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)
  - 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)

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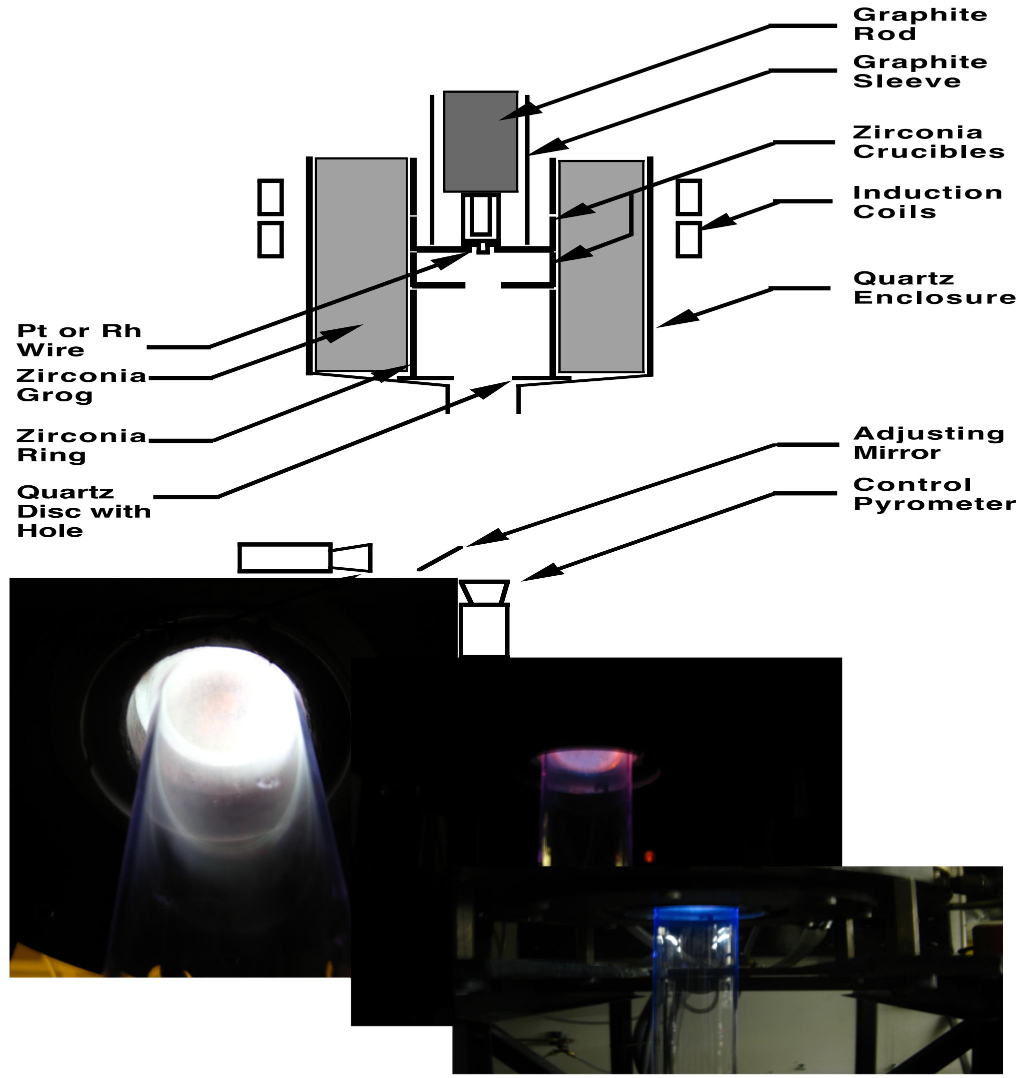
* Aids students in high temperature research.

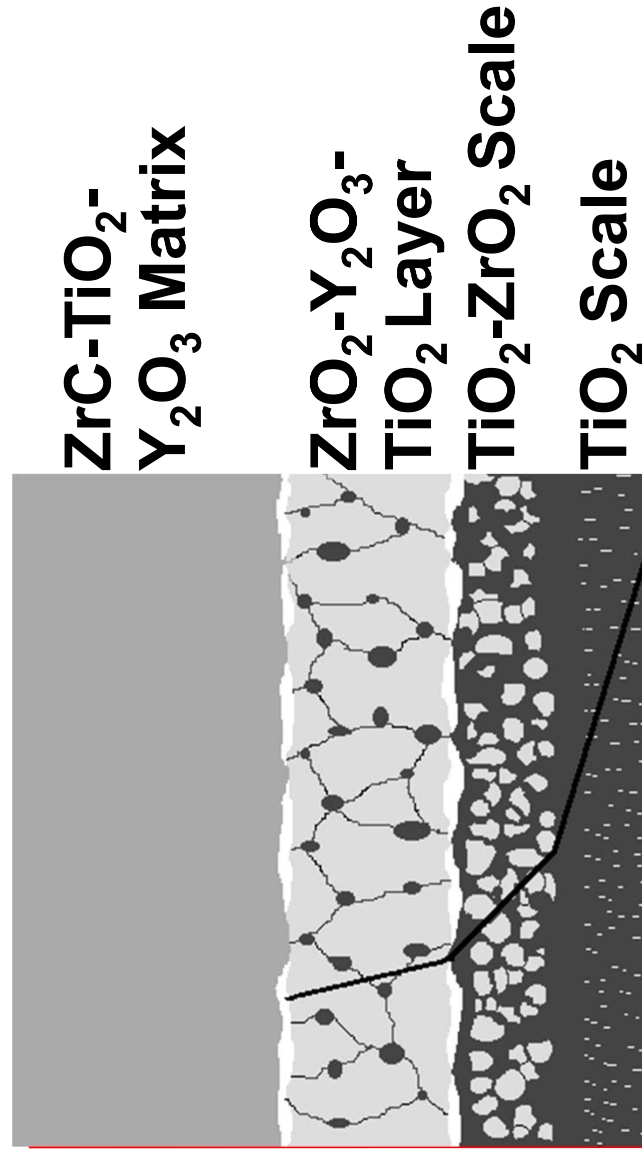
Motivation/Impact of Research

- 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.

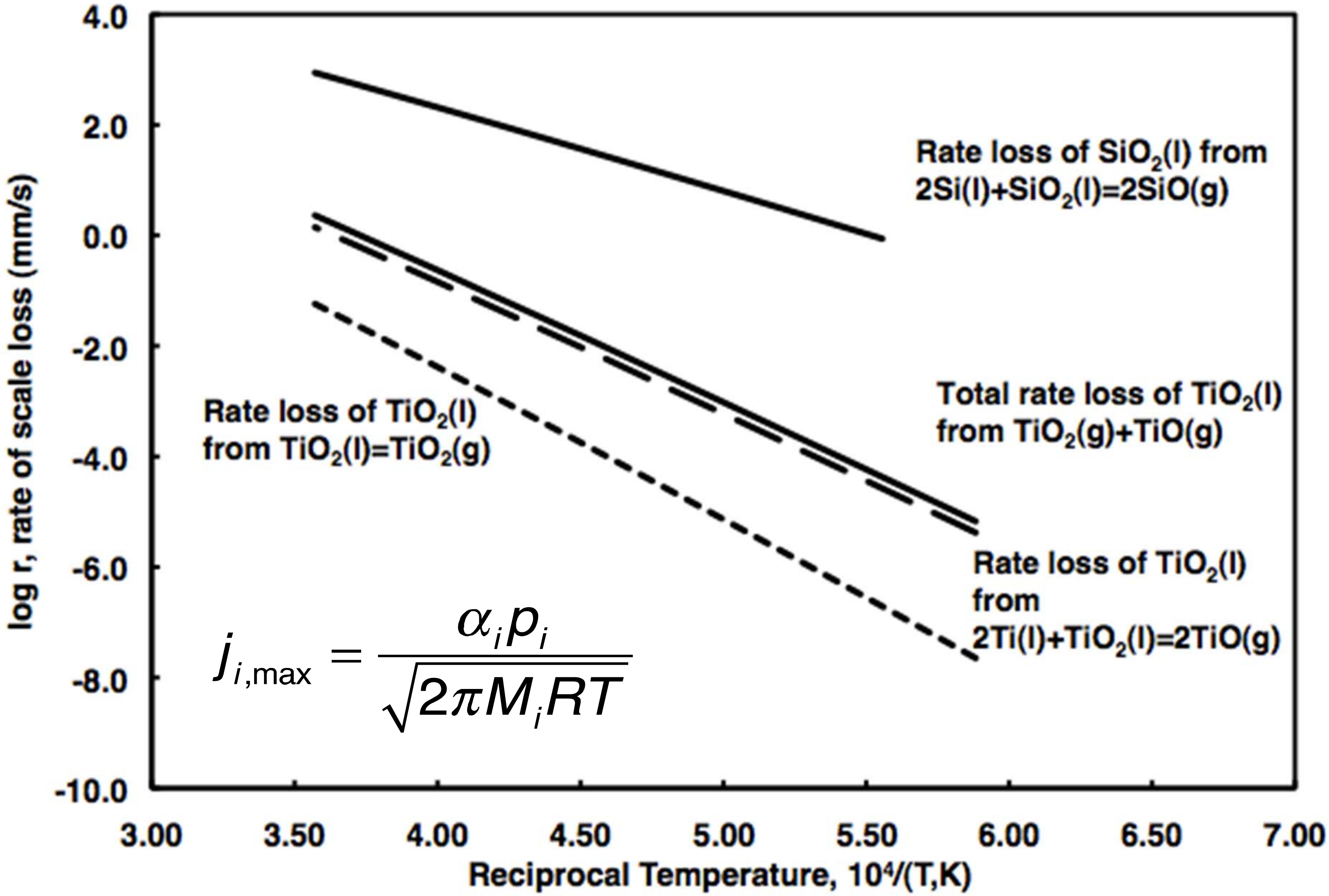


Outline of Presentation

- **Introduction – Processing**
  - **Scale of Al_2O_3 and TiO_x**
  - **Packed Bed Reactivity**
  - **Plasma Surface Reactions**
- **Computational Effort – computational thermodynamics coupled with heterogeneous kinetics infused with fluid dynamics to model plasma gas reactions**
- **Strategic Experimentation – Ti_3AlC-TiC-Y_2O_3, SiC, ZrC-TiO_2-Y_2O_3**
- **Progress and Analysis**



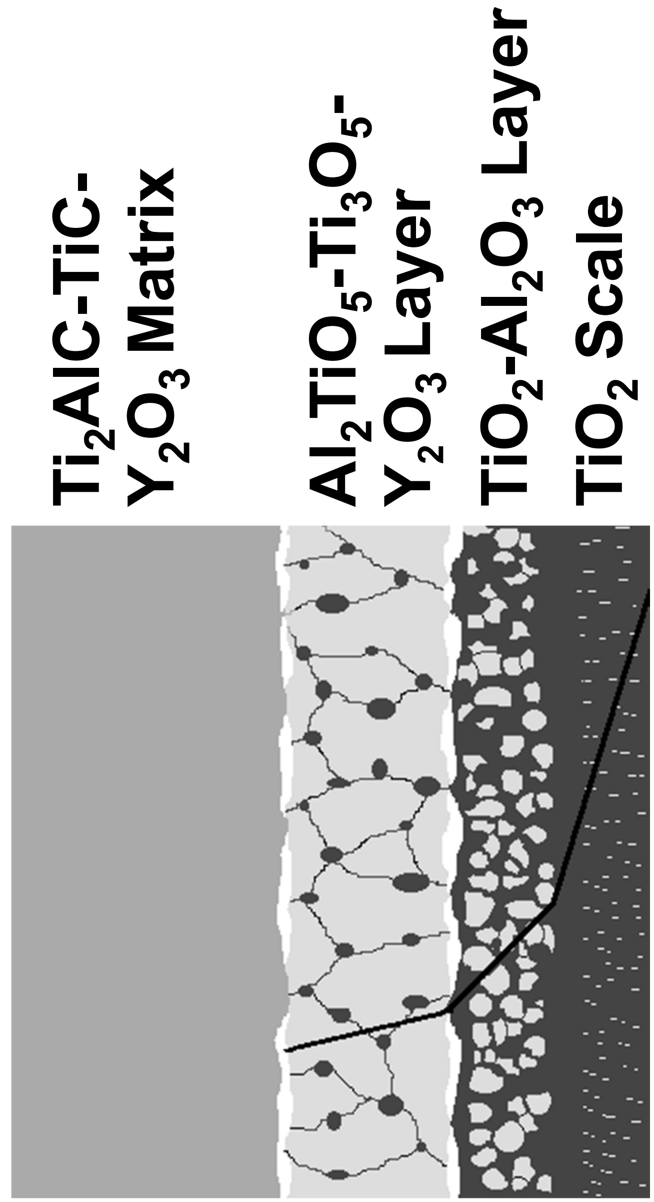
Vaporizing Flux of SiO_2 and TiO_2



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

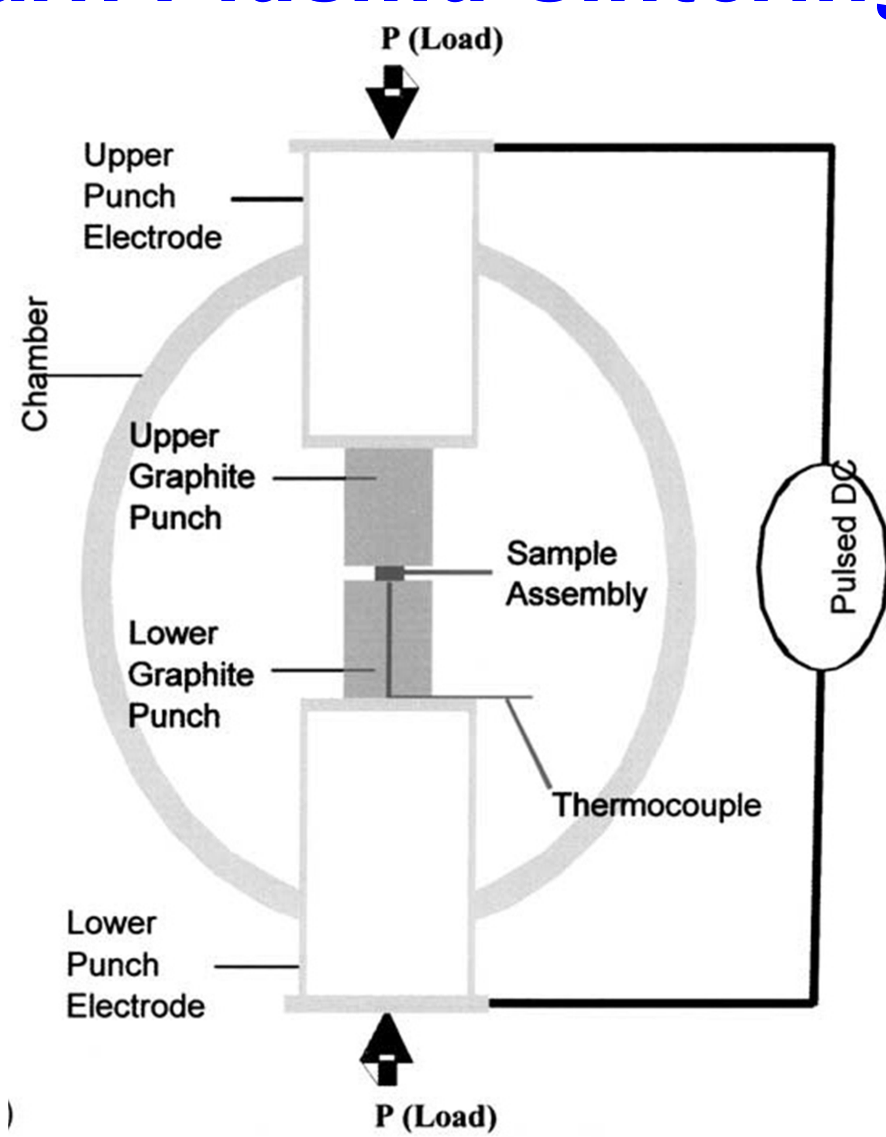
Project Objectives

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



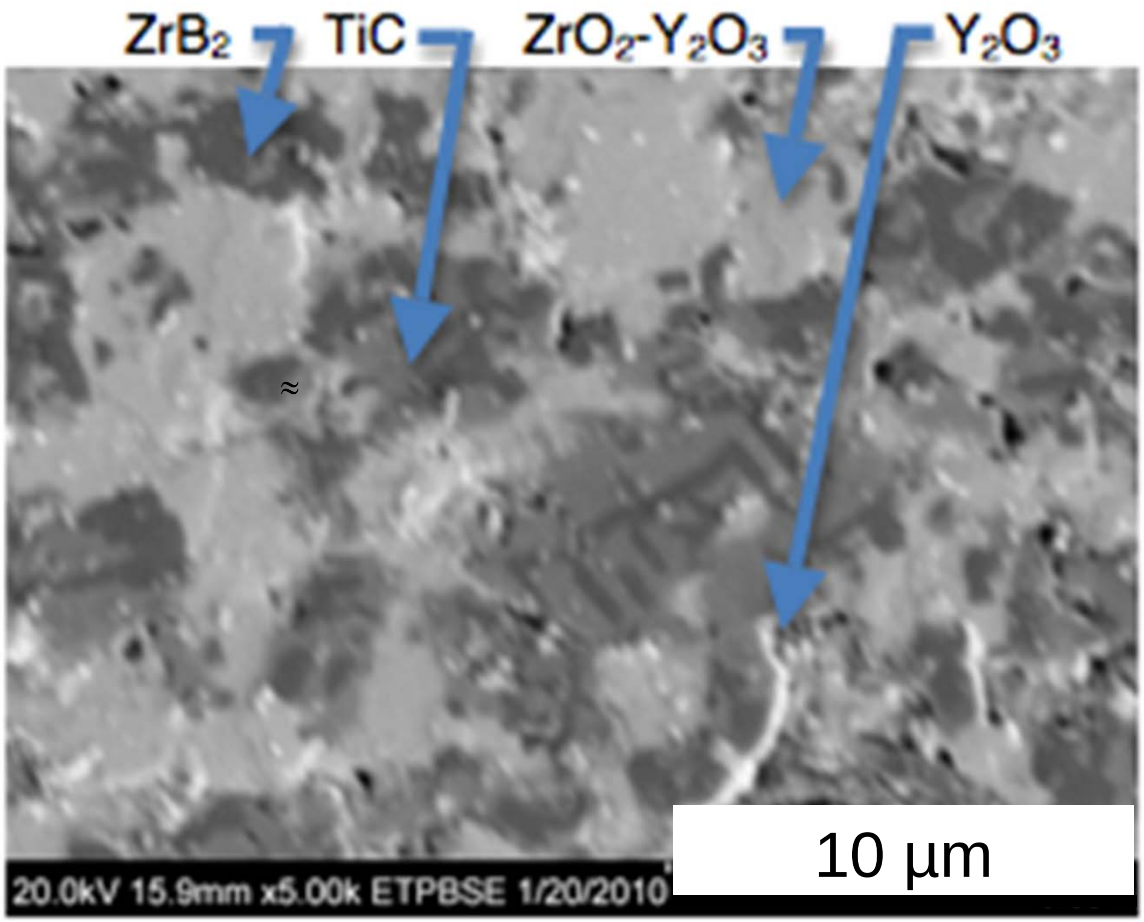
Thoughts on Spark-Plasma Sintering

- 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?



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

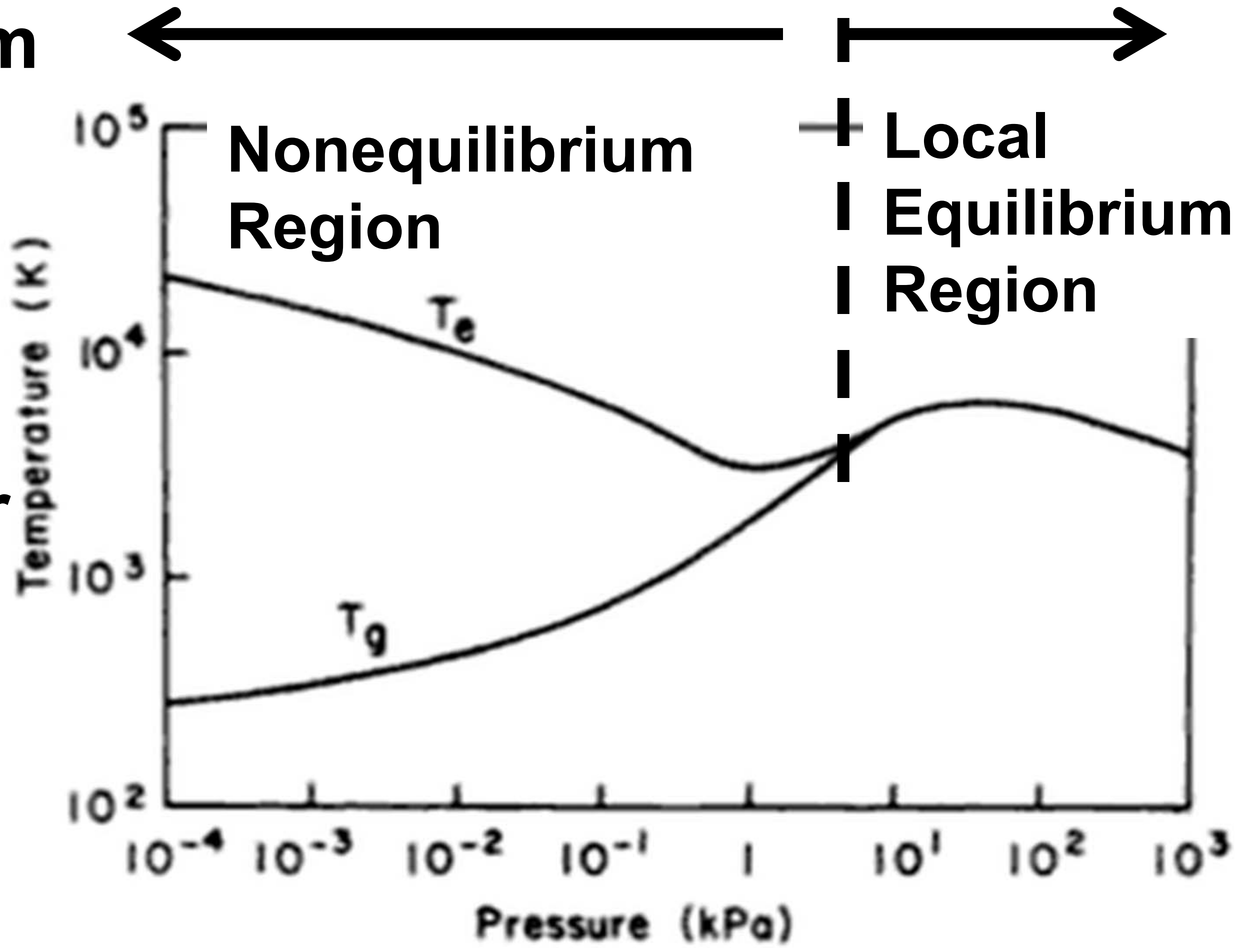
- ZrB_2 oxidizes to ZrO_2 dissolving some Y_2O_3.
- Stringers of Y_2O_3 appear in grain boundary.
- Graphite minimized TiC oxidation though TiO formed from residual O_2 in Ar.



