Computational-Experimental Study of Plasma Processing of Carbides at High Temperatures

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High Temperature Research Group

- Graduate Students
  - Alejandro Garcia (Computational - Masters) to Delfingen Inc.
  - Arturo Medina (Computational - Masters)*
  - Sanjay Shantha-Kumar (Experiment - Ph.D.)*
- Senior/Graduate Student Transition
  - Alberto Delgado (Experimental/Computational – Dual B. S. in Mechanical Engineering with B. S. in Metallurgical & Materials Engineering, MME); Now pursuing MS in MME.

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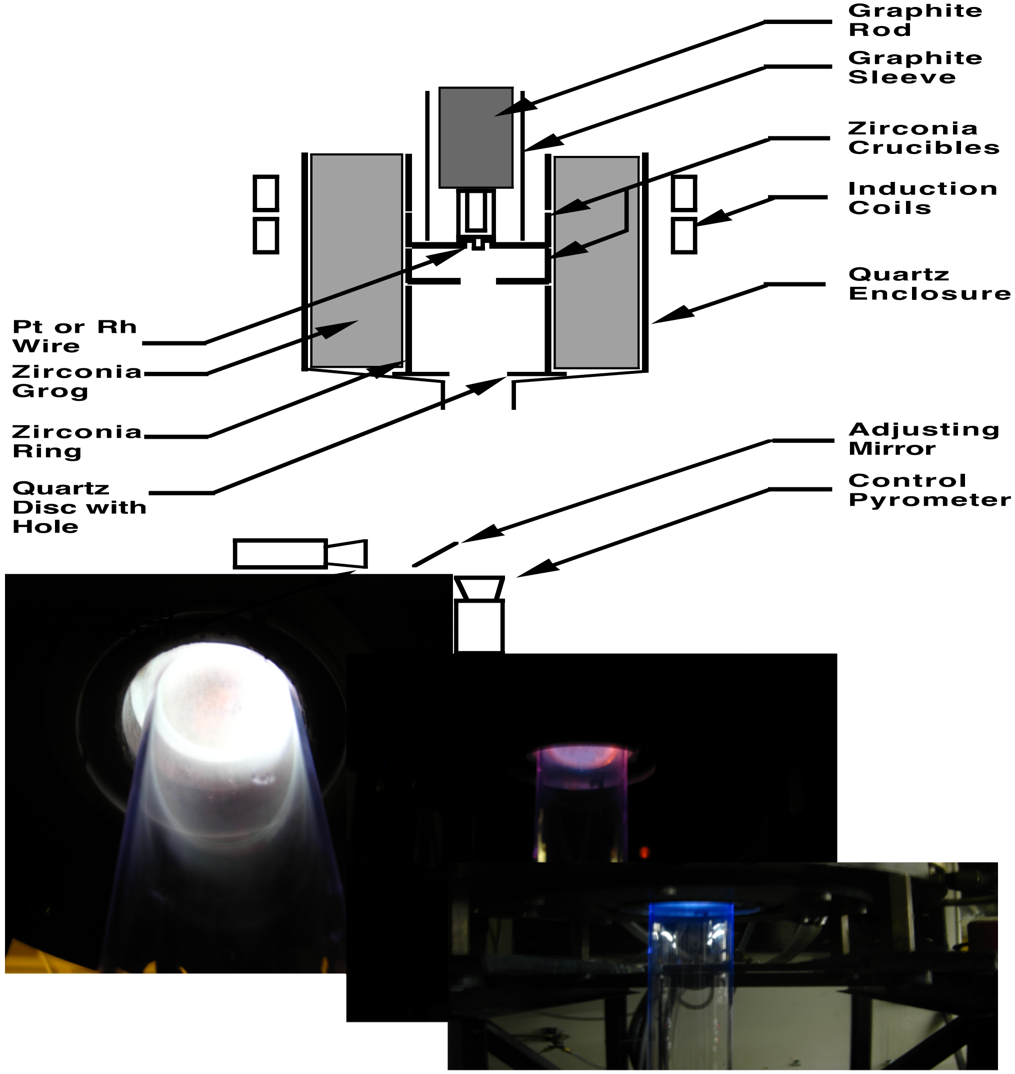
* Aids students in high temperature research.

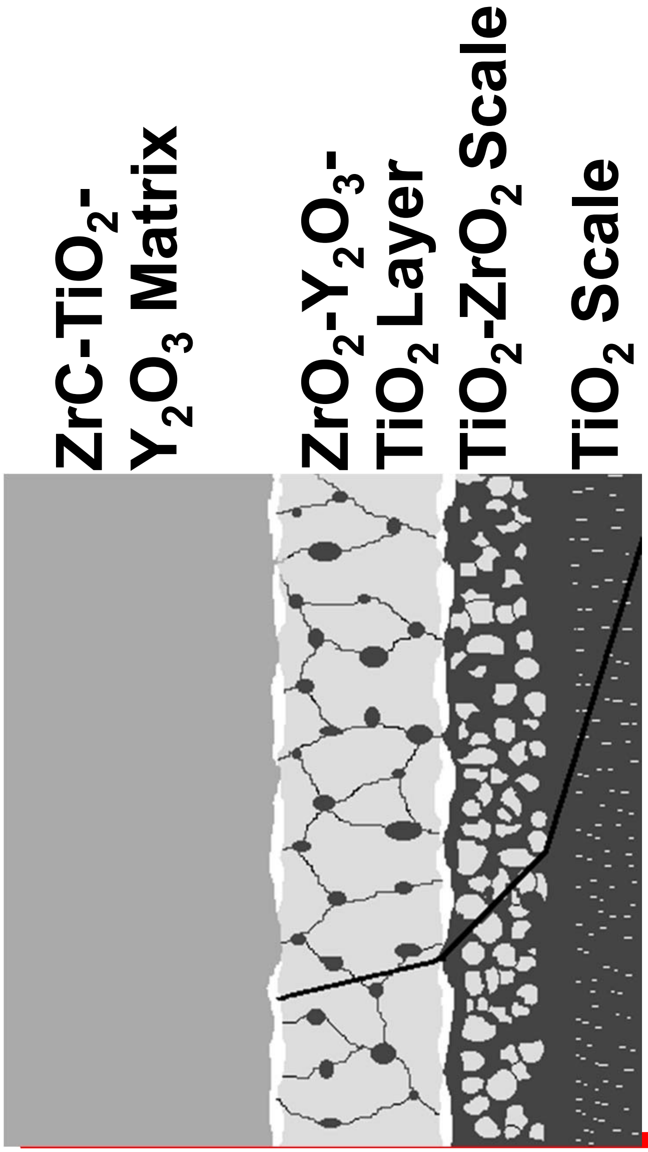
Motivation/Impact of Research

- **Use electromagnetics to control plasma surface reactions.**
- **Use plasma processing to create temperature extremes.**
- **Use temperature spikes to form metastable phases.**
- **Use electromagnetics to change diffusional flux.**

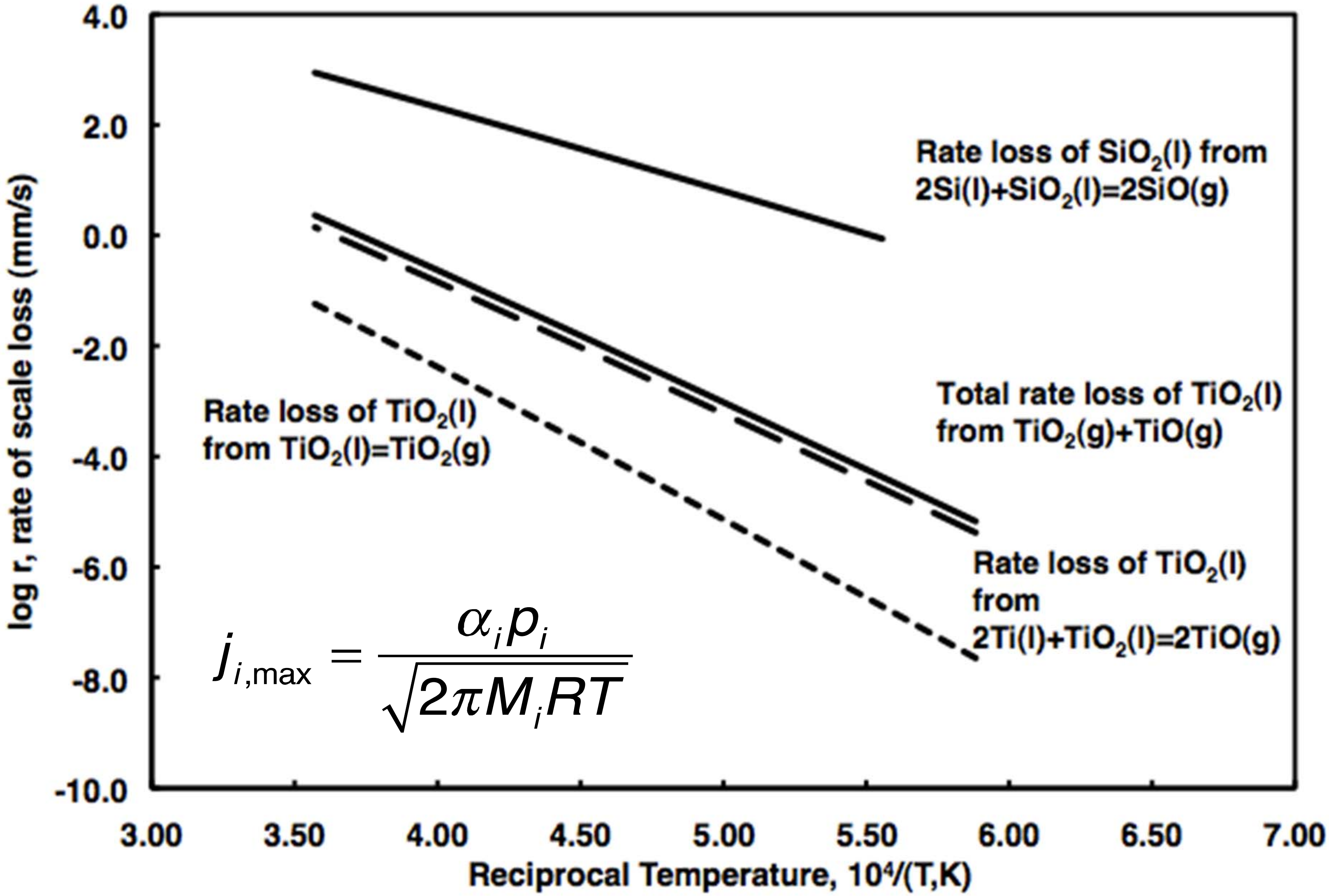


Outline of Presentation

- Introduction – Processing
  - Scale of Al_2O_3 and TiO_x
  - Plasma Surface Reactions
- Computational thermodynamics coupled with heterogeneous kinetics infused with fluid dynamics to model plasma gas reactions
- Strategic Experimentation – Ti_3AlC-TiC Processing and Oxidation
- Analysis of Plasma-Surface Reactions



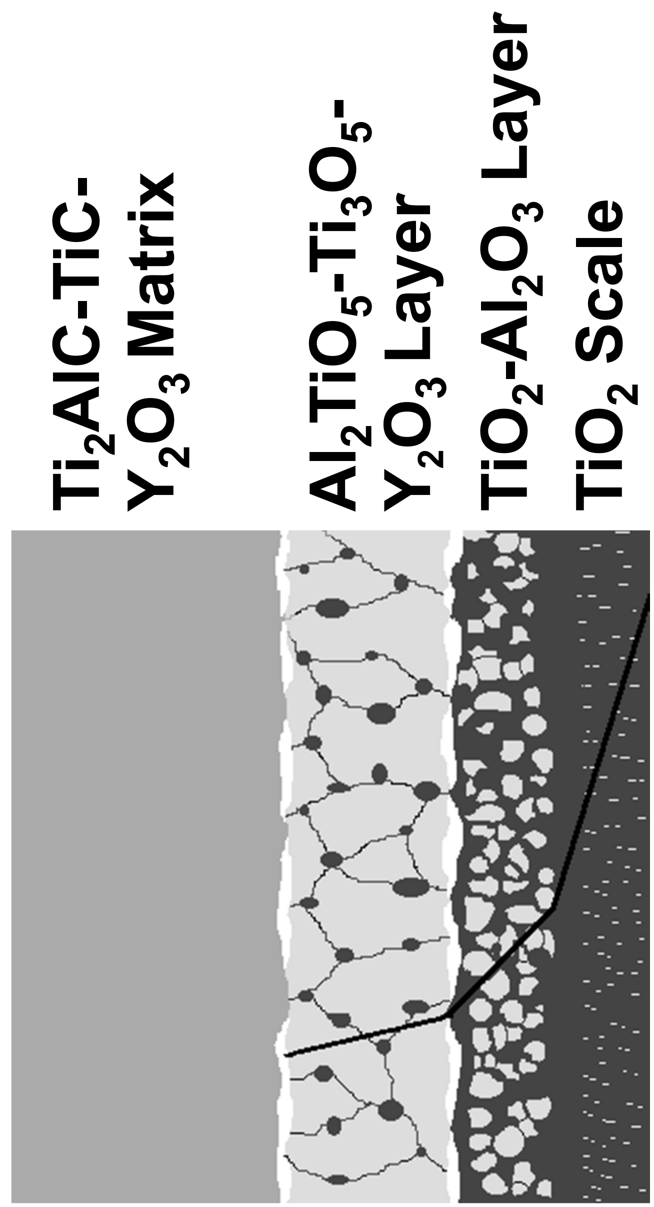
Vaporizing Flux of SiO_2 and TiO_2



$$j_{i,\max} = \frac{\alpha_i p_i}{\sqrt{2\pi M_i R T}}$$

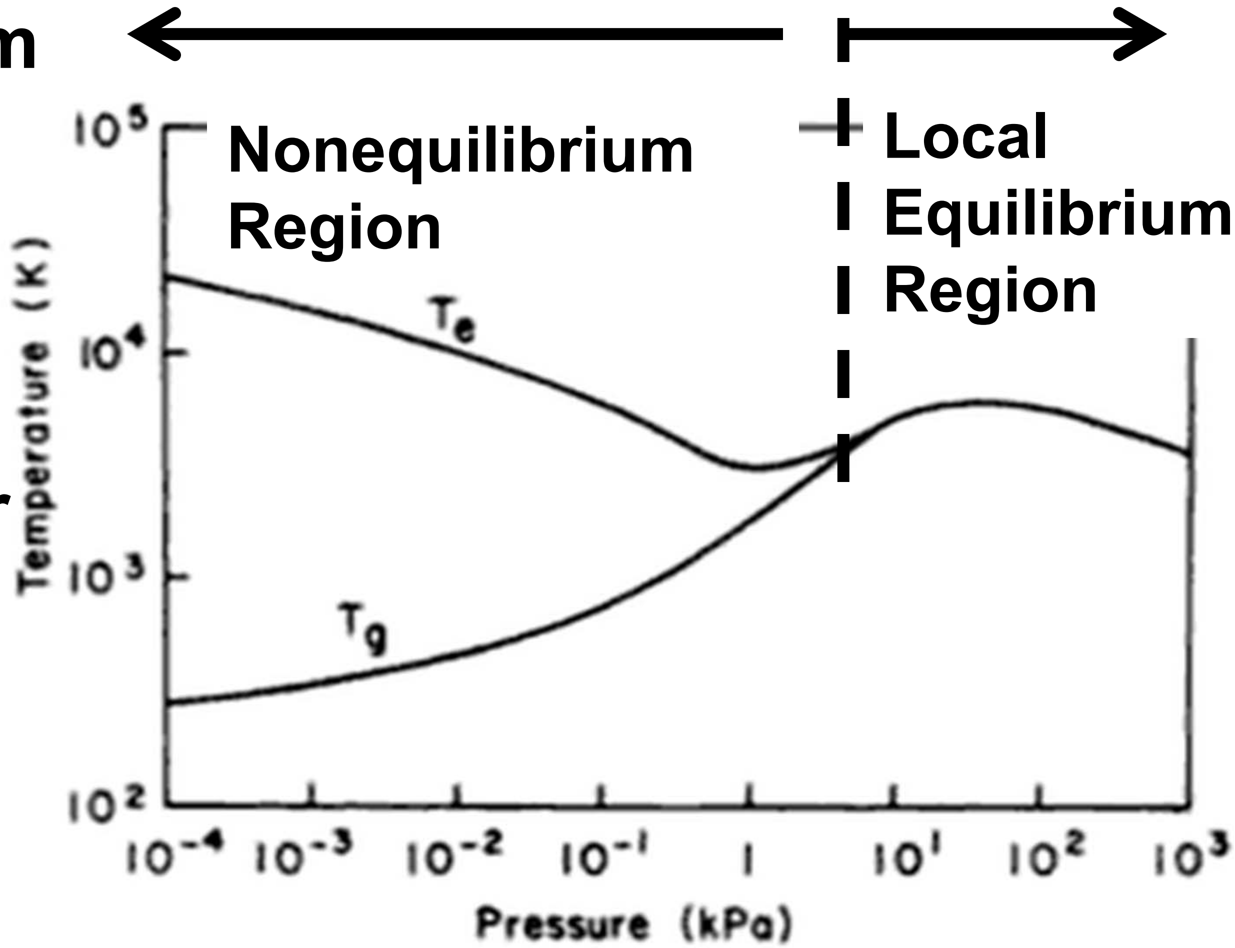
Project Objectives

- Investigate the effects of **plasma surface reactions within pores of carbide packed bed**;
- Investigate the plasma-surface reactions on high temperature carbides
- Investigate the **effect of the potential gradients of the electromagnetic field** on mass transfer



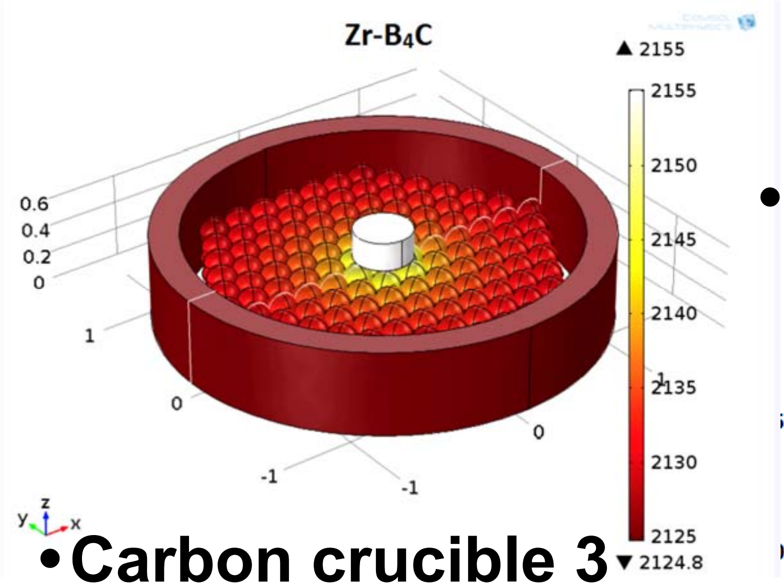
Plasma Temperatures - Pressures

- Non-equilibrium versus local equilibrium plasmas
- Plasma energy in terms of T or $(T_e-T_g)/T_e$
- Significantly lower number of studies on plasma-surface reactions.



