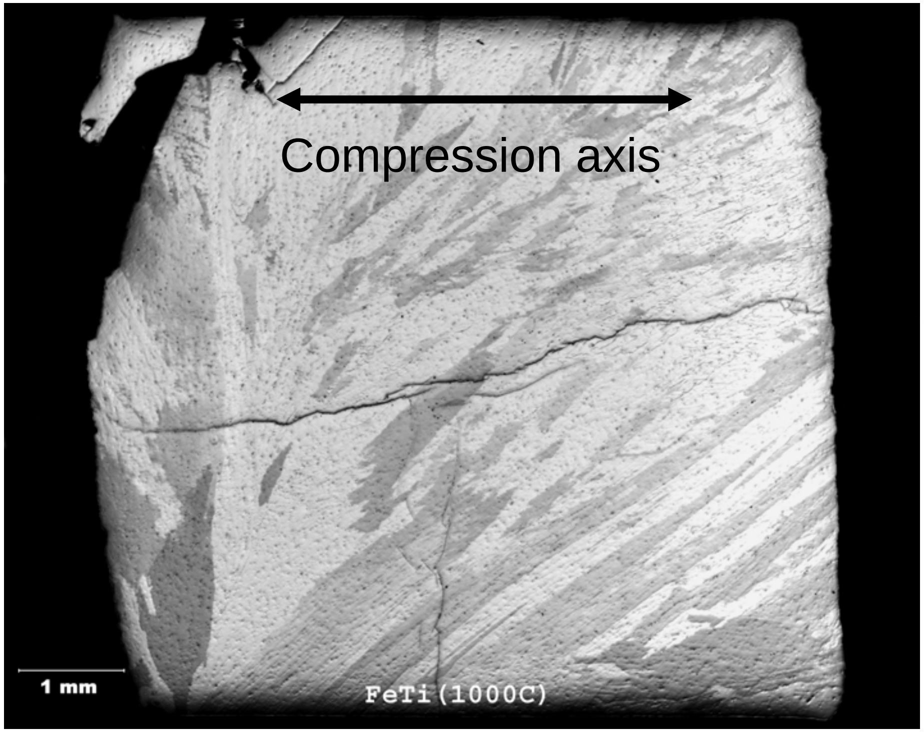
Alloys J12&J13



- J5 derivates designed using ThermoCalc (minimize Ni-Mo ppt)
- Microstructures after aging at 800°C for 40 hours
  - J5 → Ni-Mo ppt prevalent; J12 & J13 → few ppt
- Evaluating corrosion behavior (800°C-Air+3%H_2O)

Fe-Ti for Argonne National Laboratory

- Two Fe-Ti intermetallic alloys prepared by arc melting.
- Hot-hardness and hot-compression tests to determine formability
  - poor formability
  - p/m alloy
- Ingots sent to ANL
  (Terry Cruse)



Sample after compression testing at 1000°C.

Materials Performance for Heat Exchangers & Other Balance of Plant (BOP) Components for (SOFC)

Generic SOFC System Components

1. Fuel Cell Stack
2. Fuel Pre-reformer/Reformer
3. Process Gas Heater
4. Fuel De-sulfurizer
5. Air Pre-heater
6. Effluent Burner
7. Heat Recovery
8. Fuel Management
9. Air Blower
10. Control Unit
11. Power Conversion Unit
12. Back-up Power Unit
13. Purge Gas
14. Water Purification for Start-up Steam

Fontell *et al*., "Conceptual Study of a 250 kW Planar SOFC System for CHP Application," *J. Power Sources*, 131 (2004) 49-56.