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

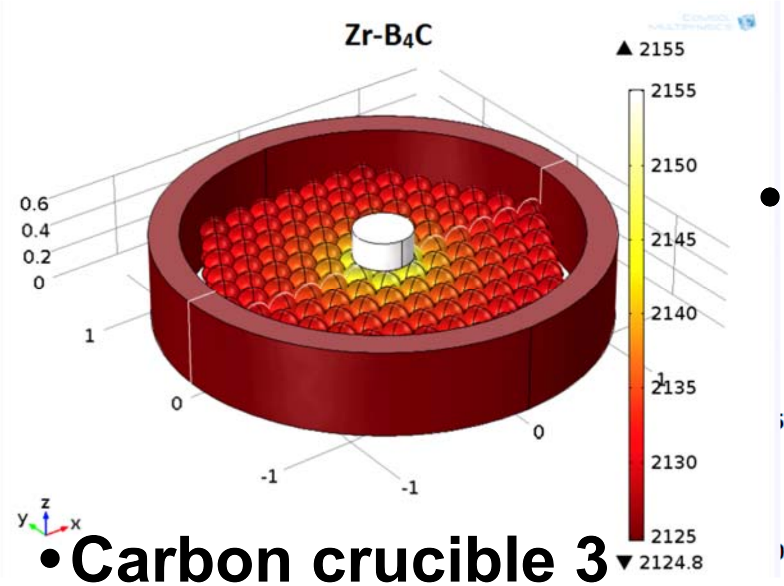
Plasma Temperatures - Pressures

- 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.



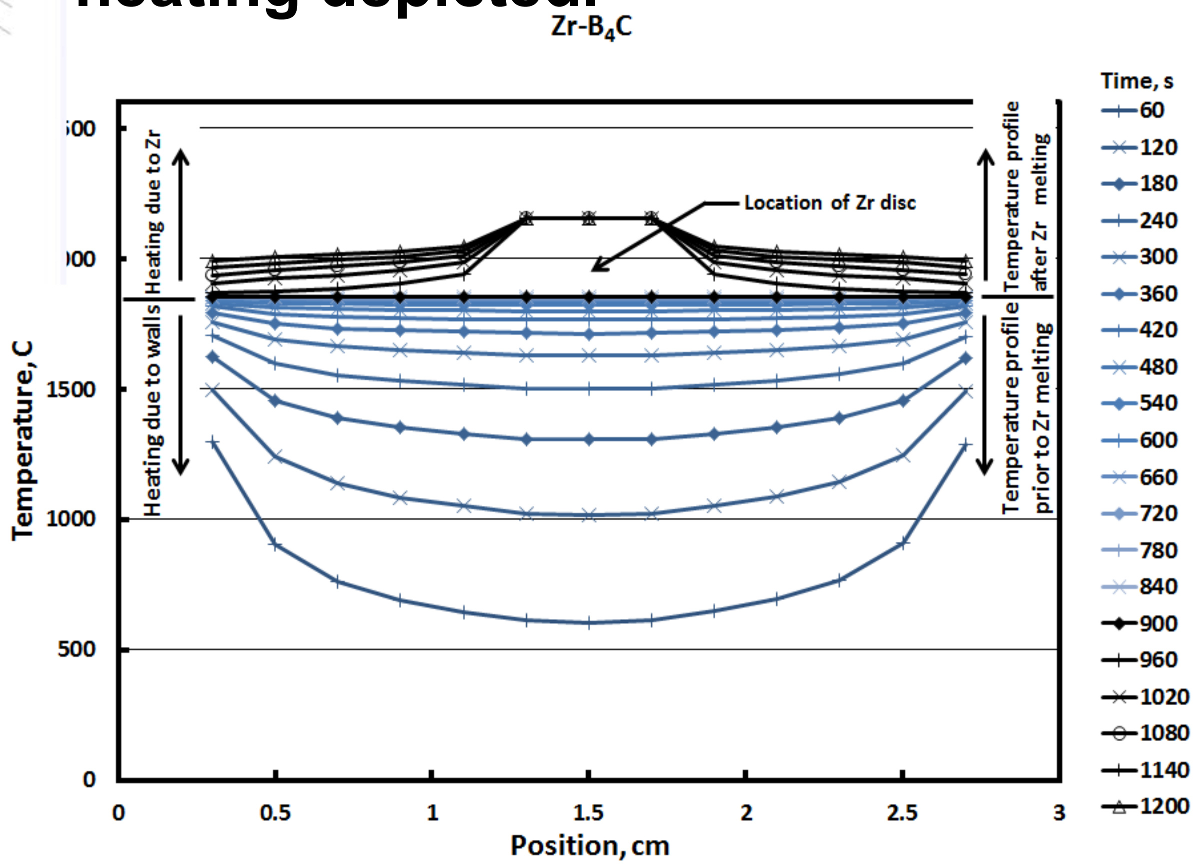
Boulous, Fauchais and Pfender--1994

Temperature Transients from COMSOL Simulations



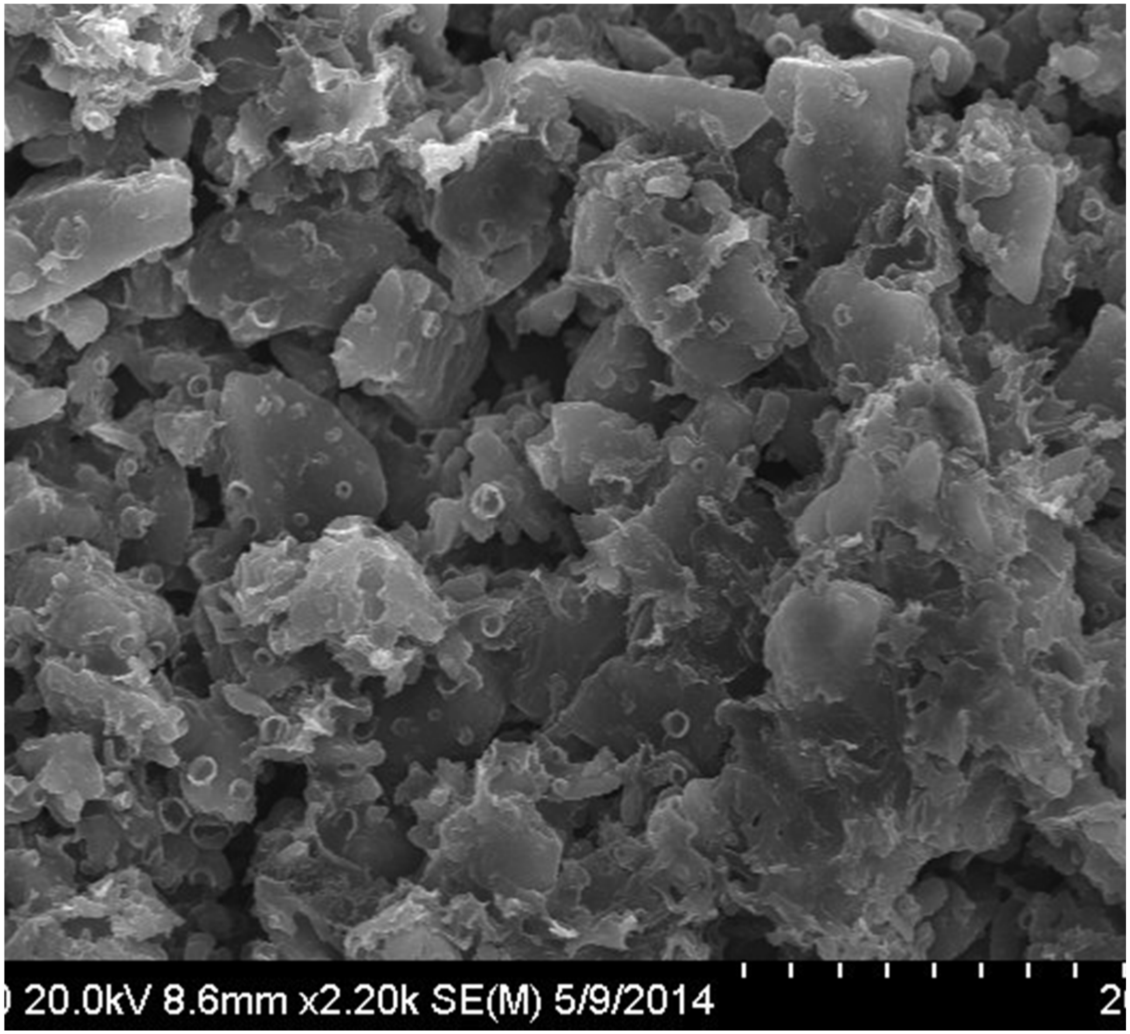
- Carbon crucible 3 cm OD-2.6 cm ID & 254 B_4C spheres.
- B_4C melts at 2450° C
- Zr melts at 1855° C
- k_{B4C}=4.5, k_{Zr}=34 W/(mK)

- 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.



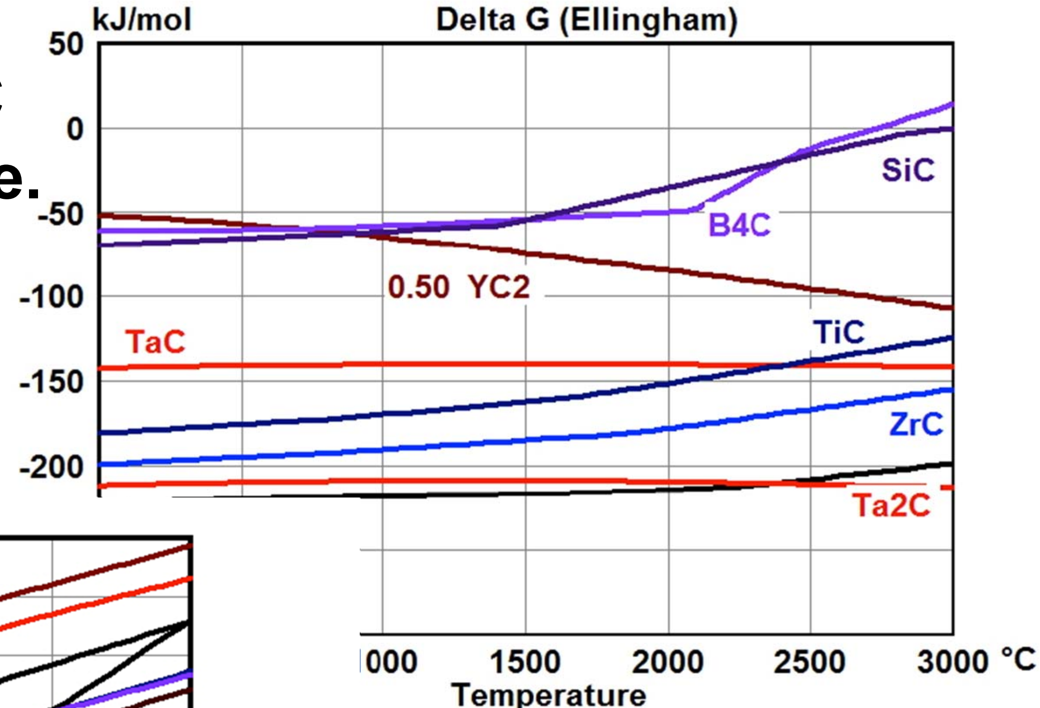
B_4C Microstructure after 1700° C Heating

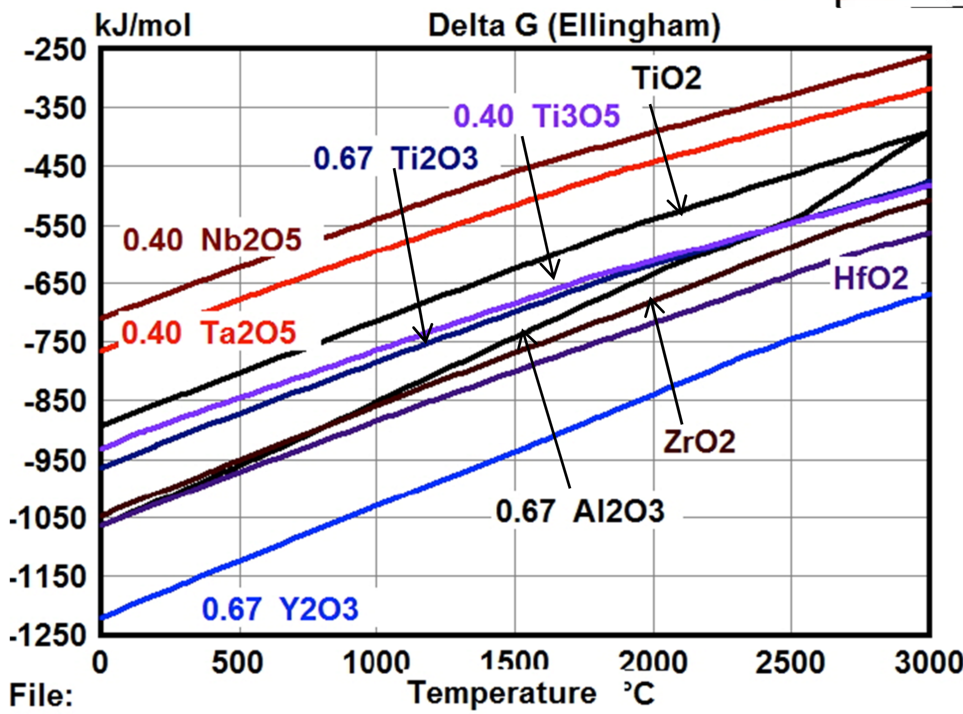
- B_4C powder averaging 10 µm was heated to 1700° C in a graphite crucible.
- Afterwards, liquid Bi was used to embed particles followed by polishing.
- Pores vary from 1 to 10 µm.



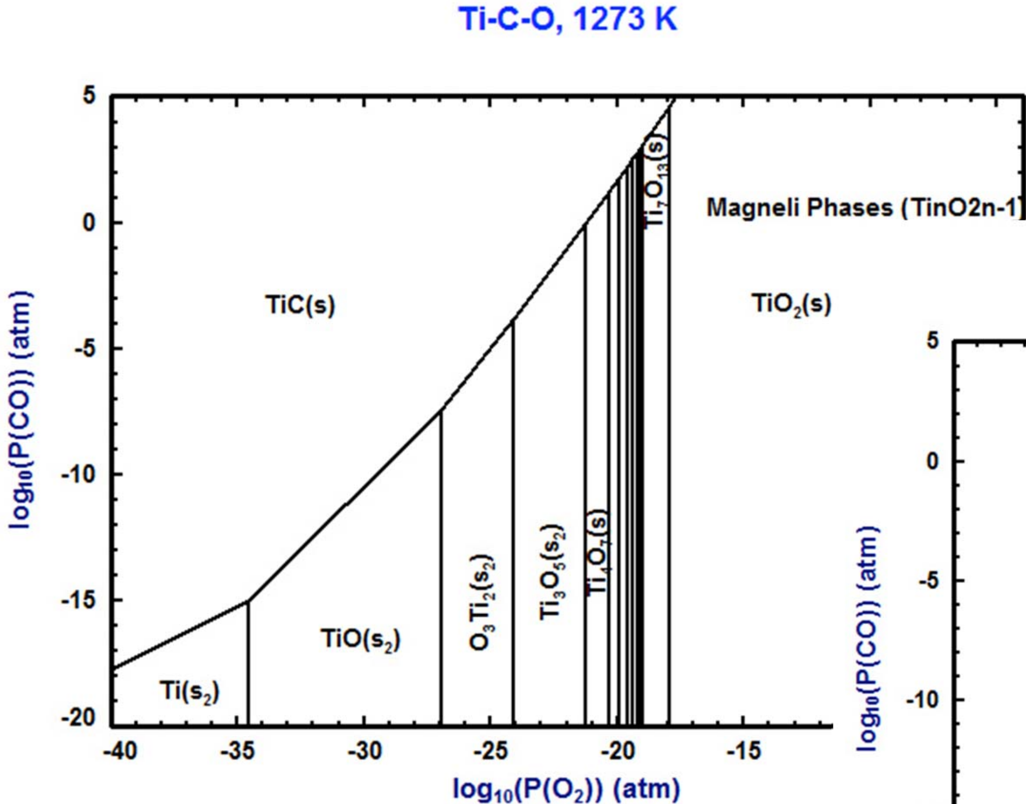
Stabilities-Oxides and Carbides

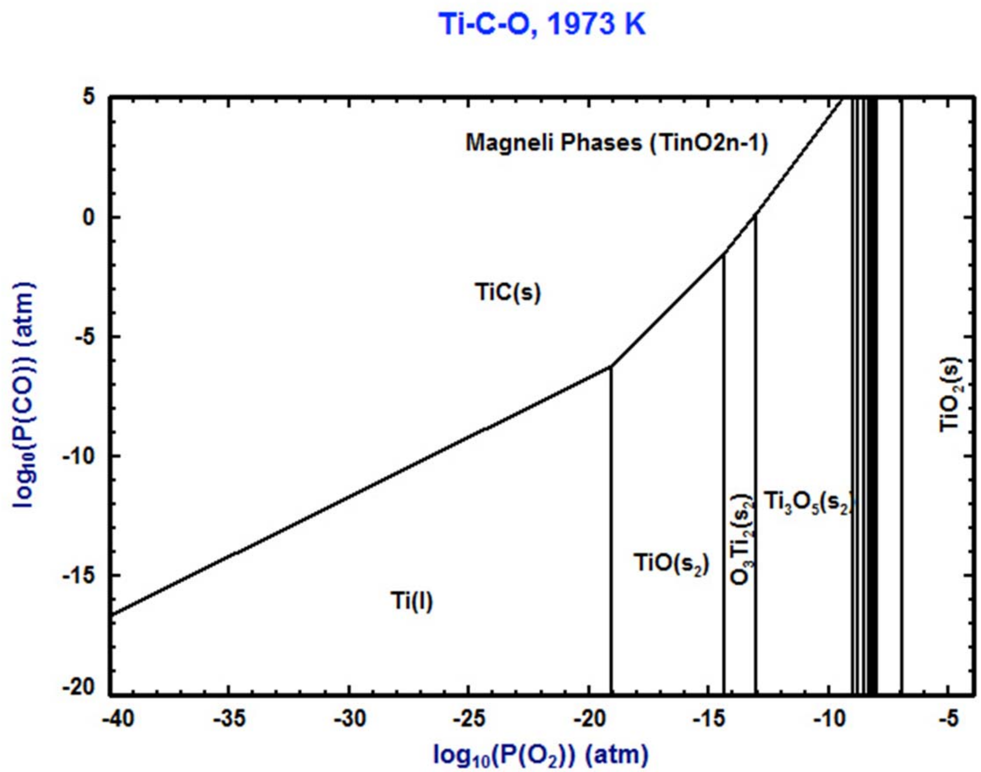
- For carbides, HfC, Ta_2C and ZrC are most stable.
- For oxides, Y_2O_3 and HfO_2 are most stable.
- Used Outotec HSC v. 7





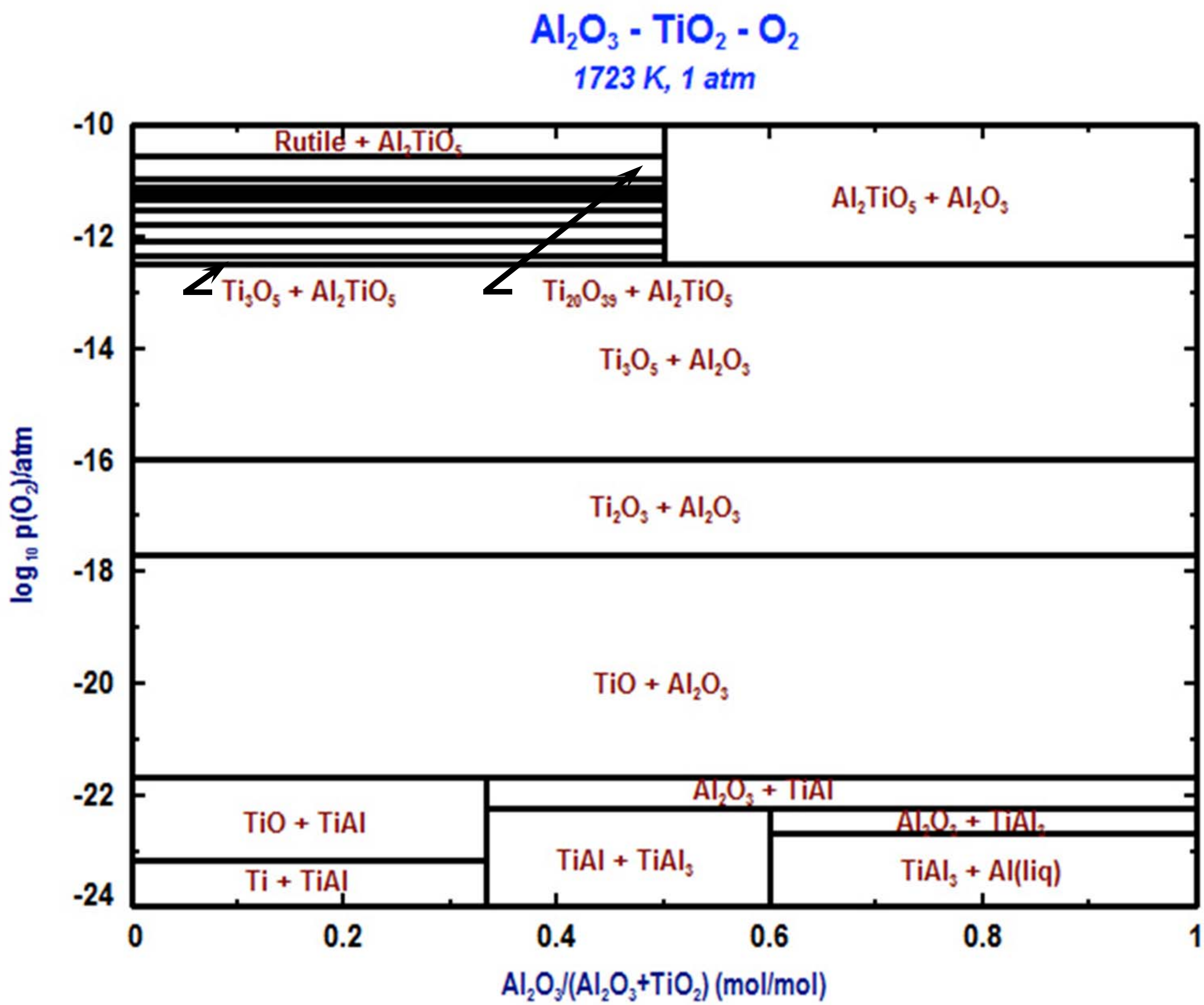
Ti-C-O Stability Diagrams at 1273 & 1973K for Expanded View of Magneli phases & p_{O2}





