Development and Testing of Ceramic Materials for Direct Power Extraction

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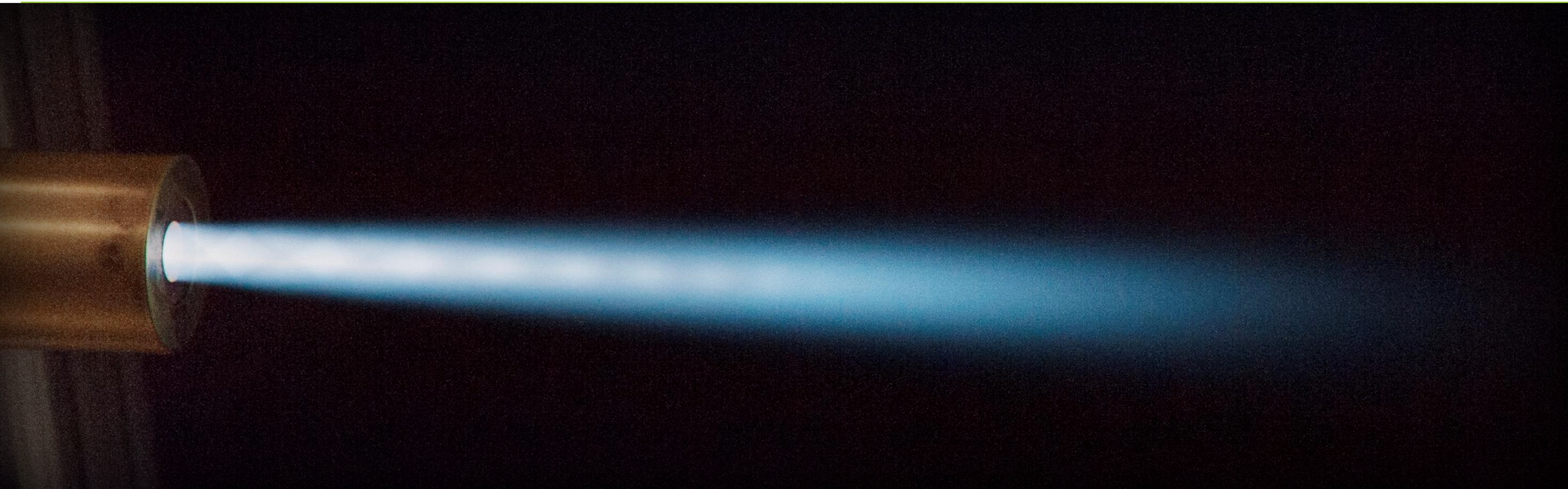
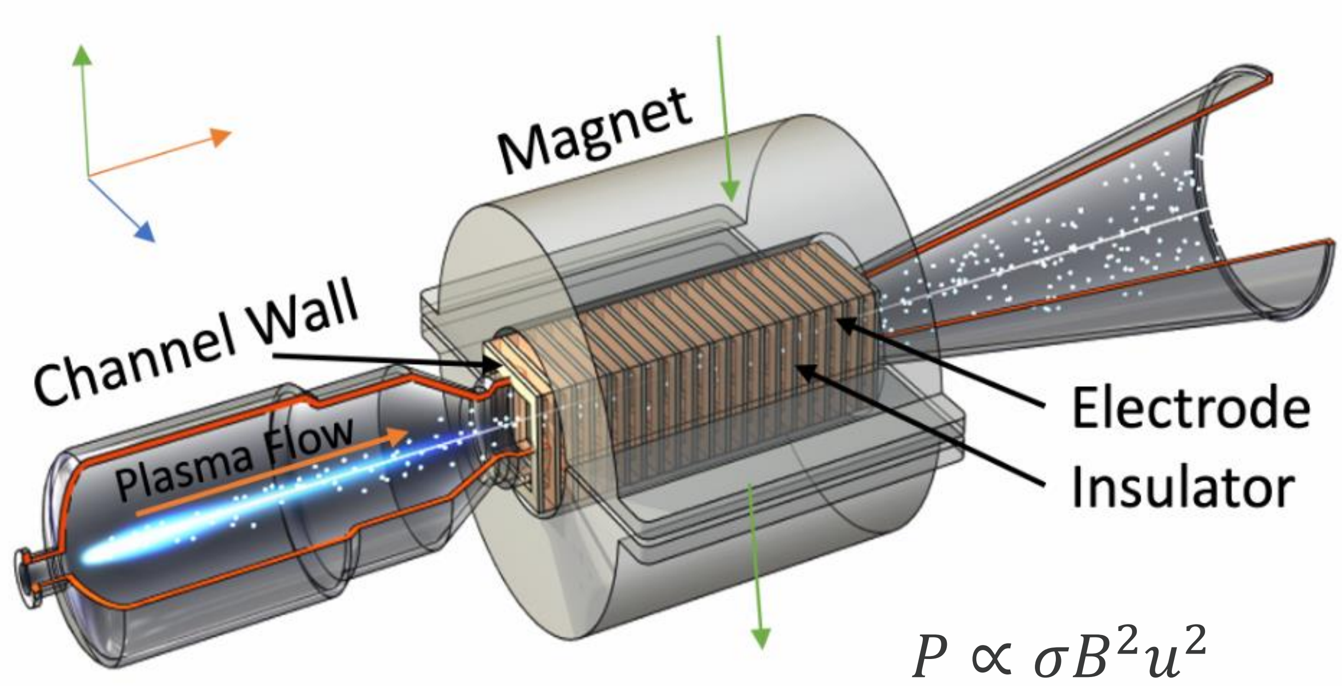


Outline

- **Introduction**
  - MHD
    - Operation
    - Legacy Research
  - Materials
    - Generator Design
    - Material Requirements
- **R&D**
  - Material selection
    - Metals, Non-oxide ceramics, Oxide ceramics
  - Characterization & Evaluation
    - High temp properties
    - Corrosion resistance
    - In-situ testing
- **Generator Design**
  - Thermo-mechanical properties
  - Structural modeling
  - Fabrication
    - Monolithic channels
    - 3D printing
    - Shrink-fit
  - Graded ceramics