Cost Structure for 250 kW SOFC System

Stack	31%
Fuel System	8%
Air System	6%
Exhaust System	2%
Start-up System	2%
Purge Gas System	0%
System Control	17%
Power Electronics	15%
Insulation	3%
Structure	2%
Labor and Overhead	15%

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= 54% (Fuel System through Structure)

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Basic Flow Sheet for an SOFC System

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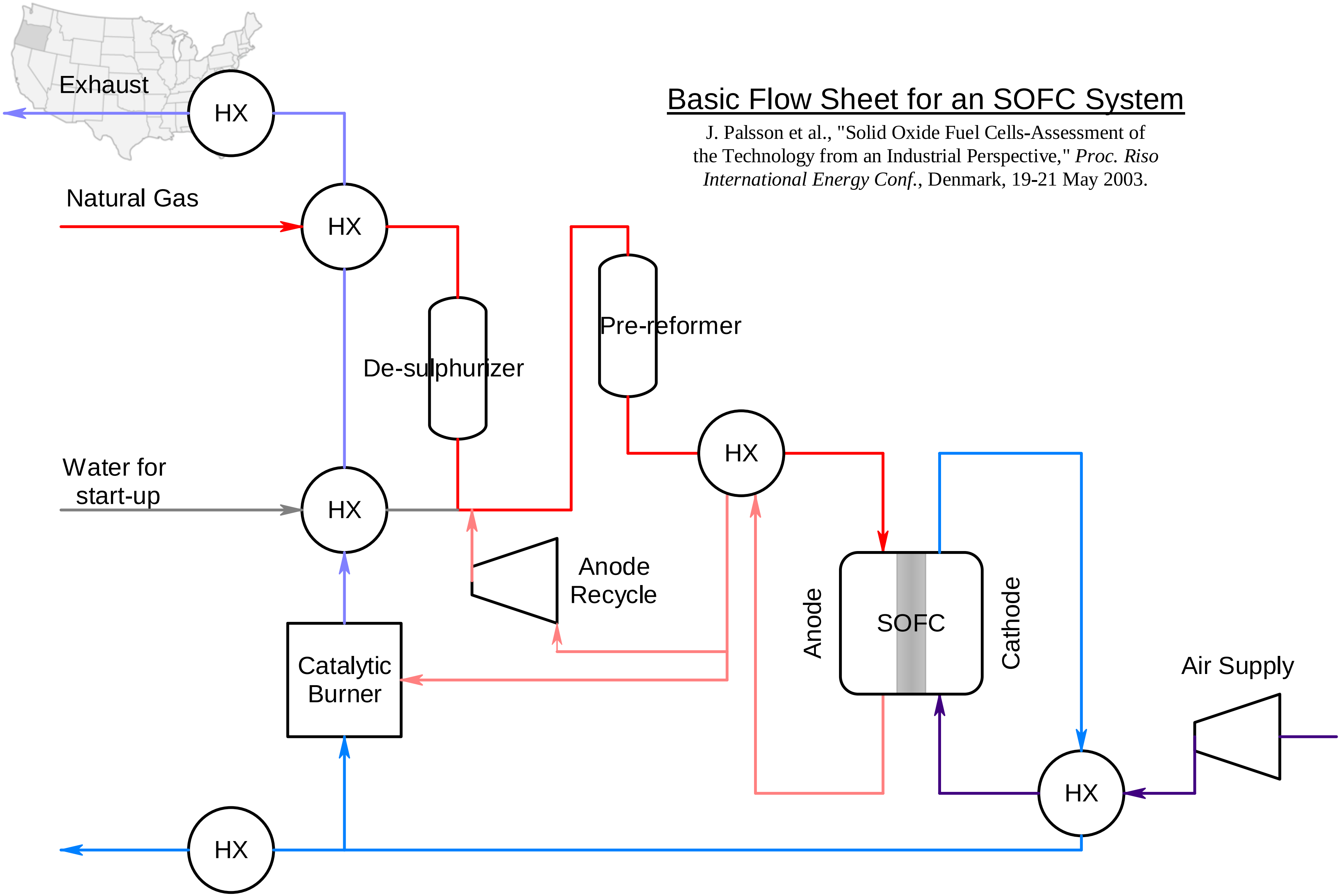