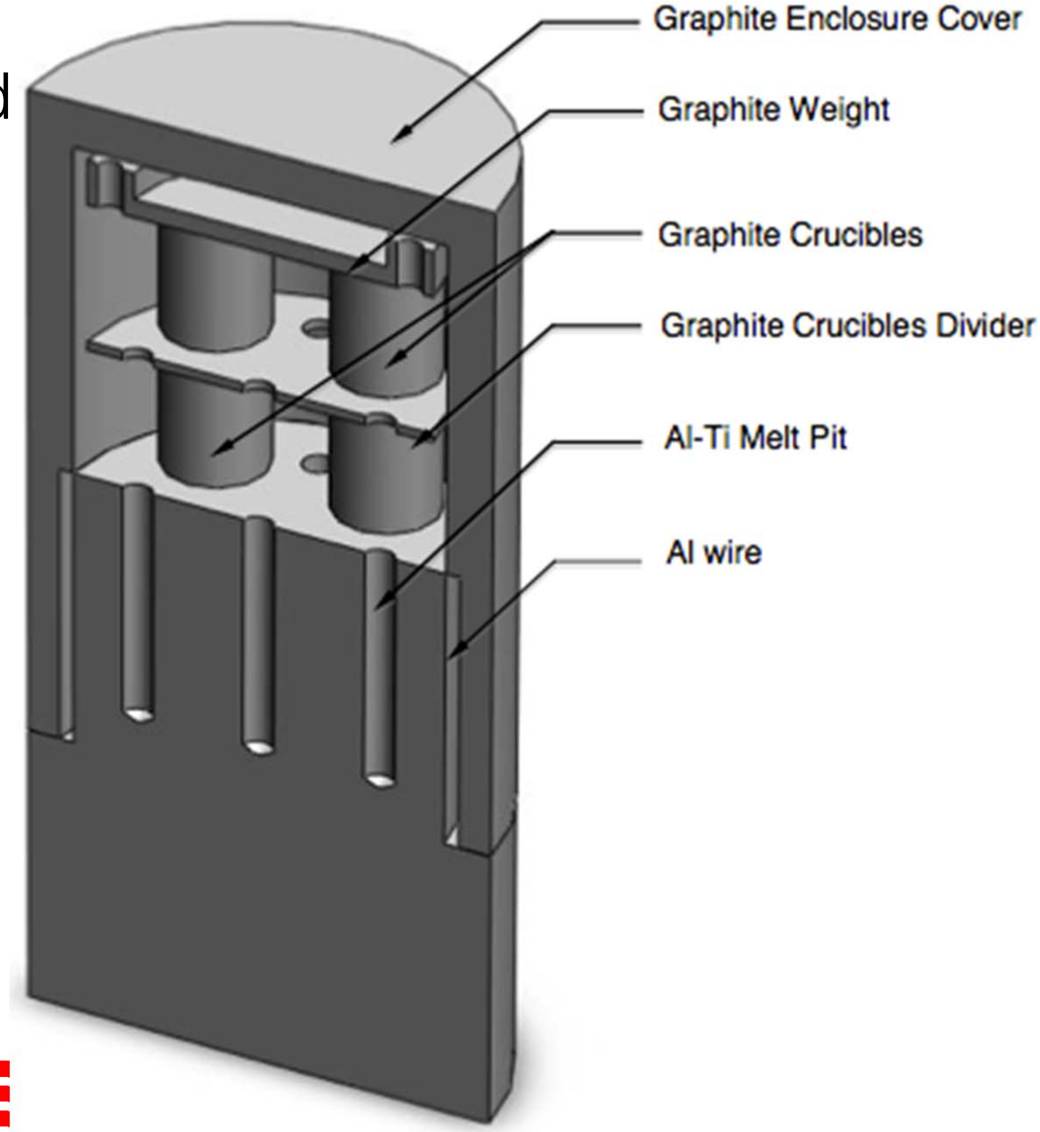
Possible Scale of Oxidized Ti_2AlC-TiC

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

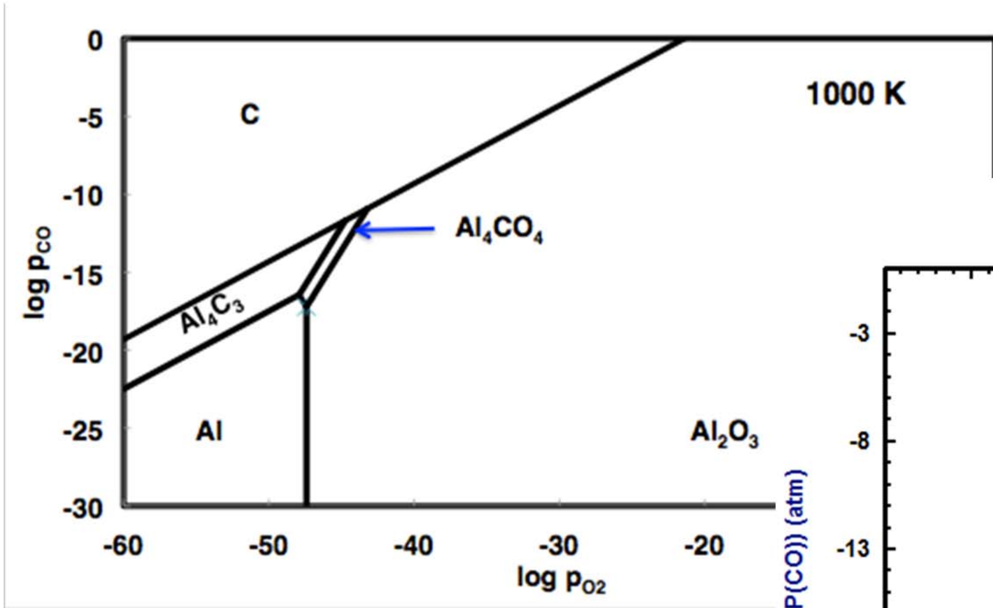


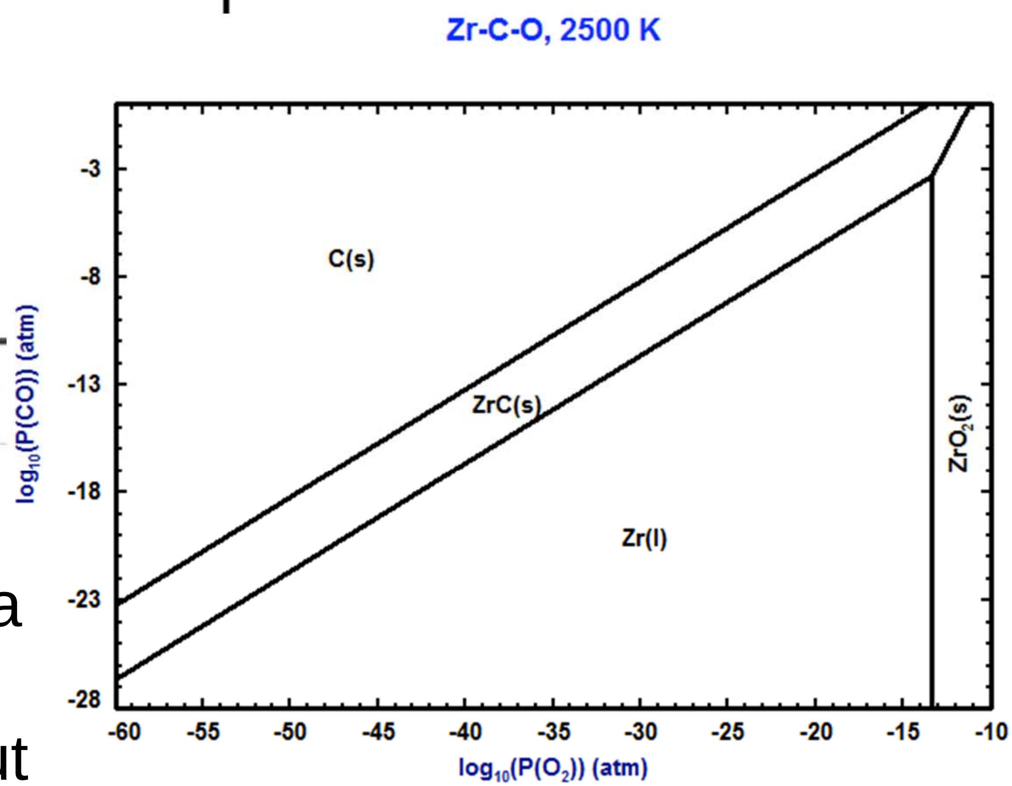
Configuration of Ti-Al-C reaction system

- 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

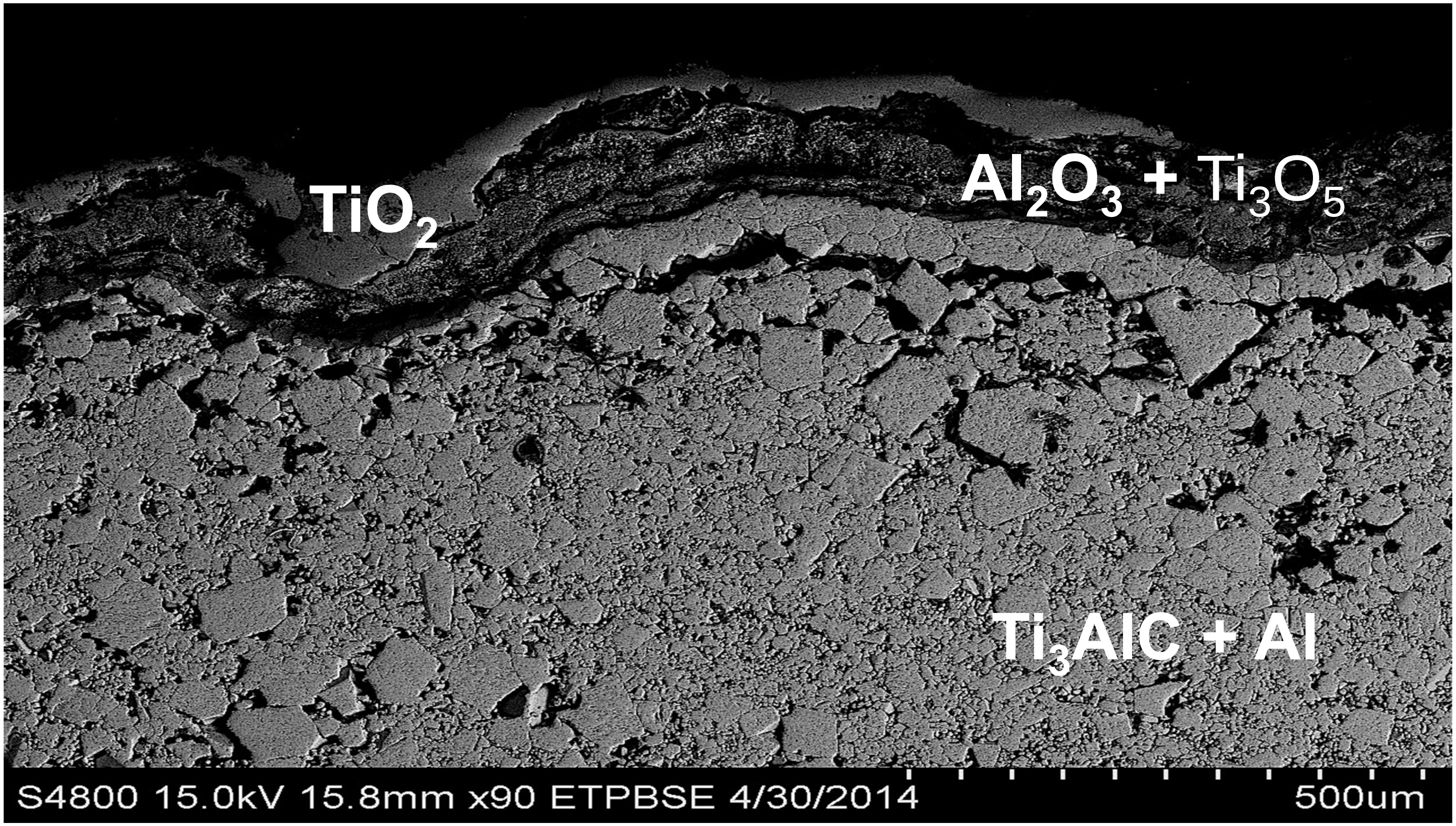




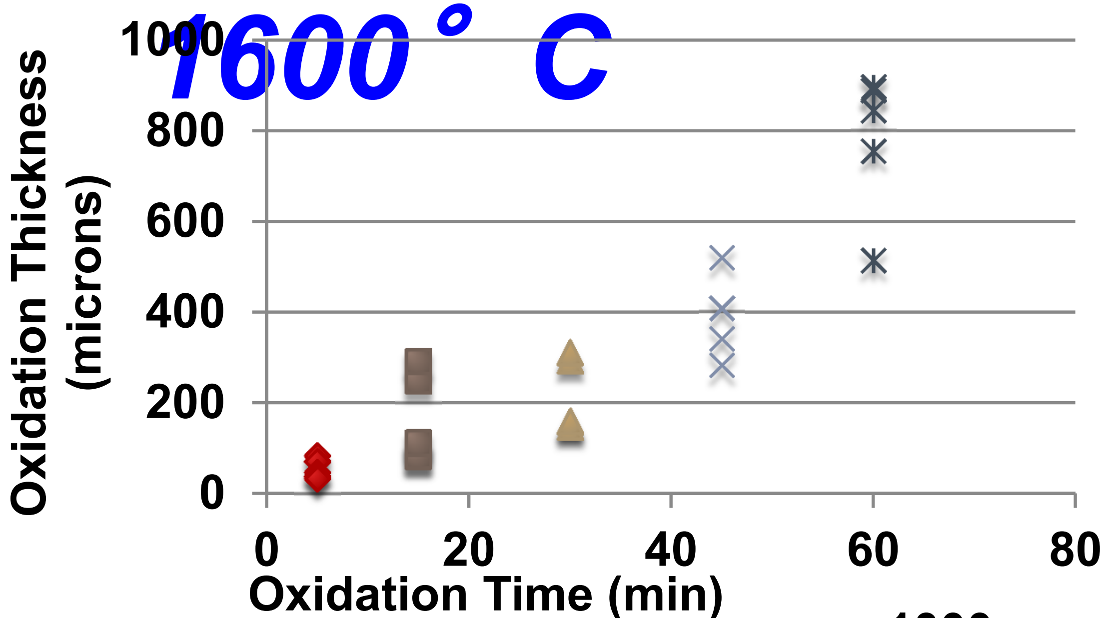
- $Al/Al_4CO_4/Al_2O_3$ estimated at 1000 K for a $p_{O2} = 10^{-47}$ atm
- Zr oxidation occurs about 10^{-13} atm.

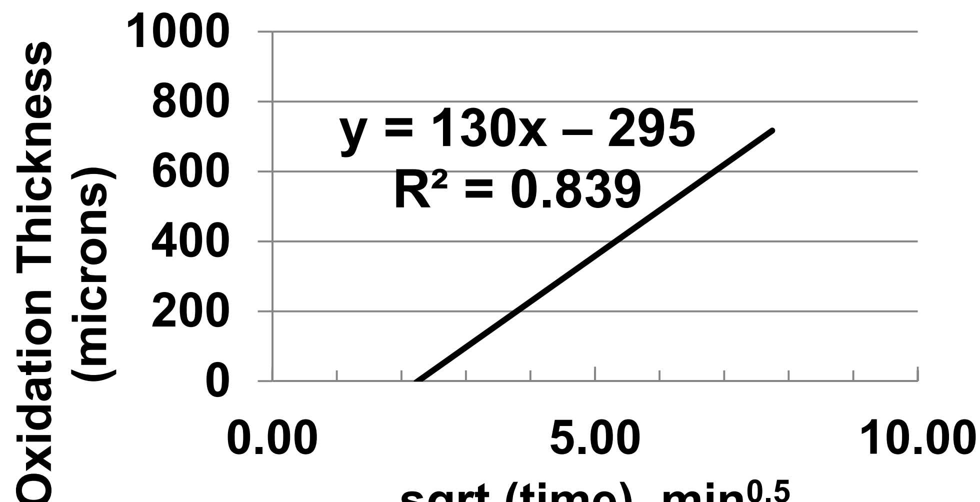
Maheswaraiah, Sandate and Bronson - 2012

Ti_3AlC core after 30 minute oxidation



Oxidizing Kinetics at 1600° C





Extending Previous Kinetic Equations

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

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

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

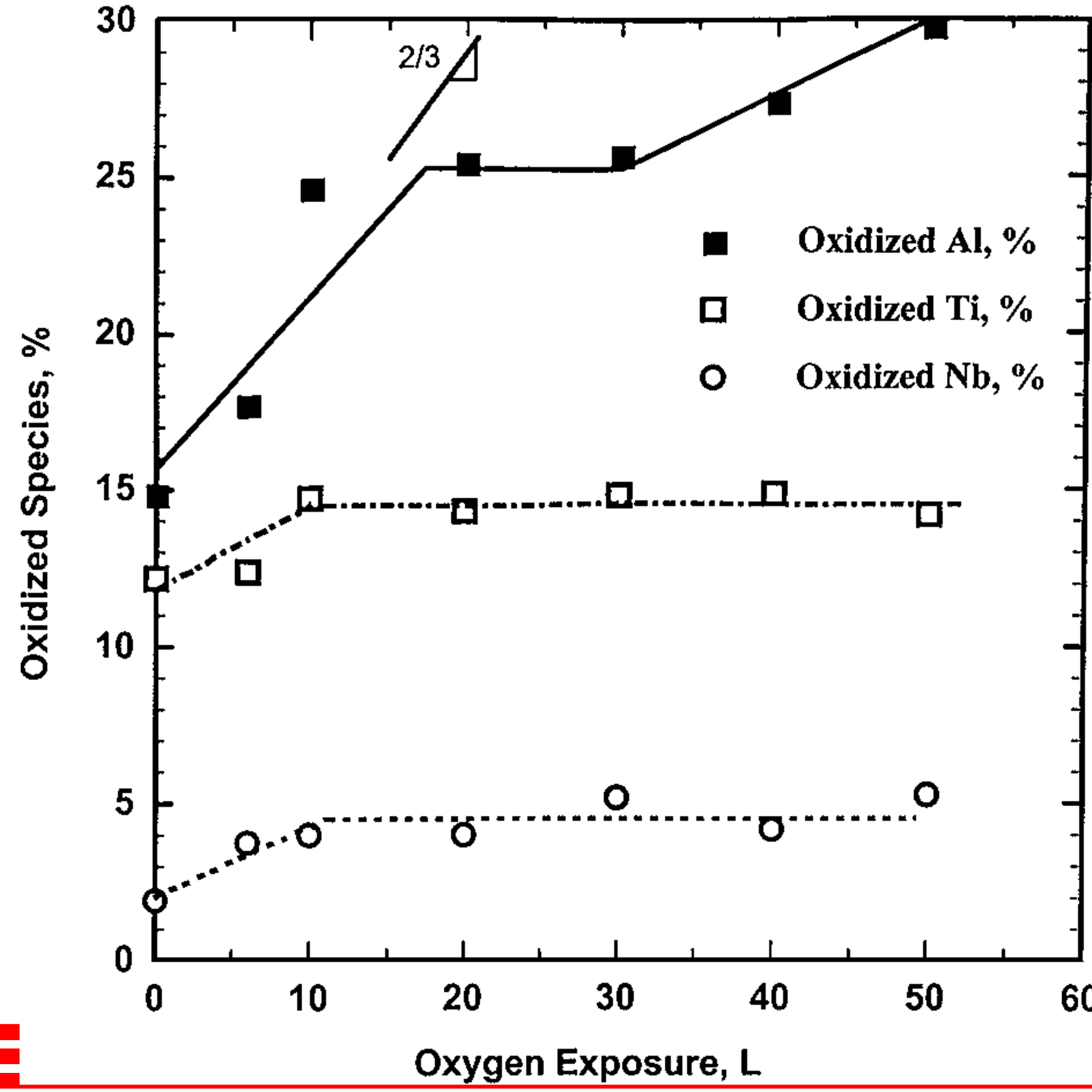
$$O_2 + 2V = 2O_{ad}$$
$$Al + O_{ad} \rightarrow AlO$$
$$AlO + O_{ad} \rightarrow AlO_2$$
$$AlO_2 + O_{ad} \rightarrow AlO_3$$

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

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

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

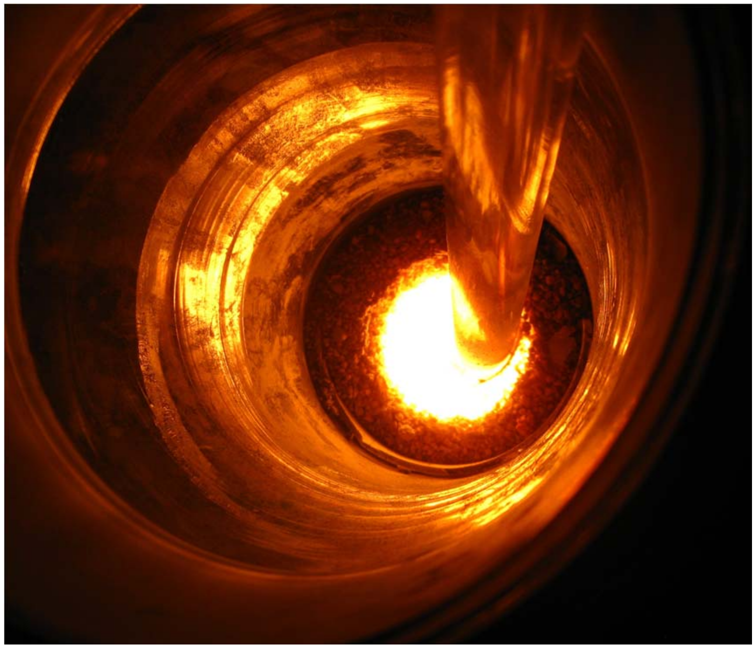
- **Oxygen exposure of L = t•p_{O2} (10^{-6} Torr•s)**
- **Slope of 2/3 acquired from kinetic rates of oxygen adsorption per AlO_3 formation (r_{ad}/r_{AlO3})**