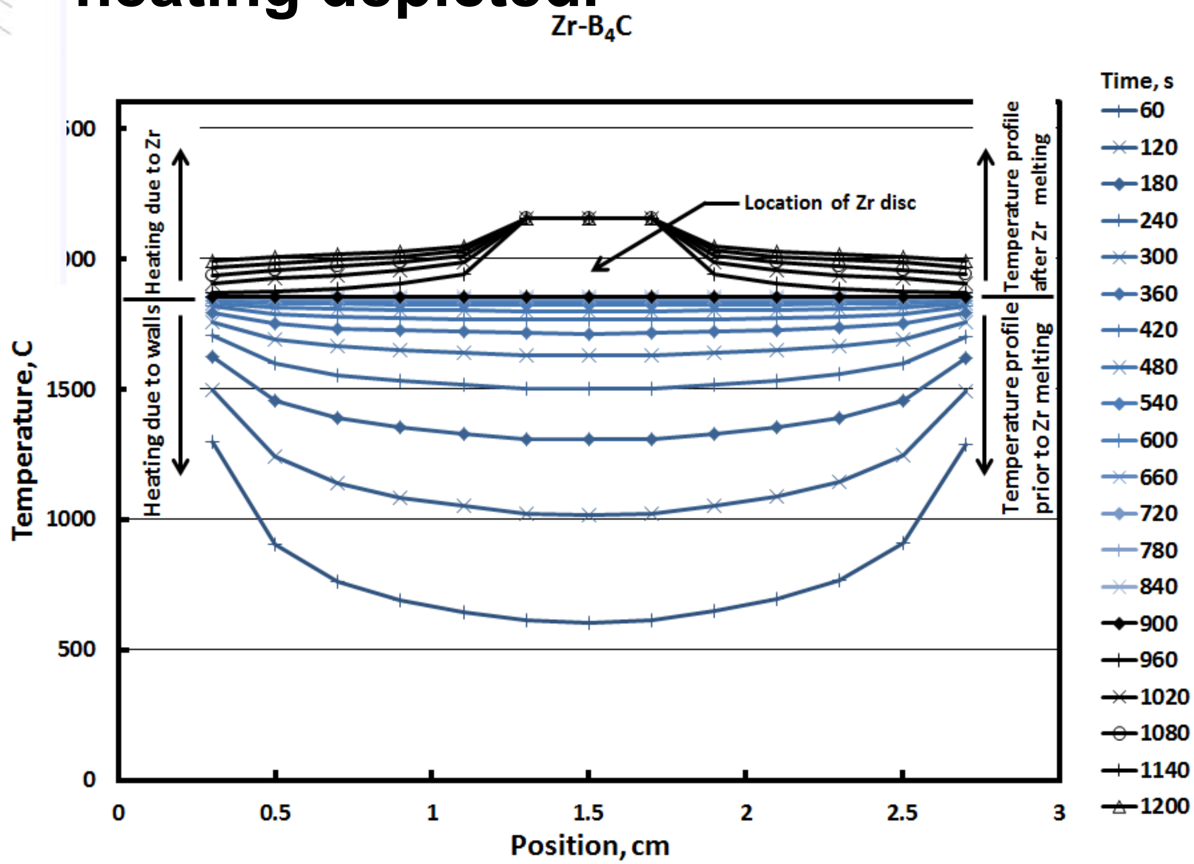
Boulous, Fauchais and Pfender--1994

Temperature Transients from COMSOL Simulations



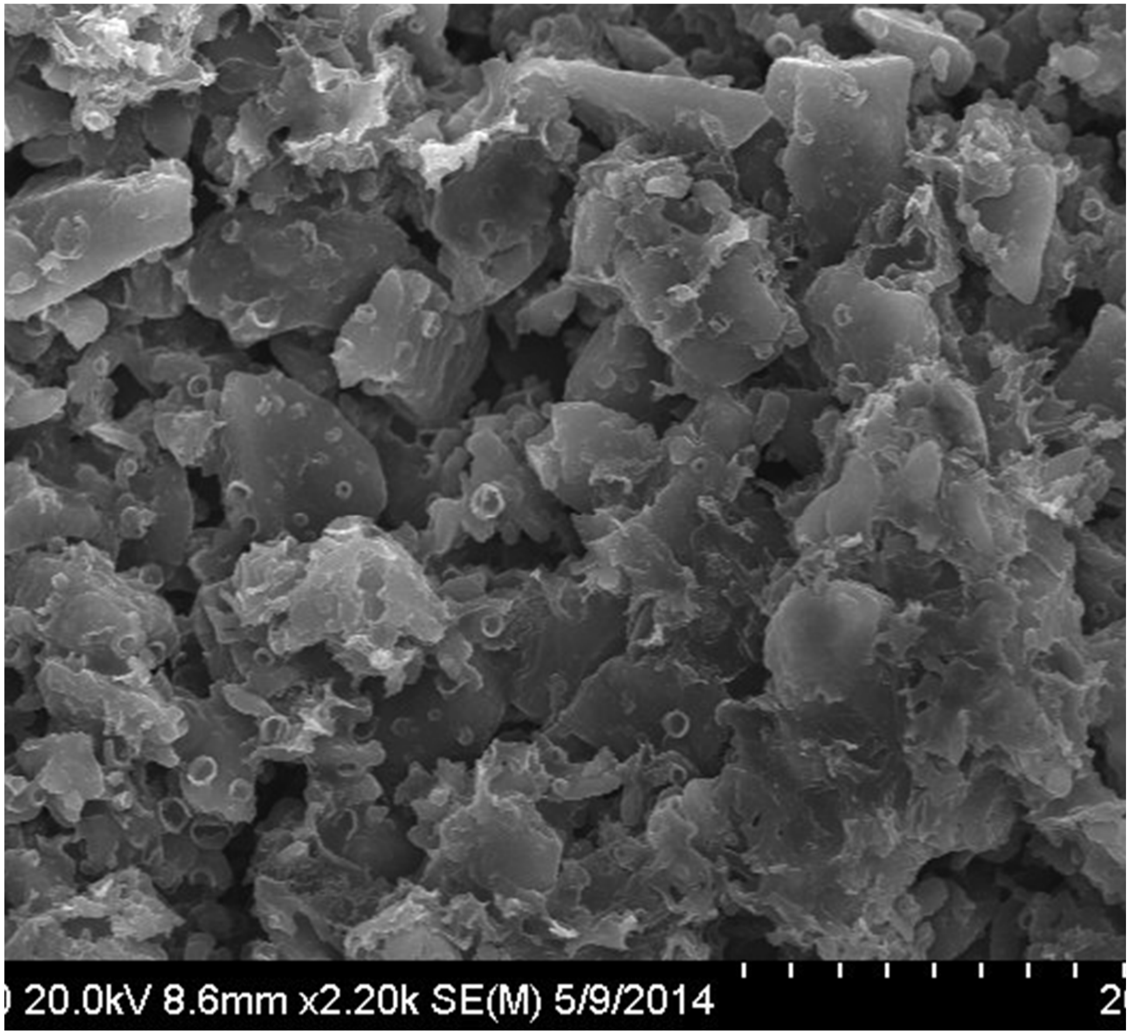
- Carbon crucible 3 cm OD-2.6 cm ID & 254 B_4C spheres.
- B_4C melts at 2450° C
- Zr melts at 1855° C
- k_{B4C}=4.5, k_{Zr}=34 W/(mK)

- B_4C packed bed (0.2 cm diameter spheres) with a Zr disc (0.4 cm diameter) placed on top of bed.
- Temperature profile of bed and Zr heating depicted.



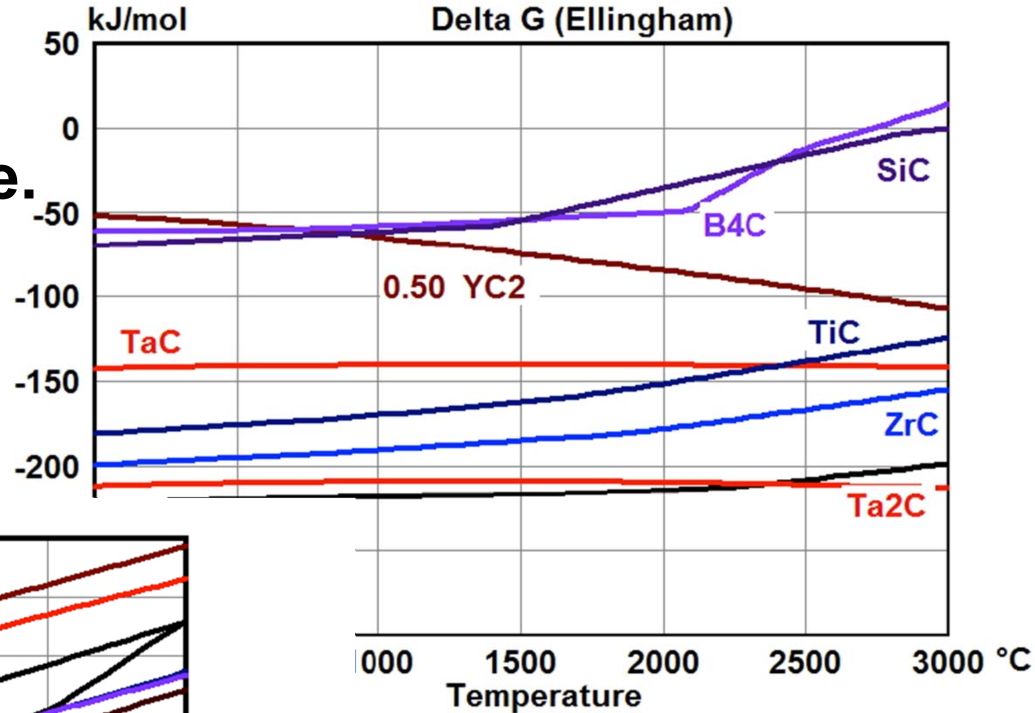
B_4C Microstructure after 1700° C Heating

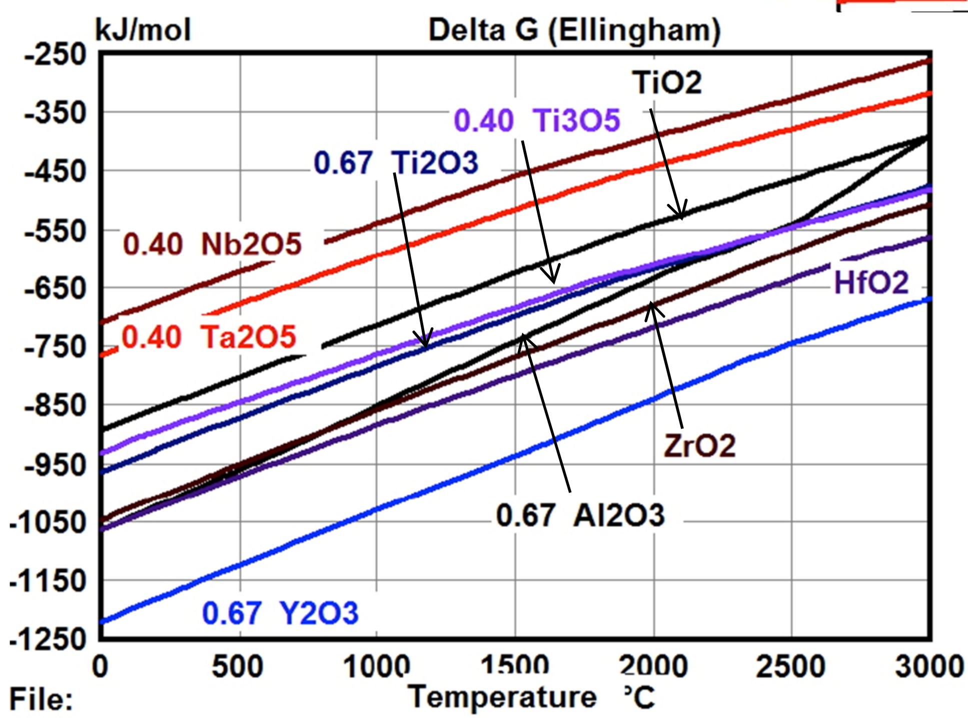
- B_4C powder averaging 10 µm was heated to 1700° C in a graphite crucible.
- Afterwards, liquid Bi was used to embed particles followed by polishing.
- Pores vary from 1 to 10 µm.



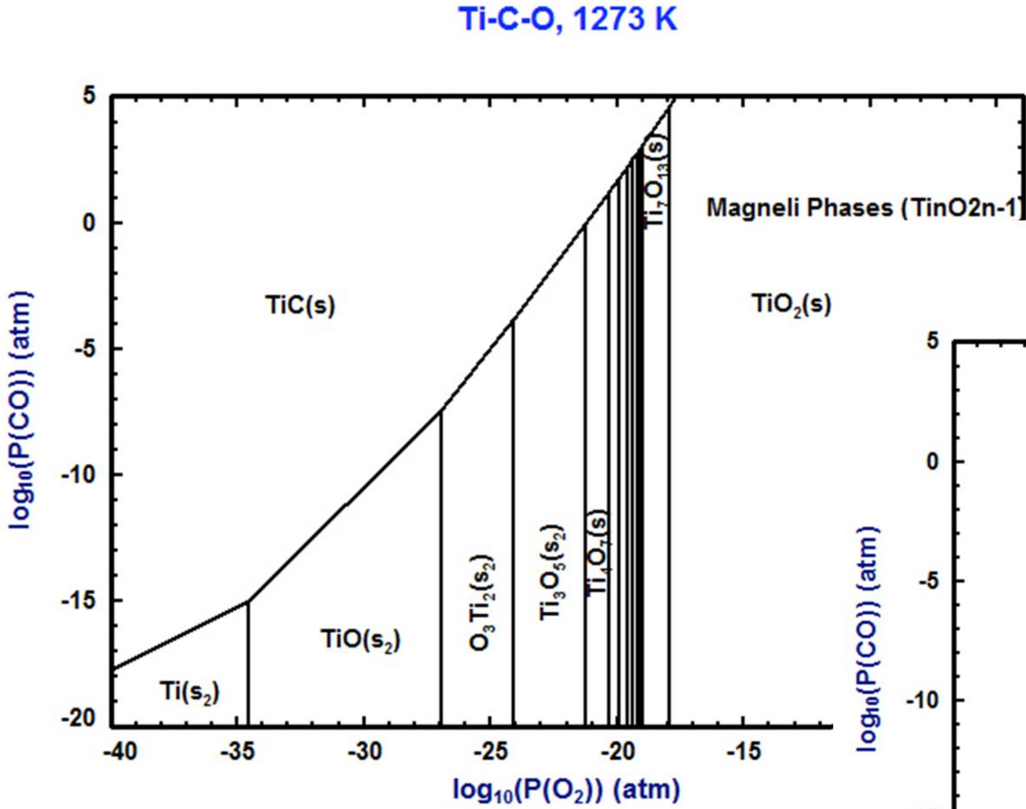
Stabilities-Oxides and Carbides

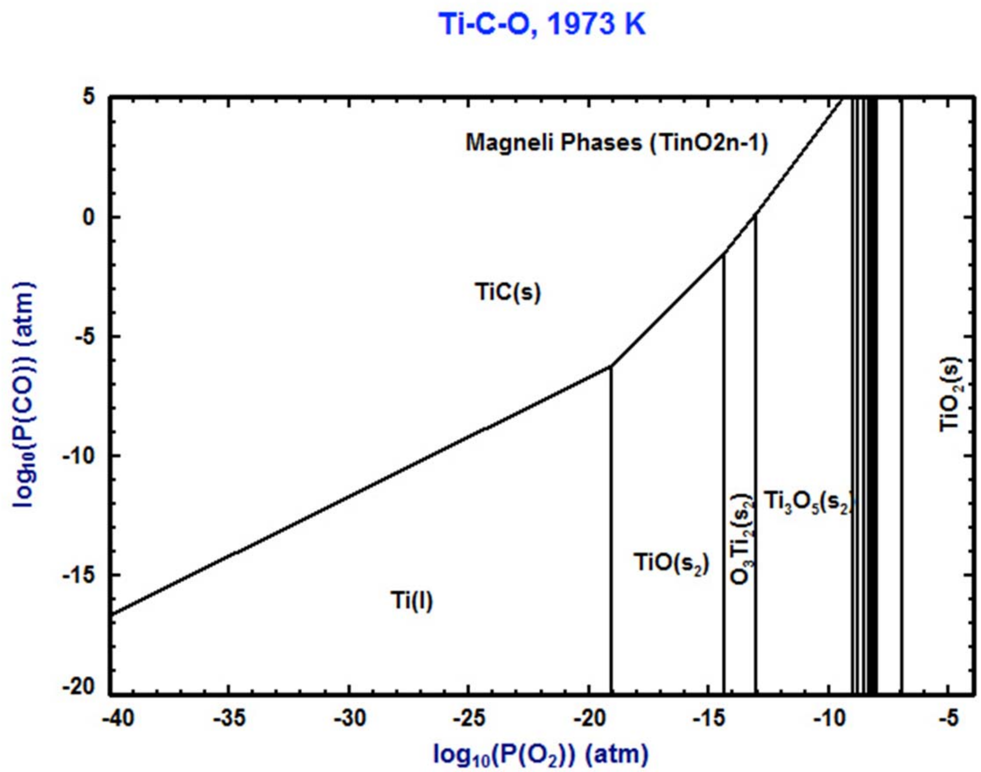
- For carbides, HfC, Ta_2C and ZrC are most stable.
- For oxides, Y_2O_3 and HfO_2 are most stable.
- Used Outotec HSC v. 7





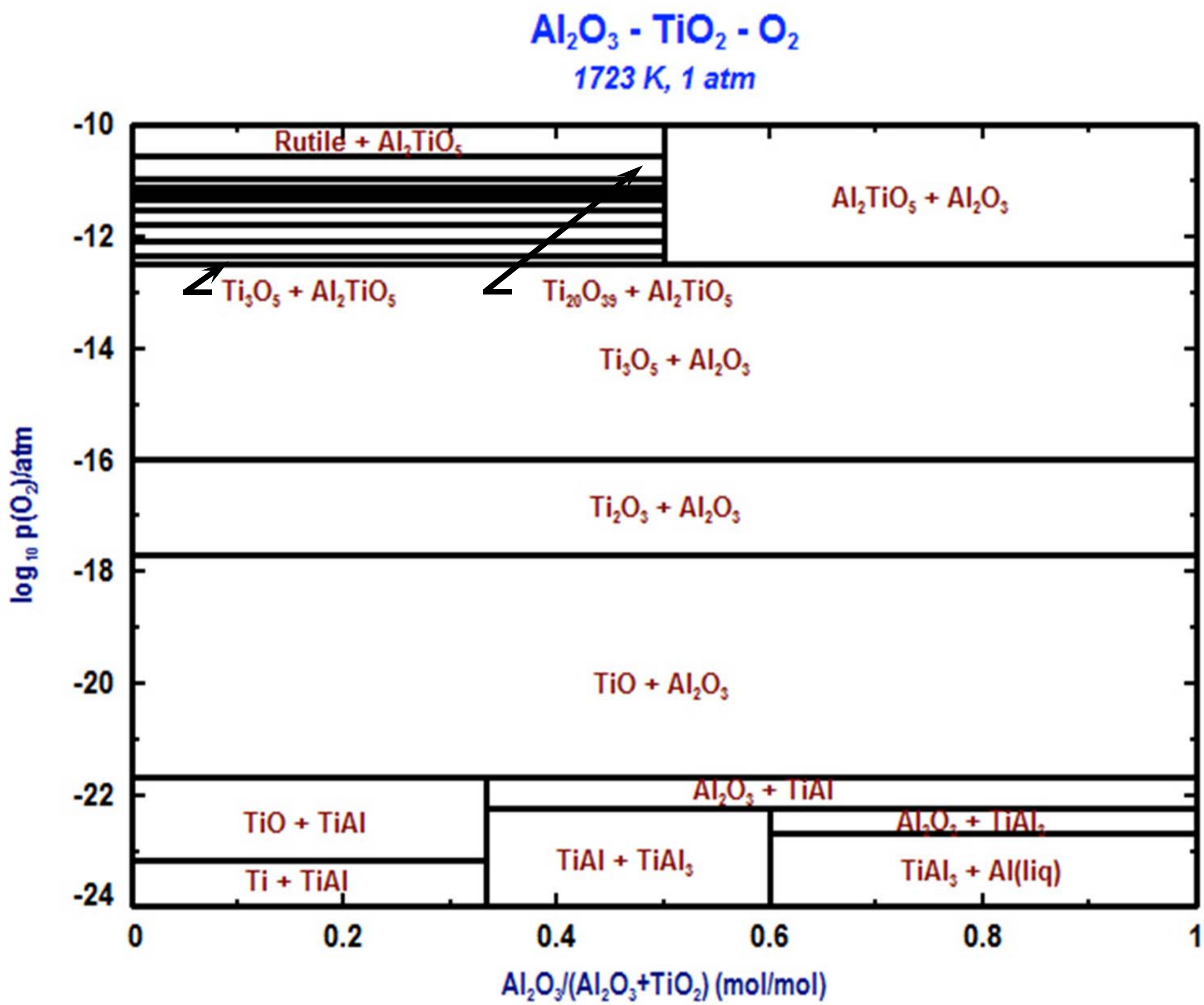
Ti-C-O Stability Diagrams at 1273 & 1973K for Expanded View of Magneli phases & p_{O2}