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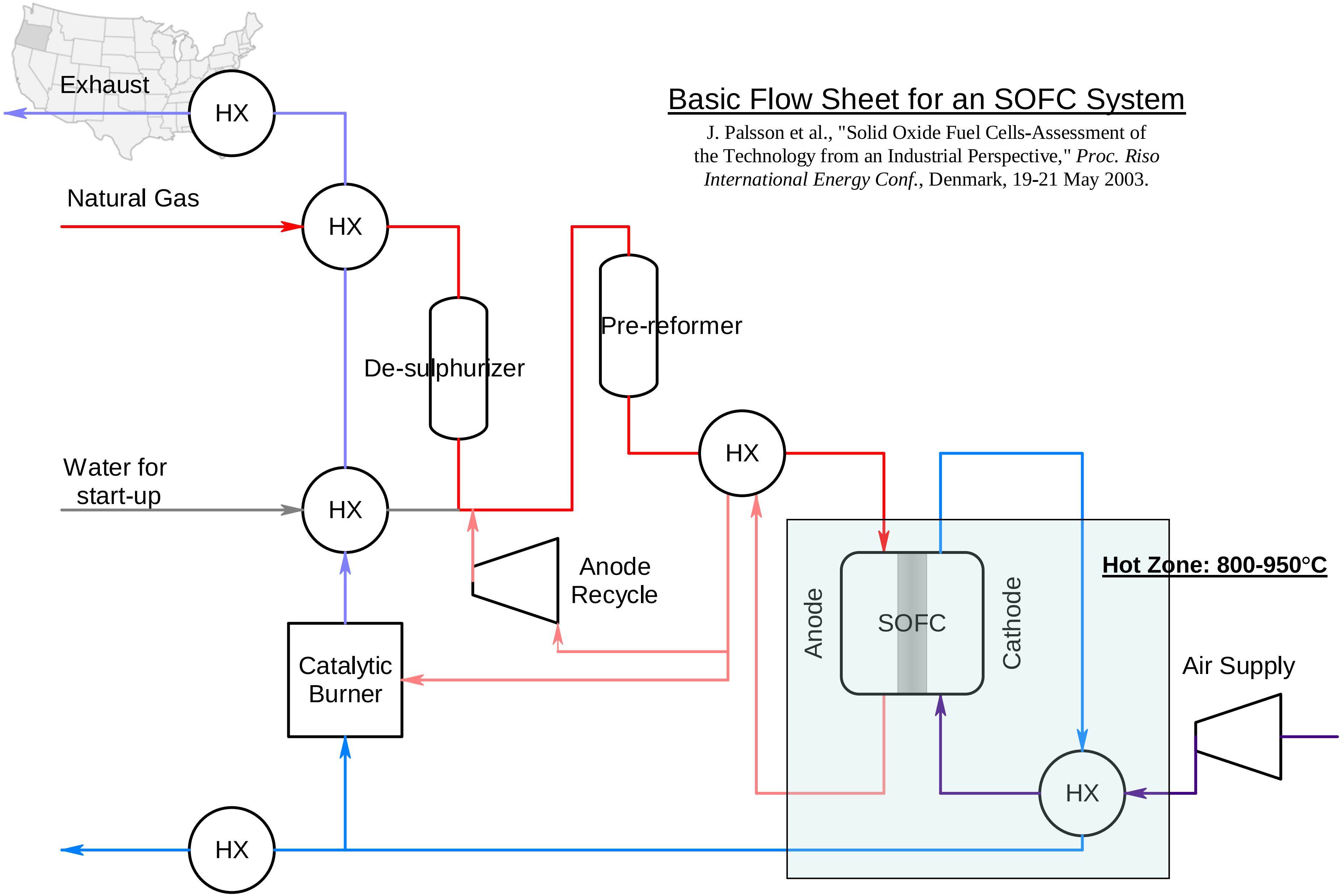