Summary

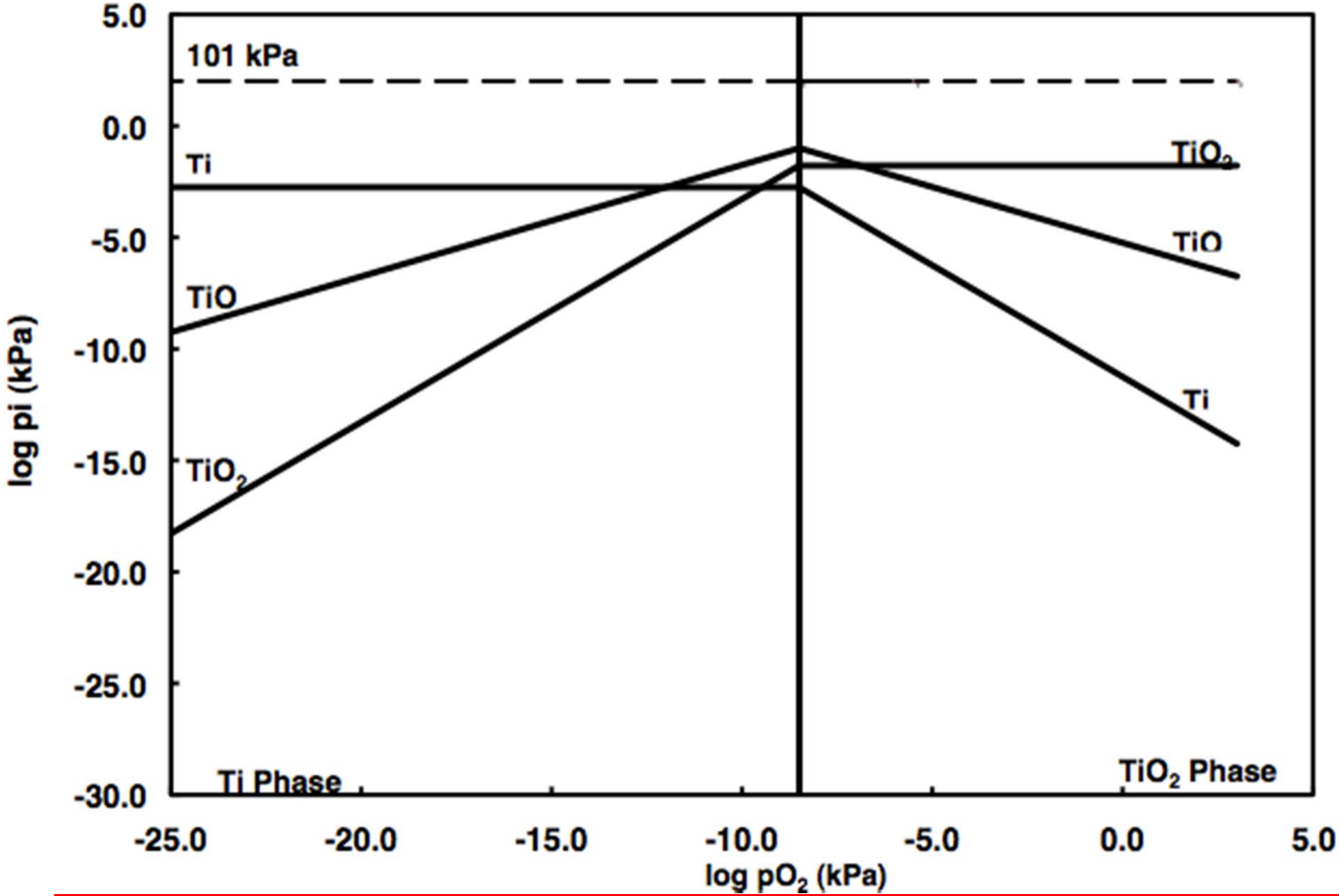
- Analyzed thermodynamic stability of oxygen potentials for TiO_x and TiO_x-Al_2O_3 for possible scale formation from Ti_2AlC-TiC components.
- Used COMSOL, a commercial software package, the temperature profile of a packed bed of B_4C.
- Controlled oxygen potential to form Ti_3AlC-Al composite which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

Questions and Comments



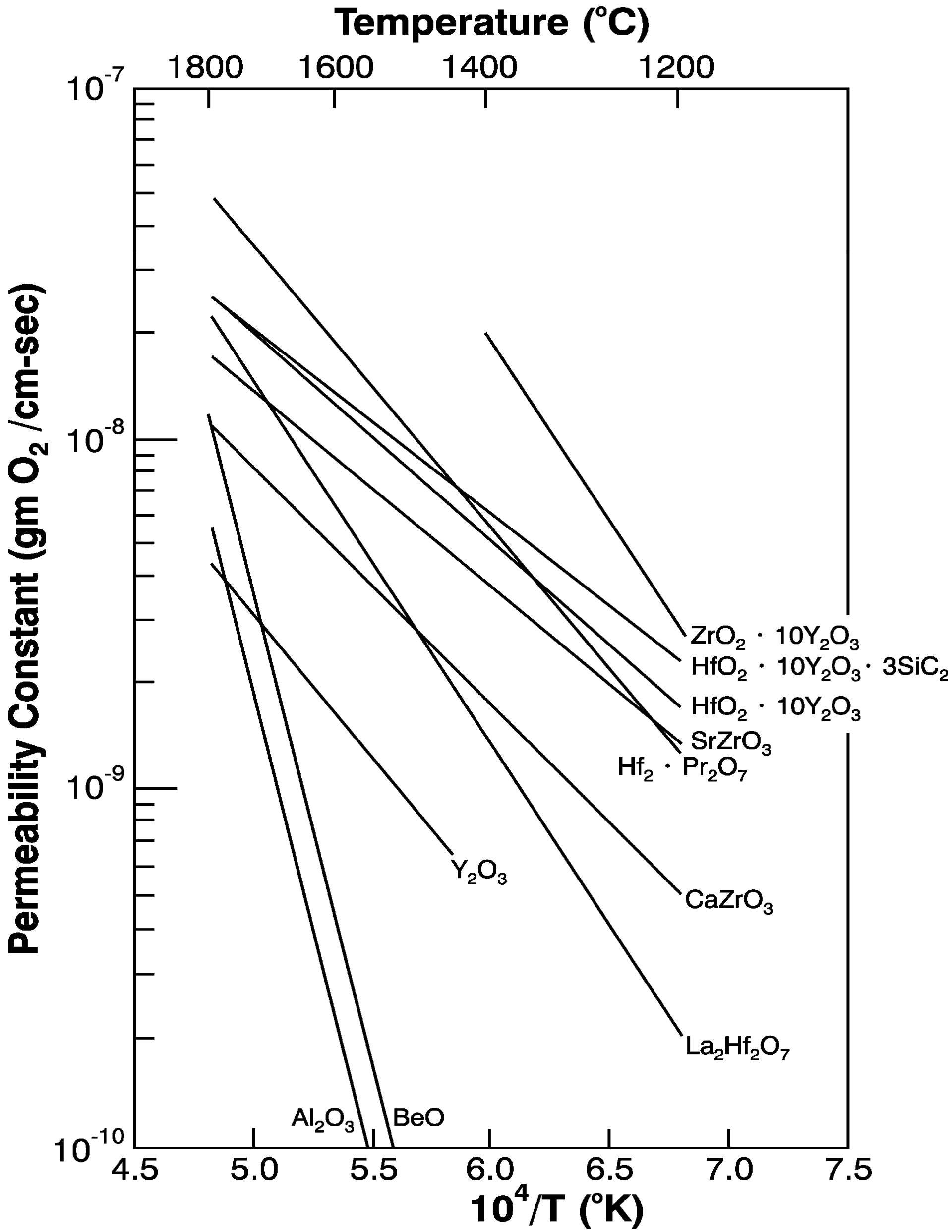
Slides to Respond to Possible Queries Follow

Kellogg Diagram for Ti-O System (2500 K)



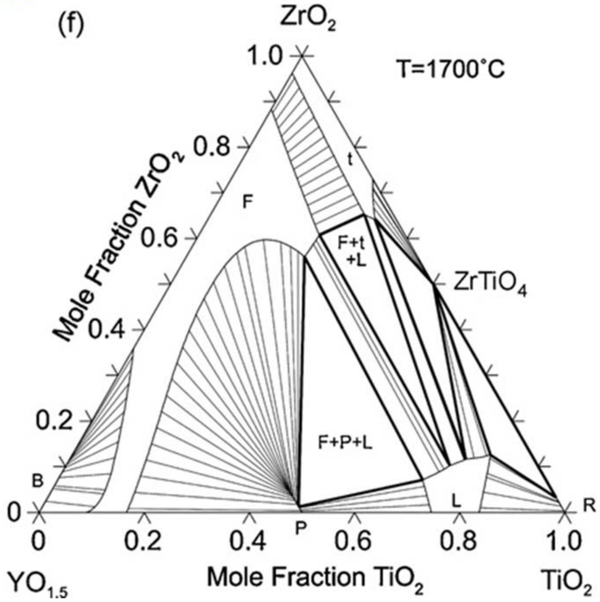
Oxygen Permeability

- For temperatures between 1700 to 1500° C Al_2O_3 and Y_2O_3 have oxygen permeability ≤ 10^{-9} gO_2/(cm-s) and $3 \cdot 10^{-9}$ 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)].

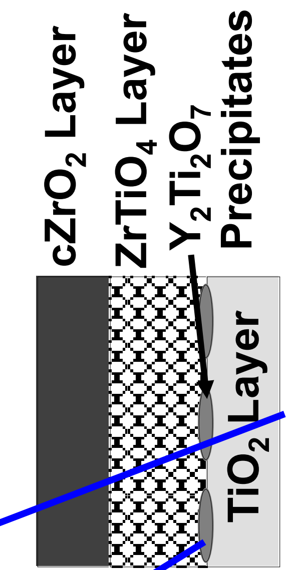


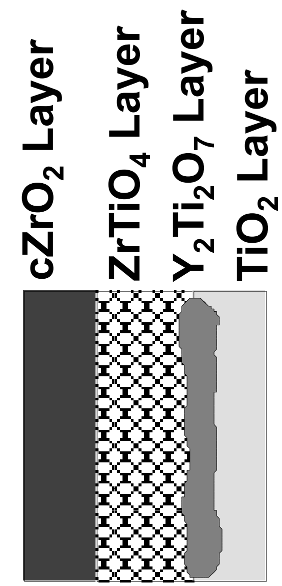
(Opeka, Talmy & Zaykoski-2004)

Wagner's Rate Equation for Scales



Calculated Diagram from Schaedler, Fabrichnaya and Levi -- 2008





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

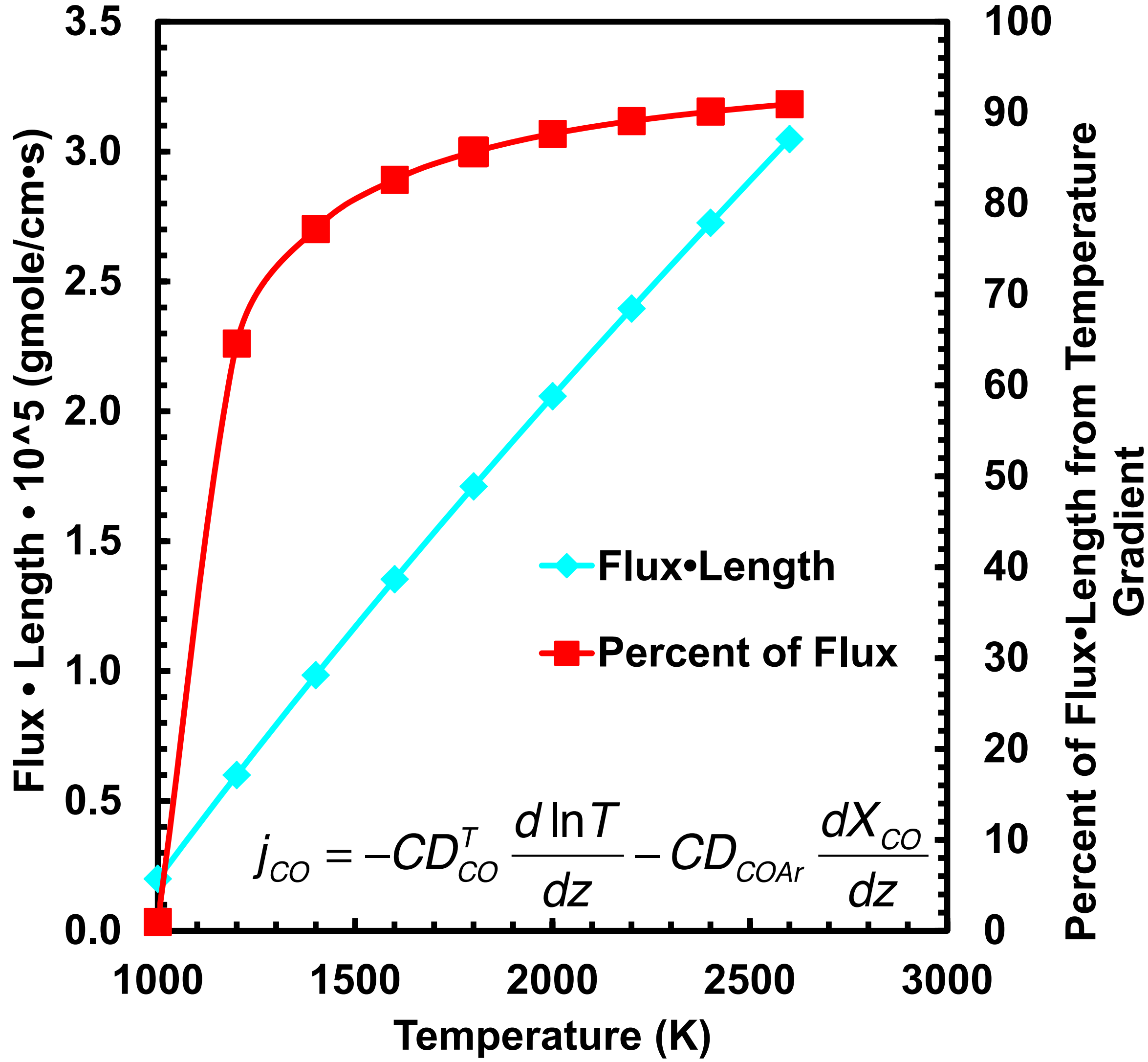
Future Efforts for Plasma Surface Reactions

- **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



$$j_{CO} = -CD_{CO}^{T}\frac{d\ln T}{dz} - CD_{COAr}\frac{dX_{CO}}{dz}$$

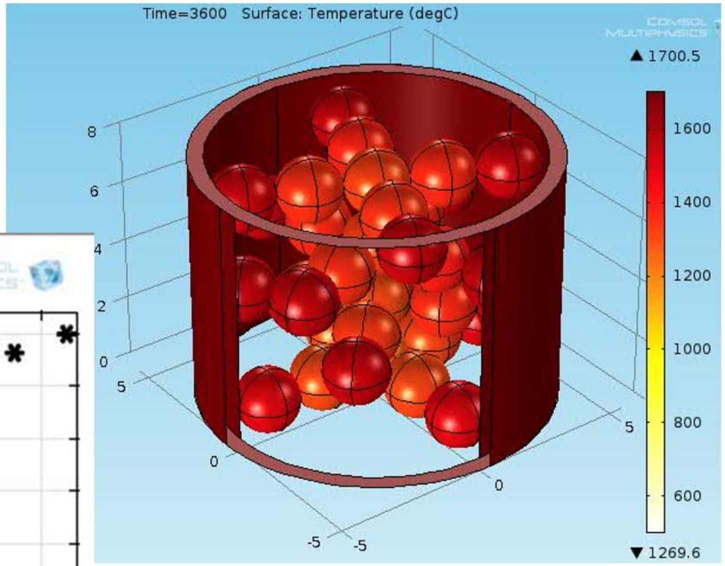
- D_{COAr} from Poirier-Geiger and checked with Chapman-Enskog Eq.
- Mean temperature

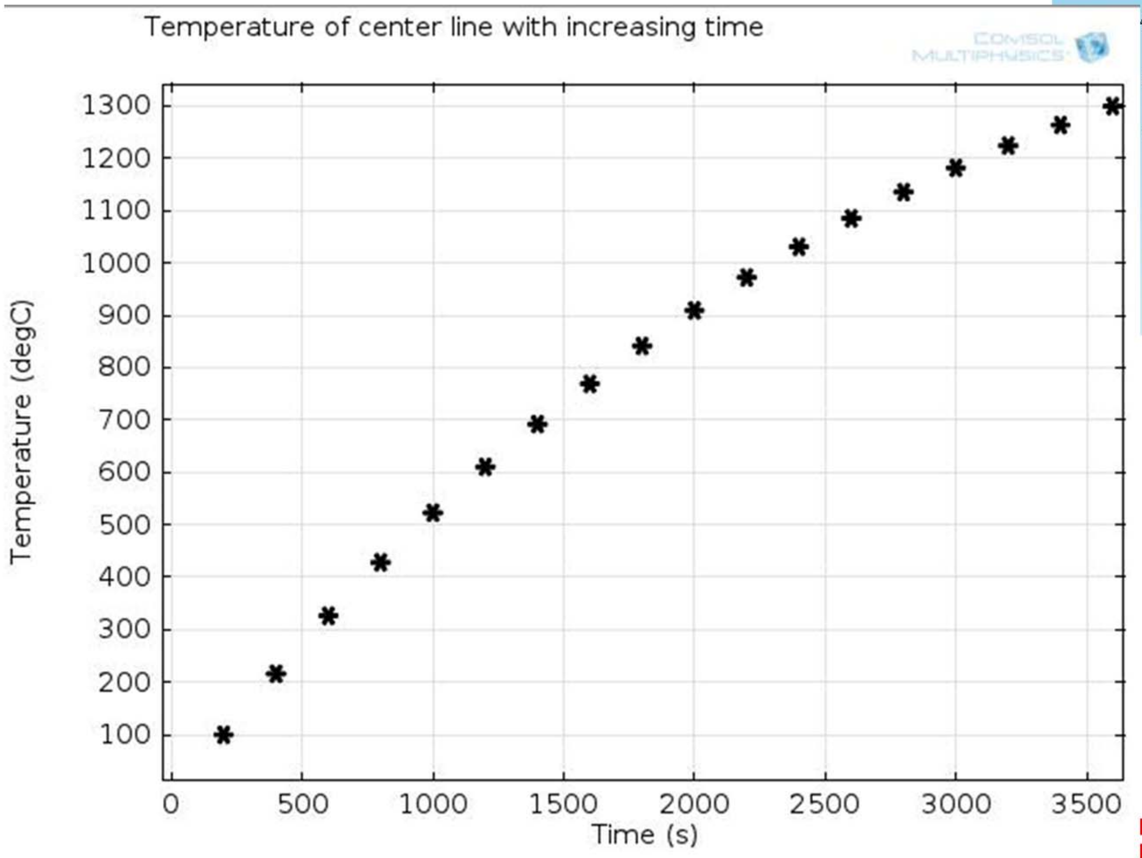
$$\frac{T_H T_C}{T_H - T_C}\ln\frac{T_H}{T_C} = 1527K$$

- $Al/Al_2O_3/Al_4CO_4$ reaction rate?

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

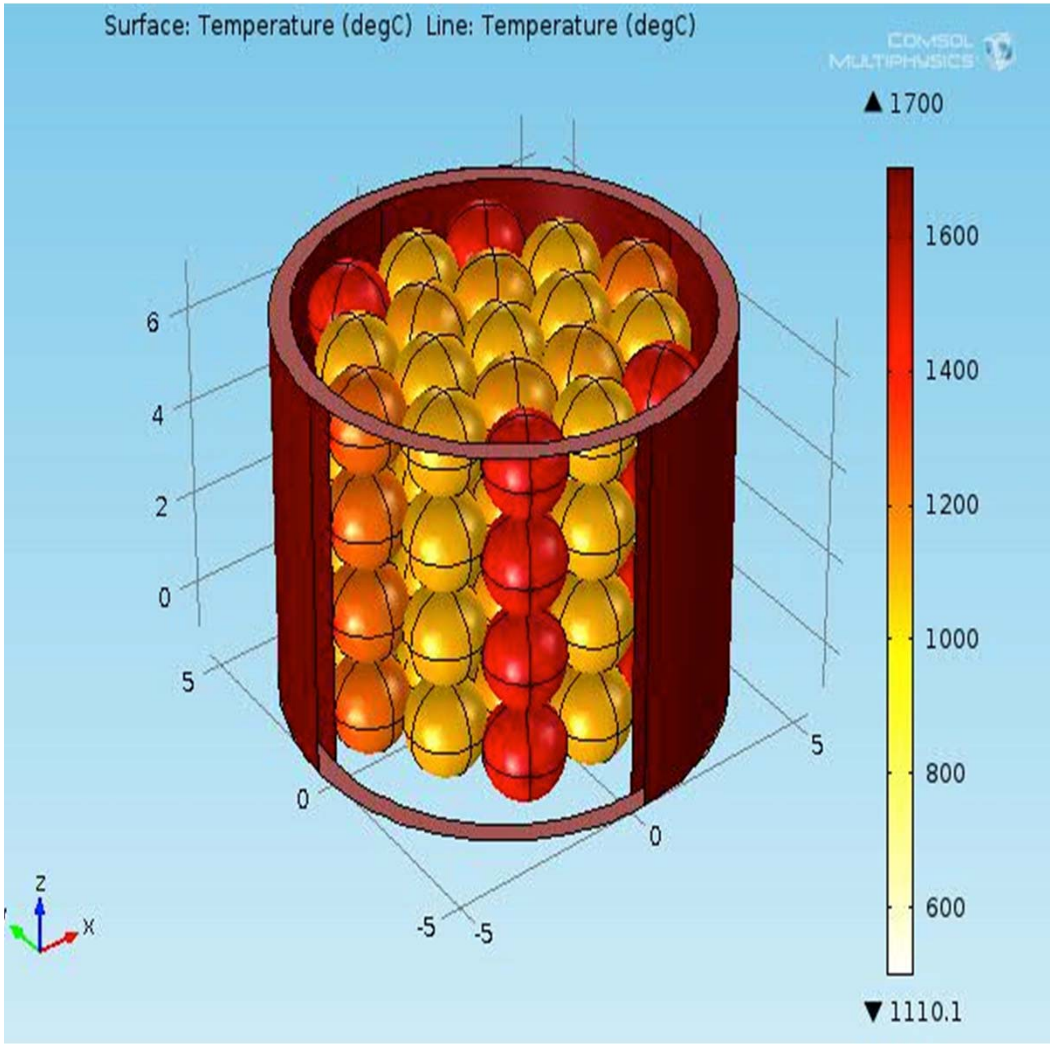
- **Carbide spheres configured in an X-pattern rotating along centerline.**
- **The spheres have an open structure.**