MHD: Principle of Operation

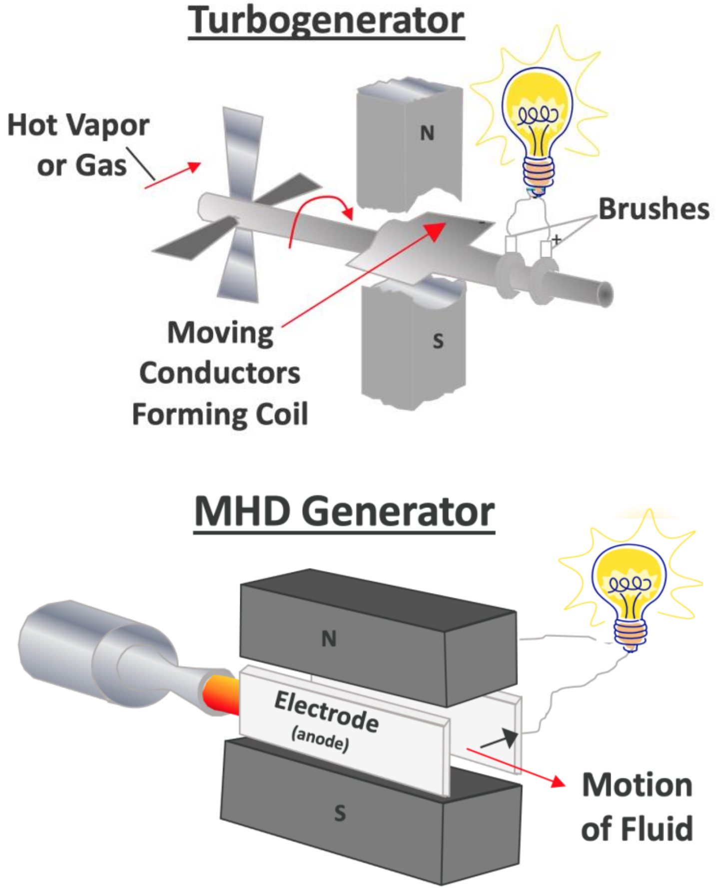
Direct Power Extraction



$$P \propto \sigma B^2 u^2$$

Figure from[2]

Figure from [1]



Magnetohydrodynamics (MHD): study of conductive fluid moving through a magnetic field

History of MHD Materials

- **Coal fired MHD (1960s-1990s)**
  - "Cold-wall" water cooled channels
    - Metal electrodes
    - Slag protective layer
- **Natural Gas: US-USSR Collab. (1970s-1980s)**
  - "Hot-wall" channel
    - Direct material exposure
    - Oxide electrodes
    - Three primary oxide materials tested:
      - Zr-Ce-Y of different concentrations – corrosive failure and material degradation[2]
      - Fe-doped $MgAl_2O_4$ – Significant degradation and corrosive failure[3]
      - Mg-doped LaCrO3 – significant degradation, Cr loss, 1700˚C limited[4]

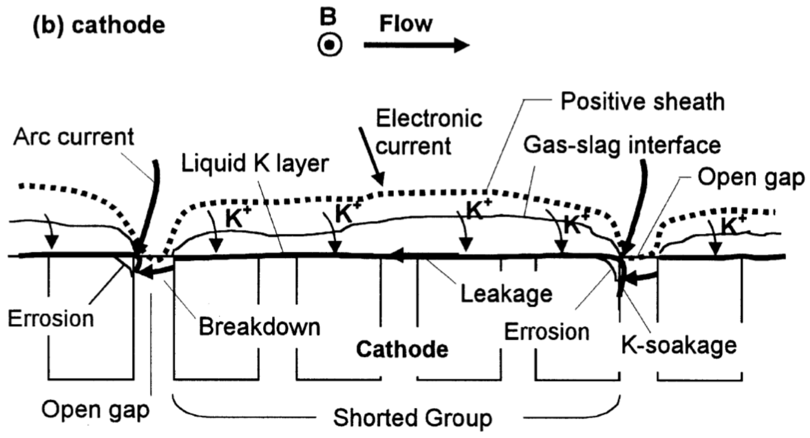


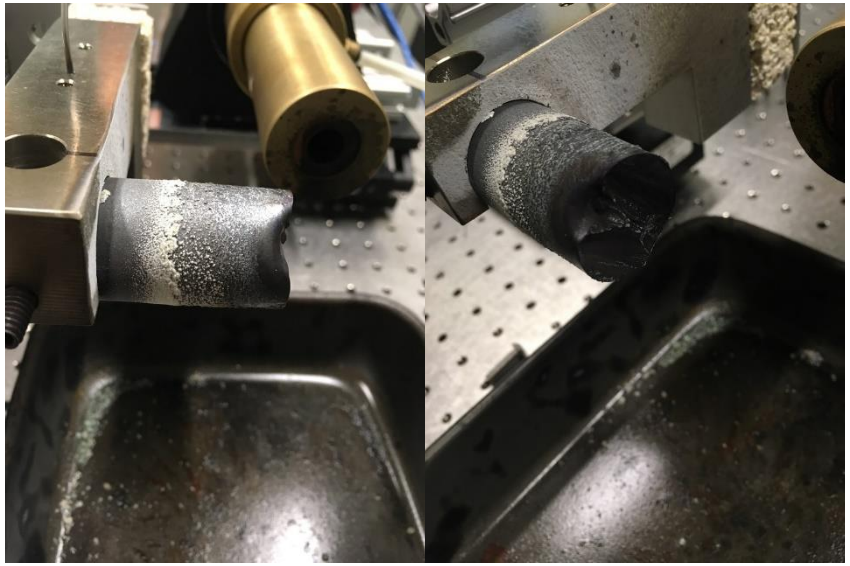
Diagram of channel wall surface and material-plasma interactions in coal-fired MHD channel. (From Kayukawa[1])

