Ultra-High Temperature Ceramics: Materials For Extreme Environment Applications V

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Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications V
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ZrC in Nuclear Applications

- Next Gen nuclear reactor technology
  - Goal: increased economic, safety, and power outputs
  - Challenges:
    - Maintain integrity of fuel element structure
    - Prevent contamination from fission products
    - Radiation Resistance
- ZrC in Nuclear Cladding
  - Provides:
    - Oxidation resistance
    - Superior material properties
      - Chemical resistance, thermo-mechanical integrity
    - Toleration of radiation damage

Motivation

- ZrC is a promising coating for advanced reactor fuels
  - Excellent resistance to corrosion
  - Fabrication results in range of stable ZrC stoichiometries
    - Sub-stoichiometric to carbon rich
- ZrC oxidation passivates under appropriate temperature and pressure conditions
  - Protective oxide layer formation
- The phenomena underlying this oxide passivation has not been studied above 1000K
  - Yet next generation nuclear reactors operate at temperatures >1873K

Literature Review

- <1000K Fickian diffusion dominates reaction before 2nd mechanism assumes control
- Katoh et al.
    - – Densification of monoclinic zirconia, CO_2 partial pressure controls reaction rate
- Shimada et al.
    - – Crystallization of cubic zirconia at 743K shifts mechanism to grain boundary diffusion
- Rama Rao et al.
    - – Formation of an intermediate oxycarbide layer alters reaction rate

Further Challenges

- Martensitic Phase Change
  - – Tetragonal ZrO_2 to monoclinic ZrO_2 transition at 1443K
- Intermediate oxycarbide layer
  - – Transient
- Contributions to Non-Fickian Diffusion
  - – Cracking
  - – Grain sizes
  - – Material crystal structure
  - – Low formation energy of carbon defects

Microscale Model

- Oxidation of ZrC
  - Finite Rate Chemistry Model
  - Developing a high temperature ZrC oxidation model with experiments at UIUC
- SPARTA Simulation Tool
  - Direct Simulation Monte Carlo Tool
    - Developed by Sandia National Laboratories
  - Model: gas-gas reactions, gas-surface interactions, gas-surface reactions
  - Leverages finite rate chemistry

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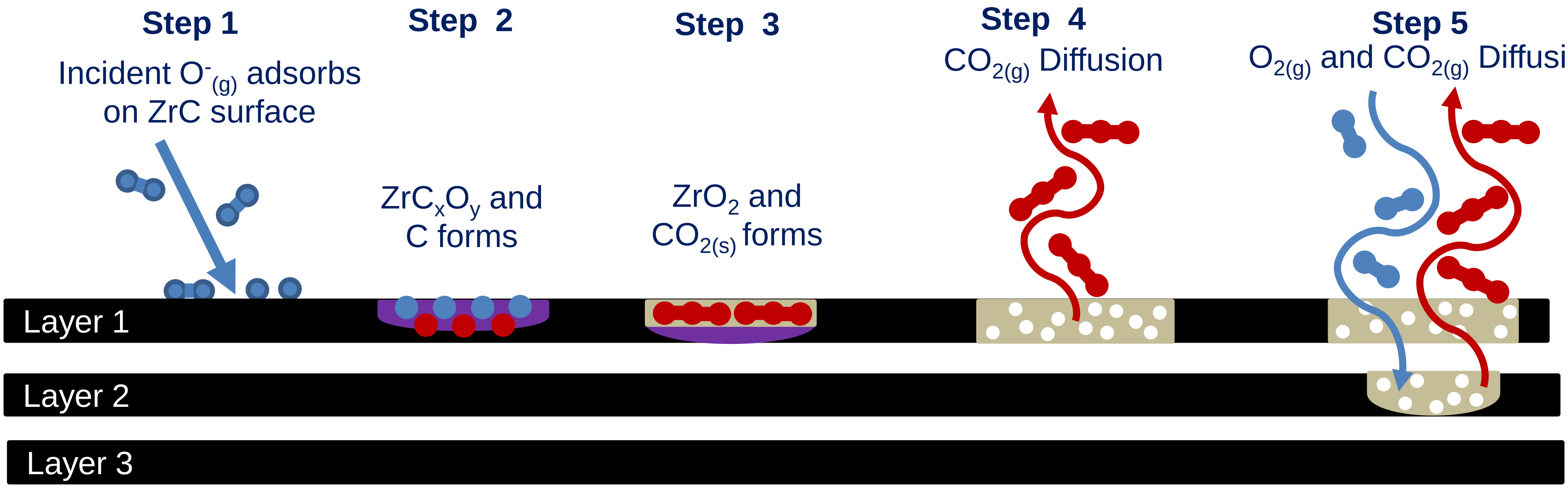
ZrC Oxidation



Step 1

Incident $O^{-}_{(g)}$ adsorbs on ZrC surface

Step 2

ZrC_xO_y and C forms

Step 3

ZrO_2 and $CO_{2(s)}$ forms

Step 4

$CO_{2(g)}$ Diffusion

Step 5

$O_{2(g)}$ and $CO_{2(g)}$ Diffusion

Fig 1.