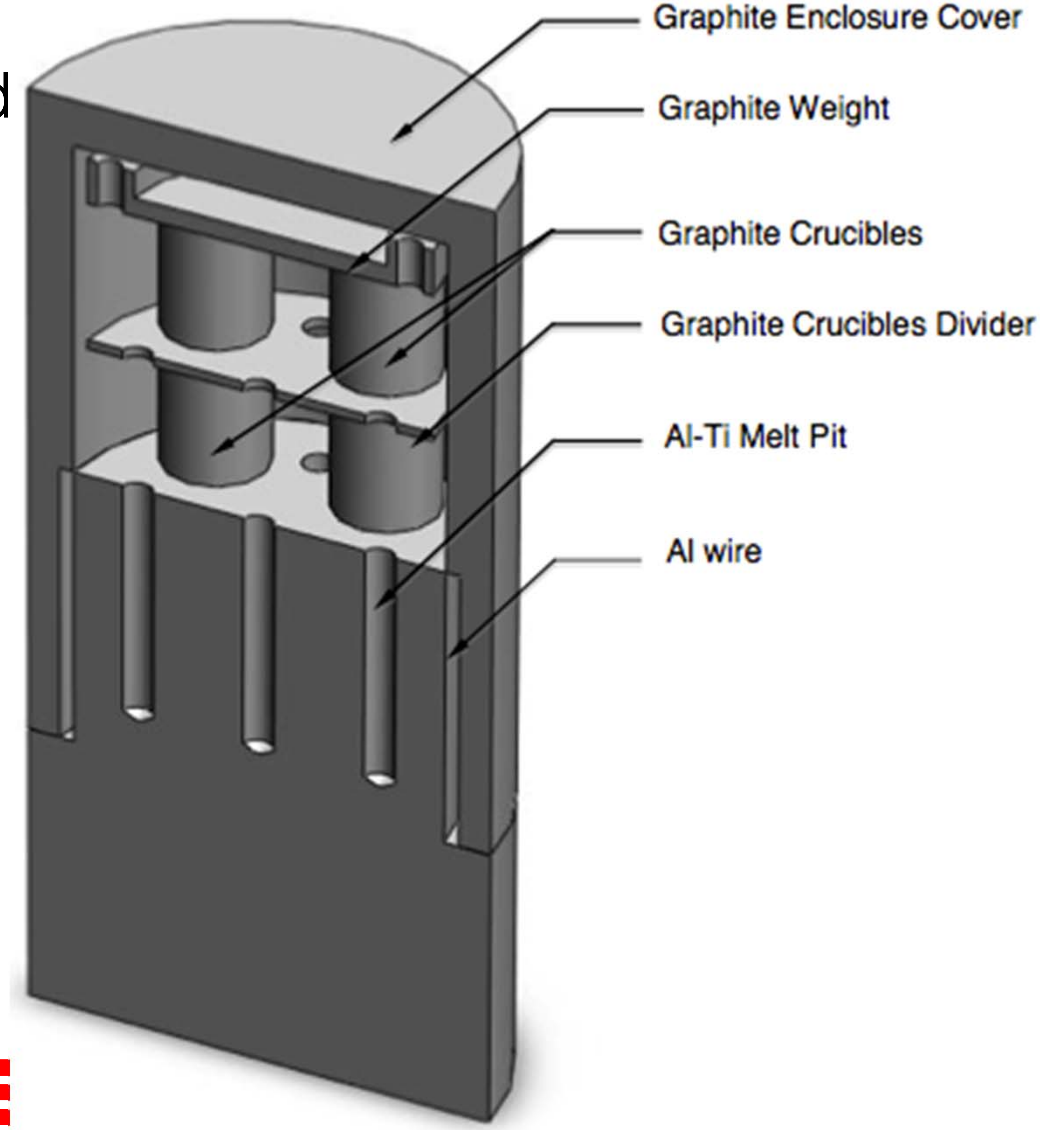
Possible Scale of Oxidized Ti_2AlC-TiC

- Ti oxides depend on pO_2 level within scale.
- Muan/Osborn showed limited solubility of Al_2O_3 - Al_2O_3•TiO_2 and Al_2O_3•TiO_2 - TiO_2 pseudobinaries.
- Al_2O_3•TiO_2 melts congruently at 1860° C as per Muan/Osborn.

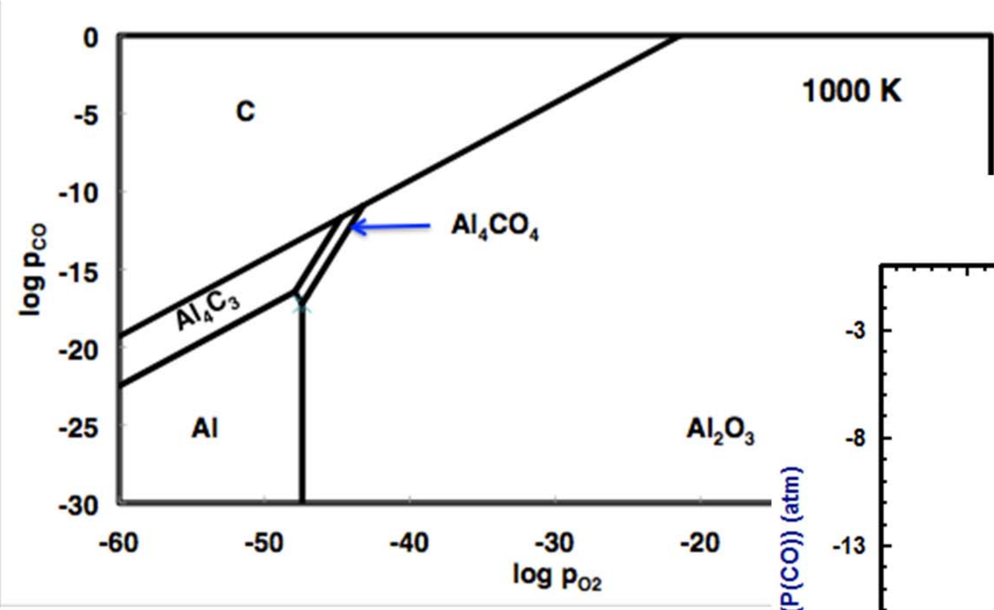


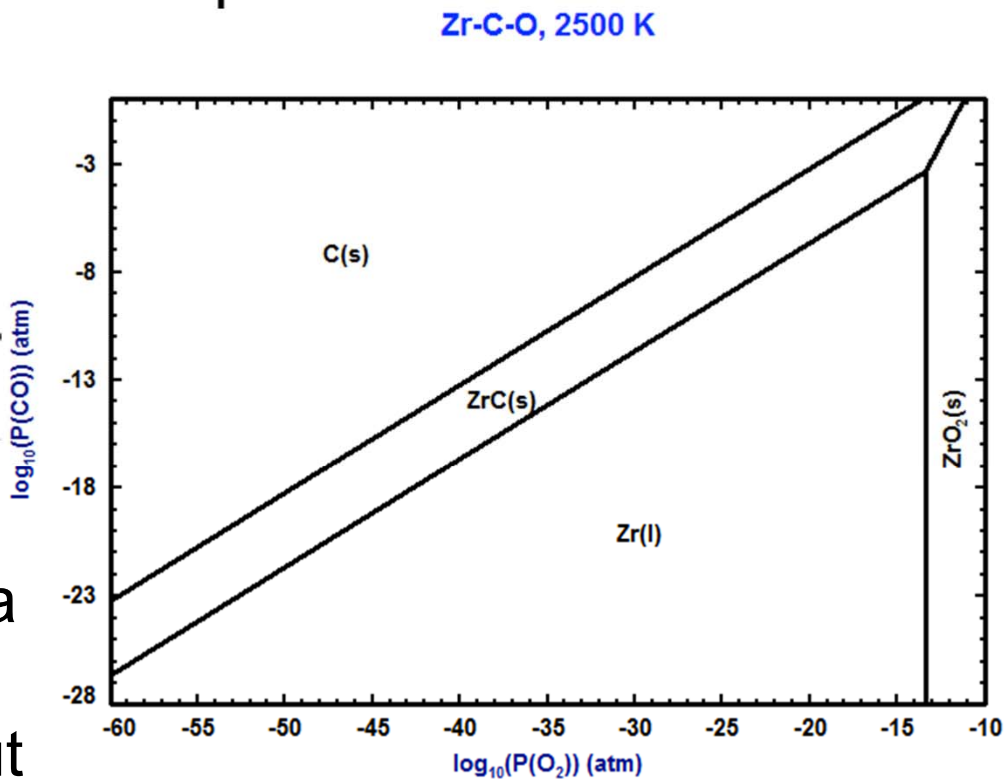
Configuration of Ti-Al-C reaction system

- Ti-Al-C charged to graphite crucibles heated to 1600-1700° C.
- Closed thermodynamic system controls oxygen potential.
- $Al/Al_4CO_4/Al_2O_3$ establishes p_{O2} at 1000 K (follows concept of Komarek research group using pseudo-isopiestic technique).



Stability of Al-C-O System at 1000 K and Zr-C-O System at 2500 K

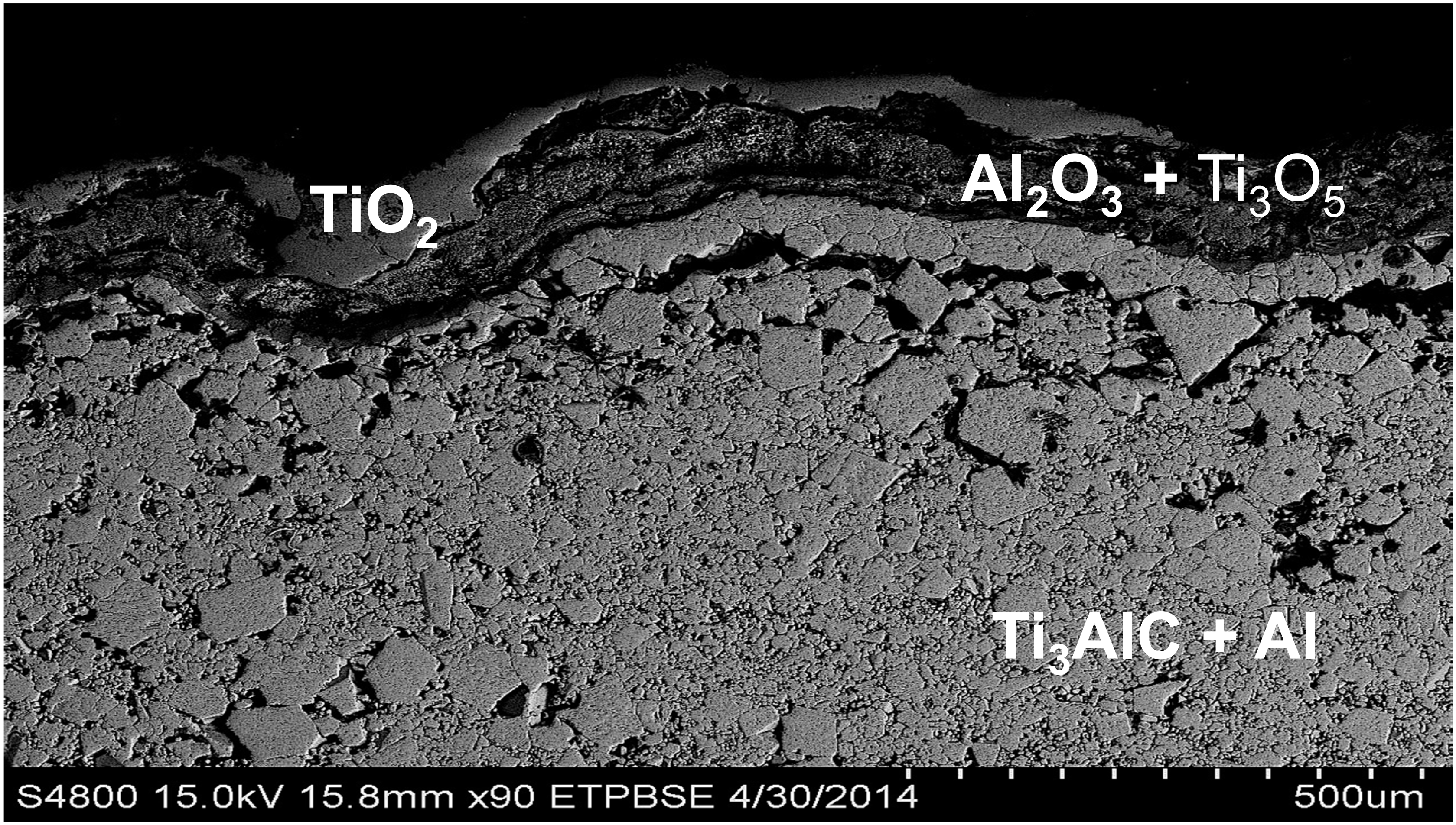




- $Al/Al_4CO_4/Al_2O_3$ estimated at 1000 K for a $p_{O2} = 10^{-47}$ atm
- Zr oxidation occurs about 10^{-13} atm.

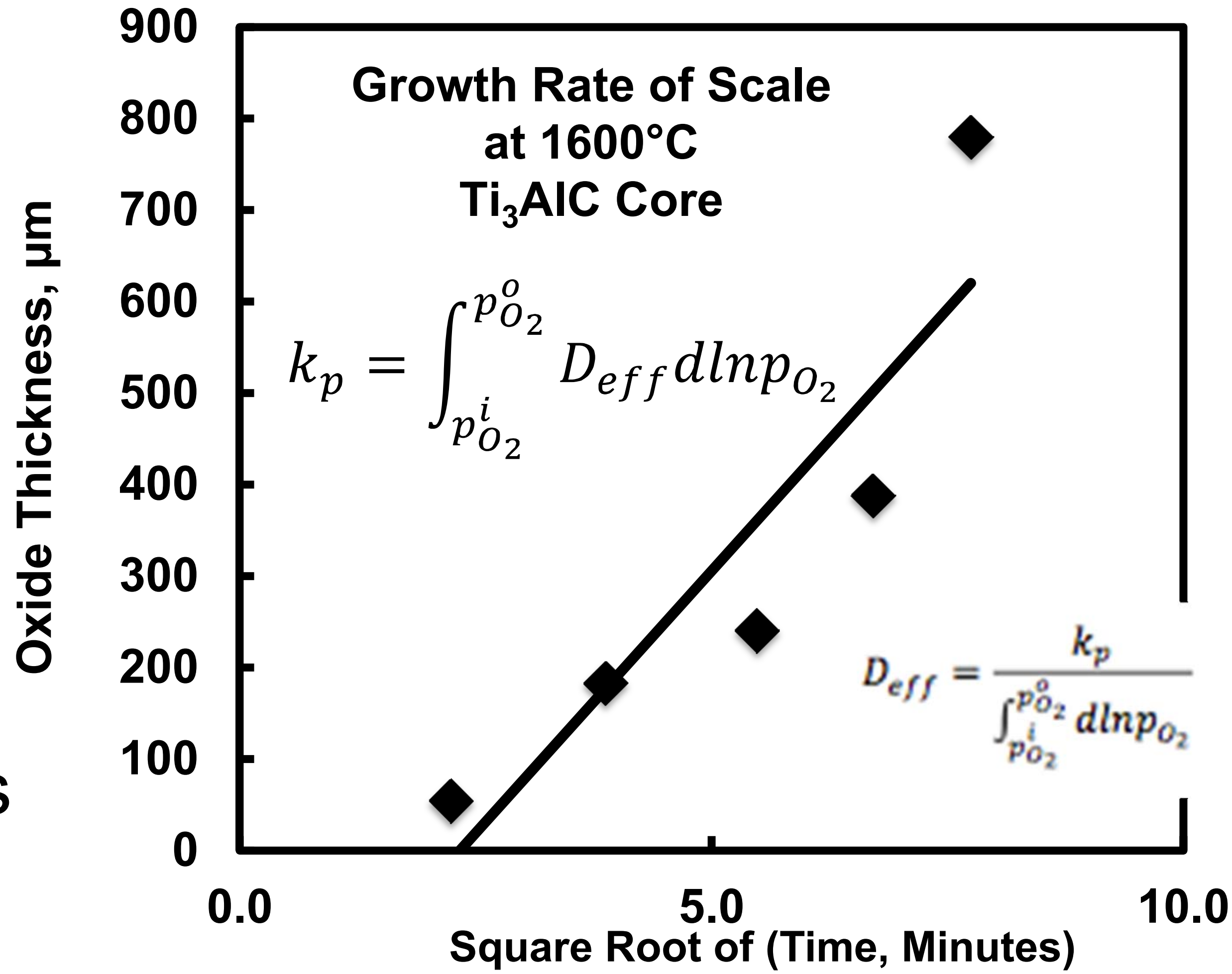
Maheswaraiah, Sandate and Bronson - 2012

Ti_3AlC core after 30 minute oxidation at 1600° C



Parabolic Growth Rate of Scale

- D_{eff} = $6.2x10^{-8} cm^2/s$ from slope via measured scale.
- For Al_2O_3 scale at 1873 K, D_{eff} = $2.6x10^{-13}$ cm^2/s Calculated from Equation of Ramanarayanan et al. -- 1984



Extending Previous Kinetic Equations

- Grabke's equations [1965 and 1970] for oxygen transfer on metals (e.g., Fe)

$$\frac{dn_O}{dt} = k a_O^{-m} p_{CO2} - k a_O^{1-m} p_{CO}$$

- Wang et al. [2003] determined oxidizing sequence for Ti44Al11Nb alloy with X-ray photoelectron spectroscopy.