Materials Selection

- **Requirements**
  - Wall temperatures > 1500°C
  - Potassium vapor ~1% conc. by weight
  - Oxygen partial pressures 10^{-9}-10^{0} atm
  - Electrical conductivity:
    - <10^{0} S/m for insulators
    - >10^{2} S/m for electrodes

- **Metals**
  - Great conductivity
  - Low melting points
  - Poor oxidation resistance
  - Water cooling necessary

- **Non-oxide Ceramics**
  - High melting points
  - Poor oxidation resistance
  - Still require water cooling



Oxidation of Molybdenum after exposure to potassium seeded plume.
Tungsten oxidized – formed tungstate with seed

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  - Oxygen partial pressures 10^{-9}-10^{0} atm
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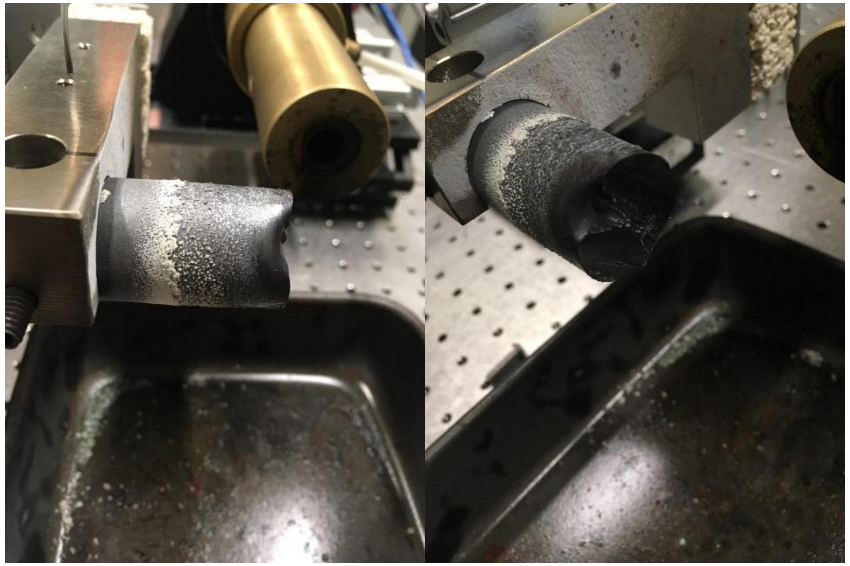
    - >10^{2} S/m for electrodes

Oxide Ceramics

Candidates of interest



Oxidation of Molybdenum after exposure to potassium seeded plume.
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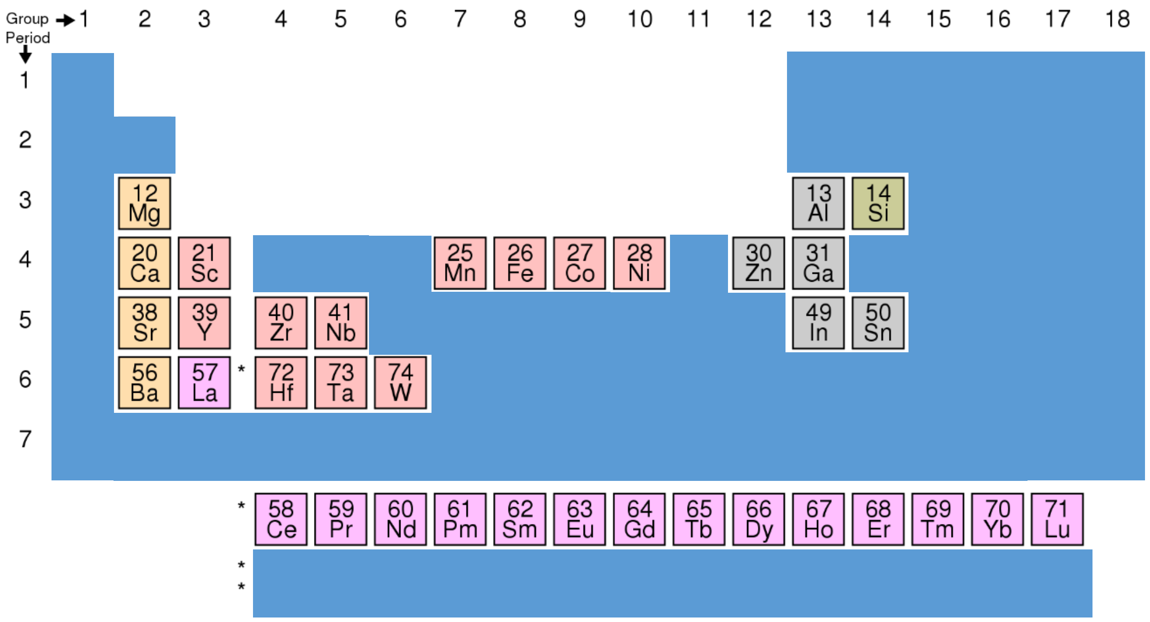
Materials Selection

Oxide Ceramics

- **Trim down periodic table:**
  - T_m>1500˚C, non-hazardous
  - High Temperature Oxides (refractory oxides)
    - Alkaline Earth Metal Oxides
      - MgO, BaO, SrO, CaO
    - Group IV Metals
      - ZrO_2, HfO_2, CeO_2
    - Rare Earths
      - Y_2O_3, Gd_2O_3, La_2O_3, Sm_2O_3 etc.
    - Others:
      - Al_2O_3, SiO_2