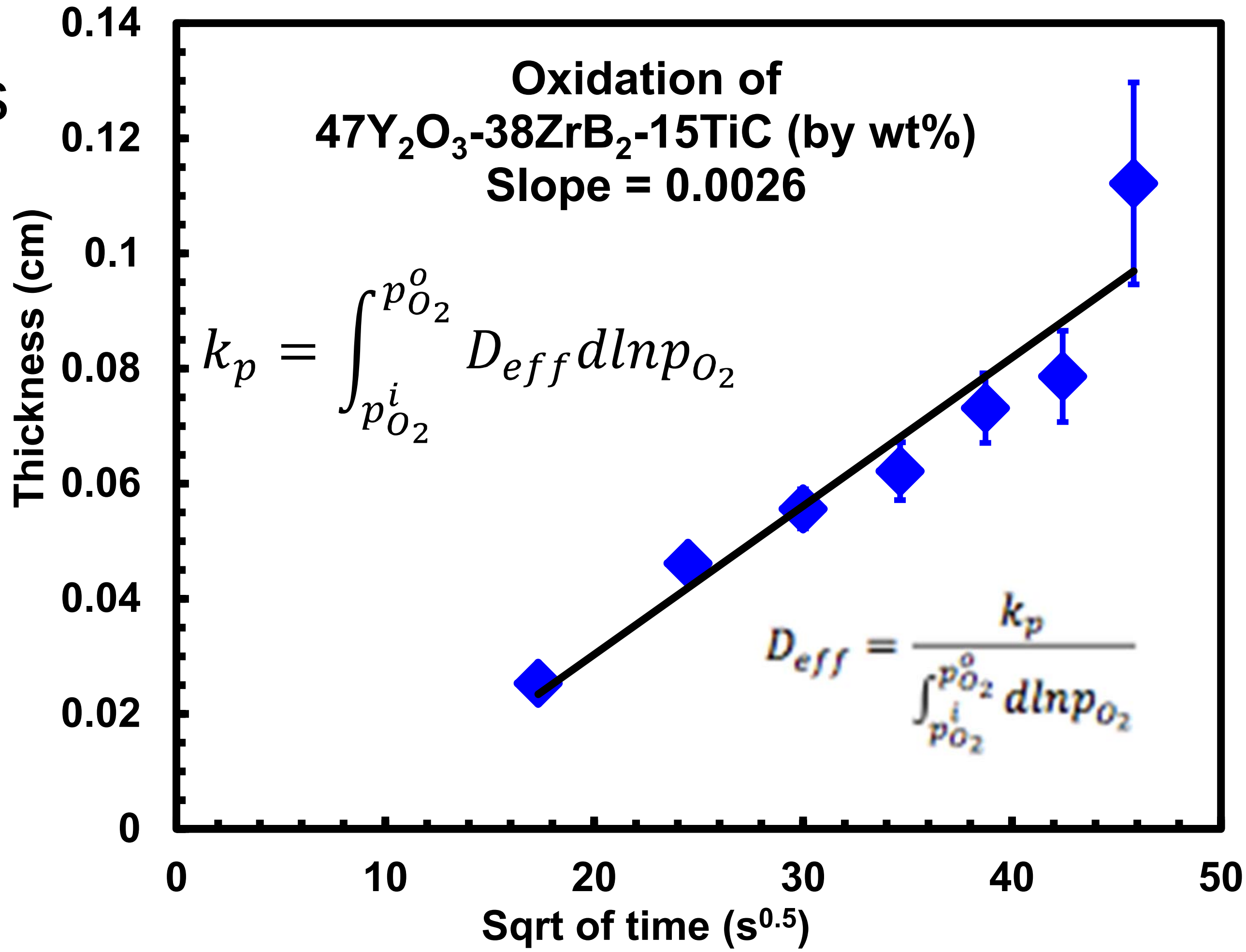
COMSOL Simulation of B_4C spheres in a packed bed

- **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



$$k_p = \int_{p^i_{O_2}}^{p^o_{O_2}} D_{eff} \, d\ln p_{O_2}$$

$$D_{eff} = \frac{k_p}{\int_{p^i_{O_2}}^{p^o_{O_2}} d\ln p_{O_2}}$$

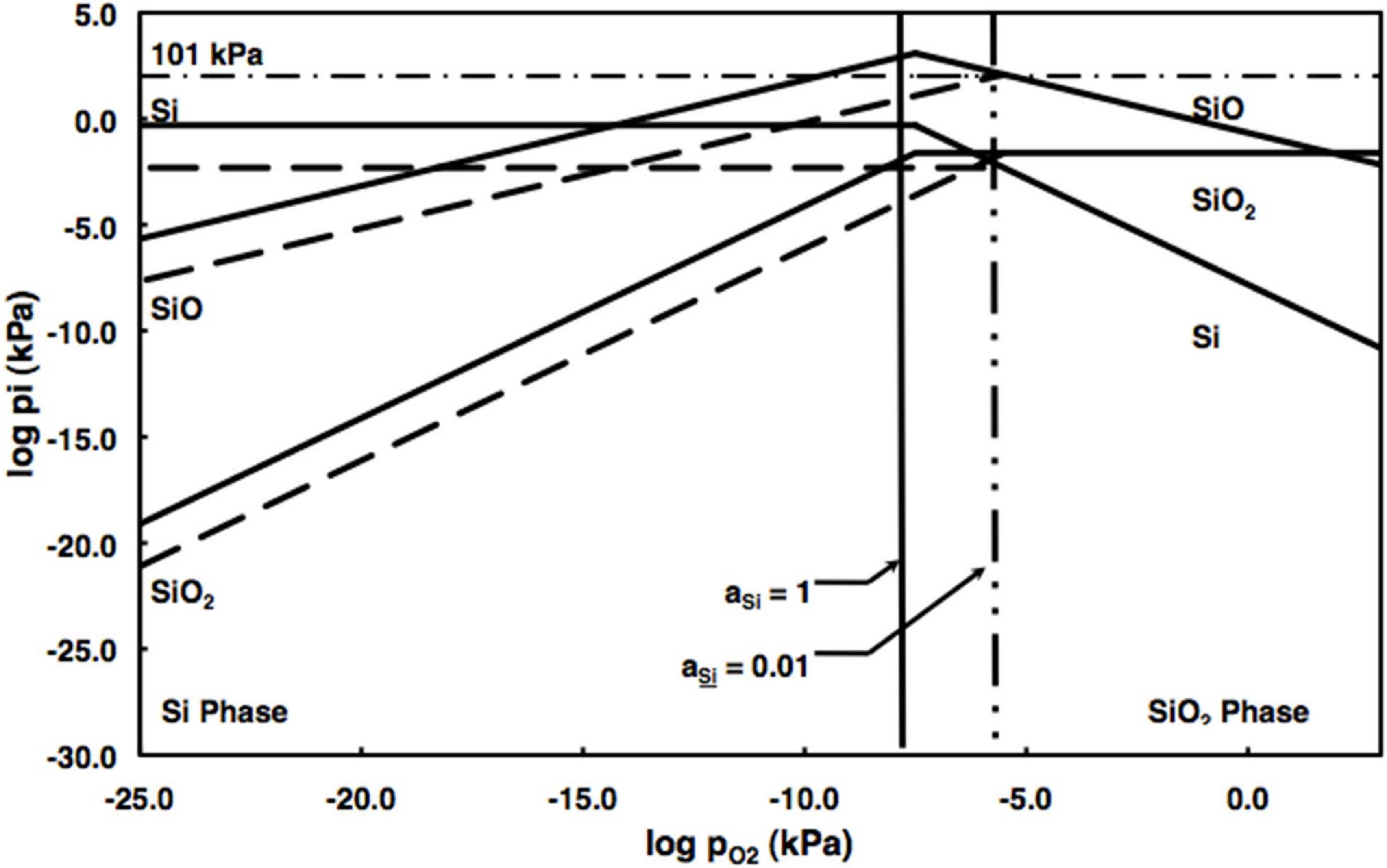
Electron-Energy Transport

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

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

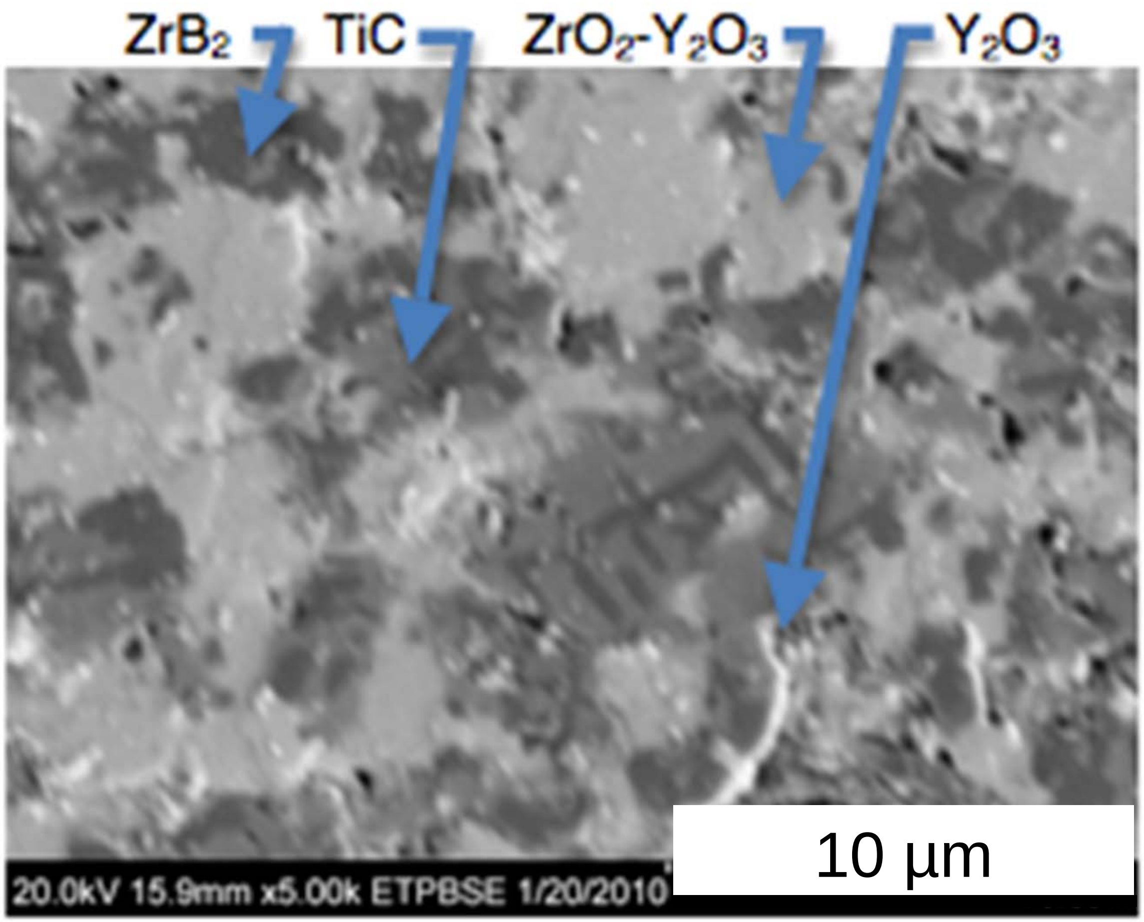
$$\frac{\partial}{\partial t}(n_e) + \nabla \cdot [-n_e(\mu_e \cdot \mathbf{E}) - \mathbf{D}_e \cdot \nabla n_e)] = R_e$$

Kellogg Diagram for Si-O System (2500 K)



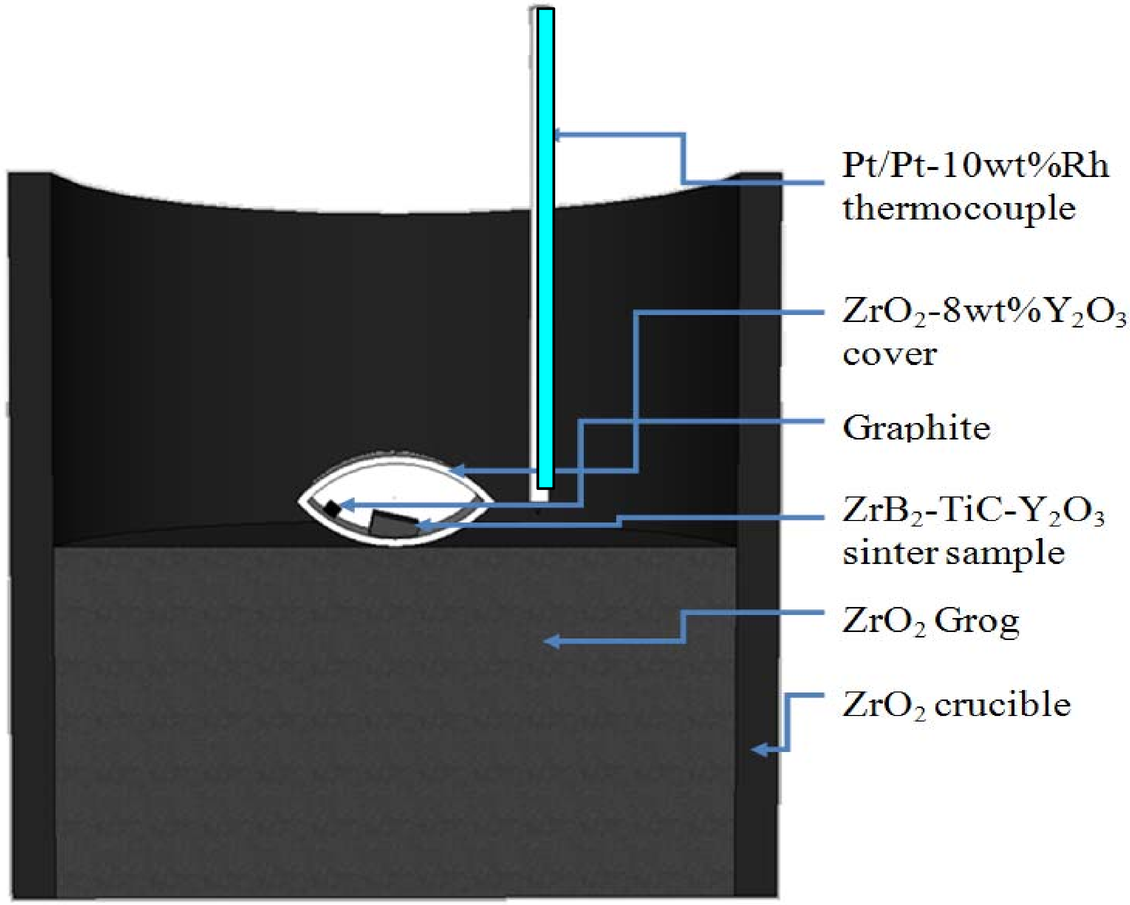
SEM image after spark-plasma sintering

- 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.



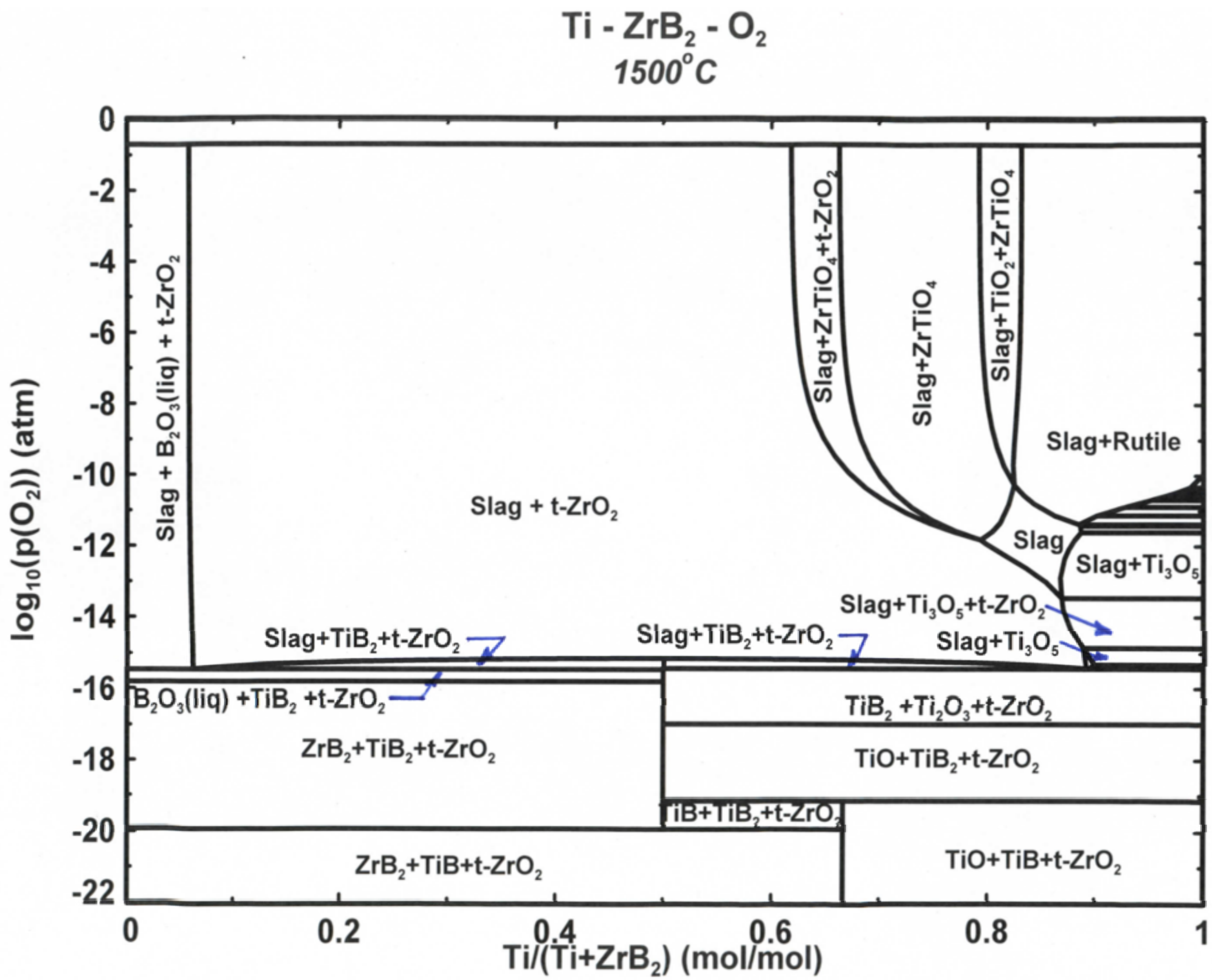
Oxidation in Silicide Furnace with air and C/CO/N_2 atmospheres at 1700° C

- 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.

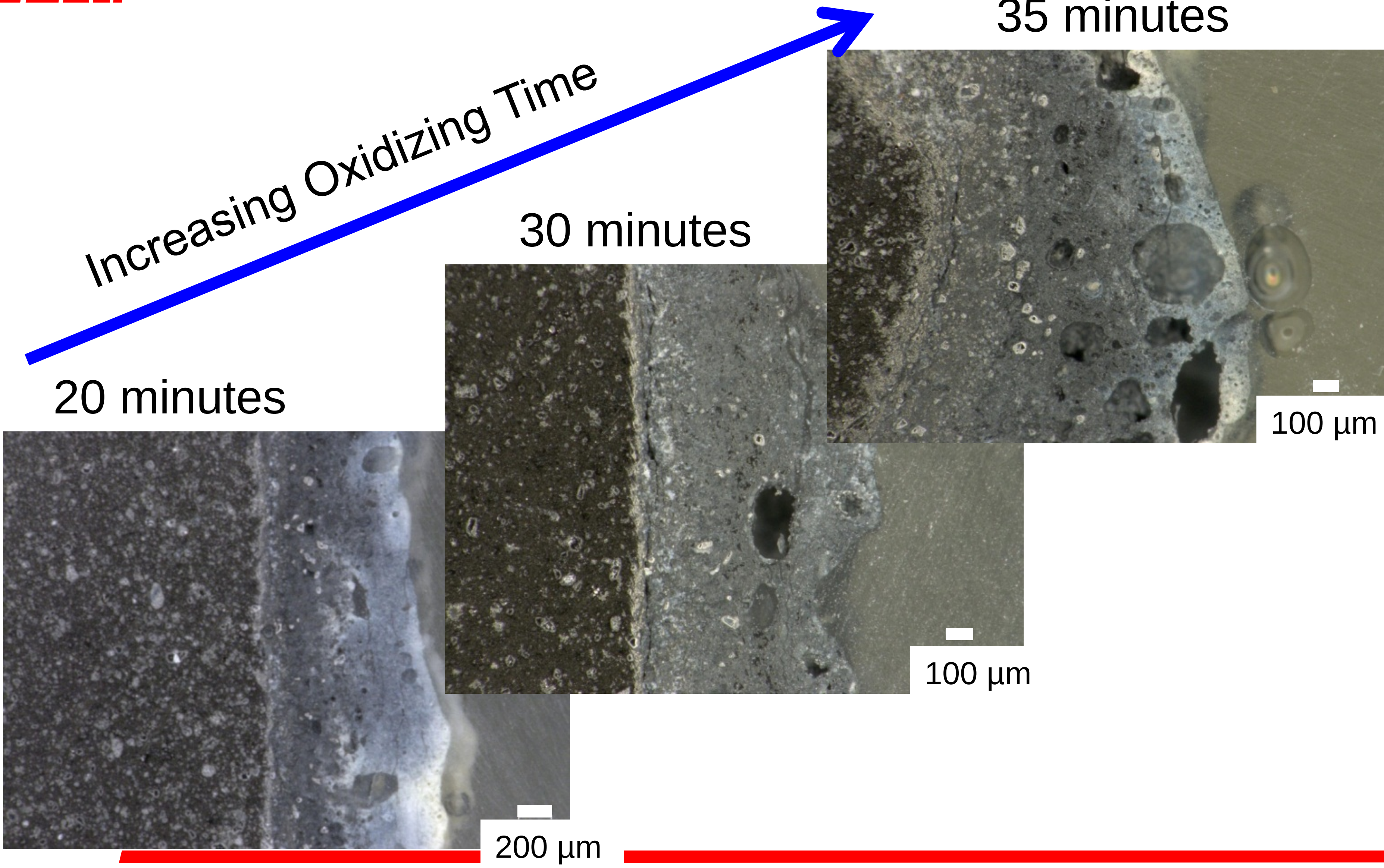


Oxygen Levels for TiO_x with Calculated $Ti\text{-}ZrB_2\text{-}O_2$ Phase Diagram