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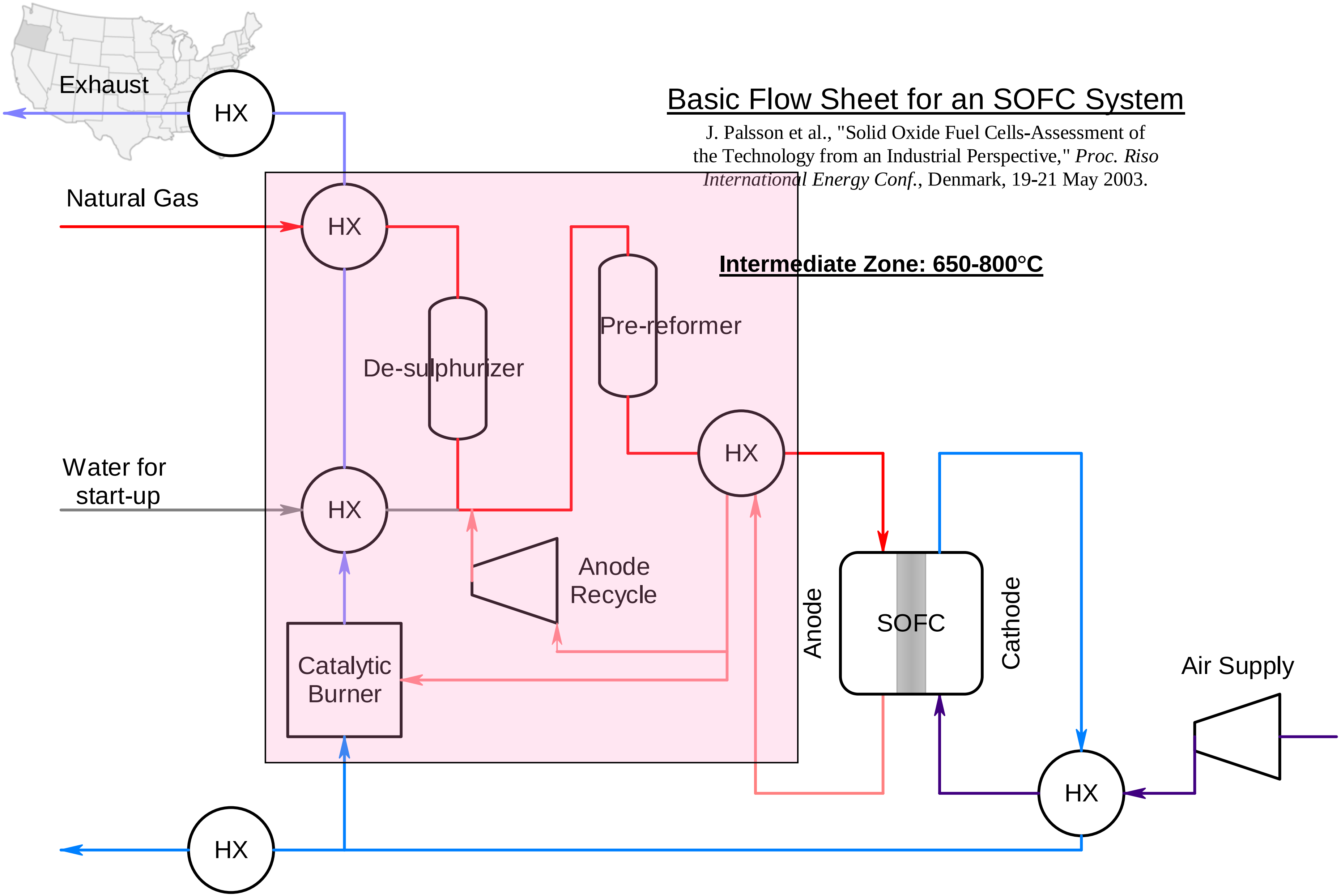