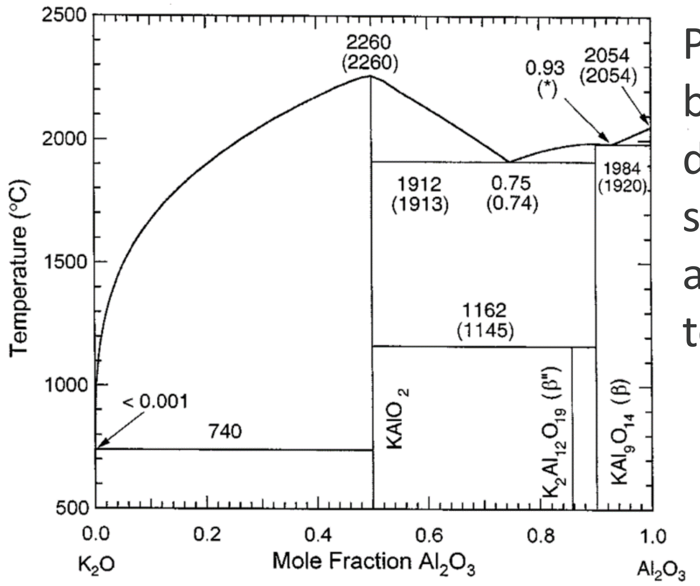
Adapted from [7]

- **These materials are worth evaluating and characterizing**
  - Evaluation: determining which candidates are viable
  - Characterization: quantifying critical properties which dictate performance

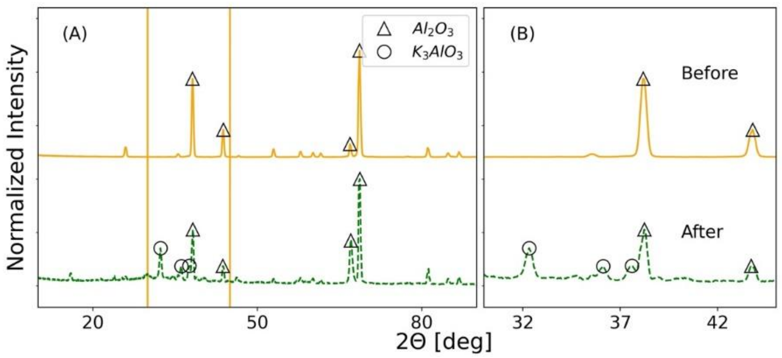
Material Evaluation: Stability

- **Temperature Stability: Criteria Met**
- **Environment Stability: Thermodynamics**
  - High potassium vapor activity
    - Extremely reactive
    - ~1% concentration (by weight)

  No handbook/table to answer this question
  - Evaluation predictors (literature review)
    - Phase diagrams
    - Observed phases - CrystallographyOpenDatabase
    - DFT – MaterialsProject database
  - Experimental evaluation (ex-situ)
    - ASTM Material Performance and Characterization article[10]



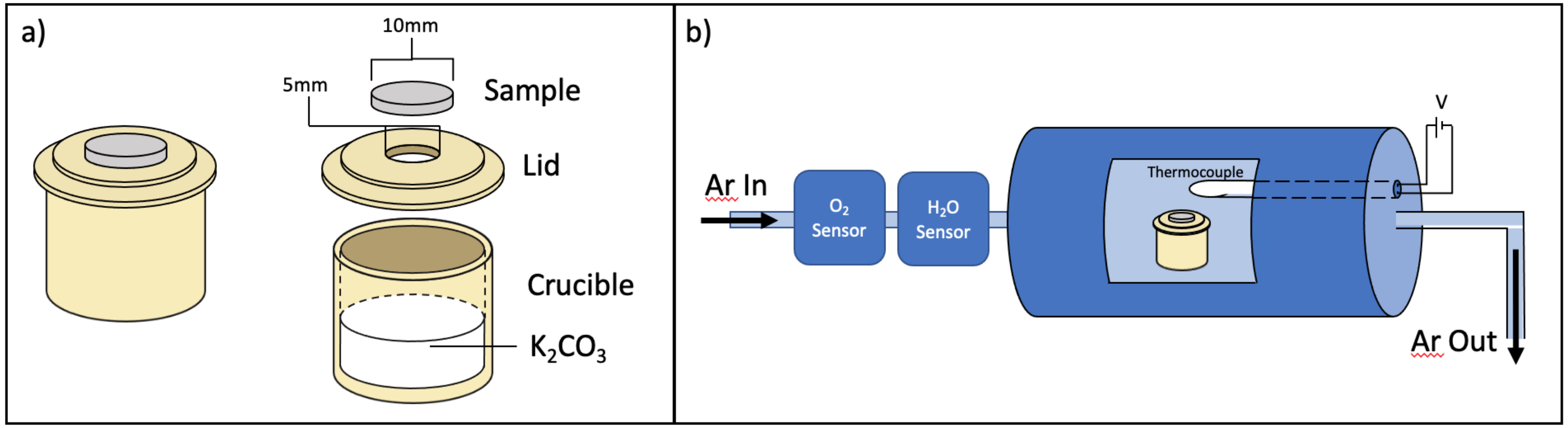
Potassium-Aluminum binary oxide phase diagram showing the stability of potassium aluminate at high temperatures.[8]



From Bowen – M.S. Thesis[9]

Ex-Situ Potassium Corrosion Resistance

Experiment Design: Adapted ASTM Method [5]



Analysis/Quantification

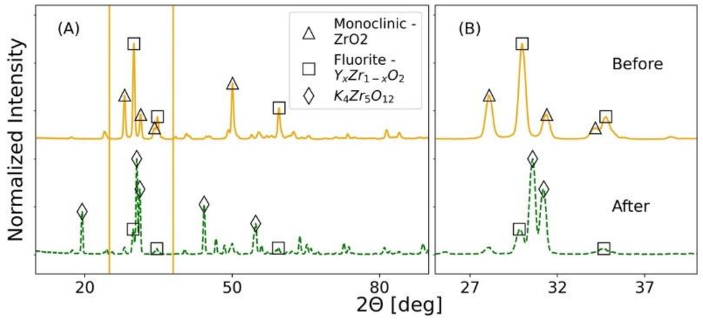
- Null test: No potassium
  - test for standard mass change
  - initial XRD pattern
- K-vapor exposure:
- Surface reaction with sample
- Track mass to 10ug
- Characterize crystal structure
  - Surface XRD of exposed face
- SEM