- 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}

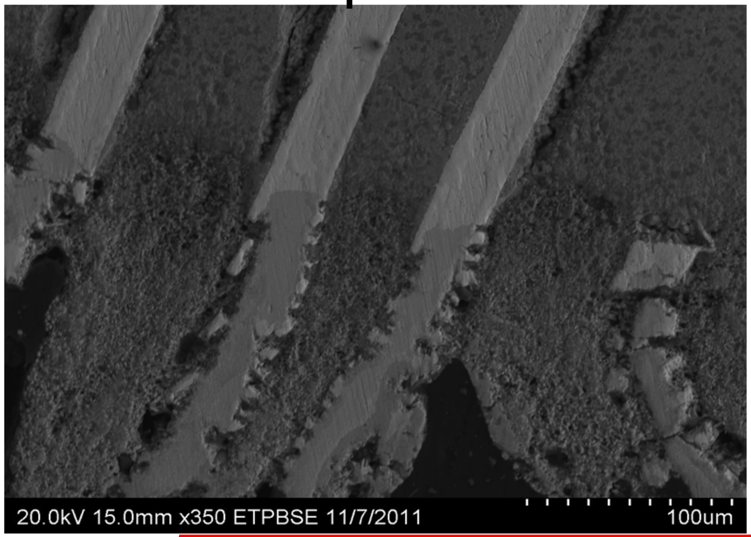


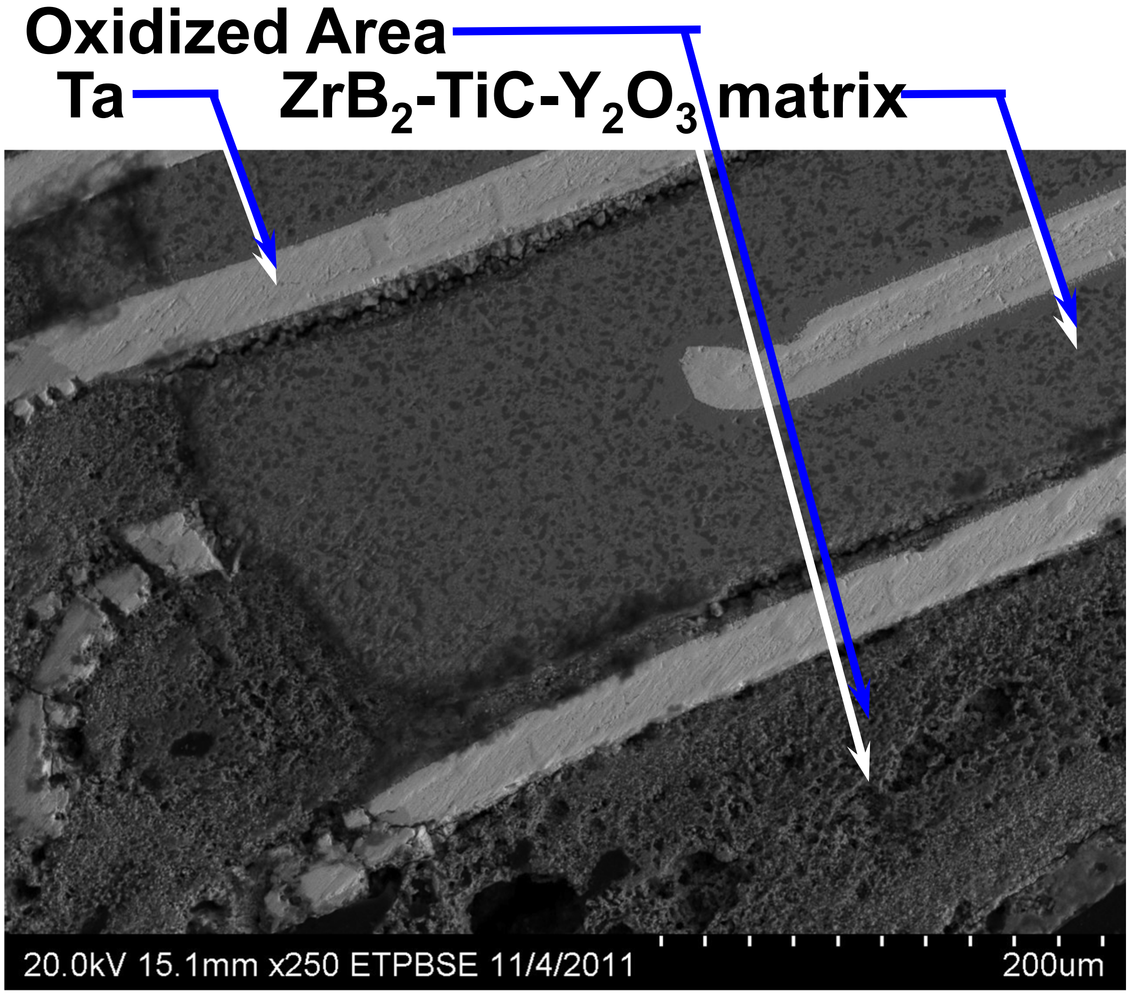
Optical Microstructures to Measure Scale



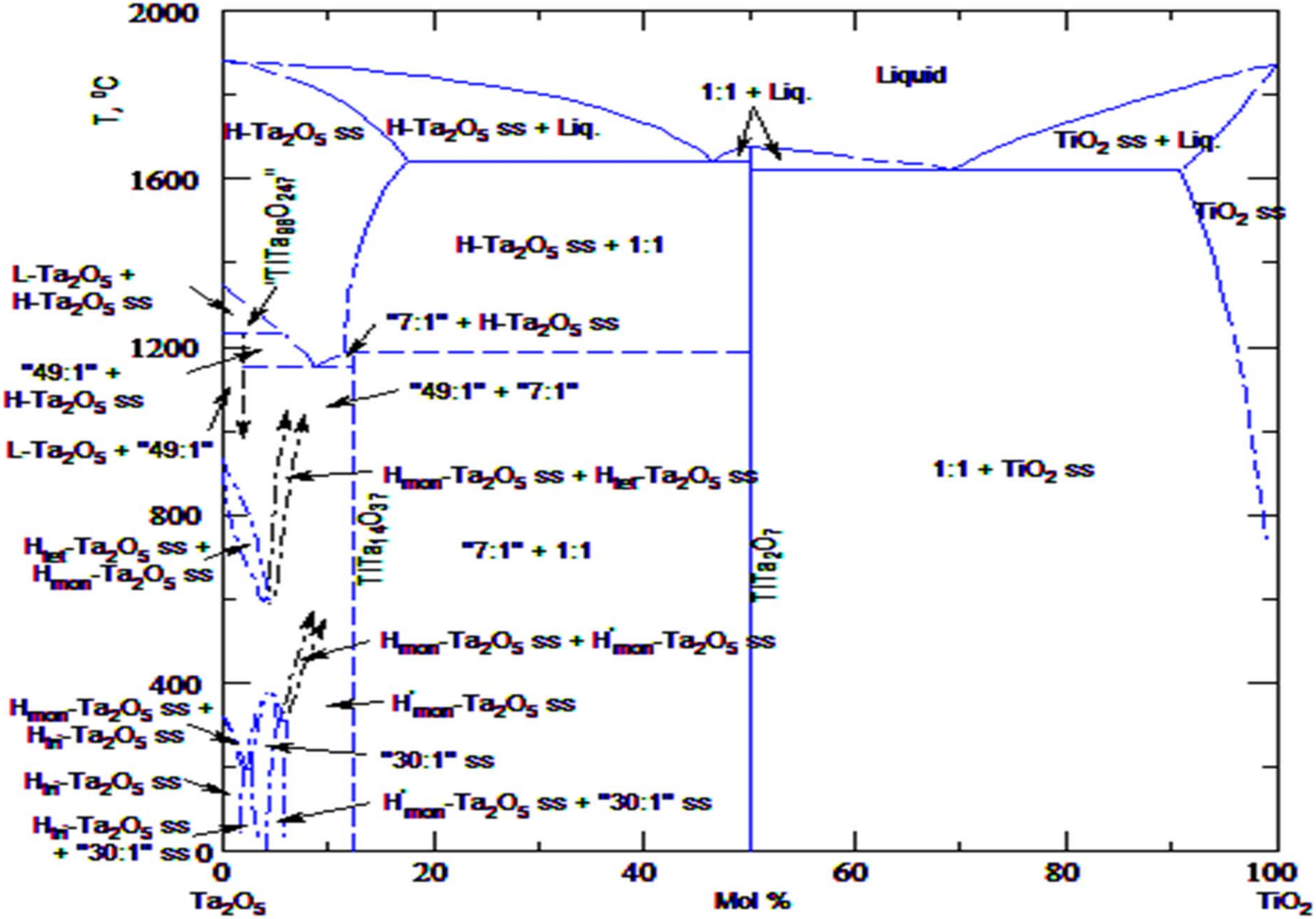
Oxidized $30ZrB_2$-13TiC-$37Y_2O_3$-20Ta sample for 3 minutes at 1700° C

- Oxidized area becomes ZrO_2-TiO_2-Y_2O_3
- Ta forms Ta_2O_5 upon oxidation with vaporization

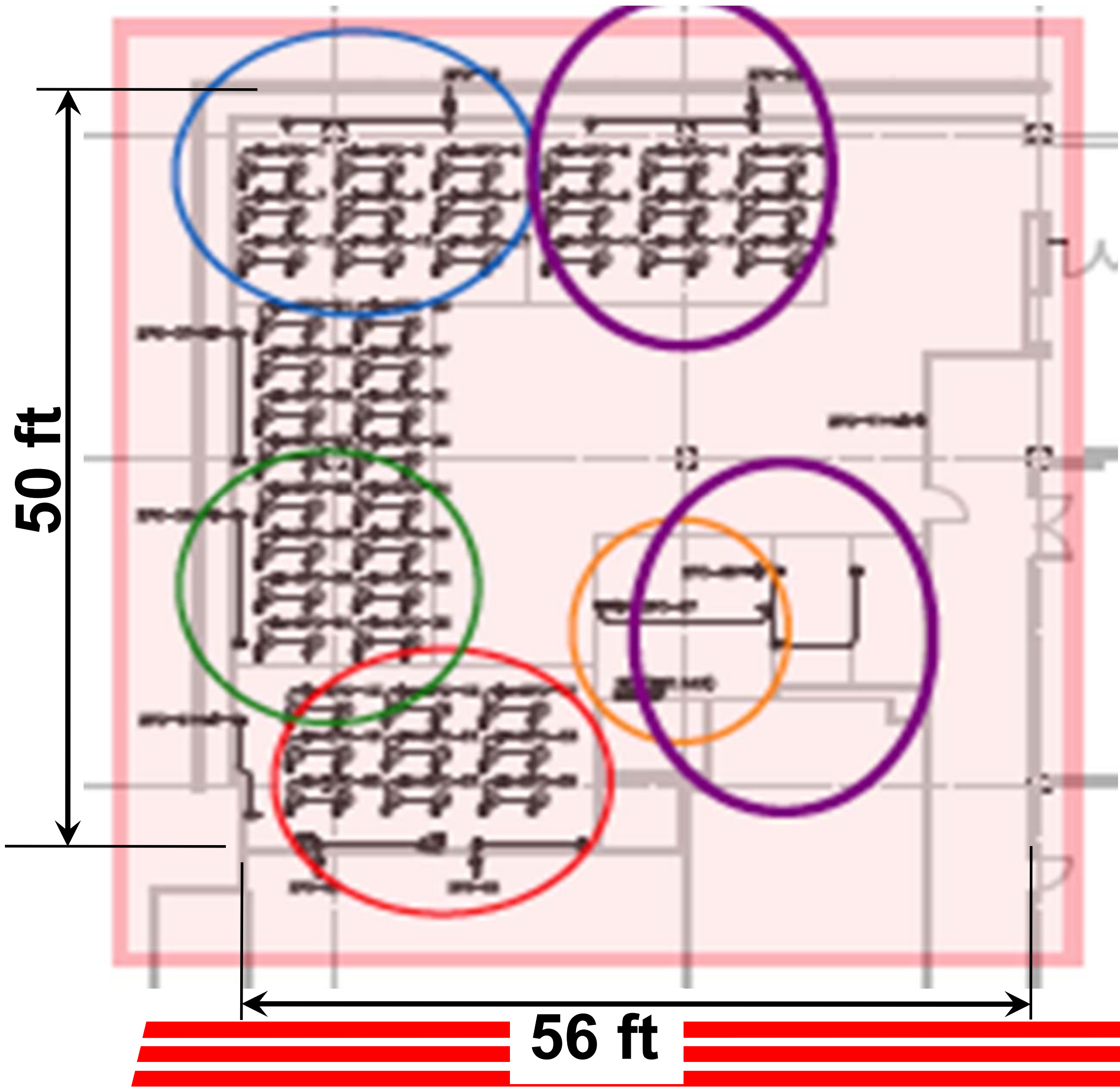




Ta_2O_5-TiO_2 phase diagram



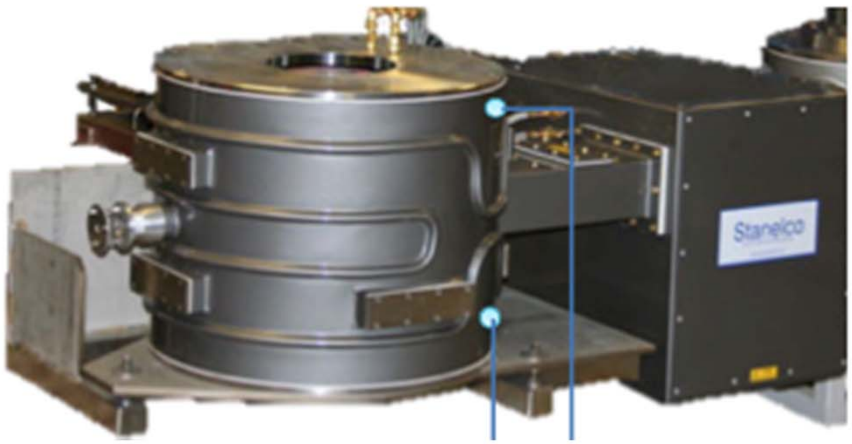
Remodeling Departmental Materials and Structures Laboratory (Dynamic)

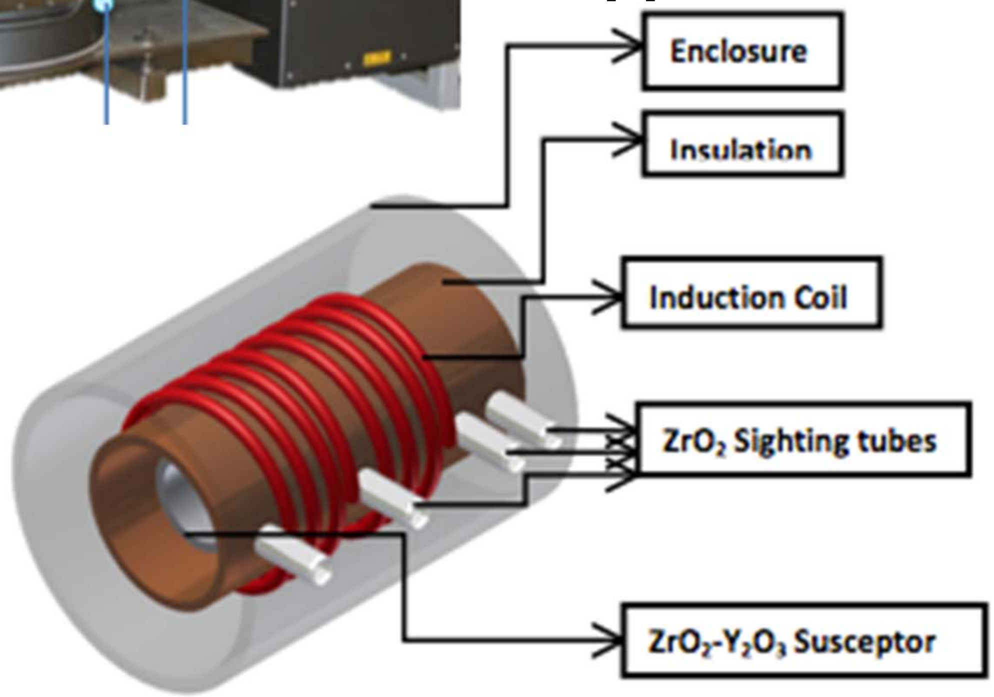


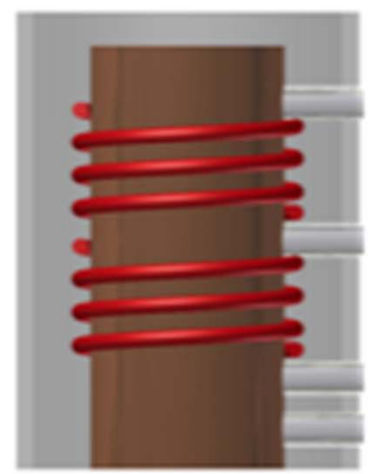
- Other than standard 120VAC, will need:3-phase,
- 480 VAC in Bay 2 (encircled - blue)120A,
- 3-Phase, 240VAC in Bay 4 (encircled - green) 40A,
- Single Phase, 210VAC in Bay 5 (encircled – red)50A,
- 3-Phase, 240VAC in Bay 5 (encircled - red)50A,
- 3-Phase, 240VAC in Bay 6 (orange) Purple Area .

Seek DURIP Request for Ultra-high Temperature Furnace

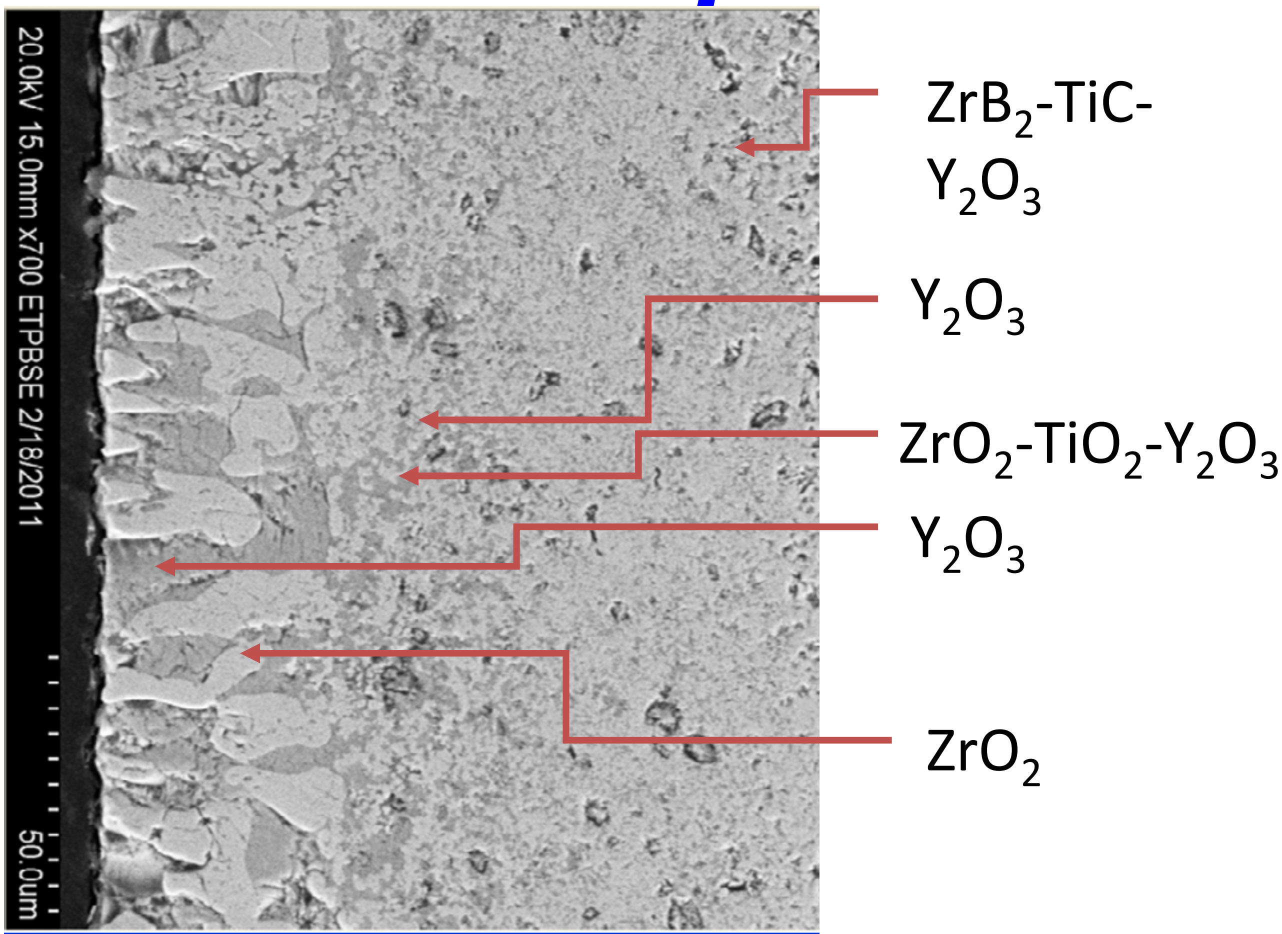
- **Dielectric induction furnace (3-7 MHz) reaching 2600 or 3500° C**
- **Four Infrared pyrometers**
- **Support AFOSR/ONR efforts**