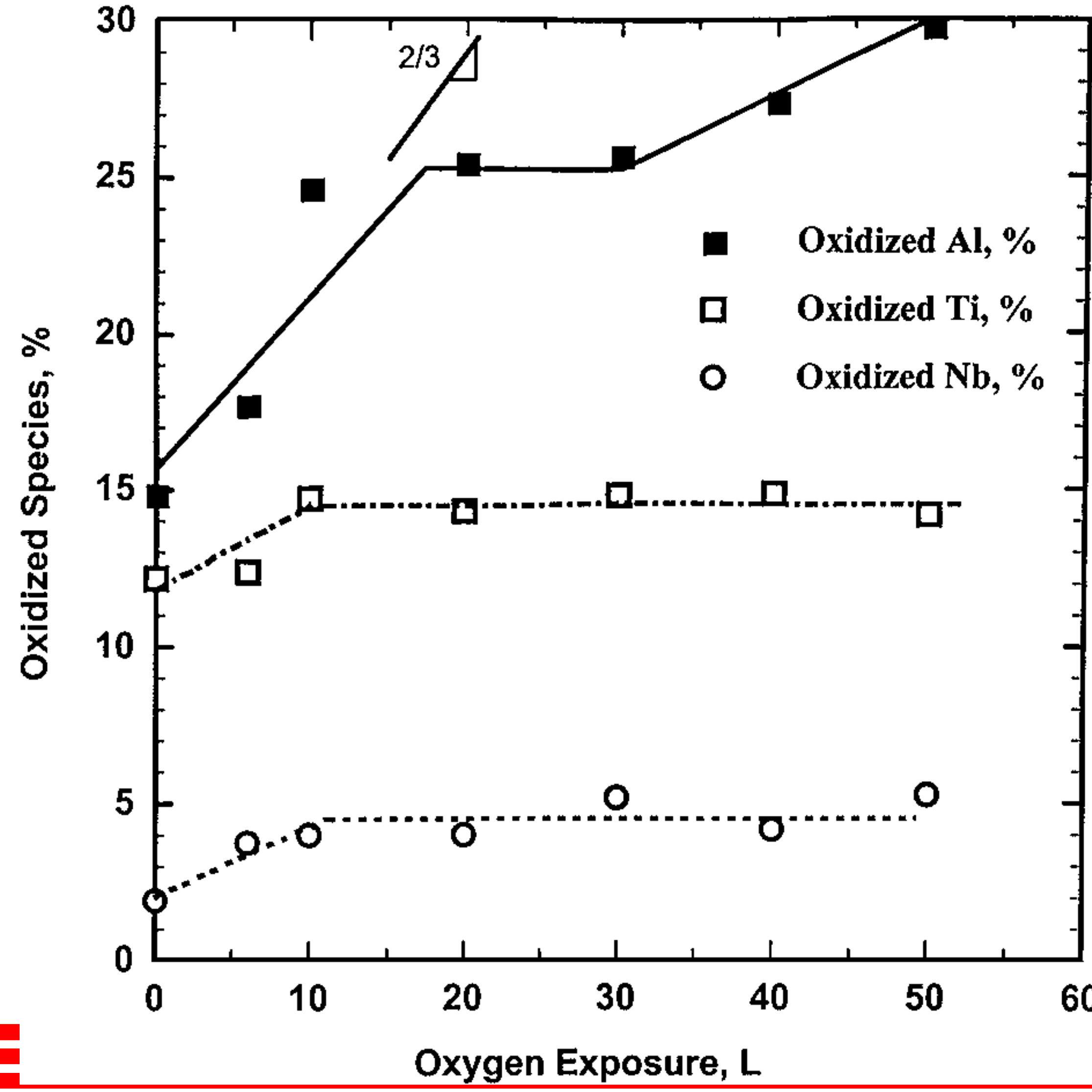
$$O_2 + 2V = 2O_{ad}$$
$$Al + O_{ad} \to AlO$$
$$AlO + O_{ad} \to AlO_2$$
$$AlO_2 + O_{ad} \to AlO_3$$

- Kurunczi, Guha and Donnelly [2006] on adsorption of oxygen (O_{ads}) on surface sites (V) from O2 plasma

$$Og + V \to O_{ads}$$
$$2O_{ads} \to O_{2(g)} + 2V$$

Oxidized Species Measured on Ti-44Al-11Nb (at%) with X-ray Photoelectron Spectroscopy

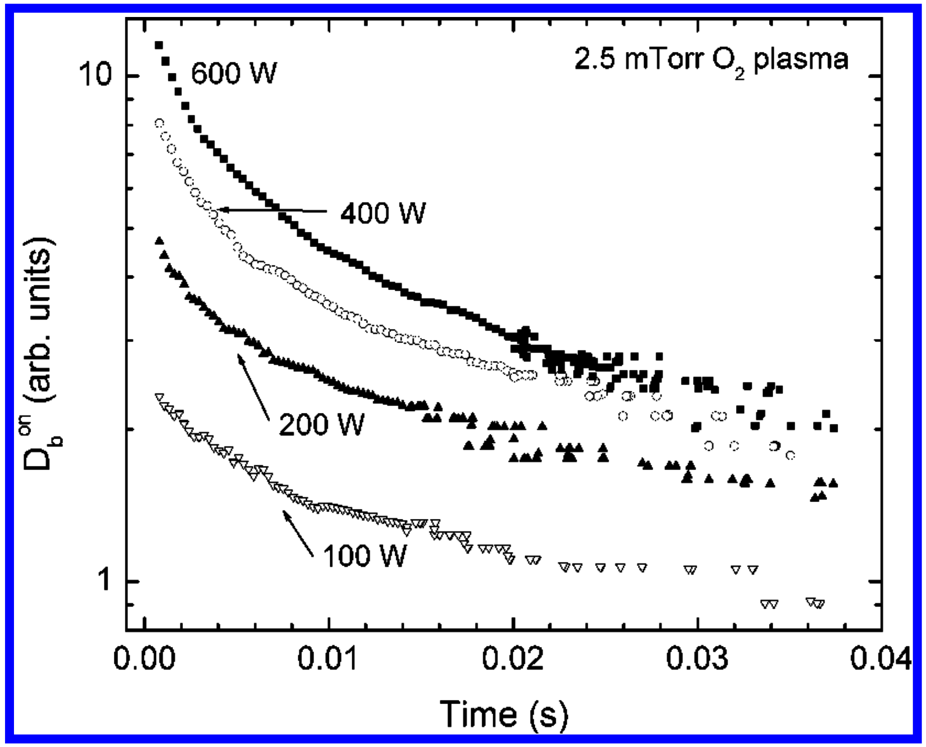
- **Oxygen exposure of $L = t \cdot p_{O2}$ (10^{-6} Torr•s)**
- **Slope of 2/3 acquired from kinetic rates of oxygen adsorption per AlO_3 formation (r_{ad}/r_{AlO3})**



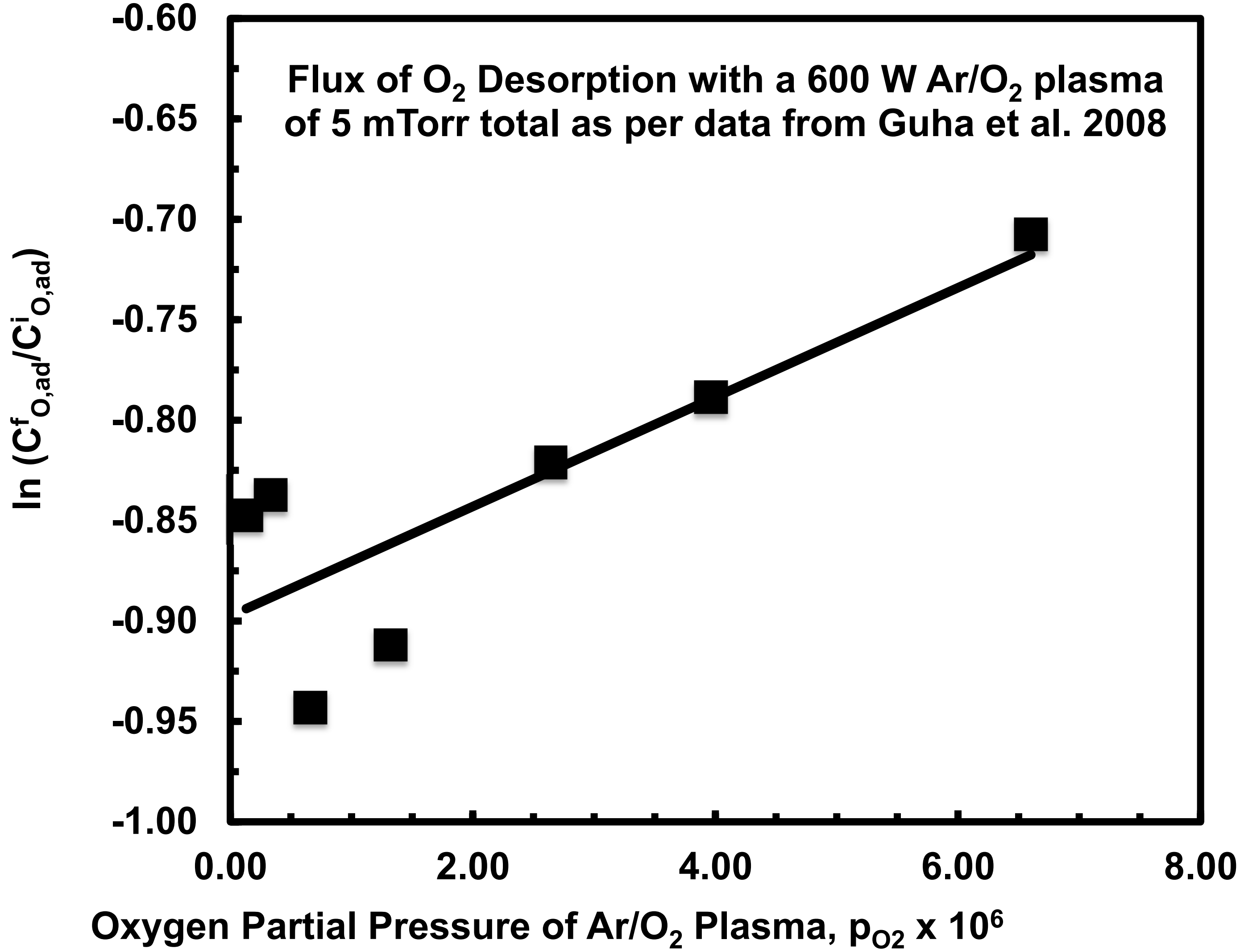
Merge the kinetics of oxygen adsorption to experimental plasma data

- Apply the reaction scheme by Wang et al. (2003) to experimental plasma data by Kurunczi, Guha and Donnelly (2006).
- Determine the effect of plasma via the ionizing power on C_{AlO3}.

$$\ln\left[\frac{C^{f}_{\mathrm{O},ad}}{C^{i}_{\mathrm{O},ad}}\right] = S\alpha t$$



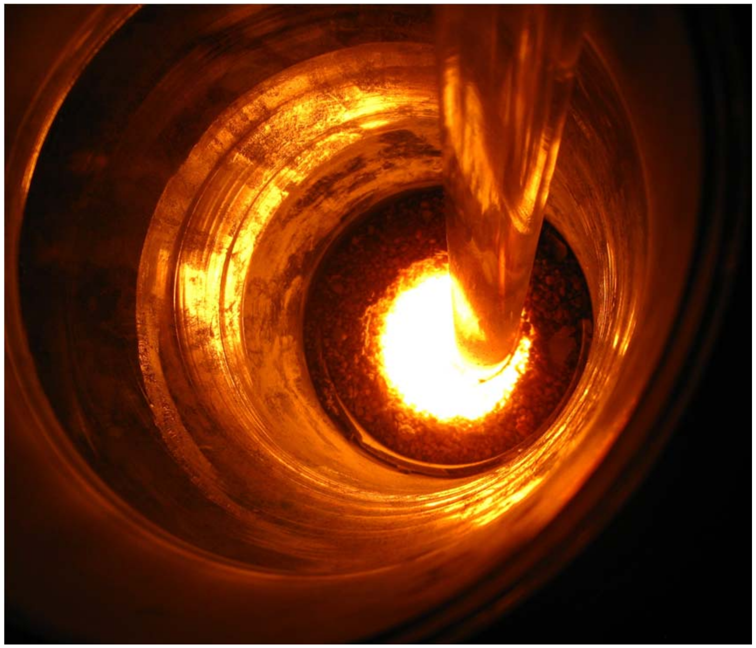
Interpretation of Desorbed Ar/O_2 Plasma



Summary

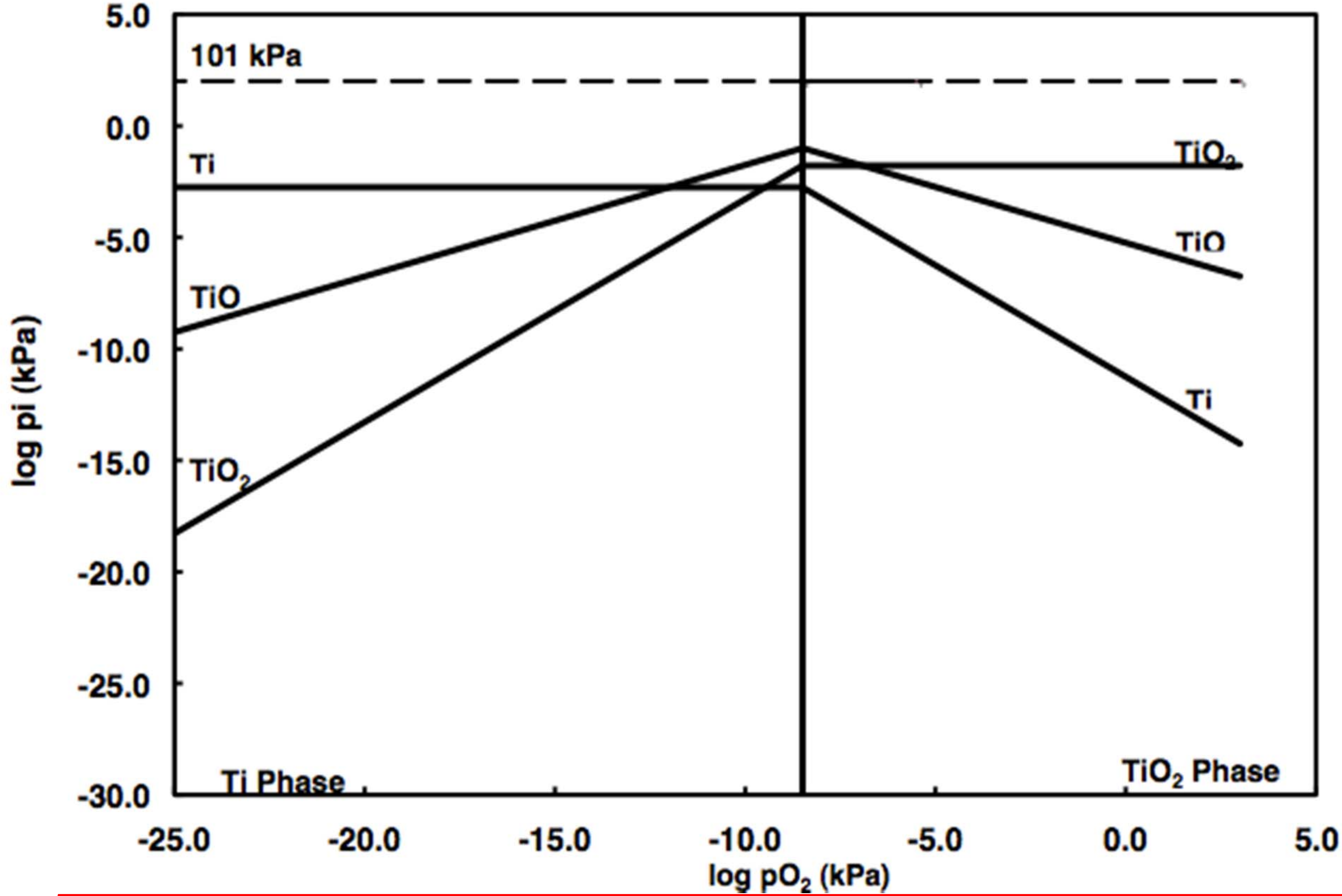
- Used COMSOL, a commercial software package, to obtain the temperature profile of a packed bed of B_4C.
- Analyzed thermodynamic stability of oxygen potentials for TiO_x and TiO_x-Al_2O_3 for possible scale formation from Ti_2AlC-TiC components.
- Controlled oxygen potential to form Ti_3AlC-Al composite which follows parabolic oxidation.
- Examined the plasma-surface reactions on Al oxide surface.
- Determining the effect of charged surface sites attracting ultimately the oxygen for surface reactions.

Questions and Comments



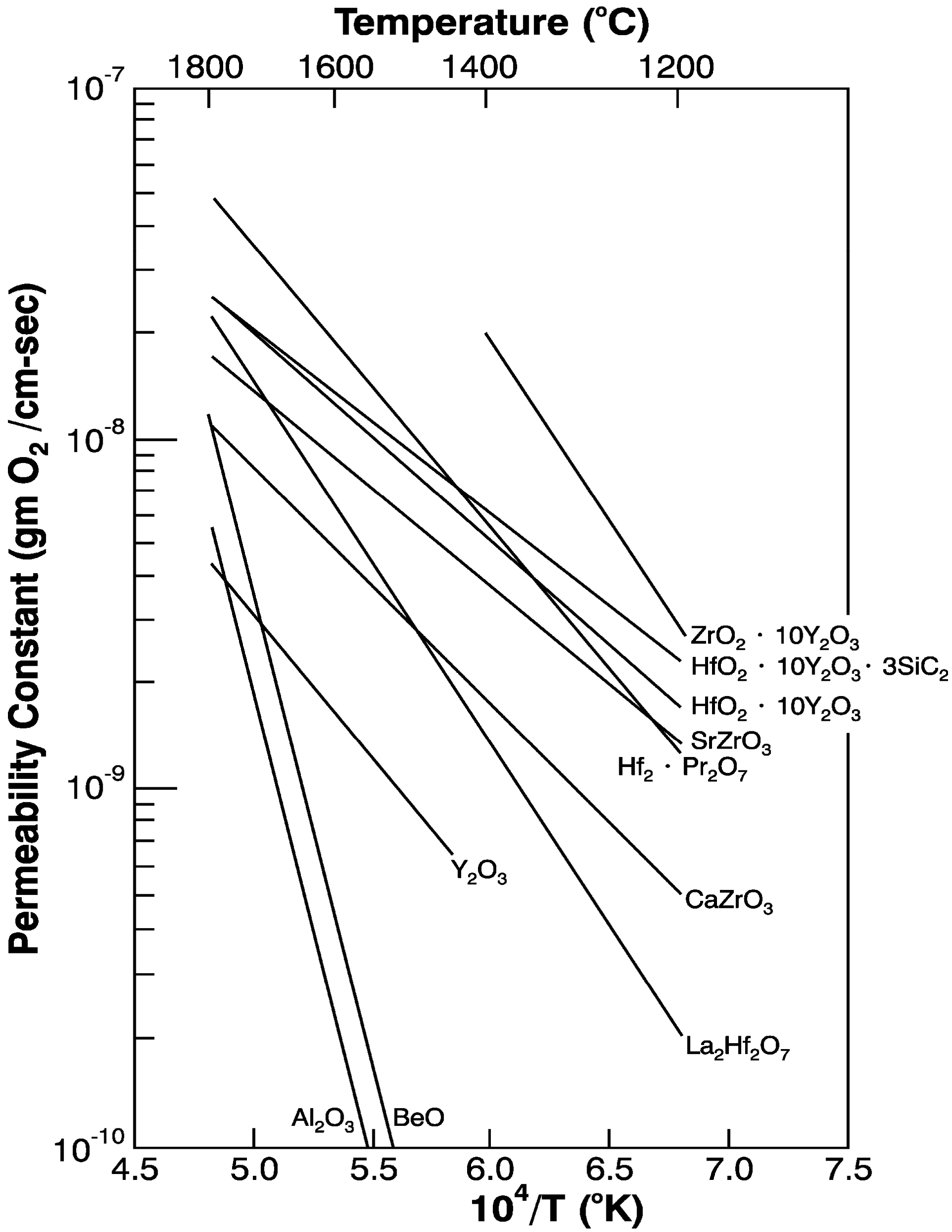
Slides to Respond to Possible Queries Follow

Kellogg Diagram for Ti-O System (2500 K)



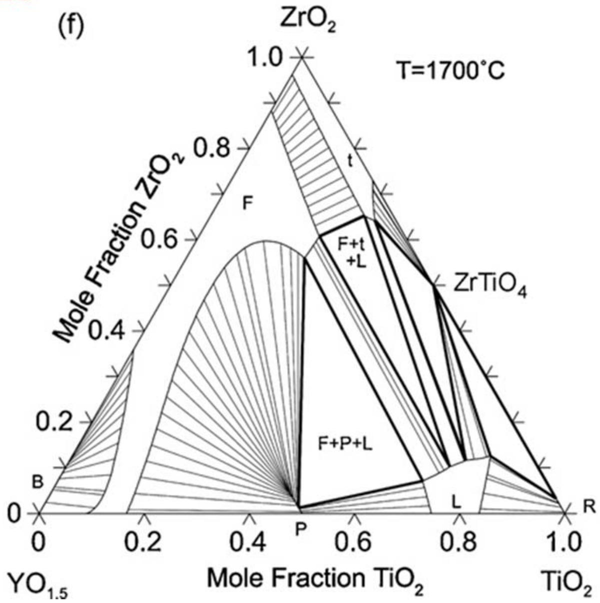
Oxygen Permeability

- For temperatures between 1700 to 1500° C Al_2O_3 and Y_2O_3 have oxygen permeability ≤ 10^{-9} gO_2/(cm-s) and $3•10^{-9}$ gO_2/(cm-s), respectively.
- Oxygen permeability of ZrO_2-Y_2O_3 and HfO_2-Y_2O_3 increases by approximately an order of magnitude [i.e., ≥ $(10)^{-8}$ gO_2/(cm-s)].