Conditions:

- 1200°C
- Ar environment: Simplest Case
- 24-hour exposure
- K is dominant species

Predicted and Observed Results

- **Group IV Oxides: ZrO_2, HfO_2, and CeO_2**
  - ZrO_2 is known to react with potassium
    - Determined reason for failure in Ce-Zr-O comps.
    - Three K-Zr-O phases have been described
    - Failure observed – cracking, spalling, joule heating
    - Used as a reference – how will failure present itself?
      - K-Zr-O crystallizes in grains on the surface



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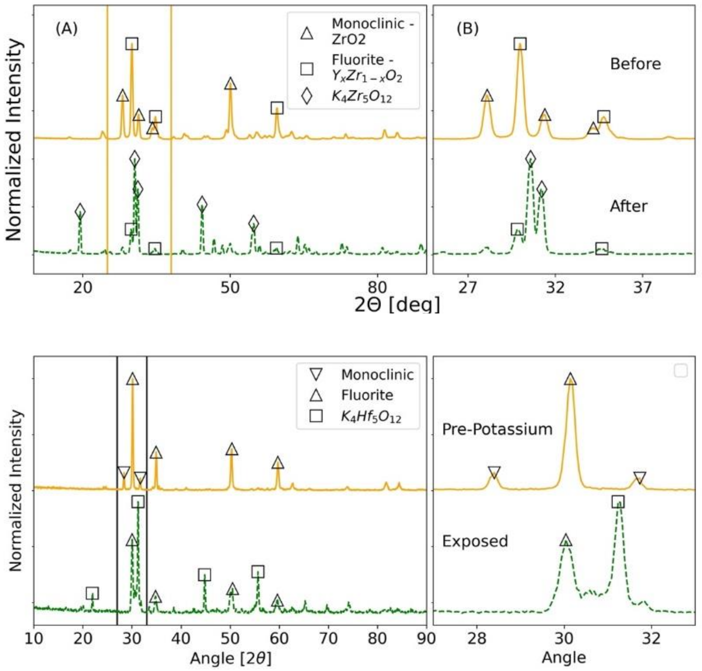
  - HfO_2 is chemically similar to ZrO_2
    - Congruent K-Hf-O phases described – match the K-Zr-O phases
    - Ex-situ tests confirm potassium reaction
      - K-Hf-O crystallizes on surface



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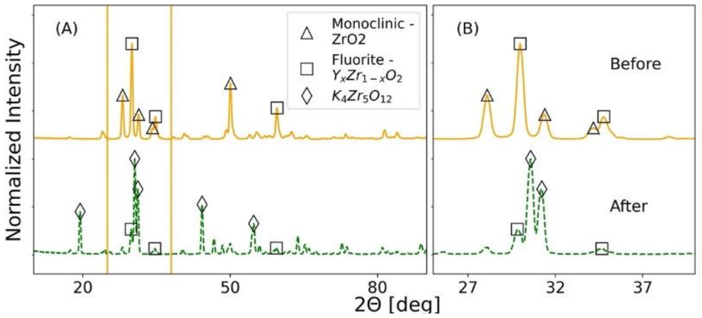
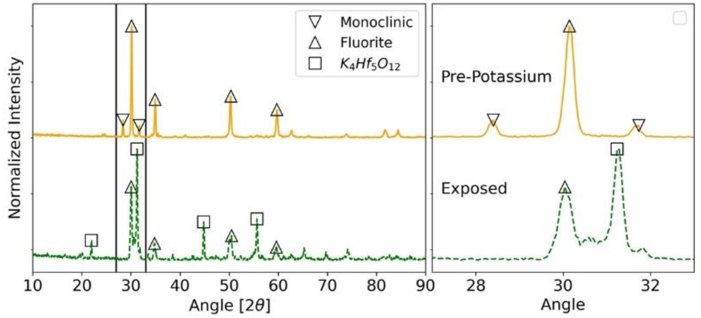
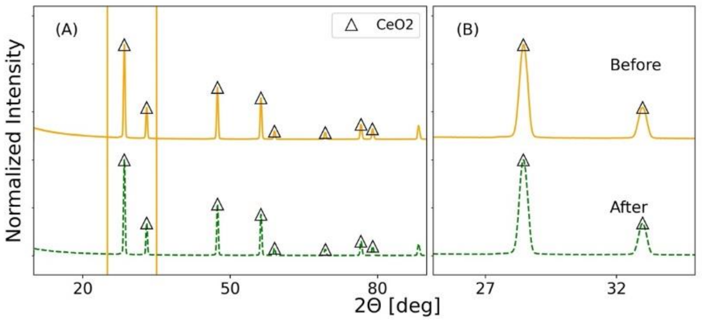
    - Congruent K-Hf-O phases described – match the K-Zr-O phases
    - Ex-situ tests confirm potassium reaction
      - K-Hf-O crystallizes on surface
  - CeO_2 shows promise with potassium corrosion resistance
    - No known K-Ce-O phases
    - No potassium reactions observed in ex-situ exposure







Predicted and Observed Results

- **Alkaline Earth Oxides: MgO, BaO, SrO, CaO**
  - MgO – tested in early research, primary insulator candidate
    - No K-Mg-O phases observed in literature or ex-situ testing
    - Some potassium infiltration to grain boundaries
  - SrO, BaO, and CaO are expected to yield similar results
    - SrO will be evaluated in $SrGd_2O_3$
- **Rare Earth Oxides: Gd_2O_3, Y_2O_3, La_2O_3**
  - Gd, La, and Y are selected based on compatibility with other materials
    - YSZ, GDC, $LaMnO_3$
  - Aside from cerium, rare earths share many chemical properties
    - Potassium reactions expected to be the same
  - At high doping levels (>10%) no potassium formations observed
    - Ex-situ testing
    - Predicted phases – only theoretical (DFT)
    - Nothing experimentally observed

No predicted or observed reactions!