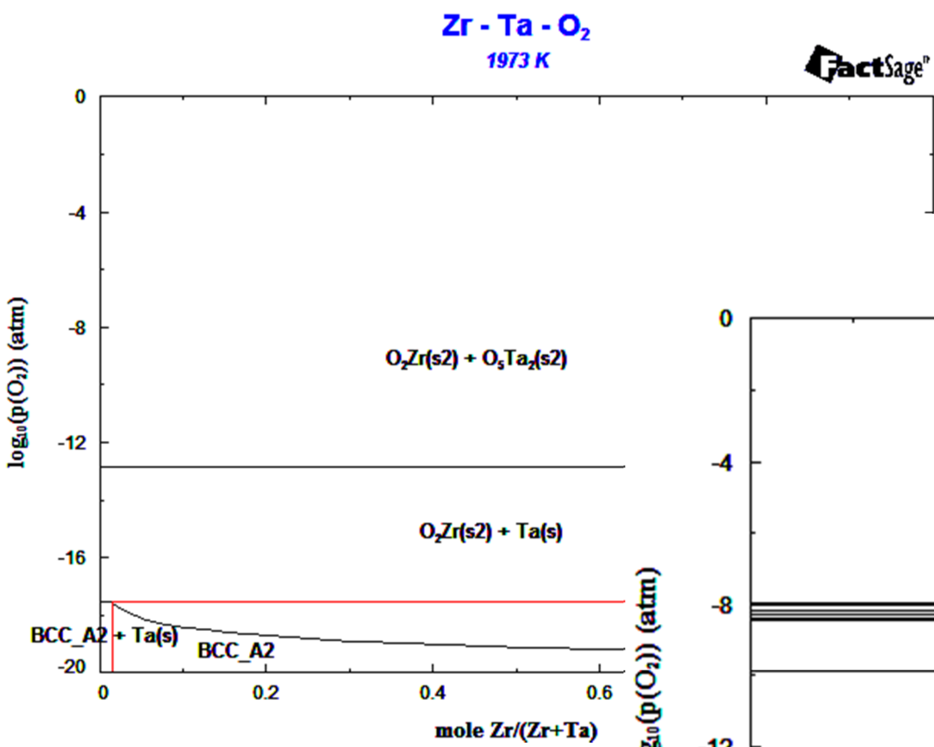


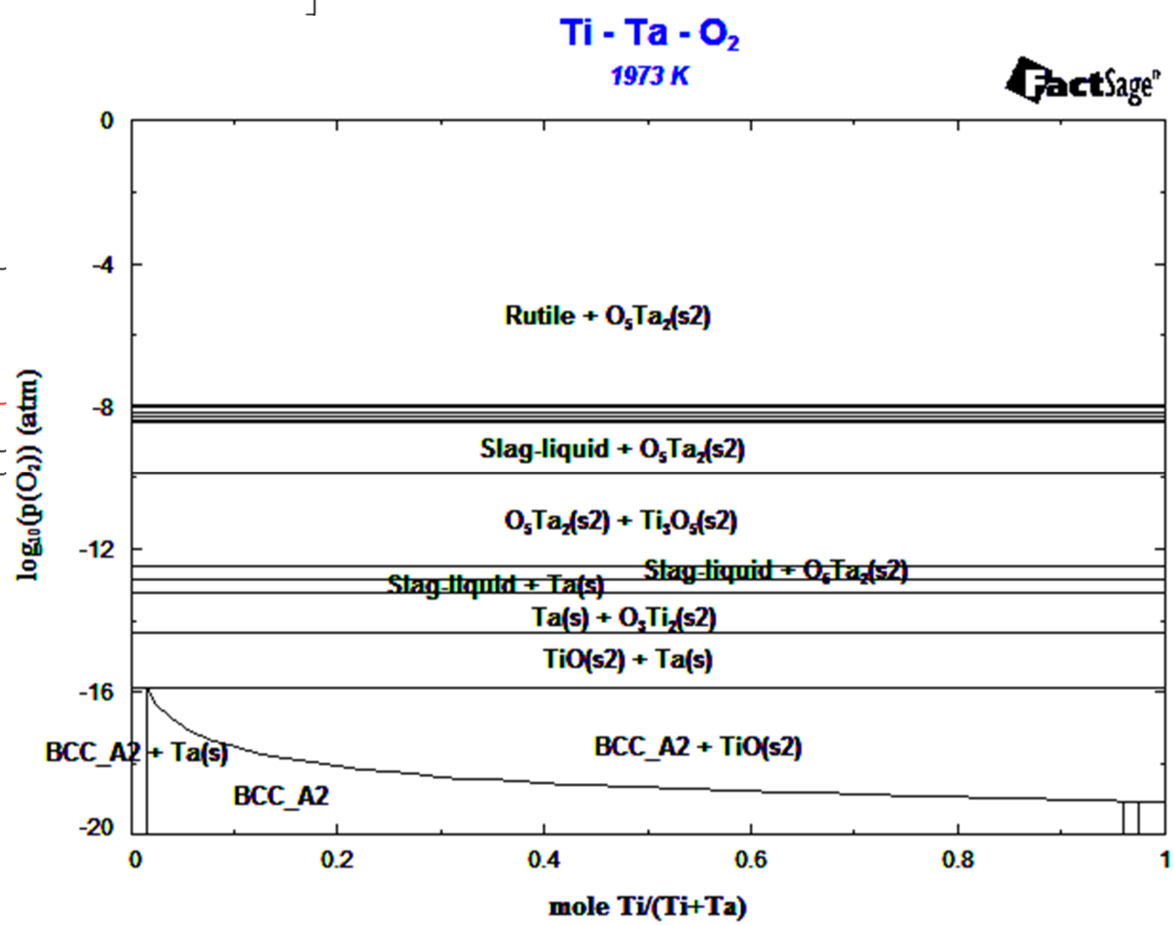


Phases identified for oxidized sample in $C/CO/N_2$



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

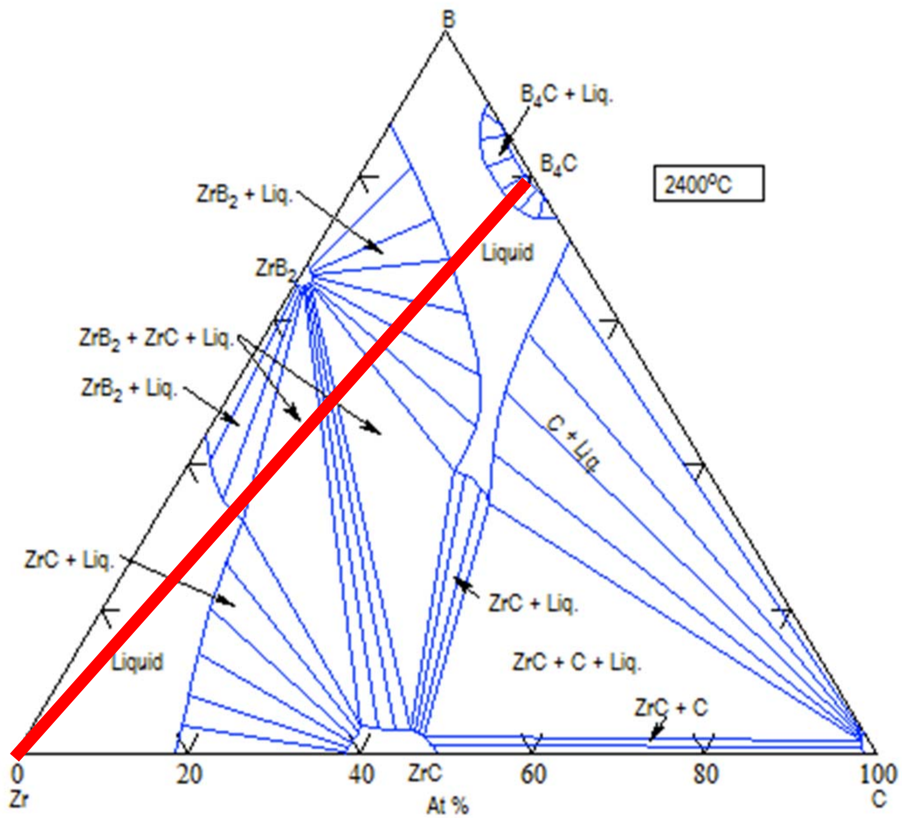




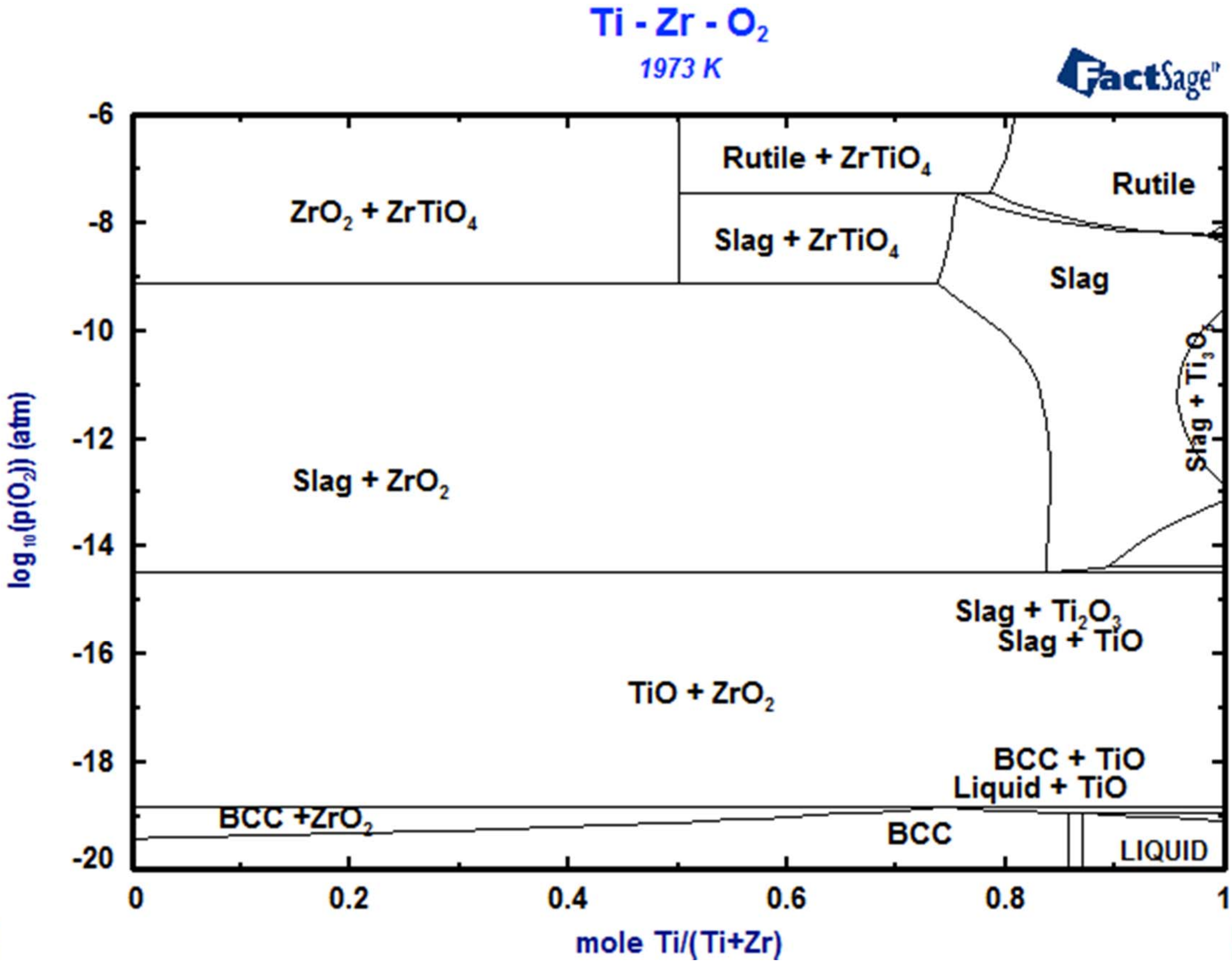
- p_{O2} level for Ta/Ta_2O_5
- $TiOx\text{-}Ta_2O_5$ liquids

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

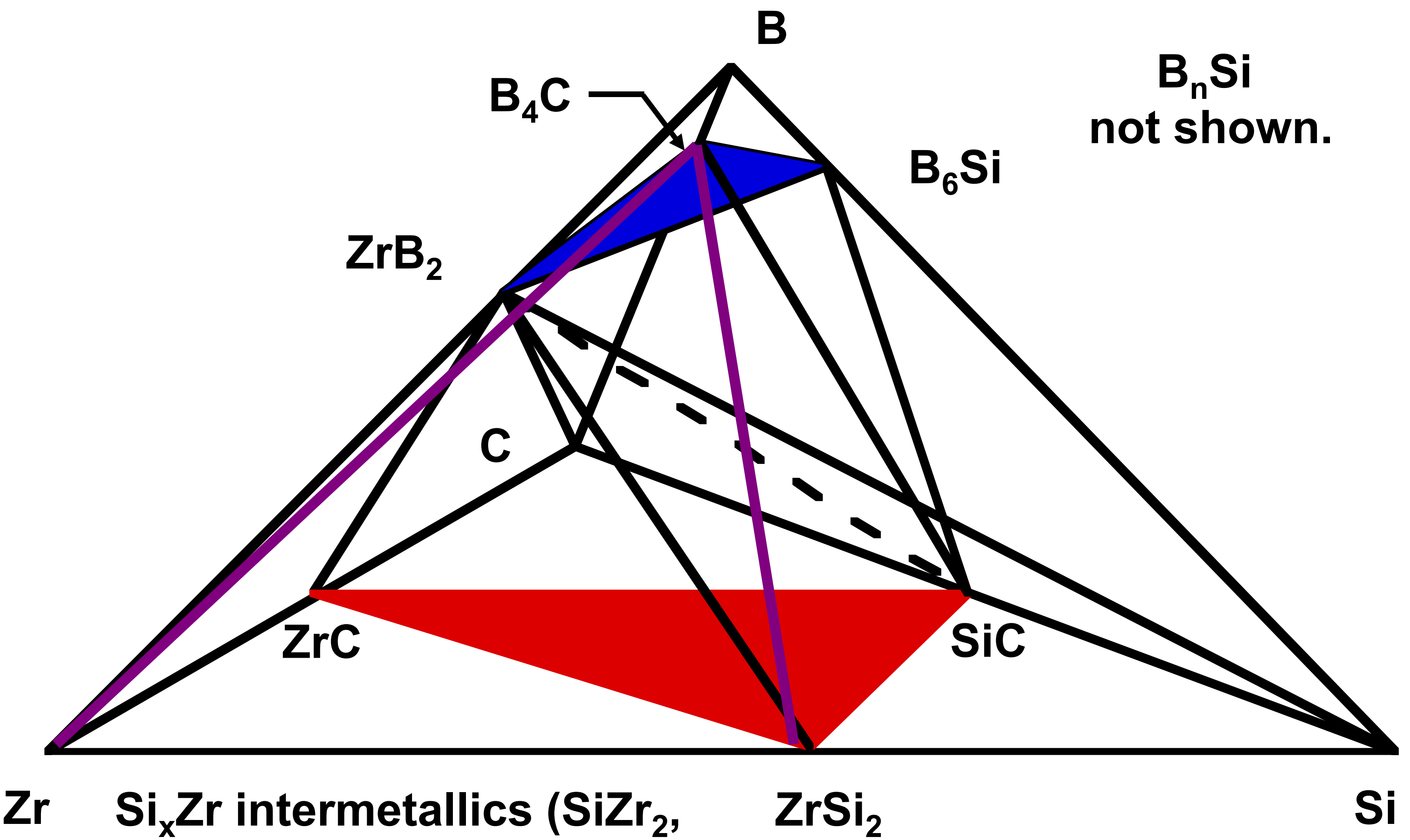
- Zr liquid changes with alloy composition
- Zr reacts with B_4C forming ZrC and ZrB_2 as a result of the mass balance.



Ti-Zr-O_2 Phase Diagram at 1973 K

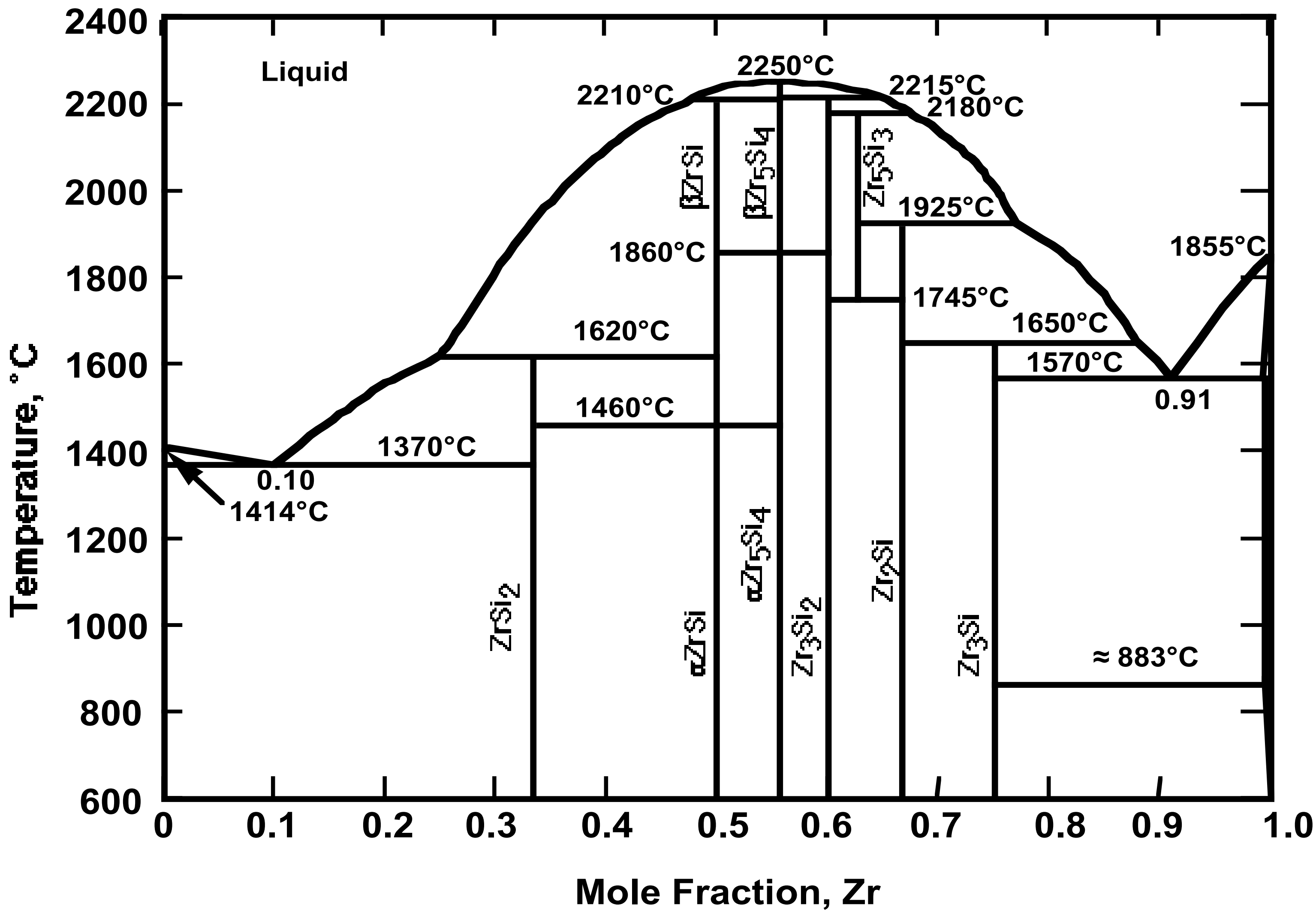


Zr-C-B-Si Quaternary (Proposed by Sorrell-1993)

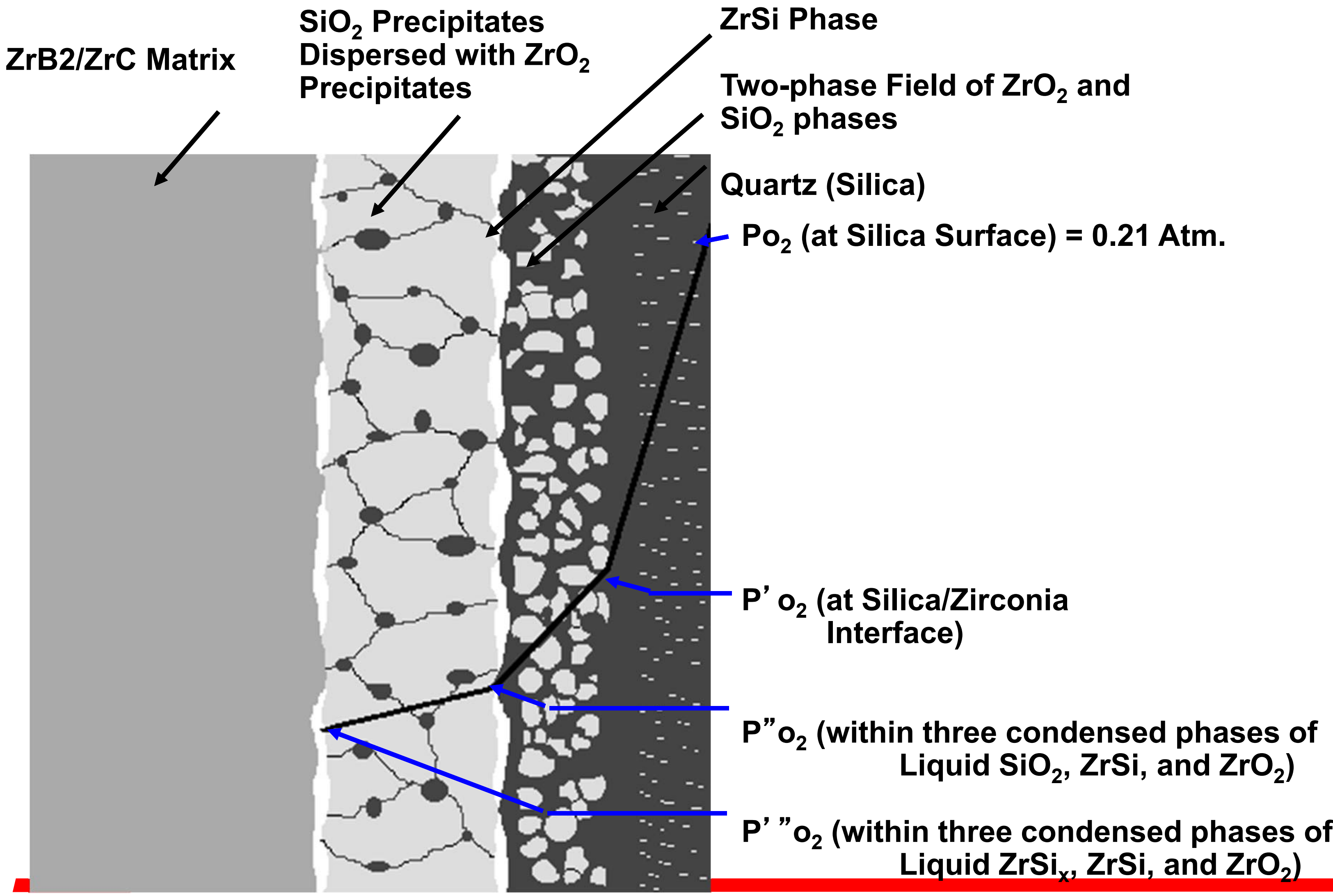


Si_xZr intermetallics ($SiZr_2$, Si_2Zr_3, Si_4Zr_5, SiZr) not shown.

Zr-Si Phase Diagram



Oxygen Partial Pressure Gradient

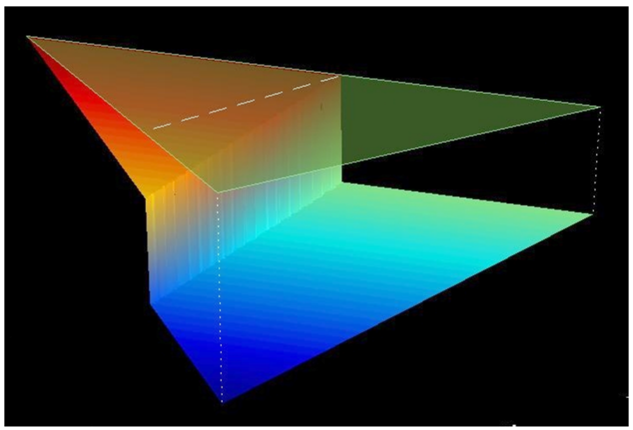


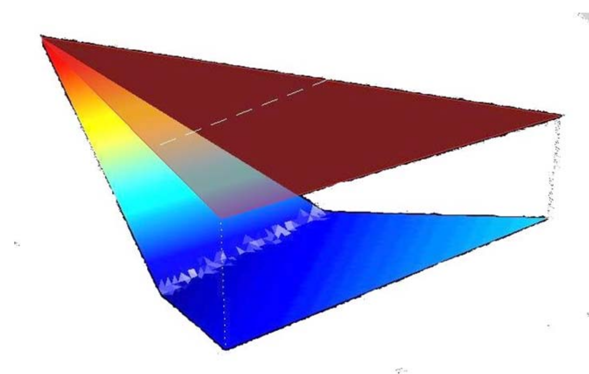
X-FEM Basics

- Extend finite element approximation space to reproduce “difficult” functions.