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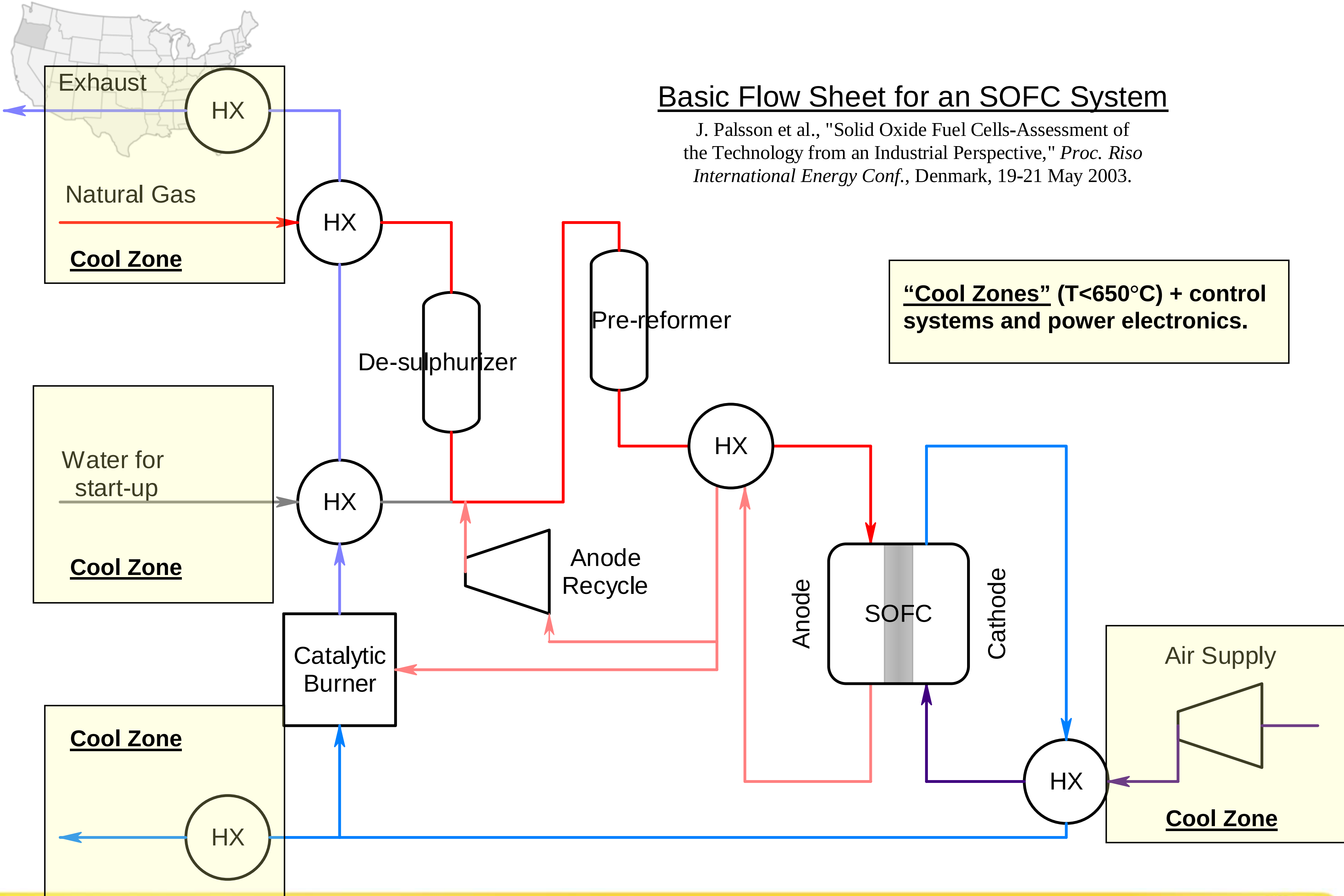
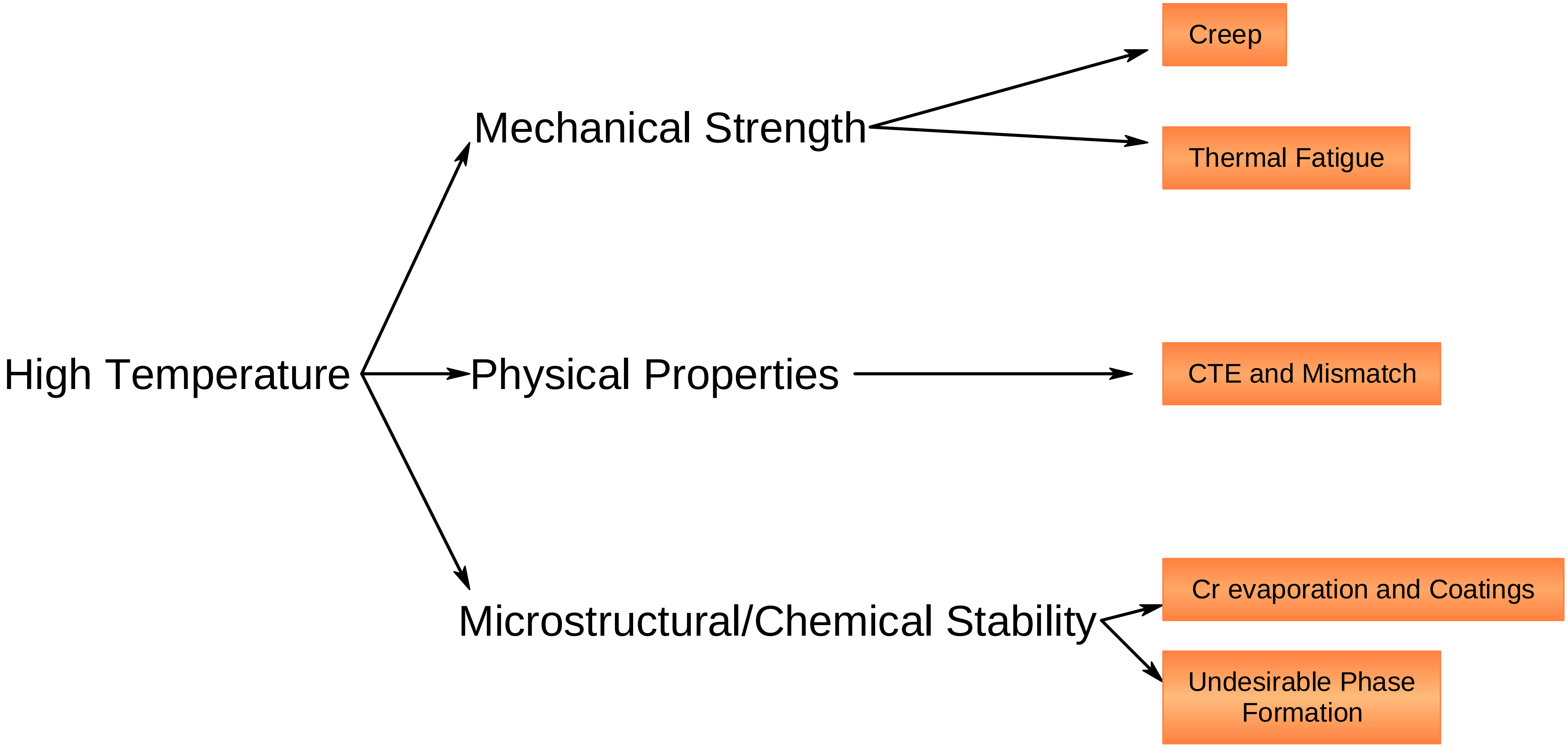