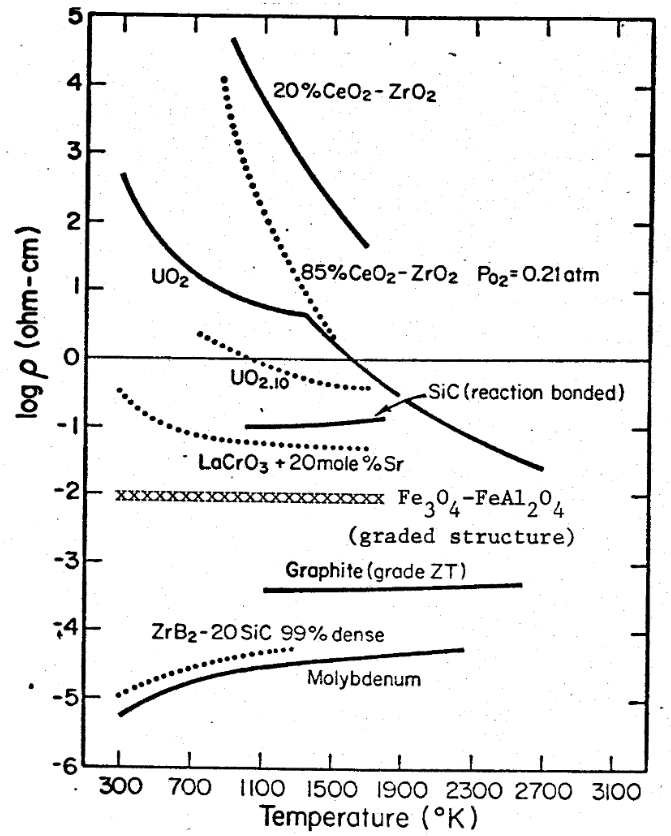
Summary of Results

- **Of the Group IV Elements:**
  - Cerium oxide is the only one to resist potassium reactions
  - Zr and Hf oxides both form a potassium containing phase on the surface when exposed, which results in spalling and surface degradation
- **Of the Alkaline Earth Elements:**
  - MgO resists potassium corrosion
    - Some potassium infiltration in G.B observed in legacy work
      - Suspected to be a result from impurities
  - Ba, Sr to be tested
- **Of the Rare Earth Elements:**
  - Gd, Y, and La appear to resist potassium corrosion
    - Not evaluated as bulk material (used as additive)
  - Others to be tested (PrO2 is only one predicted to react)

Evaluation: Electrical Performance

Electrical Characterization

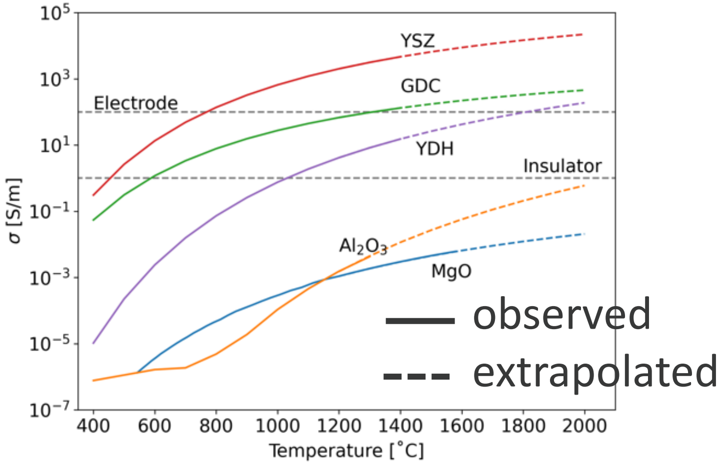
- **Conductor and Insulator**
  - Conductors > 100 S/m
  - Insulators < 1 S/m
  - Conductors should have lower activation energy
- **Little reported data in literature >1000˚C**
  - Most data shared is old
  - Measurements this high are more difficult to execute
  - OSU cooperative efforts to collect data up to 1600˚C

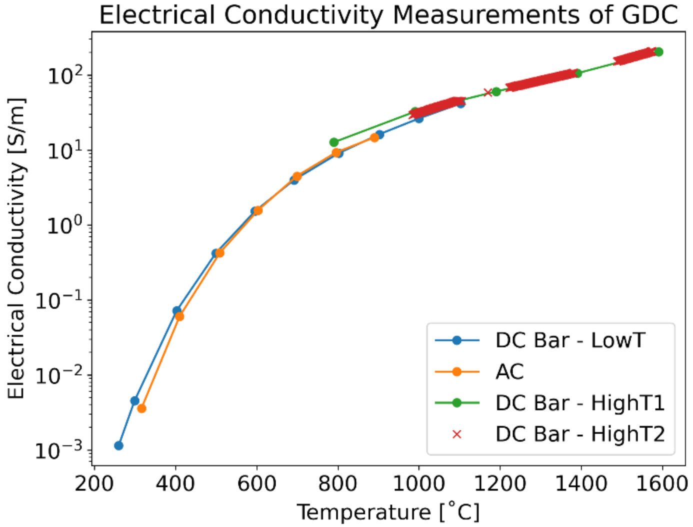


From Rudins et al[11]
MHD Electrode Material development

Summary of Results

- **Electrical Conductors:**
  - ZrO_2, HfO_2, CeO_2, $LaMnO_3$
    - Doped with rare earths
- **Electrical Insulators:**
  - Al2O3, MgO
- **Specific operating temperatures**
  - Transition electrode for int. temperatures
- **Activation energy: σ vs T**
  - Ceramics vs Metals