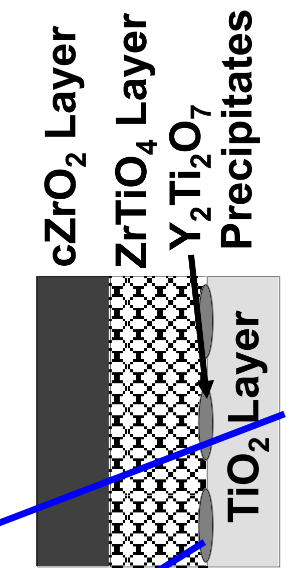


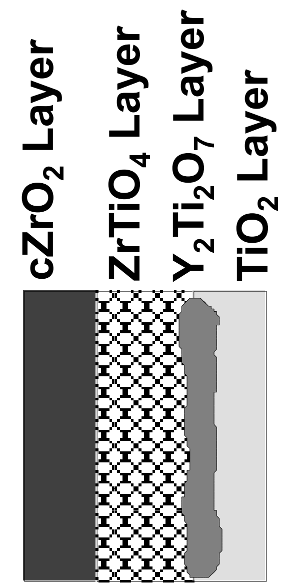
(Opeka, Talmy & Zaykoski-2004)

Wagner's Rate Equation for Scales



Calculated Diagram from Schaedler, Fabrichnaya and Levi -- 2008

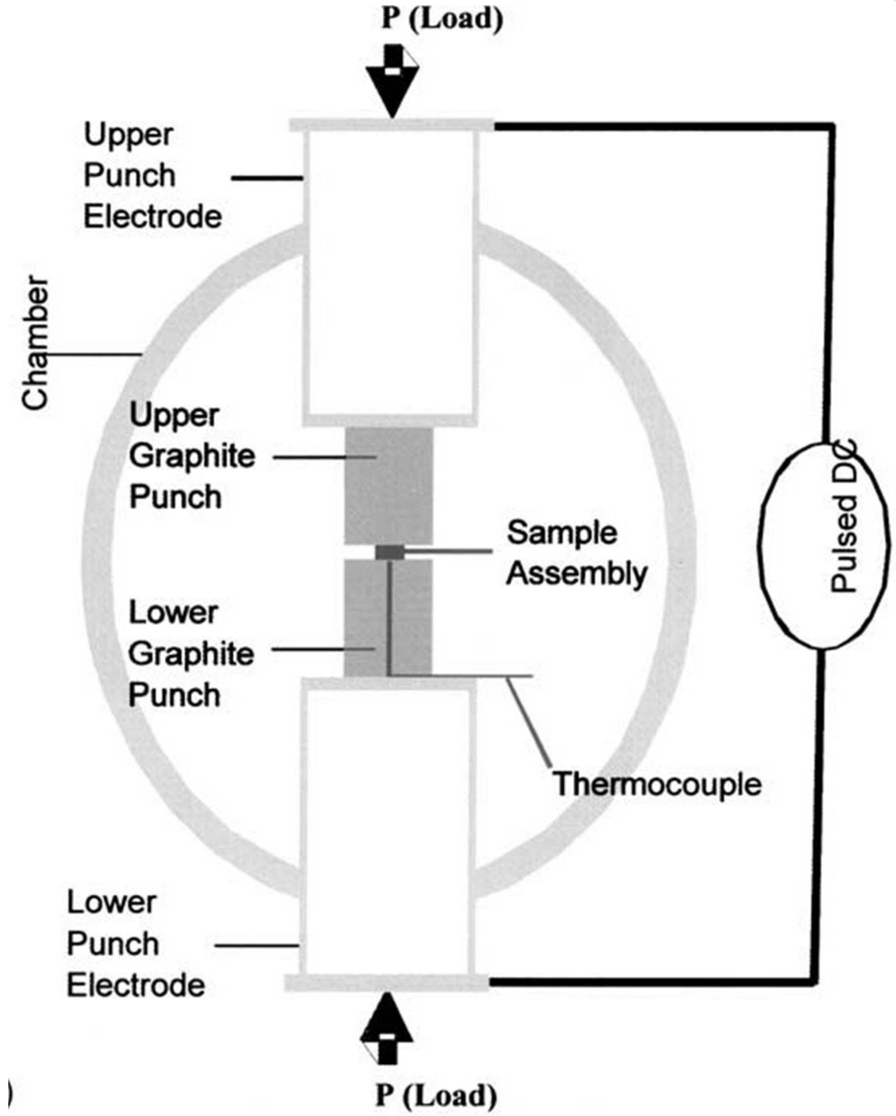




$$\frac{1}{A}\frac{d\tilde{n}}{dt}=\frac{1}{\xi}\left[\frac{\tilde{c}}{2}\int_{p_{O_2}^{(i)}}^{p_{O_2}^{(o)}}\left(\left(\frac{z_M}{z_O}\right)D_M+D_O\right)d\ln p_{O_2}\right]=\frac{\tilde{k}}{\xi}$$

Thoughts on Spark-Plasma Sintering

- Plasma has been professed to enhance sintering but without ionized gas evidence.
- Current pulses passes through graphite – sample though configuration affects the temperature extremes developed.
- What percentage of electromigration and thermal diffusion contributes to sintering?



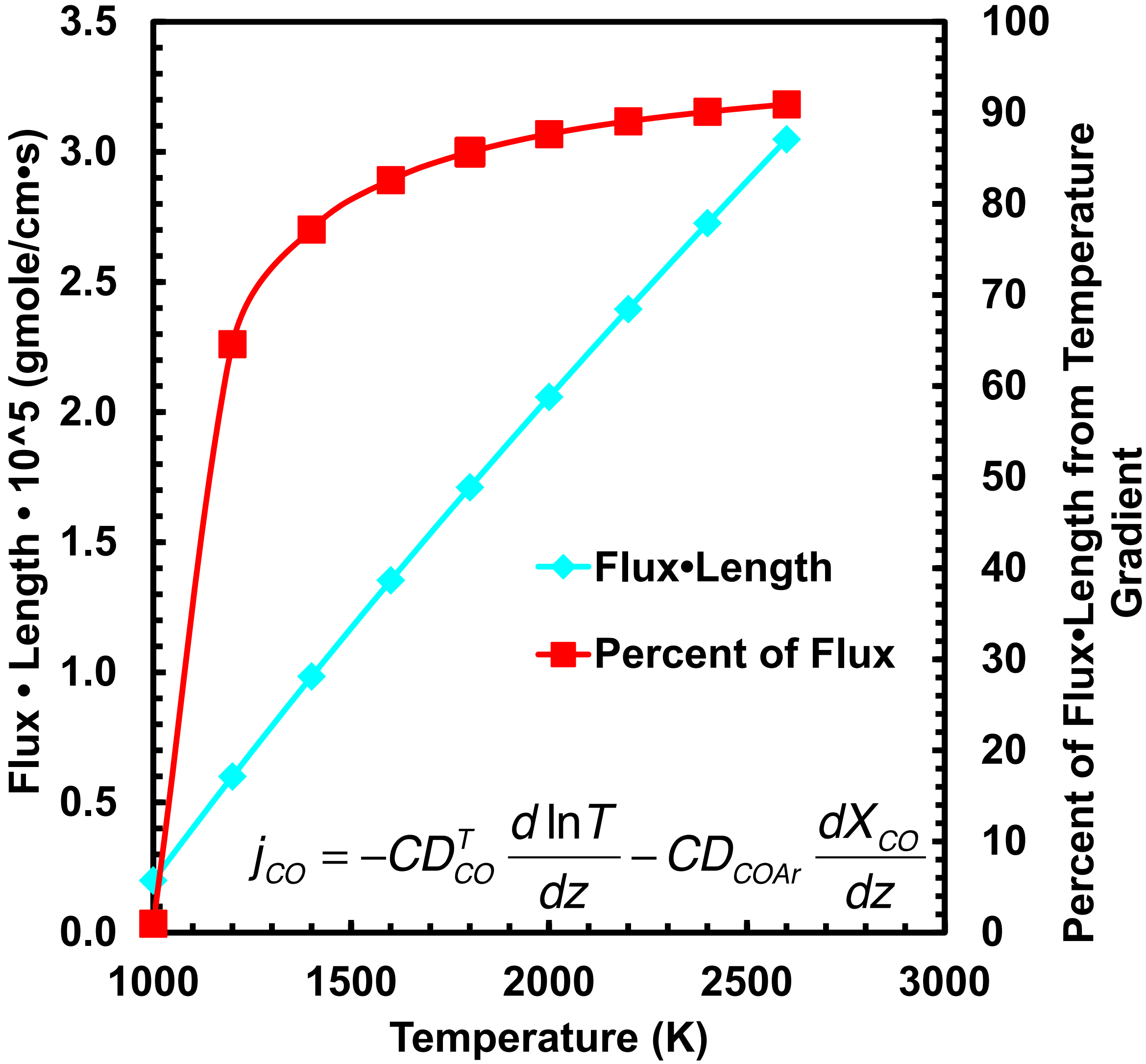
Future Efforts for Plasma Surface Reactions

- **Incorporate electron energy (e.g., electron energy density (n_ε), gradient of electron flux vector (Γ_ε) and potential field (E)).**

$$\frac{\partial}{\partial t}(n_\varepsilon) + \nabla \cdot \Gamma_\varepsilon + \mathbf{E} \cdot \Gamma_\varepsilon = R_\varepsilon - (\mathbf{u} \cdot \nabla) n_\varepsilon$$

- **Incorporate kinetics of Ar-O_2 plasma-surface reactions with SiC and Ti_2AlC.**
- **Study the effect of temperature extremes (T and dT/dx) on metastable phases and/or segregation.**

Diffusional Flux – Kinetics Issues



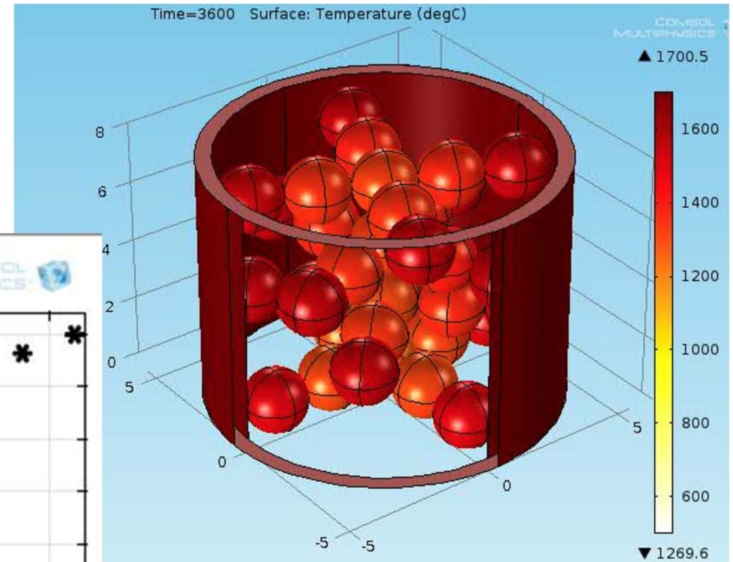
- D_{COAr} from Poirier-Geiger and checked with Chapman-Enskog Eq.
- Mean temperature

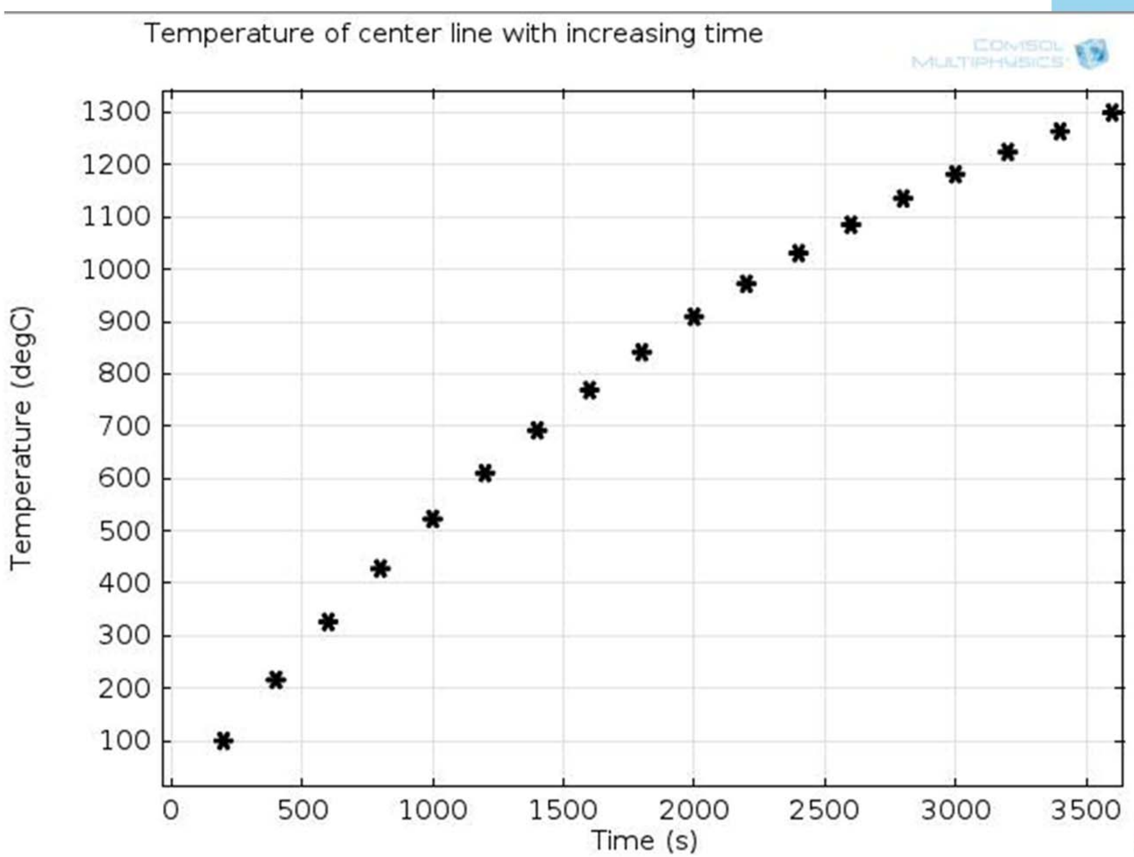
$$\frac{T_H T_C}{T_H - T_C} \ln \frac{T_H}{T_C} = 1527K$$

- $Al/Al_2O_3/Al_4CO_4$ reaction rate?

COMSOL Simulation of B_4C Spheres Basis for Packed Bed with Temperature Profile

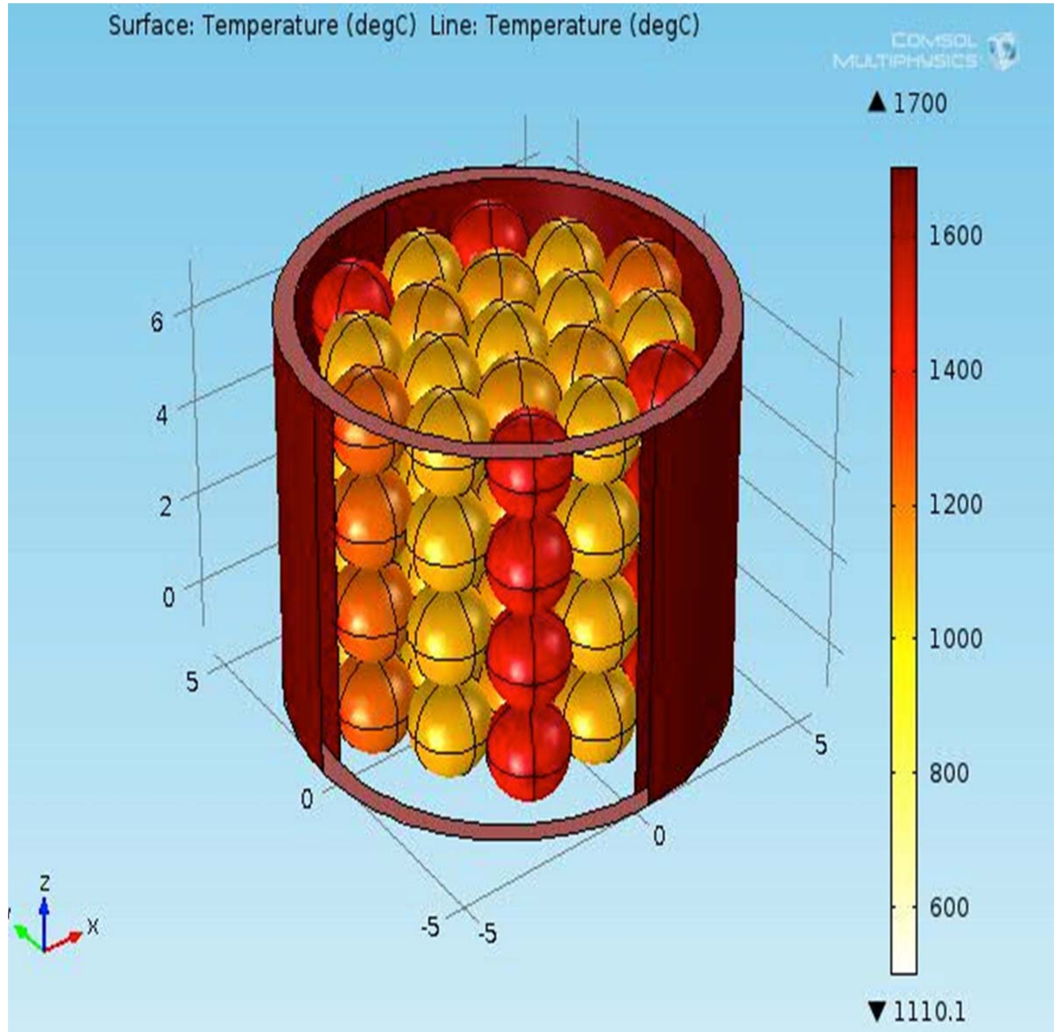
- **Carbide spheres configured in an X-pattern rotating along centerline.**
- **The spheres have an open structure.**





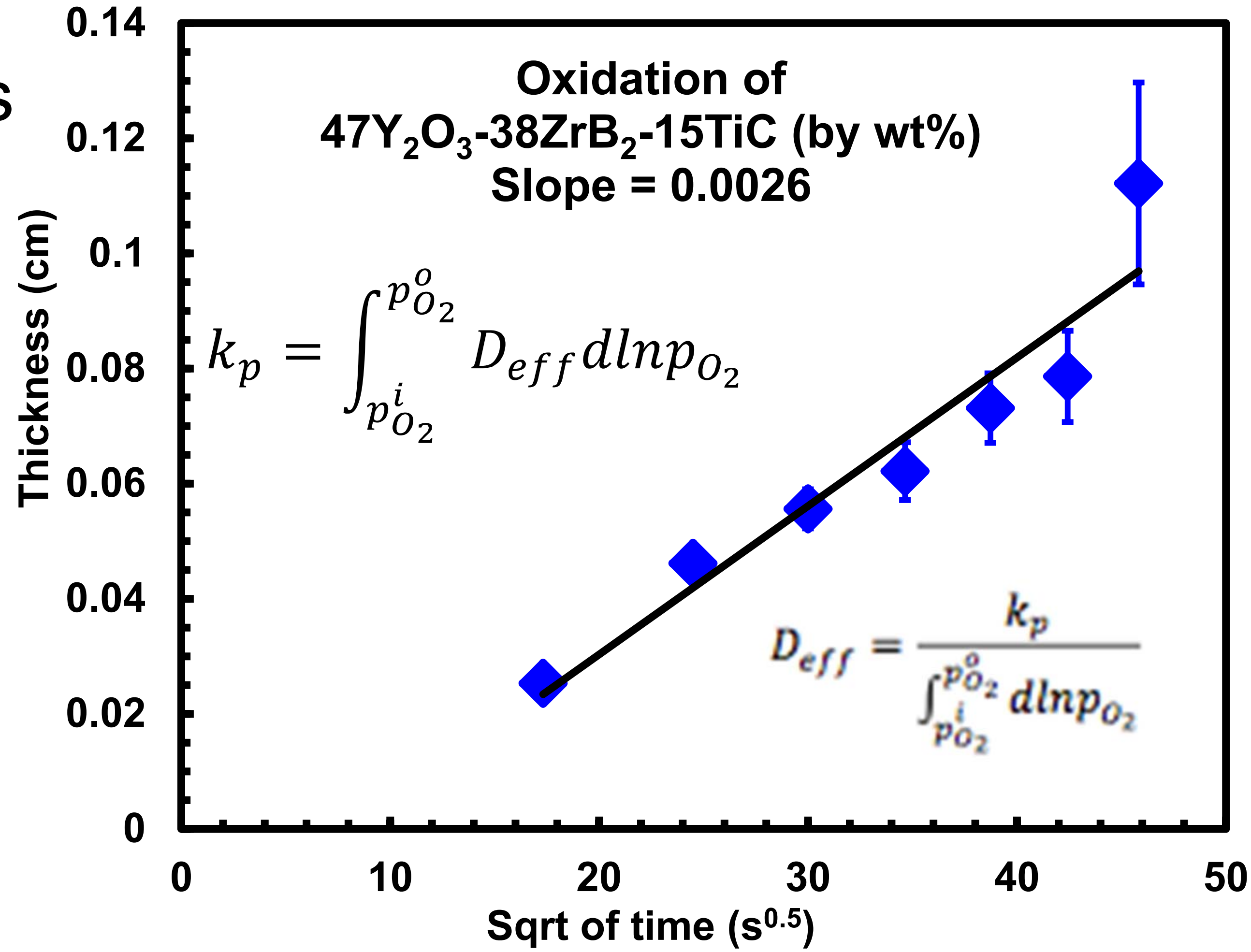
COMSOL Simulation of B_4C spheres in a packed bed

- Cylindrical graphite wall temperature is heated mimicking internal furnace wall.
- Carbide spheres touch each other with a 6-fold lateral configuration though each layer contacts uniformly.
- Spheres contacting the wall have highest temperature.
- Conductive heat transfer was used, but radiation will be added with expanded sphere number.