"Cool Zones" (T<650°C) + control systems and power electronics.

BOP Component Design and Testing Strategy

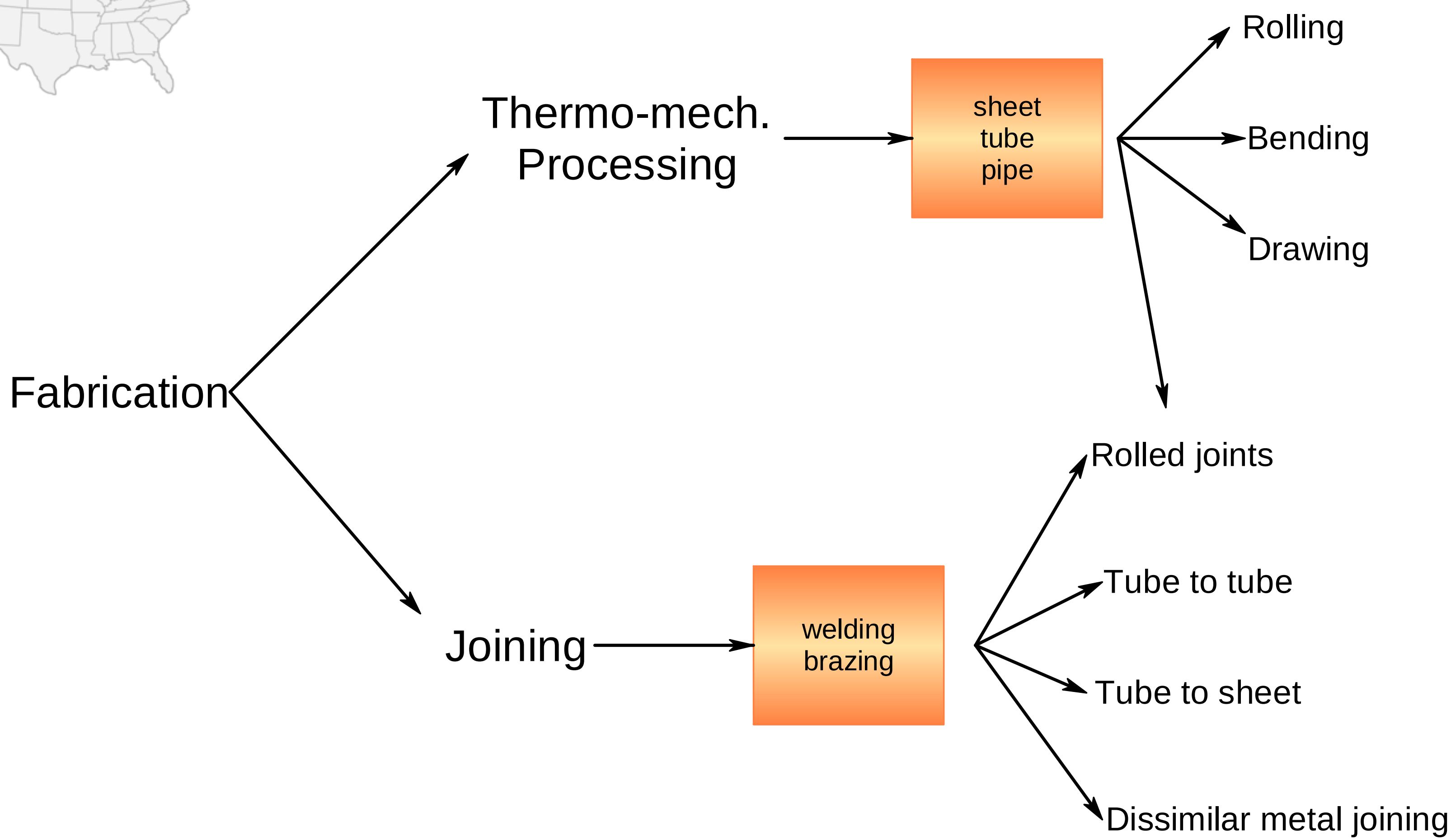
1. Define the component requirements.
2. Identify candidate materials.
3. Evaluate materials in depth.
4. Specify and select materials.
5. Establish a strategy for evaluating generic candidate BOP components.