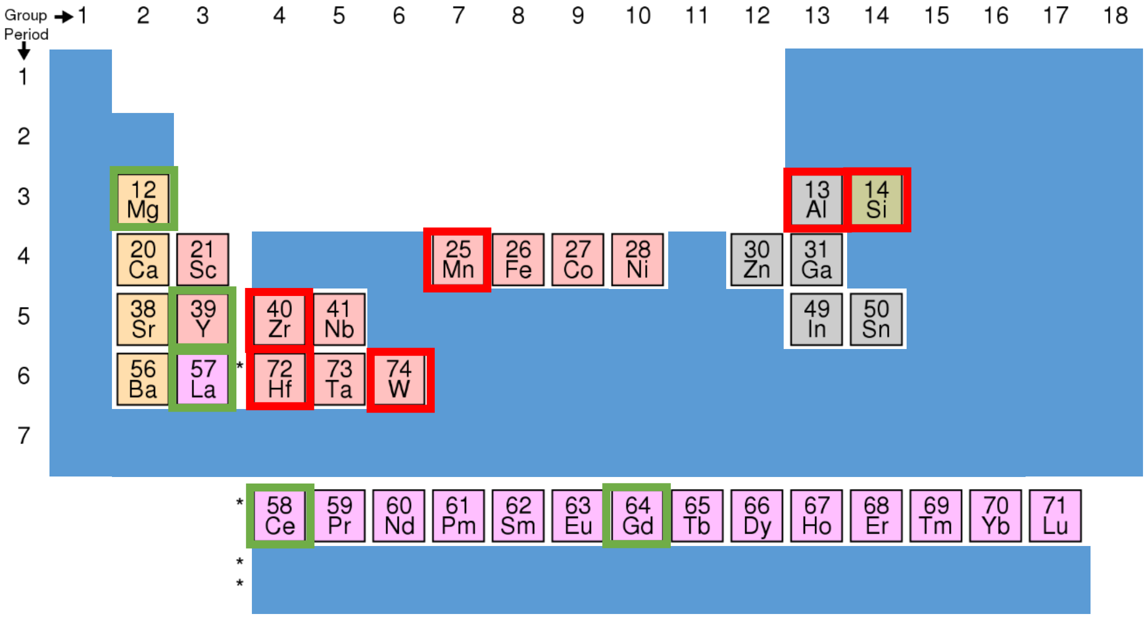


Summary of Results

Mat'l	Electrode/ Insulator	Ex-situ K corrosion?	Proceed with in-situ testing?
Al2O3	Insulator	reacts	no
MgO	Insulator	resists	yes
ZrO2 (with Y)	Electrode	reacts	no
HfO2 (with Y)	Electrode	reacts	no
CeO2	Electrode	resists	yes
LaMnO3	Electrode	reacts	no

WO_3 and SiO_2 reactions observed in uncontrolled tests

Materials tested thus far are highest melting point suspected to be most stable



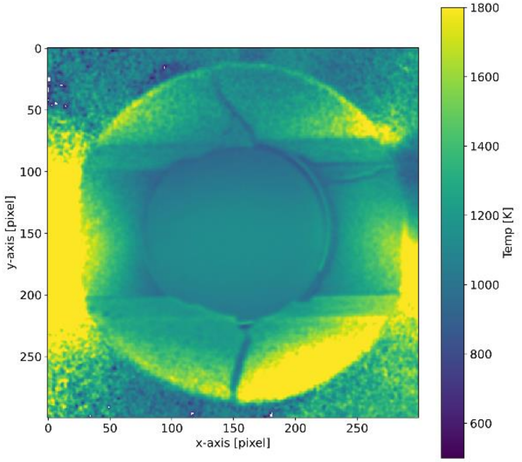
- Passed evaluation criteria

- Failed evaluation criteria

Evaluation: In-Situ Testing

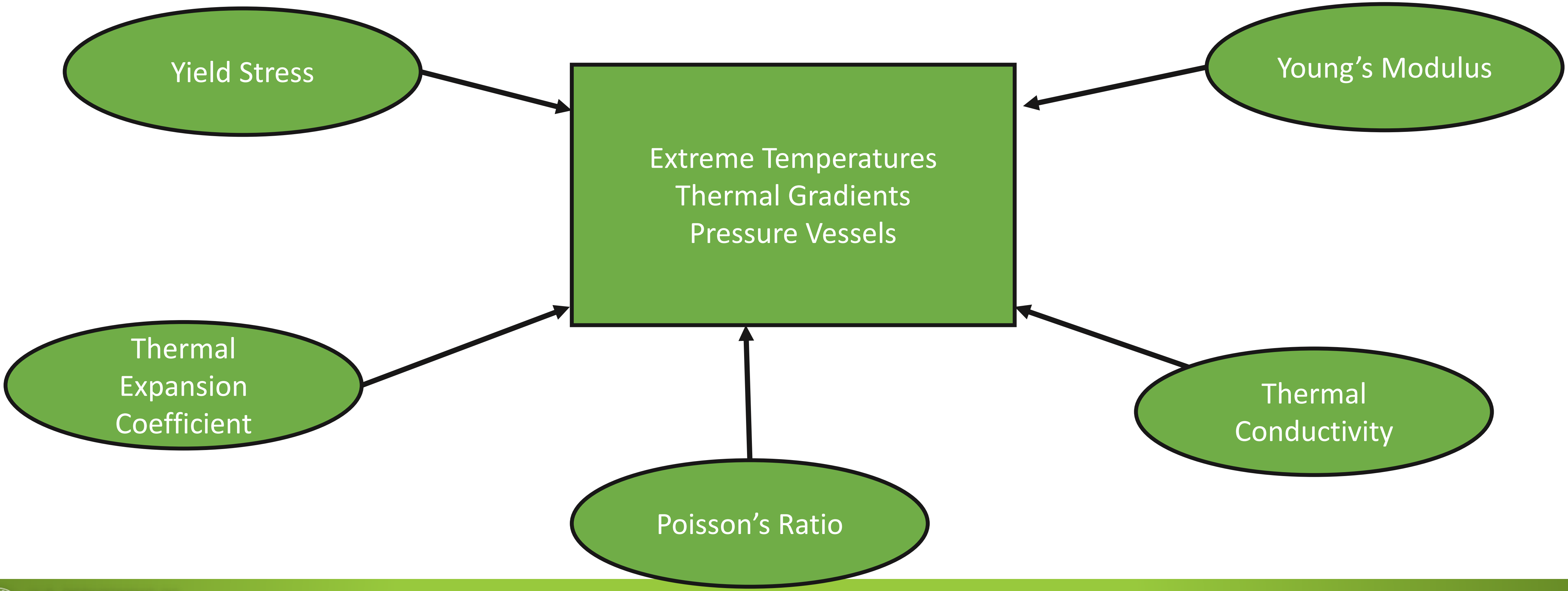
- **Evaluate material stability against true MHD operating conditions**
  - HVOF Combustion System
    - Oxy-Kerosene combustion
    - Potassium-Kerosene emulsion seed feeding
  - Surface characterization
    - XRD
    - SEM/EDX
  - Thermal performance
    - Two-color pyrometry
      - Non-contact temperature measurement for surface temperatures
    - Thermocouples
      - Contact temperature measurements