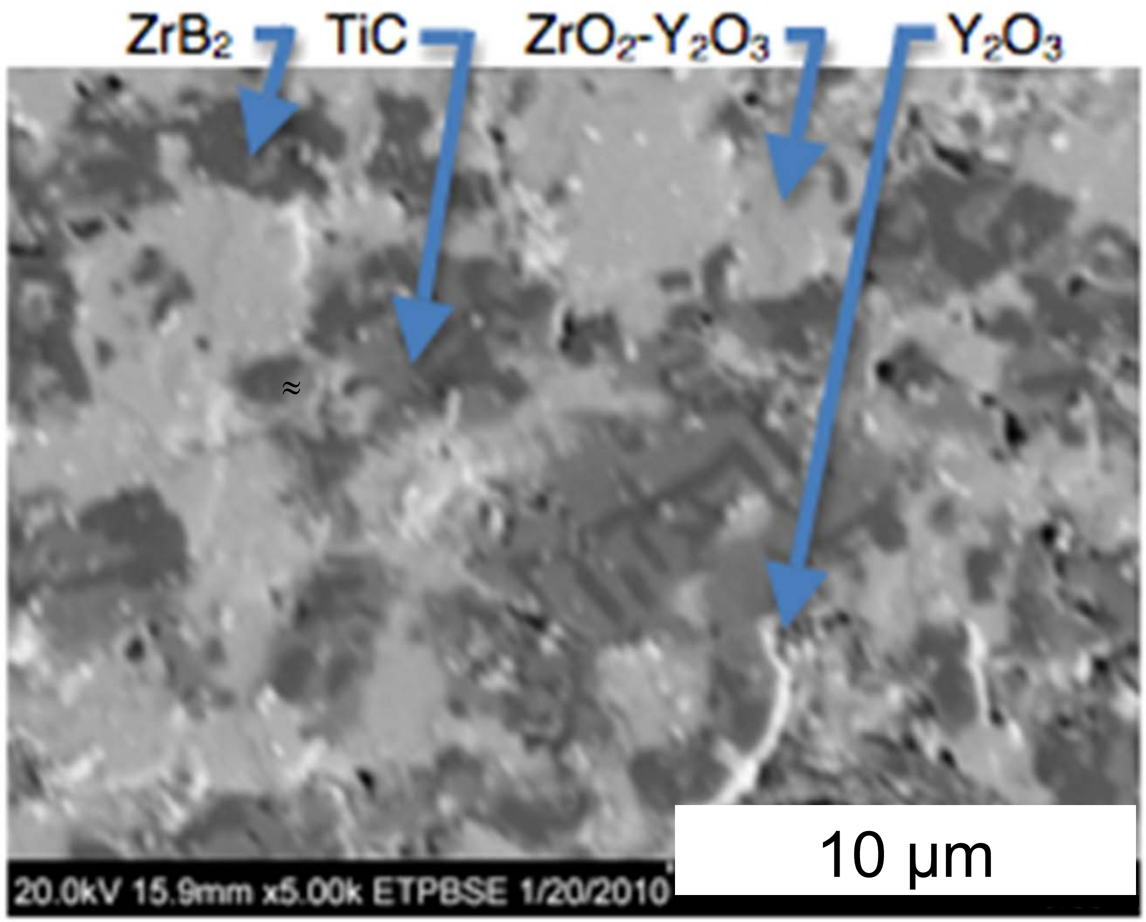
Parabolic Growth Rate of Scale

- $D_{eff} = 10^{-11} m^2/s$ for t-ZrO_2-Y_2O_3 phase as controlling layer



SEM image after spark-plasma sintering (SPS) of ZrB_2-TiC-Y_2O_3*

- **ZrB_2 oxidizes to ZrO_2 dissolving some Y_2O_3.**
- **Stringers of Y_2O_3 appear in grain boundary.**
- **Graphite minimized TiC oxidation though TiO formed from residual O_2 in Ar.**



*** SPS done at Dr. Erica Corral's Laboratory at U of Arizona**

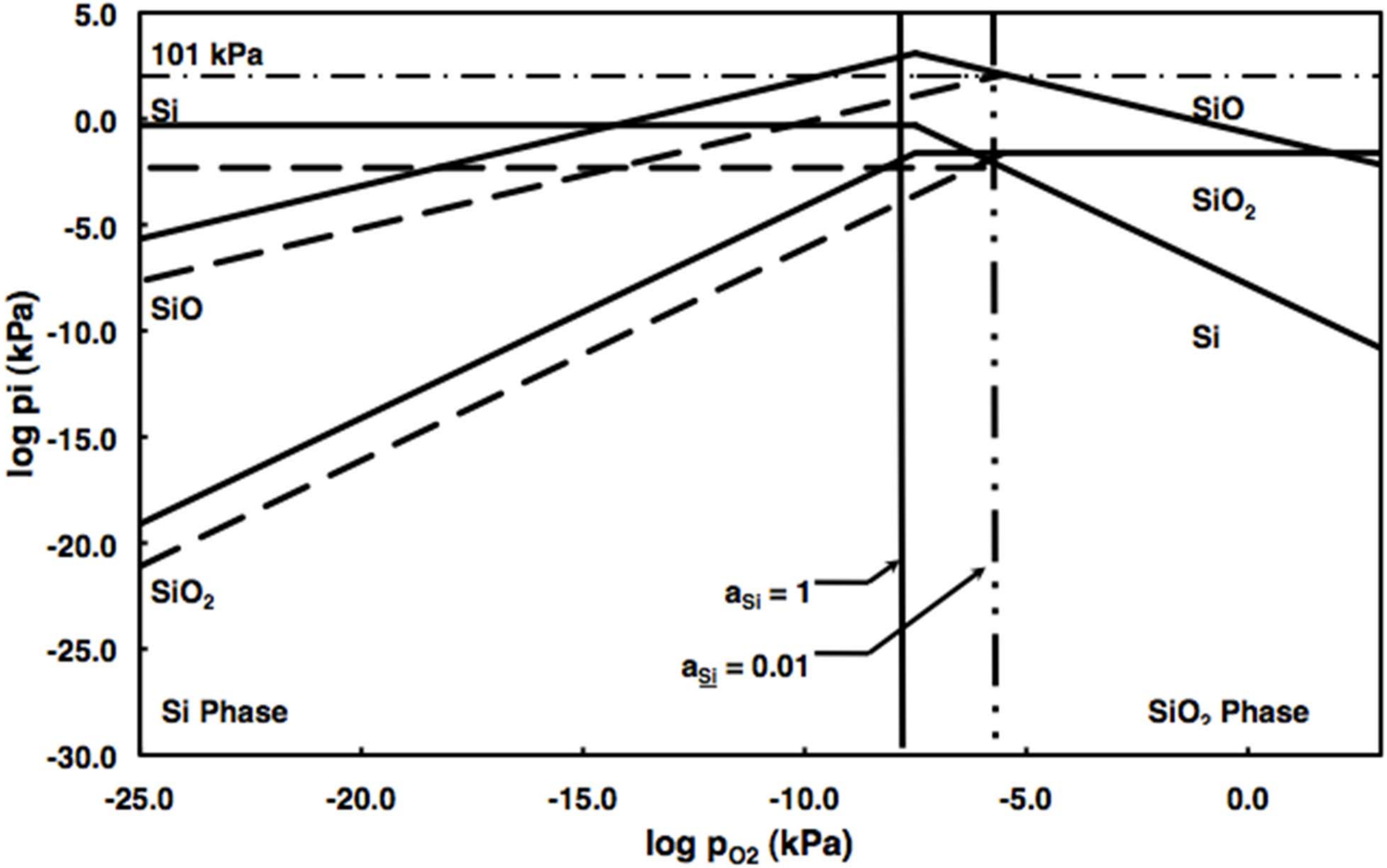
Electron-Energy Transport

- Should consider electron, ions and neutral species balance coupled with electron energy and momentum balances.

$$\frac{\partial}{\partial t}(n_\varepsilon) + \nabla \cdot \Gamma_\varepsilon + \mathbf{E} \cdot \Gamma_\varepsilon = R_\varepsilon - (\mathbf{u} \cdot \nabla) n_\varepsilon$$

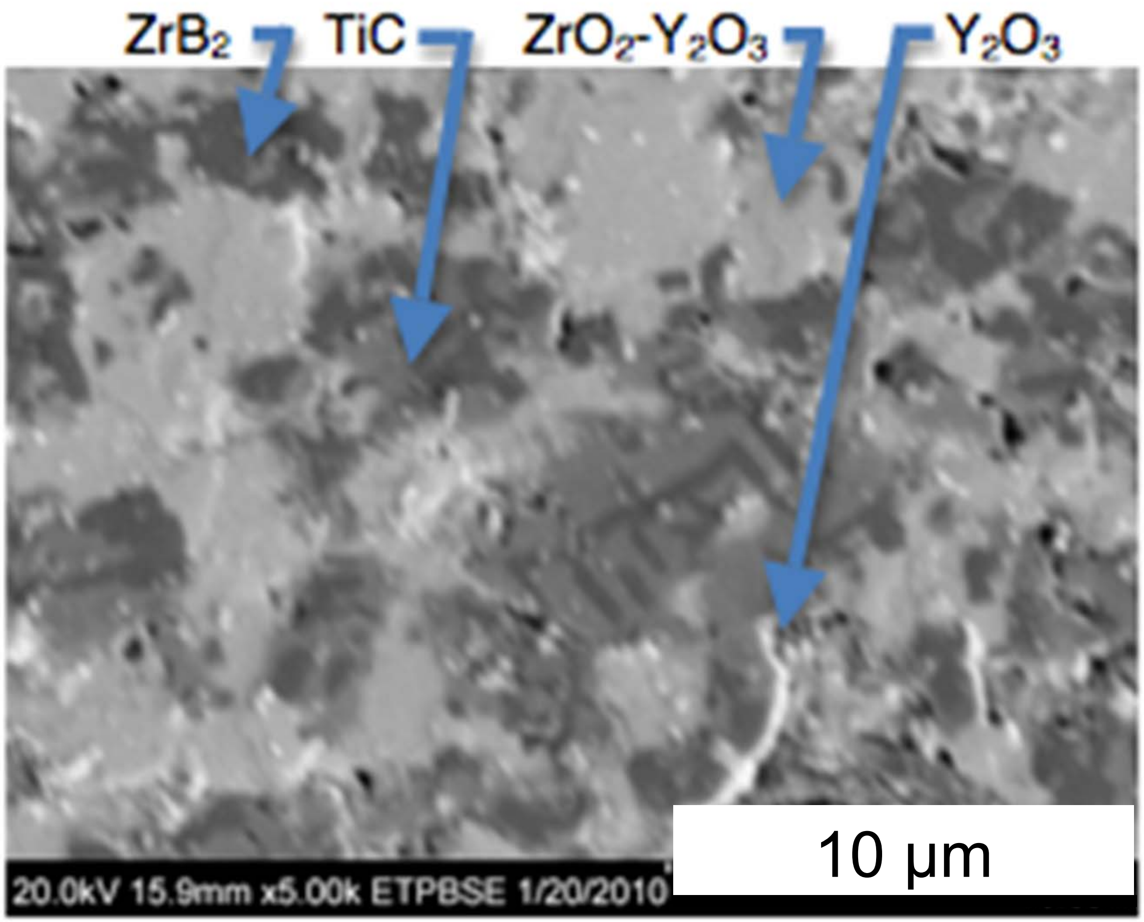
$$\frac{\partial}{\partial t}(n_e) + \nabla \cdot [-n_e(\mu_e \cdot \mathbf{E}) - \mathbf{D}_e \cdot \nabla n_e)] = R_e$$

Kellogg Diagram for Si-O System (2500 K)



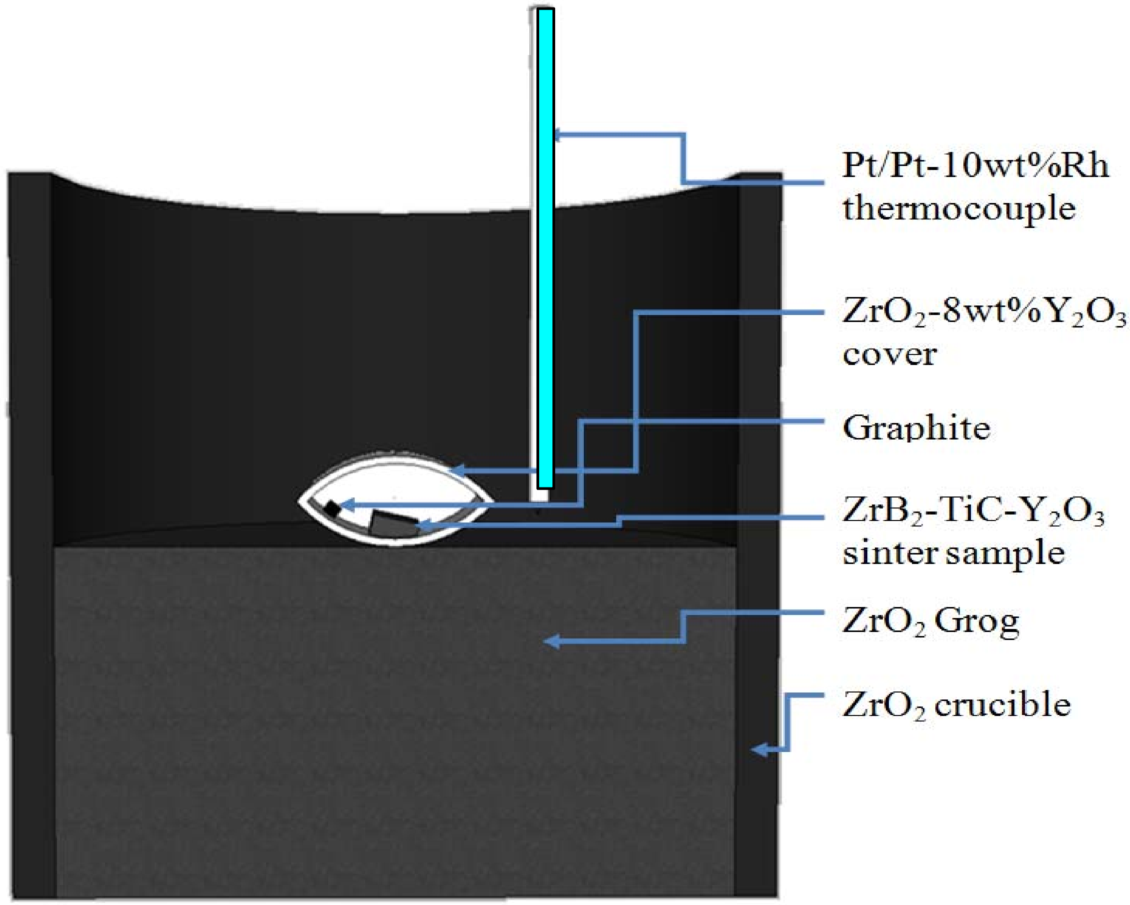
SEM image after spark-plasma sintering

- ZrB_2 oxidizes to ZrO_2 dissolving some Y_2O_3
- Stringers of Y_2O_3 appear in grain boundary
- Graphite seems to minimize TiC oxidation.



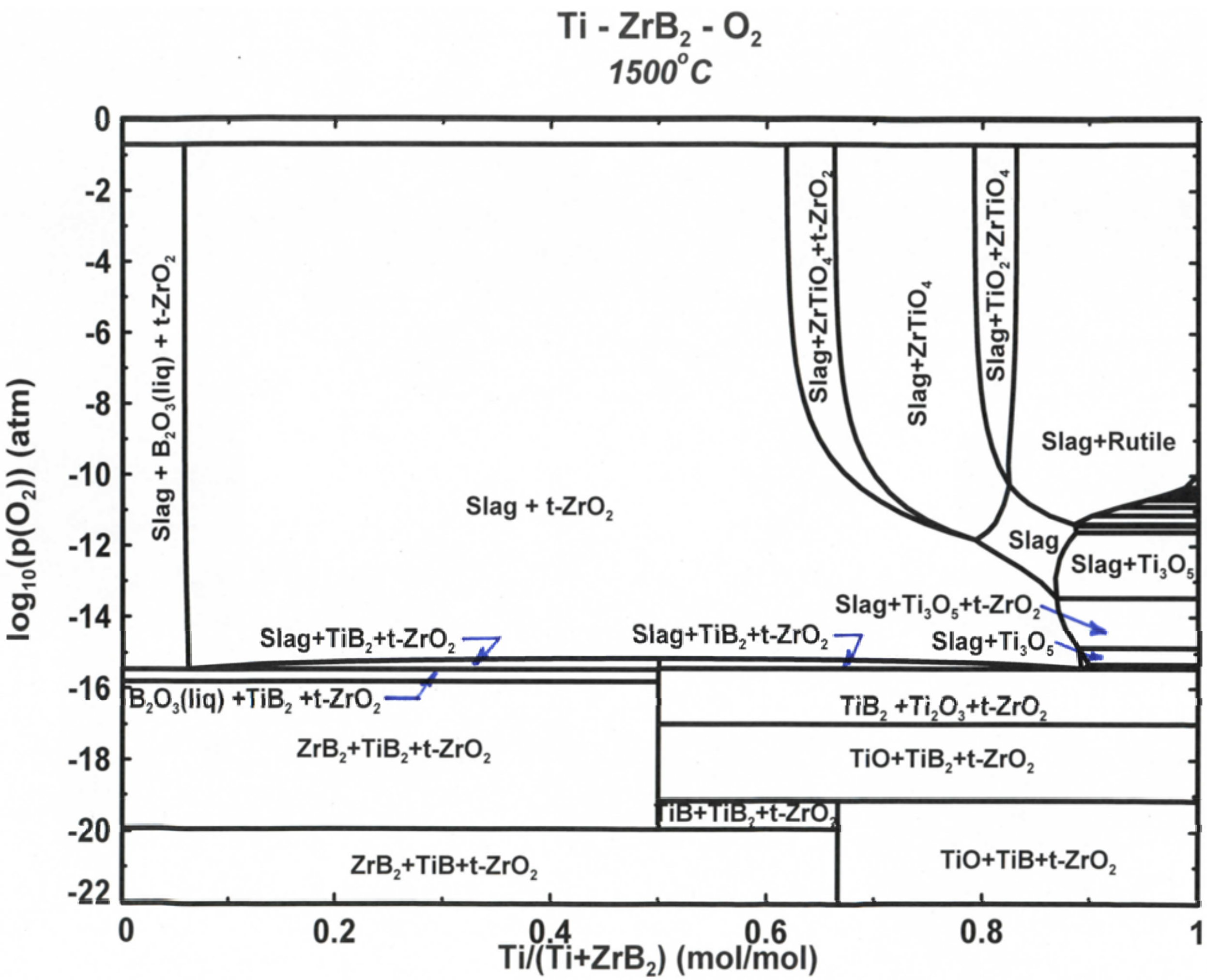
Oxidation in Silicide Furnace with air and C/CO/N_2 atmospheres at 1700° C

- Spark plasma-sintered samples
- ZrO_2-8 wt% Y_2O_3 crucible covers were used to hold samples.
- Hf foil were also used to hold samples.