Step 1: Incident $O^{-}_{(g)}$ adsorbs on ZrC surface

Step 2: ZrC_xO_y forms

Reaction: $ZrC + 2O^{-}_{(g)} \leftrightarrow ZrC_xO_y + yC$

Step 3: Adsorbed O2 reacts with ZrC_xO_y to form ZrO_2 + $CO_{2(s)}$

Reaction: $ZrC_xO_y + O_{2(g)} \leftrightarrow ZrO_2 + CO_{2(s)}$

- At this point, there are competing reactions with O_2 to form ZrO_2 or CO_2

Step 4: CO_2 diffusion creates micro-voids in matrix

Step 5: 1-4 repeat with O_2 diffusion to create further oxide layer depth.

▨ - Oxide layer (ZrO_2)

🟪 - ZrC_xO_y

●● - O_2 Molecule

●●● - CO_2 Molecule

● - O Molecule

● - C Molecule

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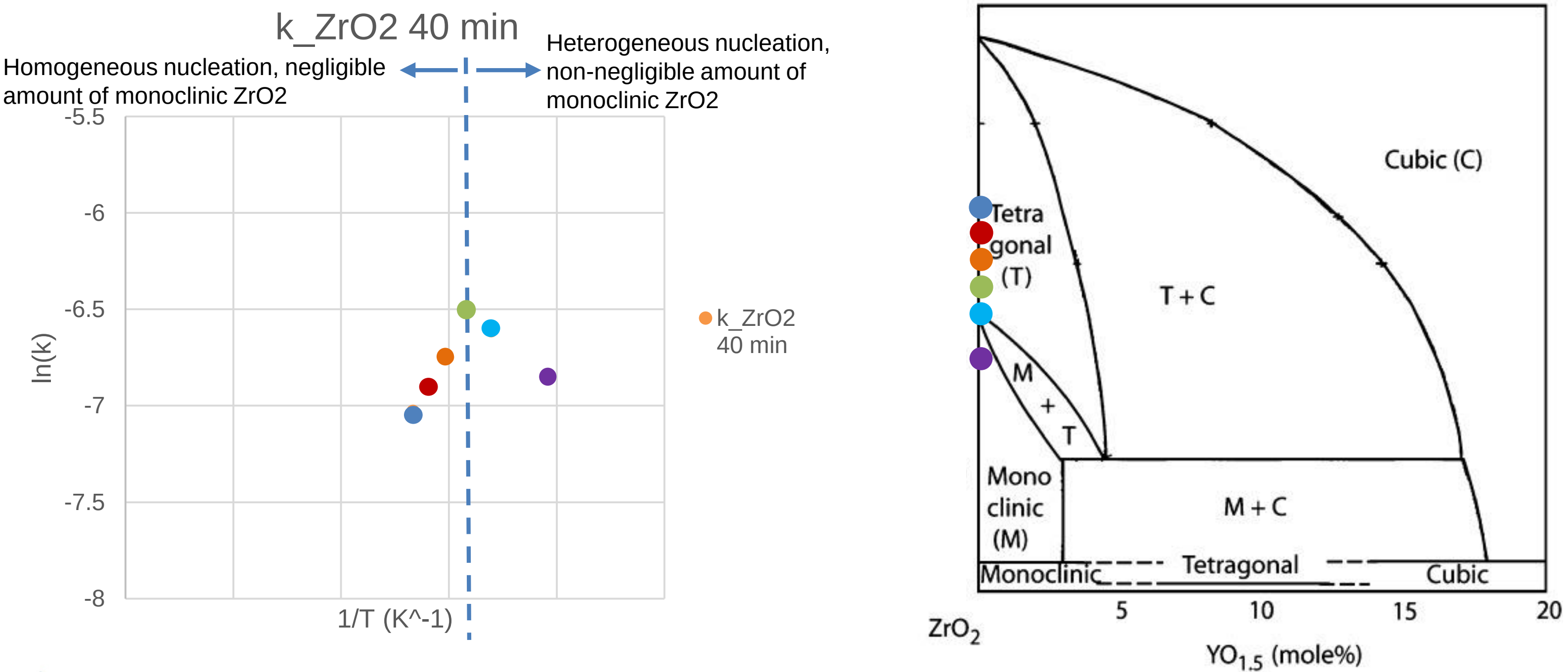
ZrC Experimental Approach