Iterative design testing:
Top left: crucible mount
Bottom left: sleeve holder
Bottom right: in-situ thermal image



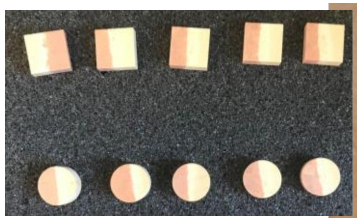
Design Considerations

Thermal and Mechanical Properties

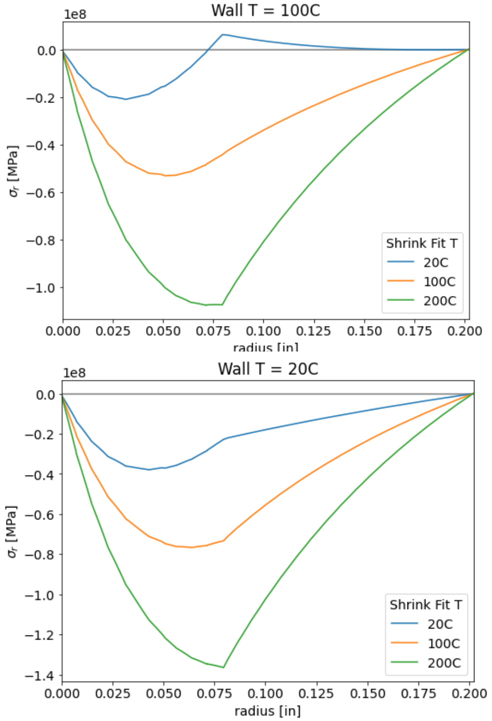


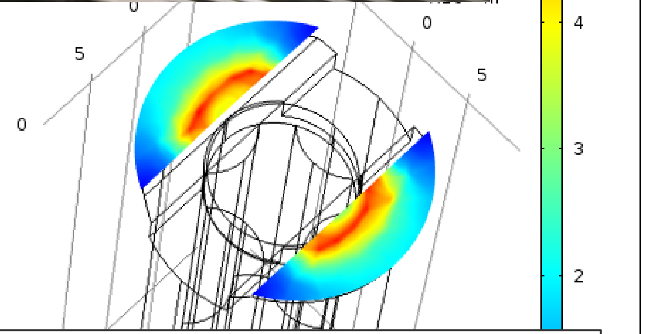
Fabrication and Modeling

- **Modeling:**
  - Thermal Stresses
    - Hoop stress
    - Interference fit
- **Fabrication**
  - 3D Printing
  - Machinable Ceramics
  - Monolithic channels
    - Unibody rather than multi-component
  - Graded Ceramics

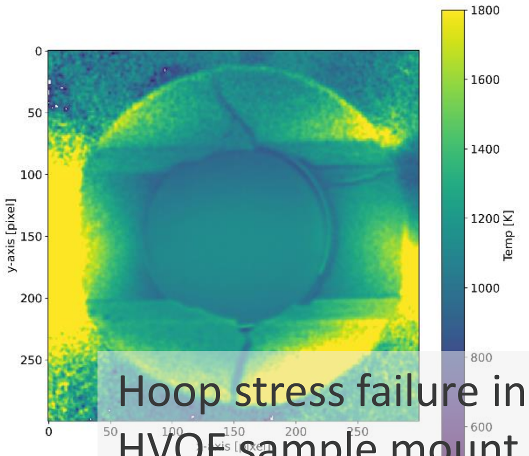

Graded ceramics


3D Printed SiO_2 Channel

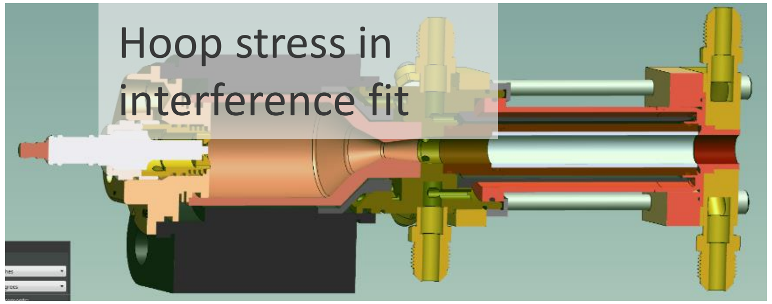




Failure in MgO sleeve – sample mounting apparatus for HVOF exposure
Model vs Experiment



Hoop stress failure in MgO Sleeve: HVOF sample mount apparatus



Hoop stress in interference fit

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