High Temperature
Mechanical Strength
Physical Properties
Microstructural/Chemical Stability
Creep
Thermal Fatigue
CTE and Mismatch
Cr evaporation and Coatings
Undesirable Phase Formation

Environment + Temperature → Corrosion → Oxidizing / Reducing

monolithic
surface modified
composite
cladded


Fabrication
Thermo-mech. Processing
sheet
tube
pipe
Rolling
Bending
Drawing
Rolled joints
Joining
welding
brazing
Tube to tube
Tube to sheet
Dissimilar metal joining

Heat Exchangers

1. Plate and fin
2. Shell and tube
3. Finned tubes
4. Tube-in-tube

Materials of Construction

1. Ferritic stainless steels
2. Austenitic stainless steels
3. Nickel alloys
4. Ni-base superalloys
5. Ceramics
6. Hi-temp composites

Raw materials
Alloy processing
Fabrication
Joining
HX production method

Increasing Cost

Decreasing temperature

BOP Systems Approach
(Identify-Evaluate-Specify)

- ARC Alloy Design/Development
- Laboratory Materials Testing
- BOP Prototype Component Testing

Alloy Design/Development

Use lowest cost alloys to achieve desired SOFC performance standards for BOP components.

Investigate low cost material alternatives:

- Identify coating/surface modification strategies.
- Develop application strategies for any material/component configuration.
- Optimize for lowest cost and greatest protection.
- Evaluate efficacy of approach.

Laboratory Materials Testing

- Exposure to air
- Exposure to fuel gas/effluent

  (with and without S)
- Exposure to dual environment

Develop empirical equations to quantify material wastage in SOFC environment.

Prototype Component Testing

Serve as a test platform for SOFC-BOP prototype components:

- Test single components
- Test “system” components
  - Upstream of the FC stack
  - Downstream of the FC stack

<u>**For a set of SOFC conditions**</u>: ***(1) measure component efficiency***
(2) determine material wastage
(3) perform forensic analysis of spent component

Research Approach

1. Construction of BOP Component Testing Facility
2. Material and Component Testing of High Temperature Heat Exchangers and Other BOP Components
3. Fuel Chemistry: Effects of Sulfur on BOP Components
4. SOFC/BOP Efficiency Optimization

Construction of BOP Testing Facility

Approach

Simulated combustion environment using a “furnace/hotbox” with feed through connections for air and fuel/effluent gases.

Material and Component Testing of High Temperature Heat Exchanger

- Mechanical and Physical Property Behavior of BOP Candidate Materials
- Prototype BOP Component Testing
- Microscopic Investigations
- Characterization of Scales

Prototype BOP Component Testing

- Test facility must be flexible enough to use:
    - different fuel chemistries
    - different operating temperatures
    - different operating pressures (but not pressurized)
- Must be modular in design to facilitate the easy insertion and removal of BOP components
- Allow easy post mortem analysis of BOP components
- Allow evaluation of operating efficiency of the "system" for both the SOFC and the BOP components

General Summary

- Identify, evaluate (test as needed) and specify materials for use as BOP components in SOFC applications. Explore coating/surface modification strategies to extend operational range.
- Design and construct a BOP component and BOP component system test facility.

Summary

(Mechanical and Physical Property Behavior)

1. Physical characterization of the potential materials of construction for BOP components.
2. Analysis of mechanical behavior of materials of construction for BOP components.
3. Evaluation of the microstructural stability of BOP materials after long-term, high temperature exposure.
4. Evaluation of BOP materials after long-term, dual-atmosphere, high temperature exposure.
5. Characterization of the microstructure and integrity of joints between similar and dissimilar materials in BOP components.

Summary

(Proposed BOP Material and Component Test Conditions)

Temperature		Pressure	Environment	Flow Rate
IT	HT	✂110 kPa (internal)	Fuel Gas Effluent Air H_2O (w/ and w/o S)	100 slpm (or any other suggestions)
500°C to 700°C	700°C to 900°C			

Summary

(Proposed BOP SOFC Environmental Conditions)

Air	Fuel Gas	Effluent
Laboratory Air	76.0 N_2 15.0 O_2 6.5 H_2O 2.5 CO_2 (Sulfur)	46.5 N_2 27.0 H_2 6.0 H_2O 3.5 CO_2 13.0 CO 4.0 CH_4 (SO_2)