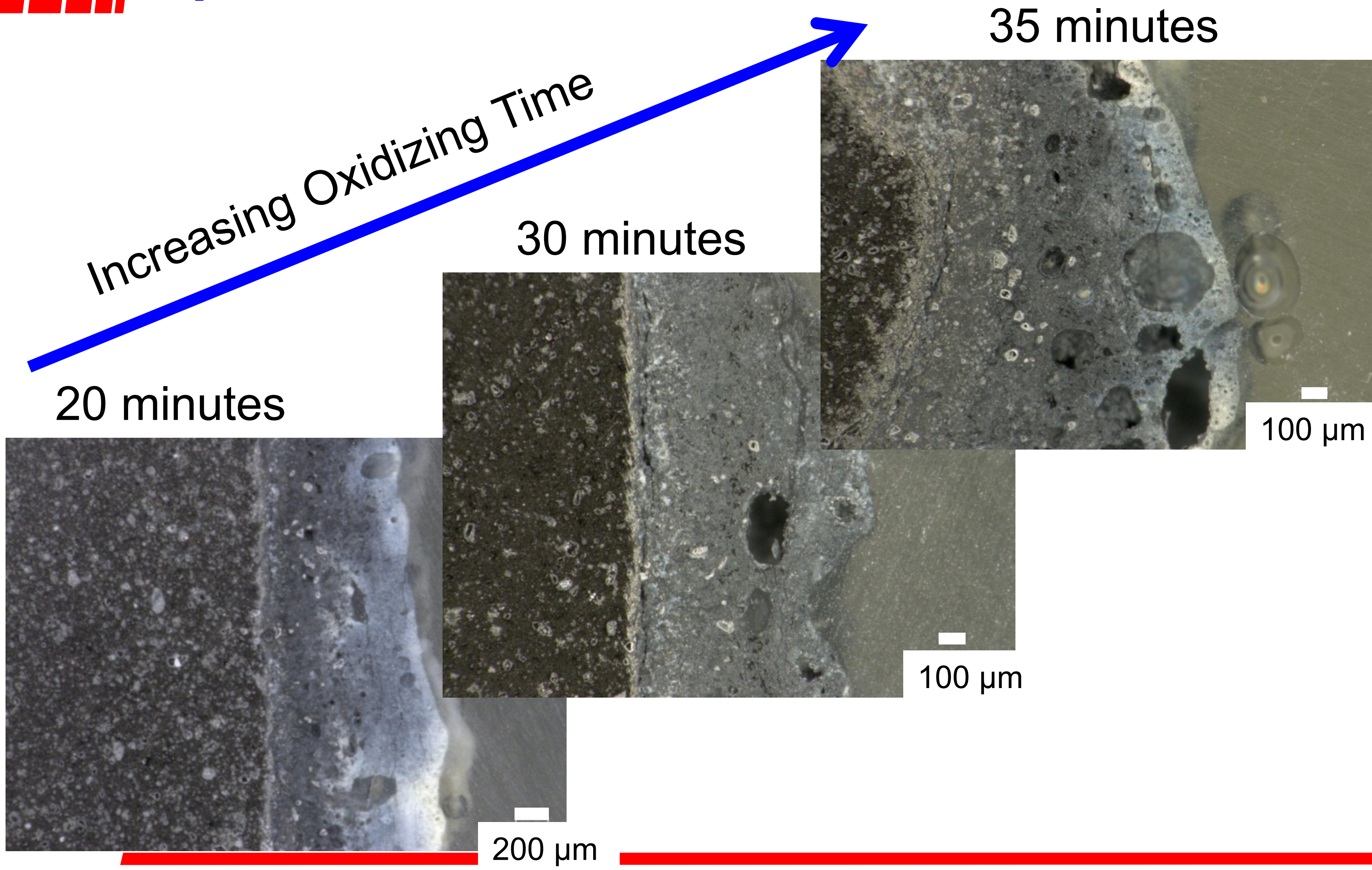


Oxygen Levels for TiO_x with Calculated Ti-ZrB_2-O_2 Phase Diagram

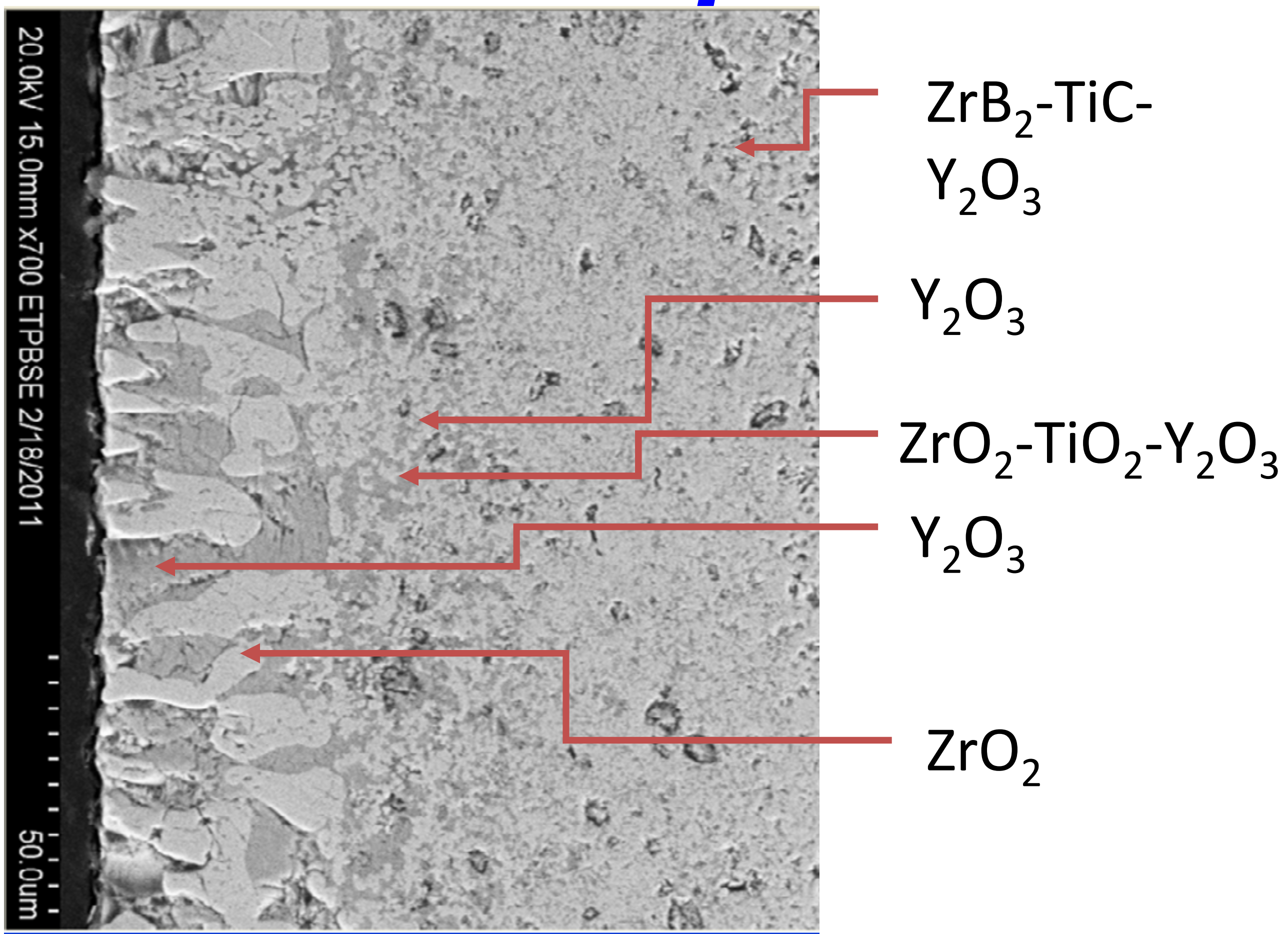
- Ti oxides start to form near $p_{O2} > 10^{-22}$ atm with TiO.
- Ti_2O_3/Ti_3O_5 has $p_{O2} = 10^{-15.5}$ atm
- ZrB_2 oxidizes to t-ZrO_2 with Ti oxides.
- Liquid oxides form with increasing p_{O2}



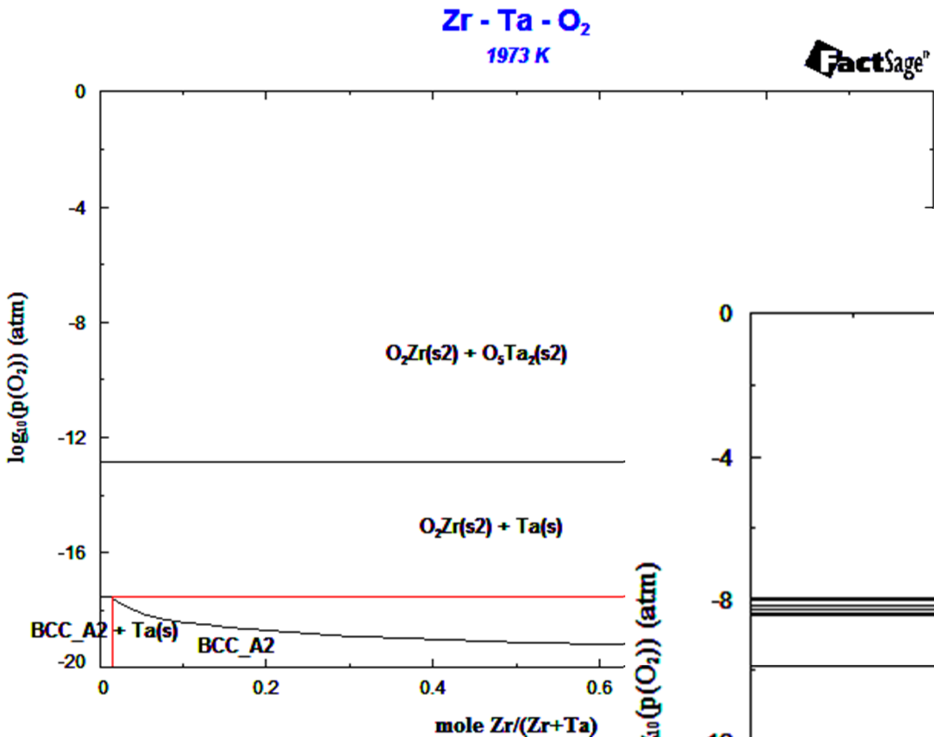
Optical Microstructures to Measure Scale

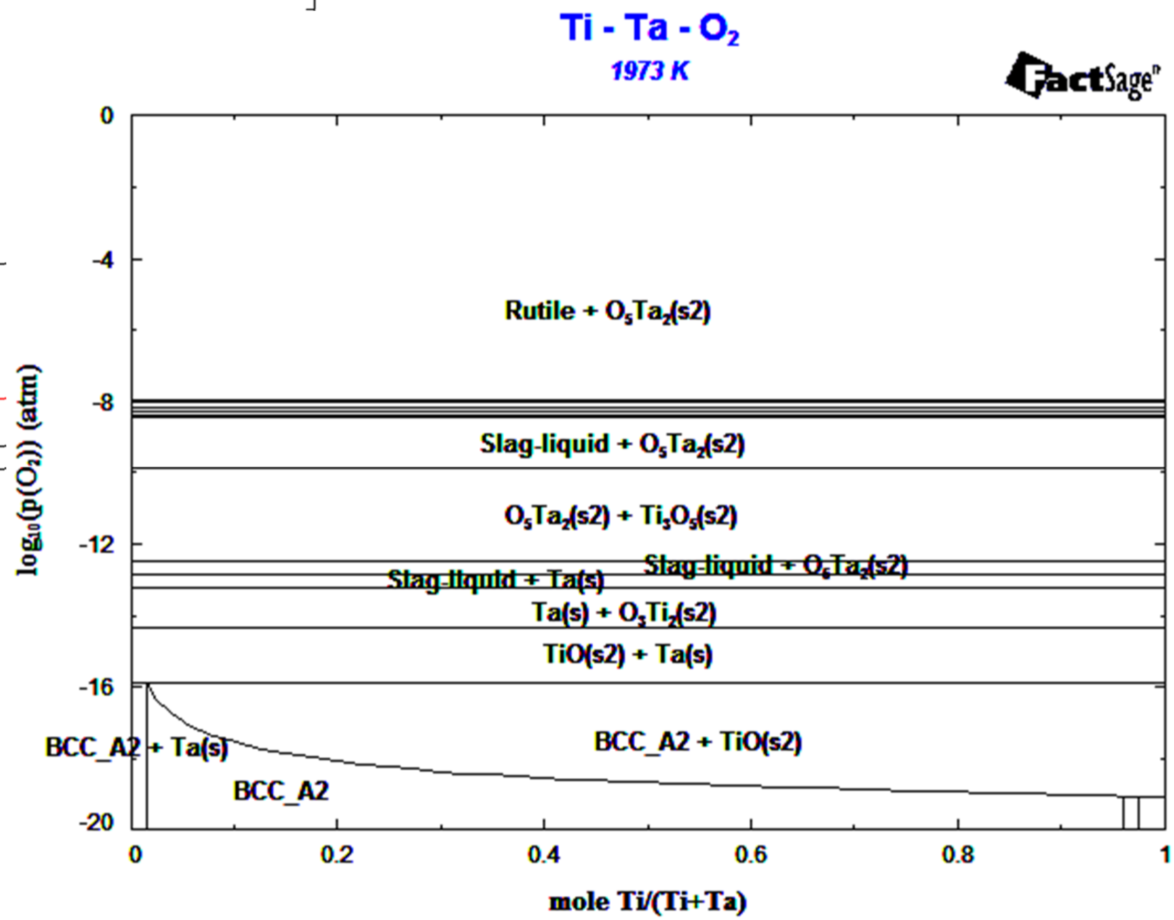


Phases identified for oxidized sample in C/CO/N_2



Calculated Zr-Ta-O_2 and Ti-Ta-O_2 phase diagrams

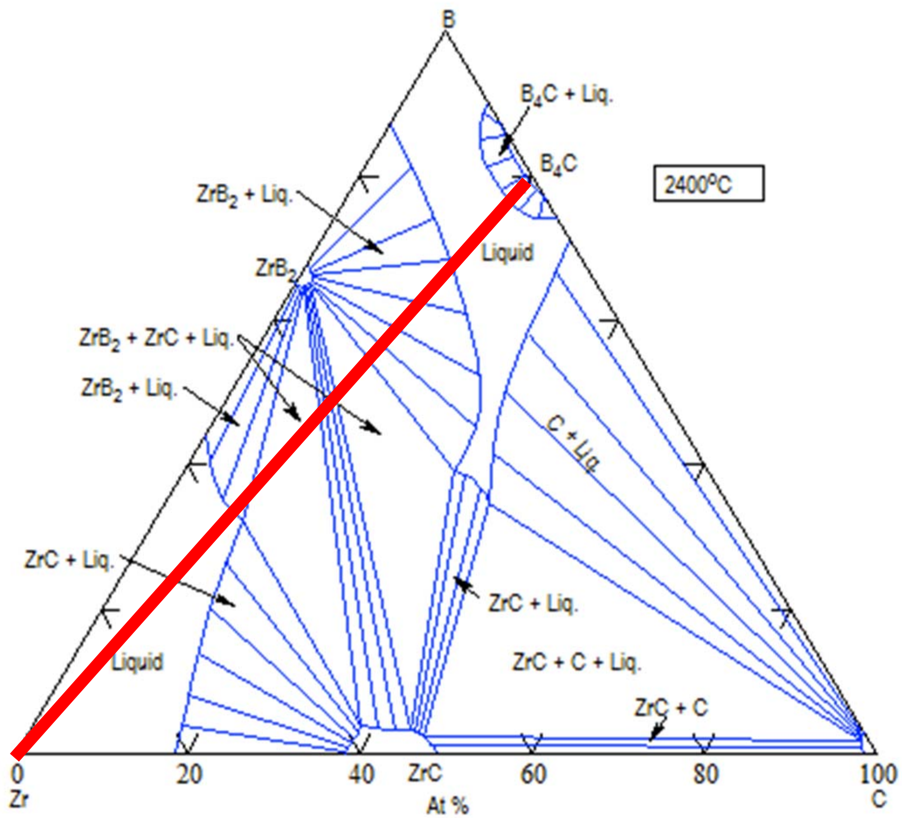




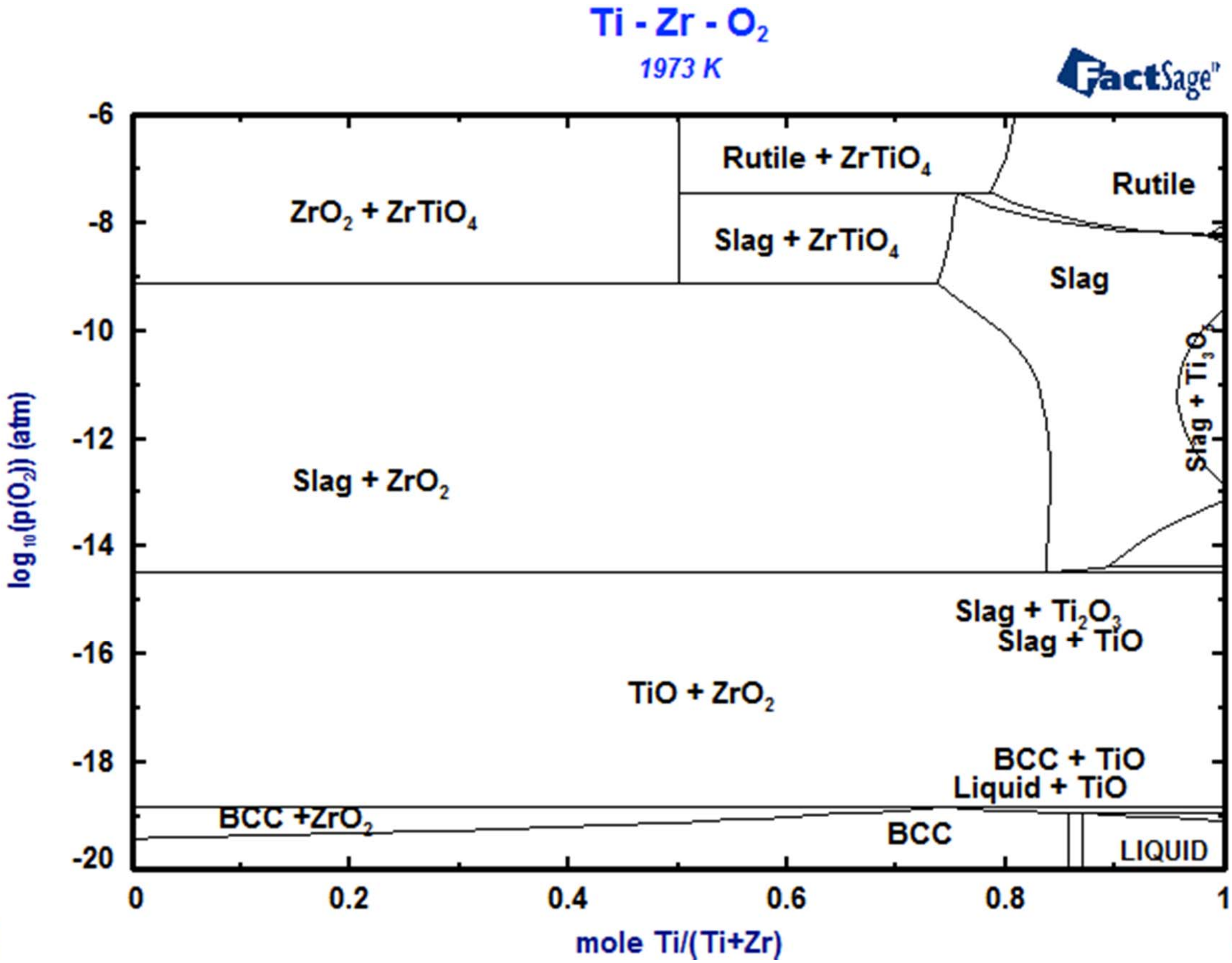
- p_{O2} level for Ta/Ta_2O_5
- TiOx-Ta_2O_5 liquids