- Material
  - ZrC Sputtering targets
  - 99.9% purity
  - ZrC0.63
- Structure
  - Face centered cubic with Carbon defects
- Furnace Setup
  - Isothermal heating, flow tube furnace
  - 20% Oxygen, 80% Nitrogen
- Conditions
  - Elevated Temperature Range
  - 10-40 minute runs

Kinetic Rates

- Arrhenius fitting of rates derived from furnace experiments (10 min) yields two fits:
    - Mixed Regime: k = 0.1265*exp((-69.5 kJ/mol)/RT)
    - High Temperature Regime: k = 105.41*exp((-168.8 kJ/mol)/RT)
    - Observe change in rates with time, indicating densification of the oxide layer
    - Differences in porosity and quality of the oxide layer

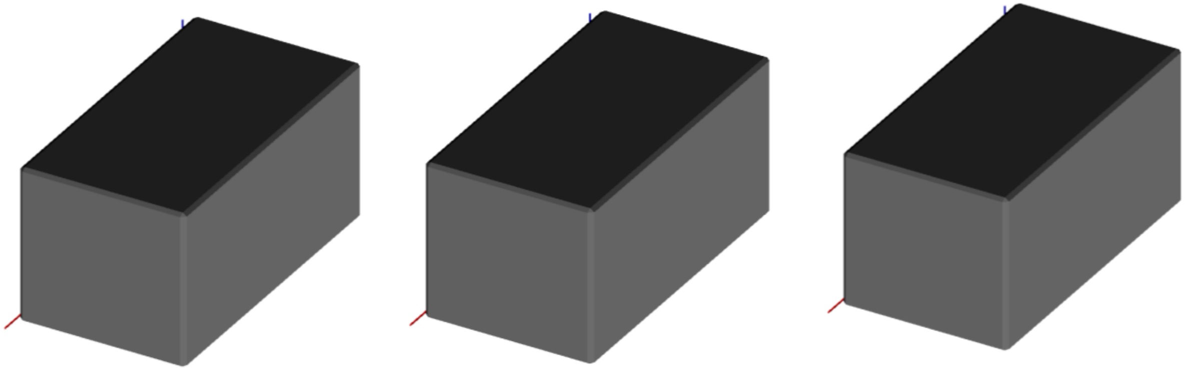

Homogeneous nucleation, negligible amount of monoclinic ZrO2

Heterogeneous nucleation, non-negligible amount of monoclinic ZrO2

Fig 2. Arrhenius Graph and Phase Diagram demonstrating the correlation of kinetic rates with phases of ZrO2. Phase diagram reproduced from Witz et al.

ZrC Rates

- 3 Different Oxide layer formation regimes
  - High Temp Regime: dense protective oxide layer forms
  - Mixed Regime: porous protective oxide layer forms
  - Low Temp Regime: powderization of sample
    - Rate in this regime was captured by Rama Rao et al.
- Rates implemented in SPARTA for appropriate temperature regimes
  - Currently assumes all active sites are available to react
- As oxide layer forms, impedes further oxidation of ZrC
- Capture overall ZrC oxidation response
  - Time and temperature



HT Regime Reaction Front

Mixed Regime Reaction Front

LT Regime Reaction Front

Fig 3. Videos of ZrC oxidation rates in each identified regime, from left to right (High Temp, Mixed, Low Temp)

Future Developments

- Refine and Develop Sparta Simulations
  - Develop and refine outputs
  - Verify ability to recreate furnace experiments and predictive model capability
  - Implement thermal transport phenomena and cracking into model

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Supplemental Slides

ZrC Fabrication

- Solid Phase reactions
  - Reduction of ZrO_2 with Carbon
  - Intermediate oxycarbide phases
- Powder sintering
  - Potentially Non-isotropic
  - Stoichiometry depends on Zr:C molar ratio
    - Customizable if properly controlled
- Solution based fabrication
  - Diffusional reaction
  - Long timescales required
  - Residual oxygen impurities
- Vapor Phase
  - Low porosity, limited impurities
  - Difficulty due to use of zirconium halides as feed gas
  - Provide control over density and stoichiometry
  - Specific to coatings

Influences on ZrC Properties

- Carbon to Zirconium molar ratio
- Chemical impurities
  - Additives and stabilizers
  - Oxygen impurities at carbon defect sites
- Secondary phases
  - Ex. Grain boundary phases
- Grain size, morphology, orientation, and texture
- Porosity, pore size, tortuosity