Zr as primary component in B_4C reaction on Zr-B-C phase diagram

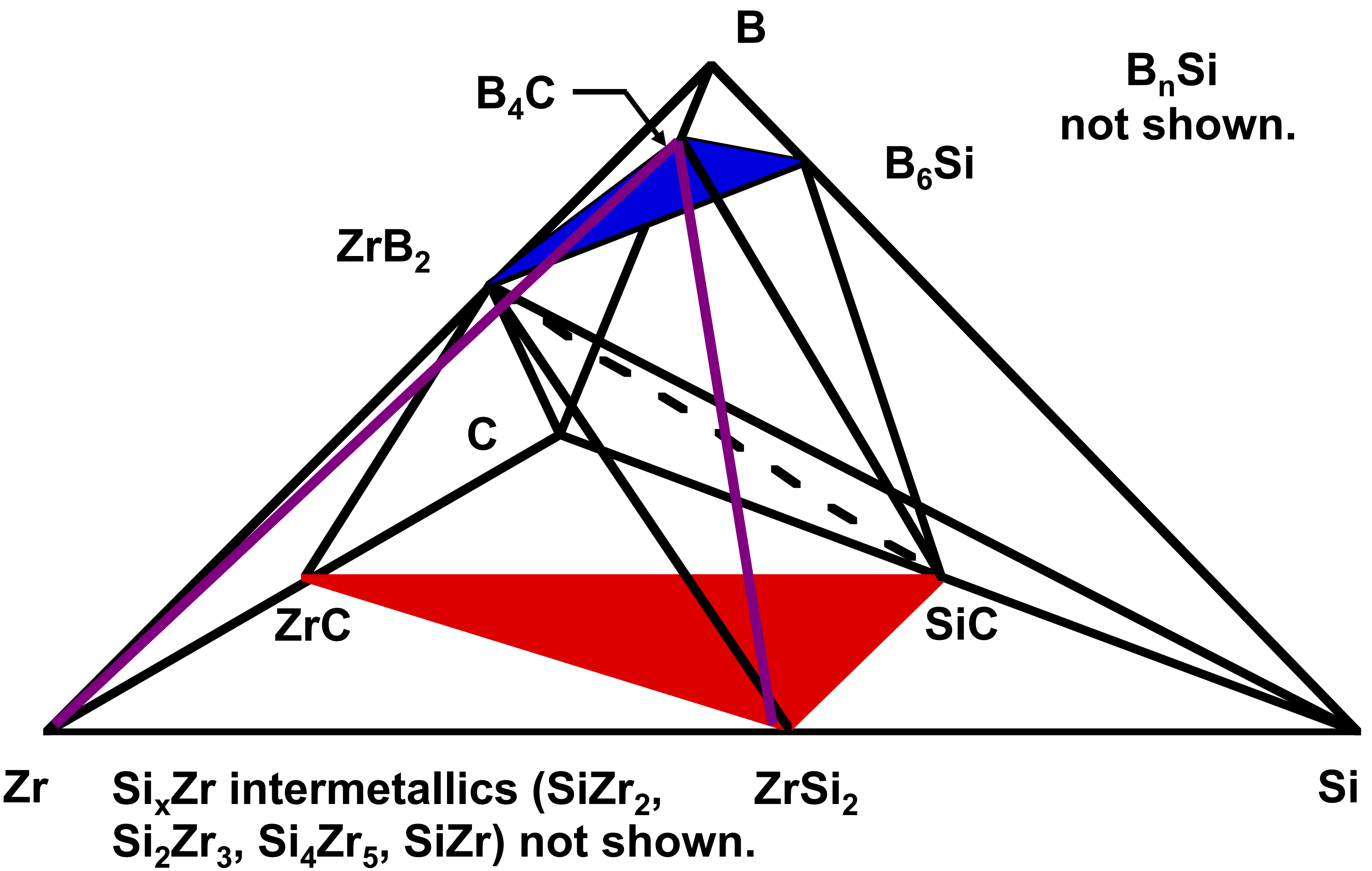
- Zr liquid changes with alloy composition
- Zr reacts with B_4C forming ZrC and ZrB_2 as a result of the mass balance.



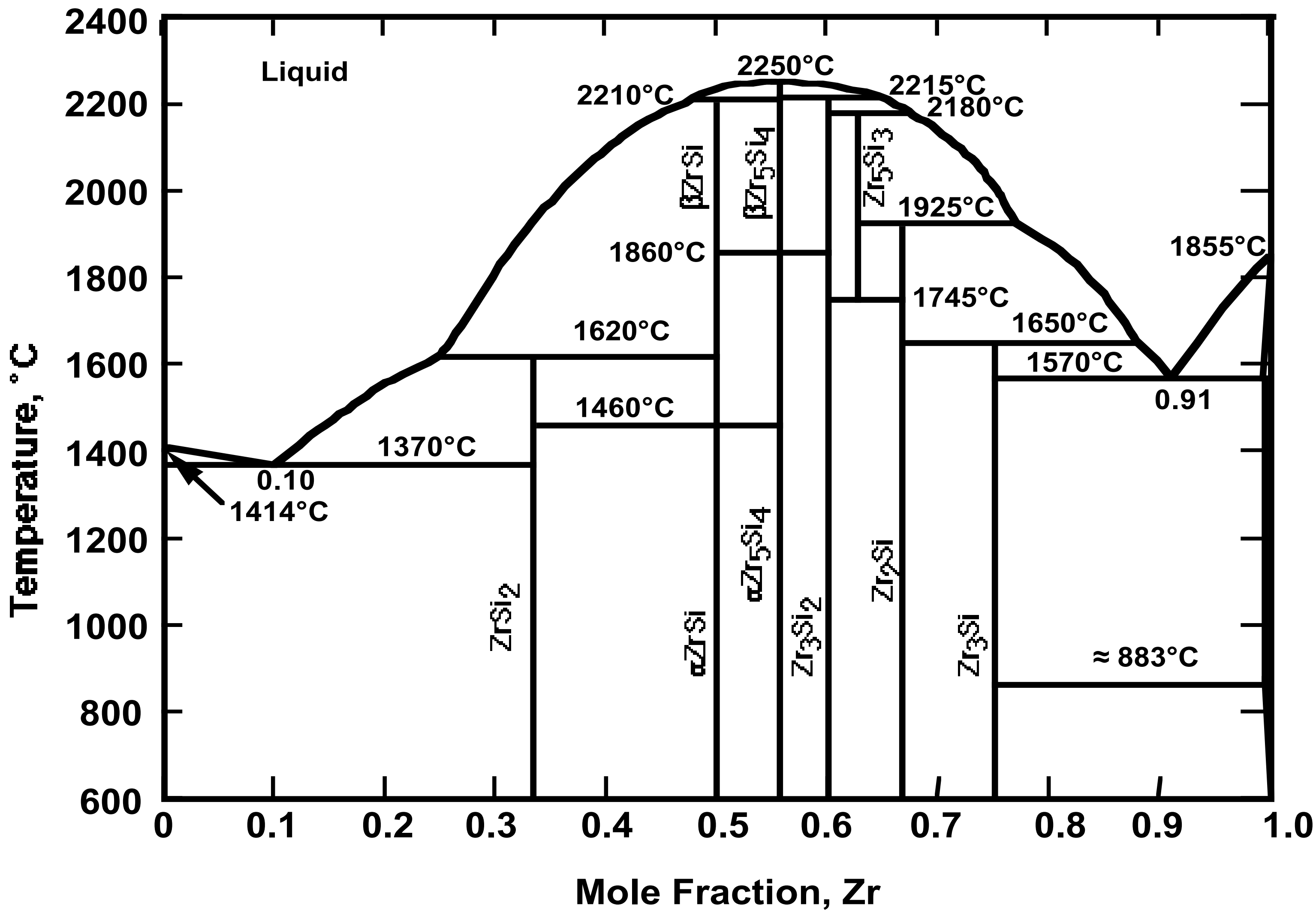
Ti-Zr-O_2 Phase Diagram at 1973 K



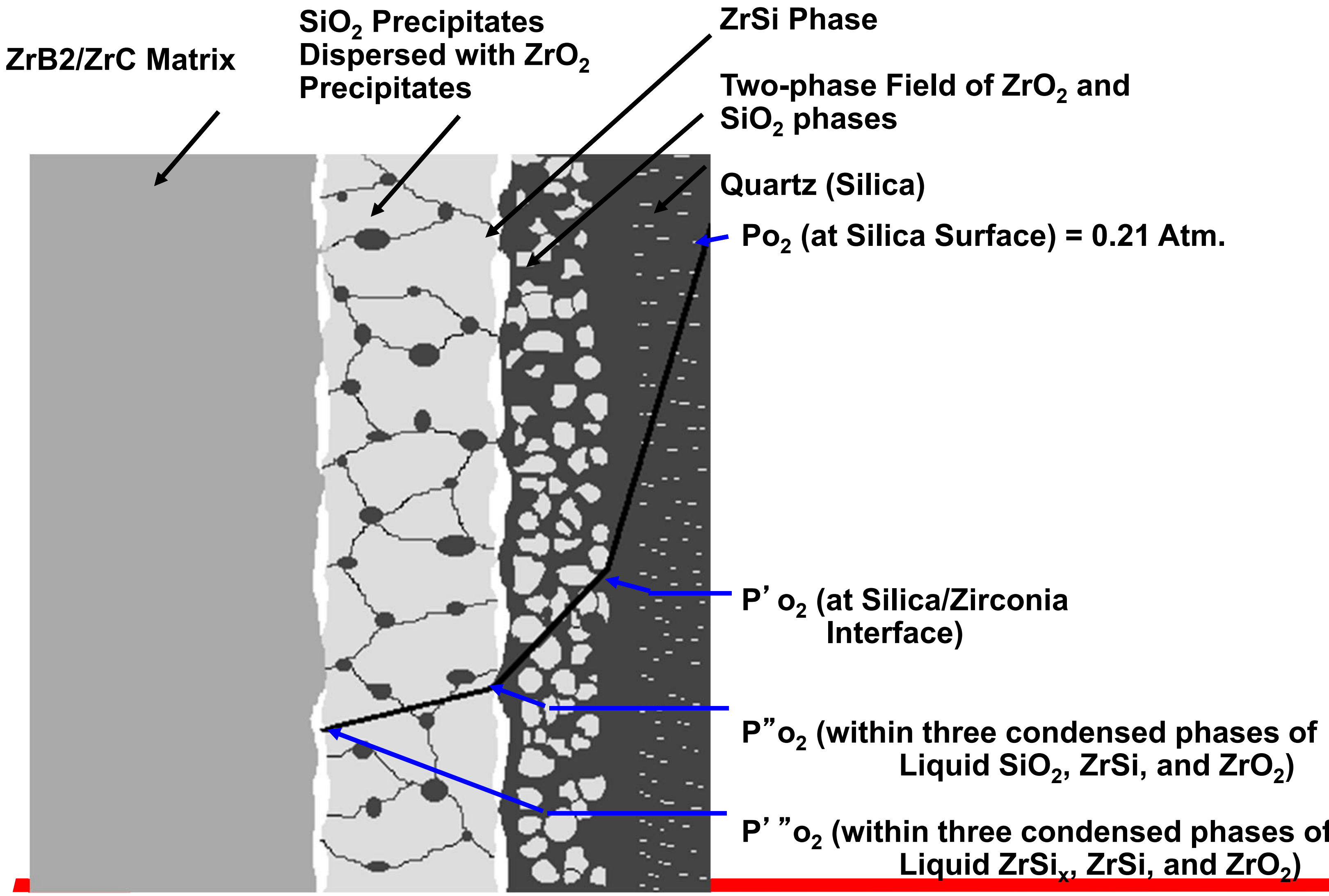
Zr-C-B-Si Quaternary (Proposed by Sorrell-1993)



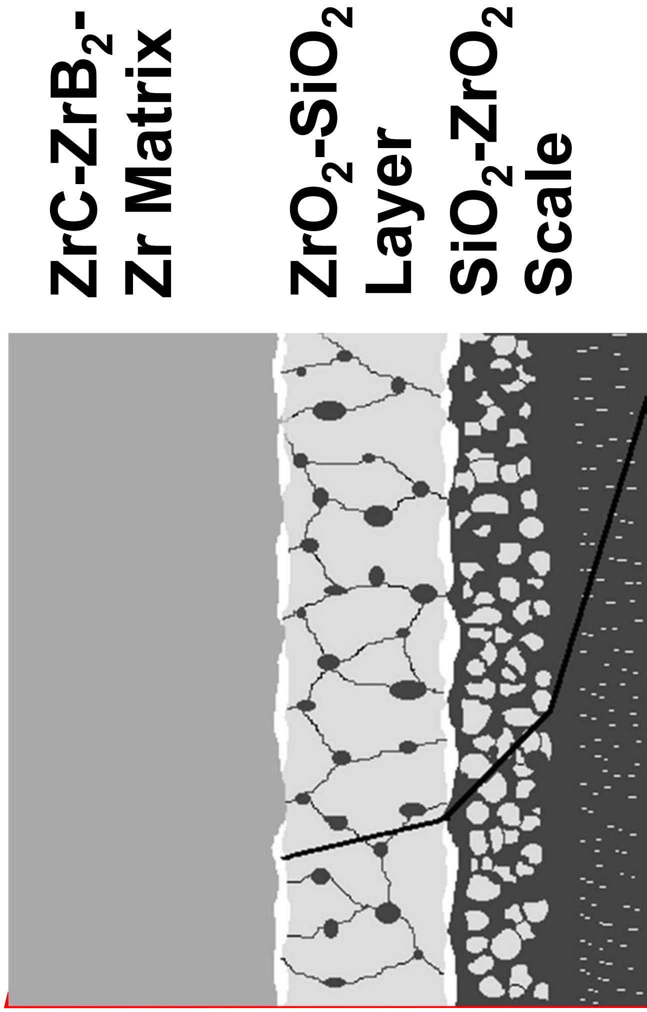
Zr-Si Phase Diagram

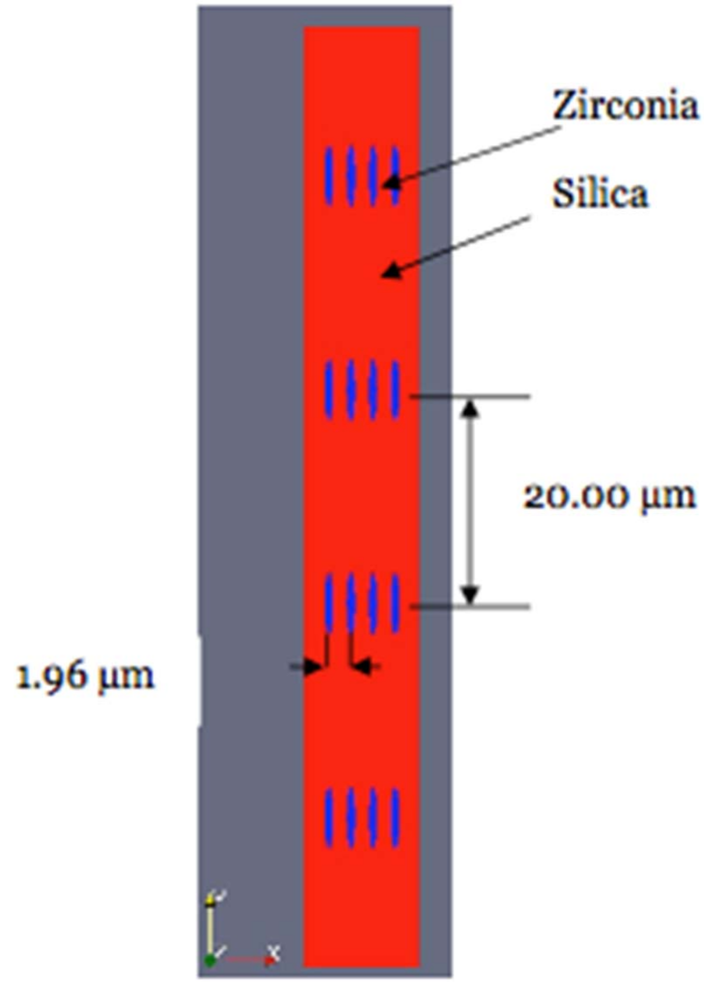


Oxygen Partial Pressure Gradient

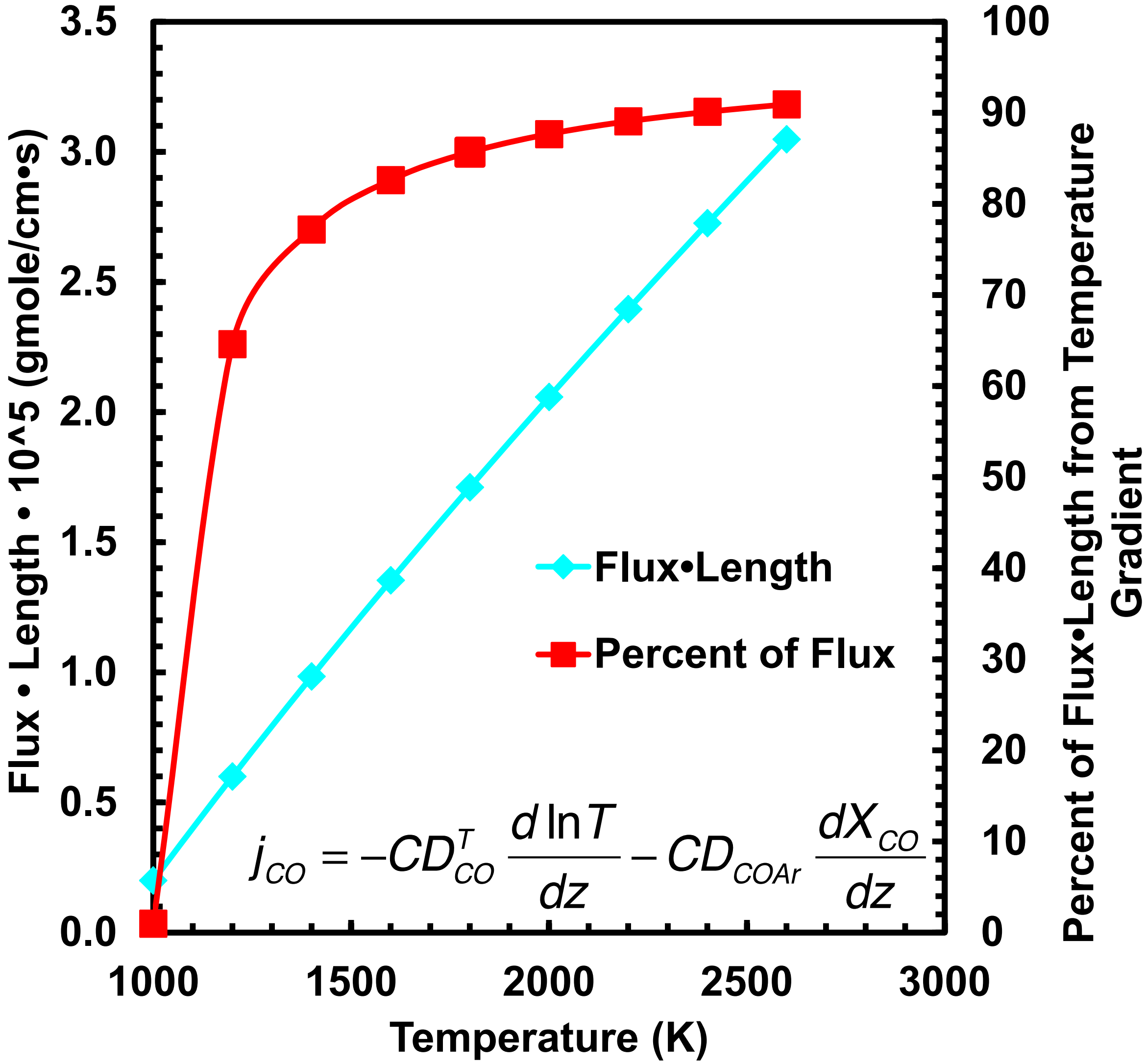


Optimal Configuration of ZrO_2 Precipitates in SiO_2 Matrix





Diffusional Flux – Kinetics Issues



- D_{COAr} from Poirier-Geiger and checked with Chapman-Enskog Eq.
- Mean temperature

$$\frac{T_H T_C}{T_H - T_C}\ln\frac{T_H}{T_C} = 1527K$$

- $Al/Al_2O_3/Al_4CO_4$ reaction rate?

Surface Energies for Hf Alloy Melts Determined from Elements