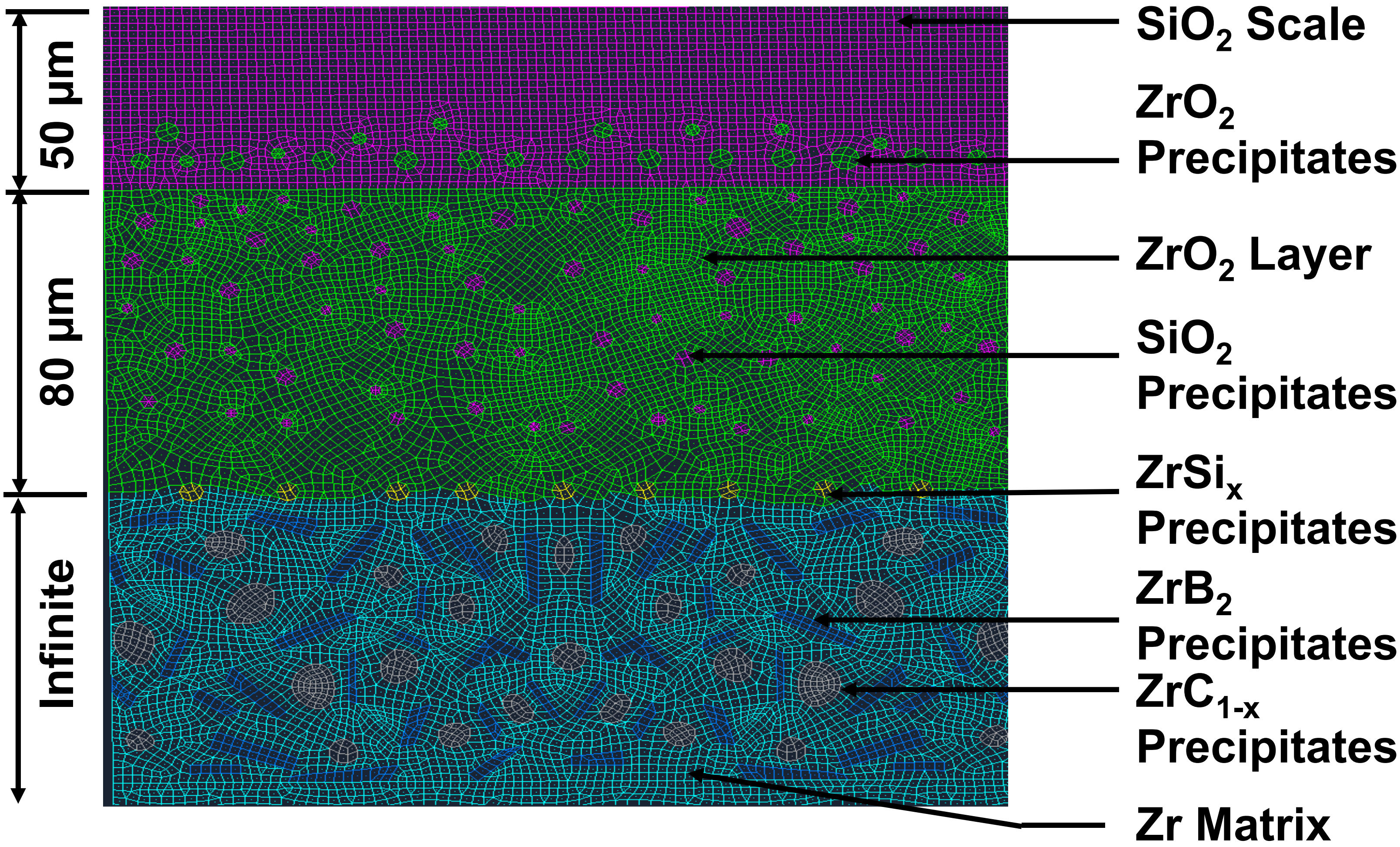
$$u^{XFEM}(x) = \sum_{I \in \mathcal{N}} N_I(x) u_I + \sum_{J \in \hat{\mathcal{N}}} N_J(x) \Psi(x) a_J$$

Standard Part Enriched Part



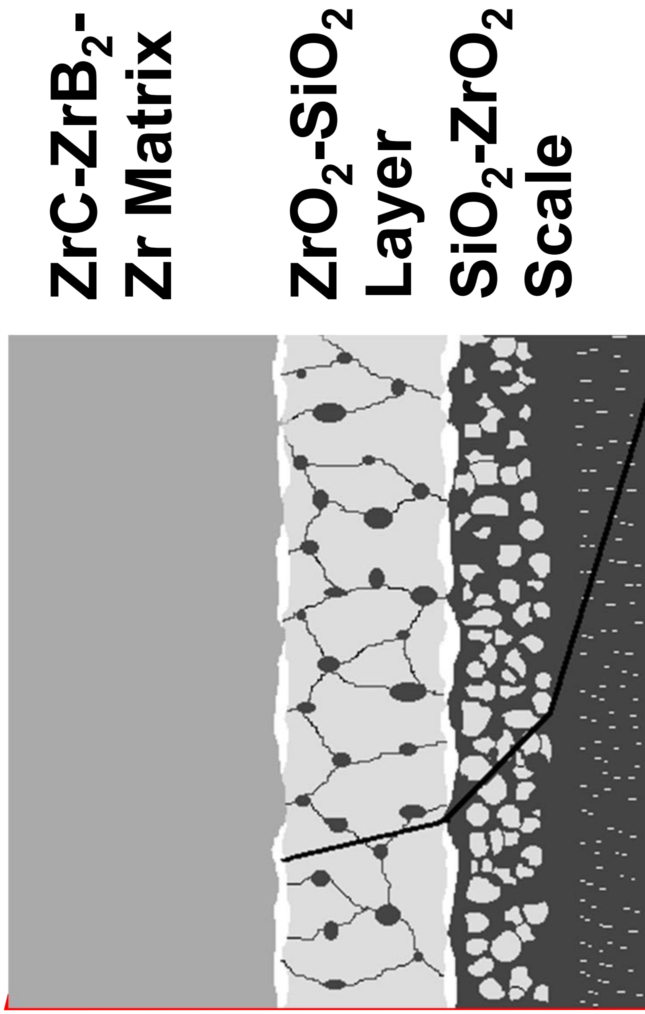


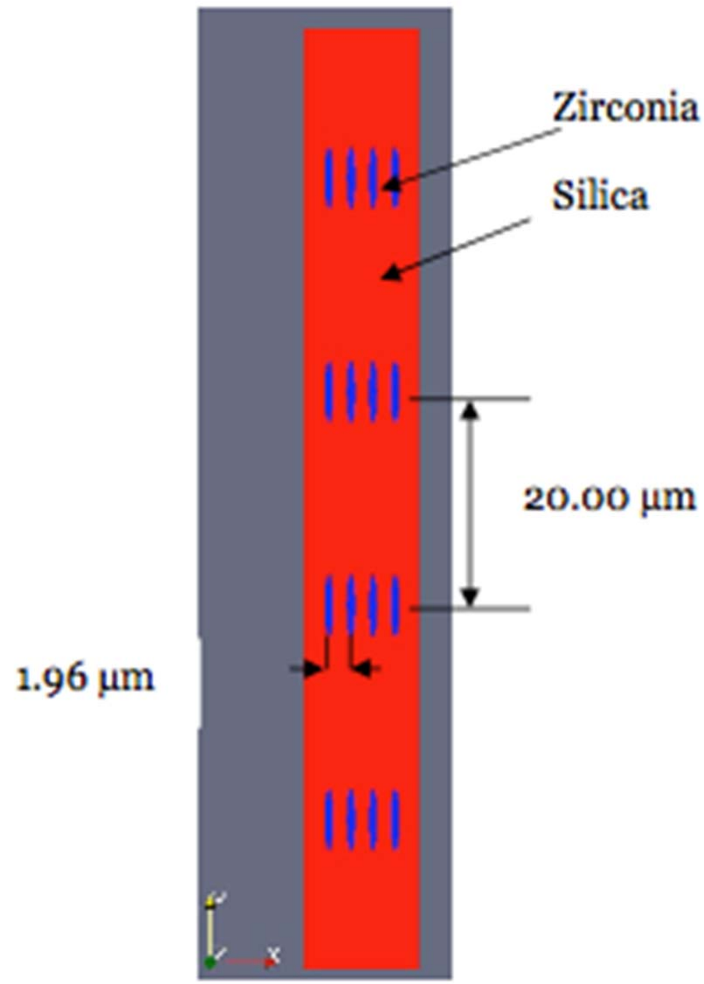
FEA MODEL OF THE MICROSTRUCTURE OF ZrB_2 / ZrC_{1-x} / Zr-Si_x SYSTEM



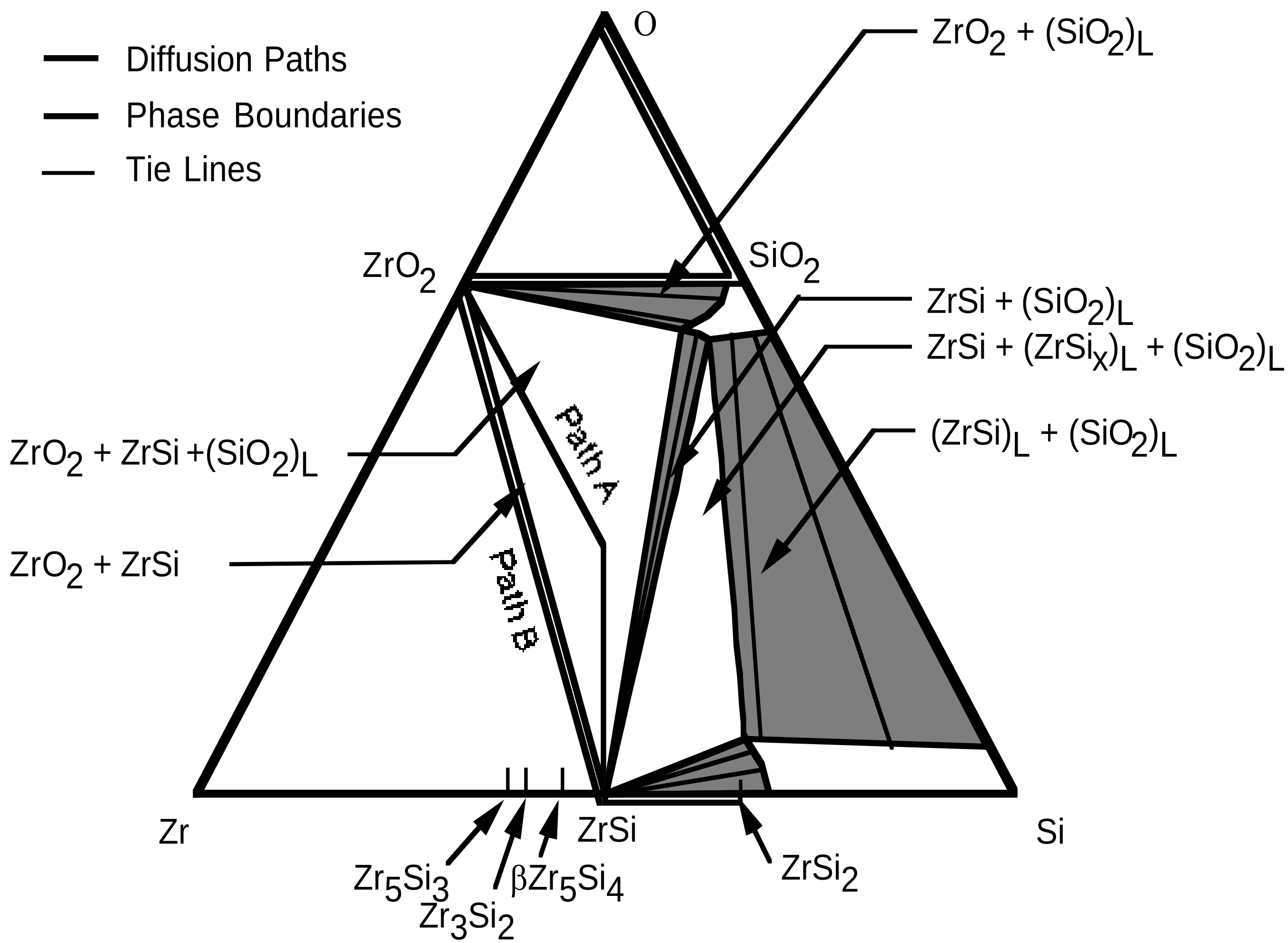
Baseline mesh of the microstructure of ZrB2 / ZrCx / Zr-Si SYSTEM

Optimal Configuration of ZrO_2 Precipitates in SiO_2 Matrix

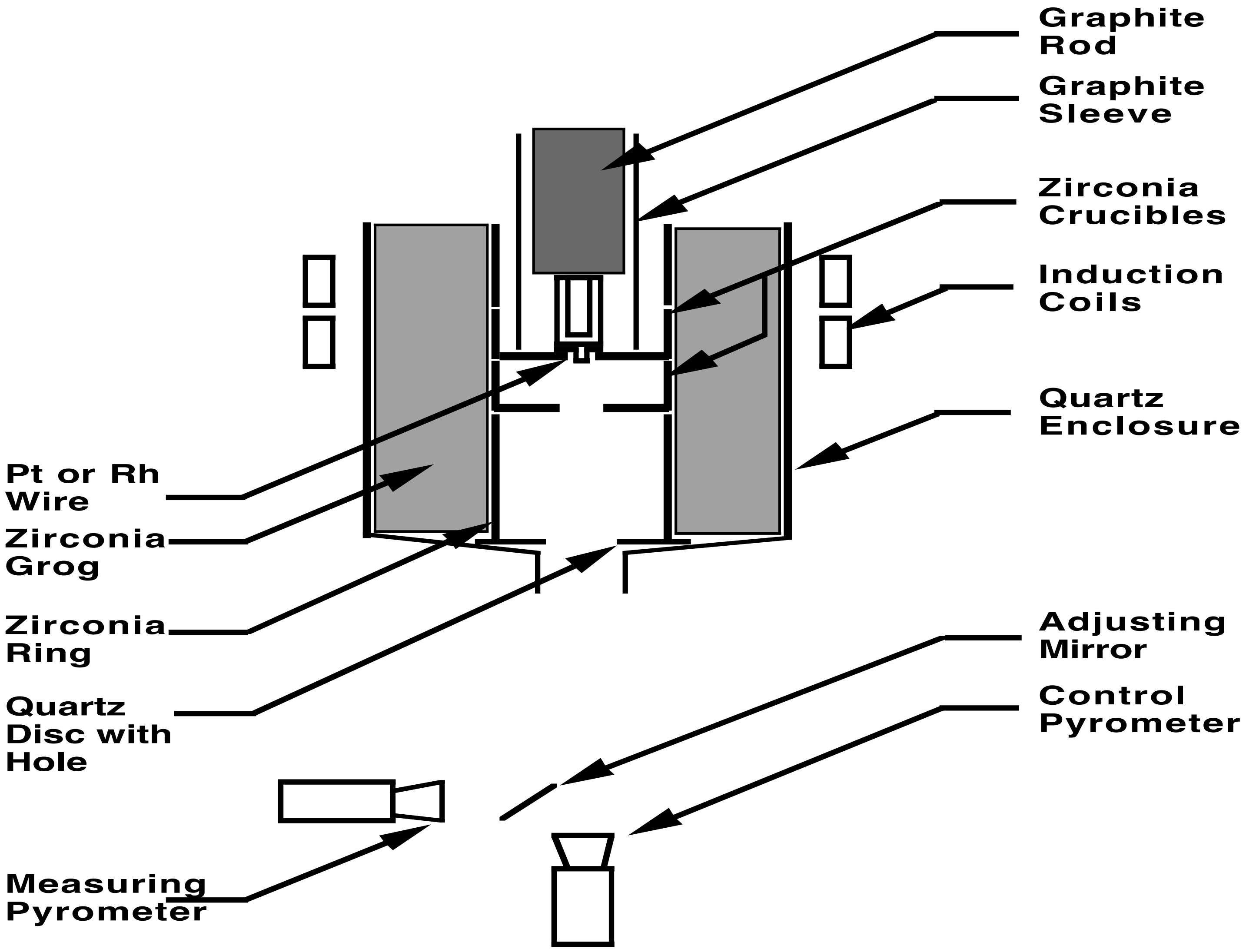




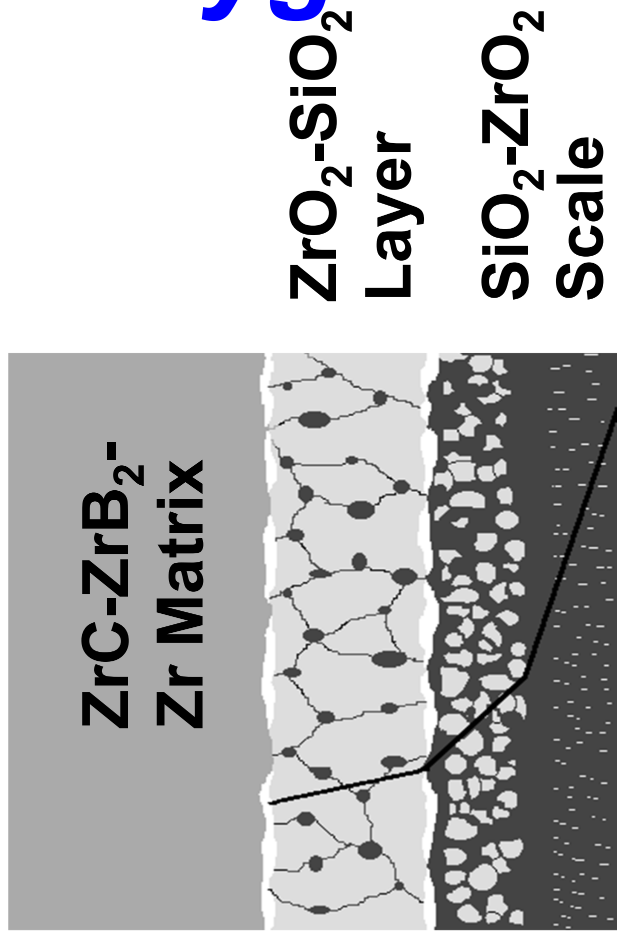
Zr-Si-O Ternary at 1800° C



Furnace Assembly



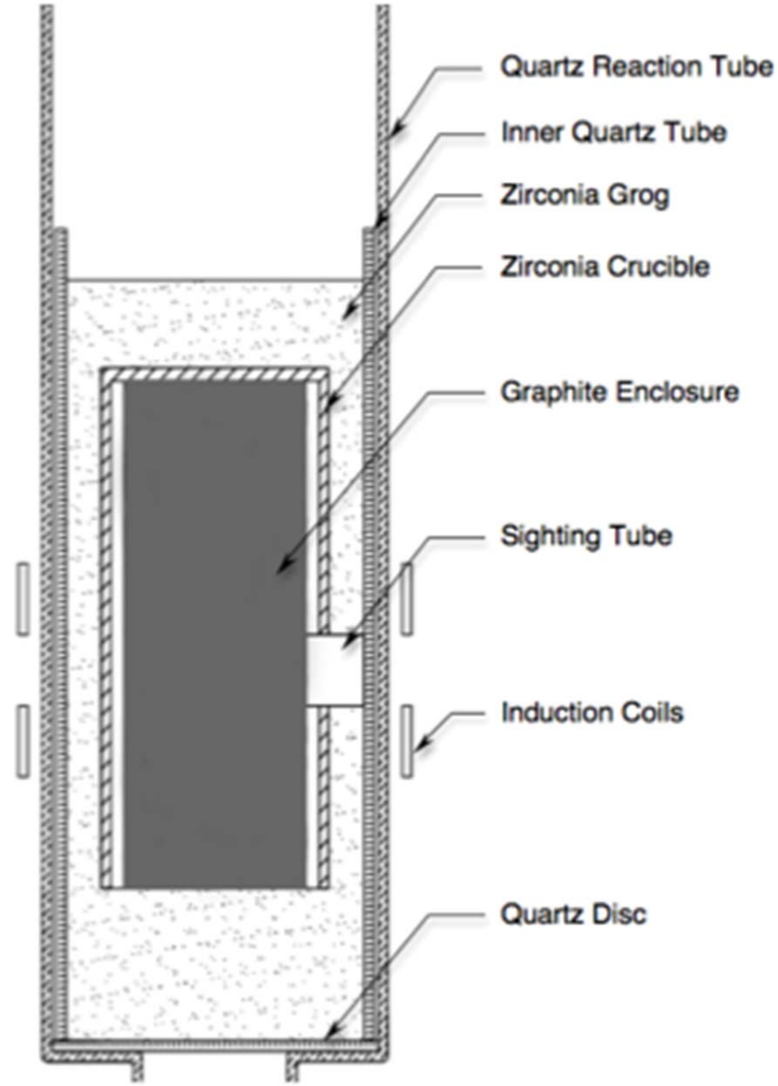
Sketch of Oxygen Diffusion



$$D_{Oxygen}^{ZrO_2} > D_{Oxygen}^{SiO_2}$$

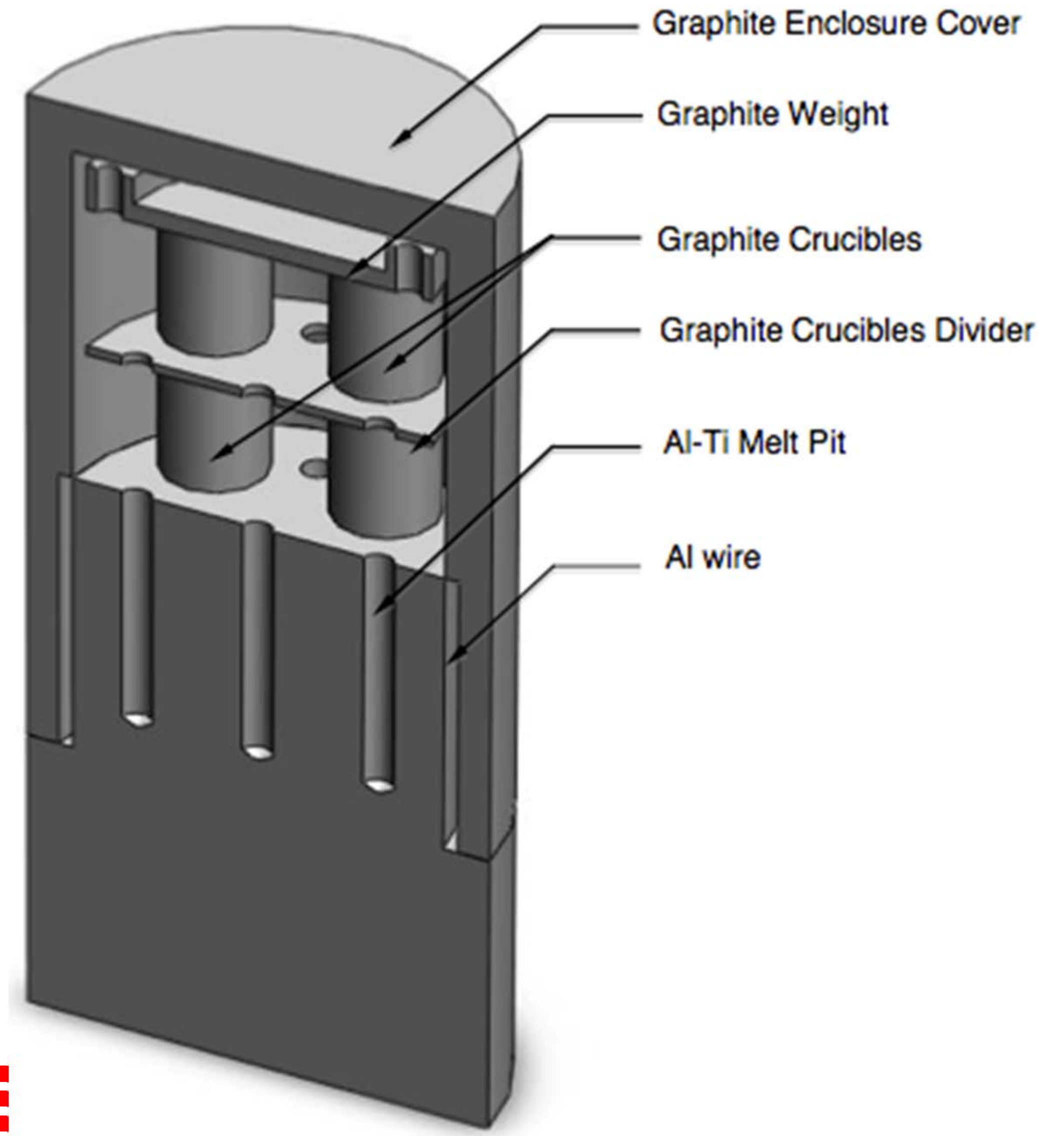
Graphite Enclosure in Dielectric Induction Furnace

- Melted previously ZrO_2 (2983 K)
- Control plasma formation with He and flow rate
- Deoxidized Ar and He flows
- Should improve temperature measurement

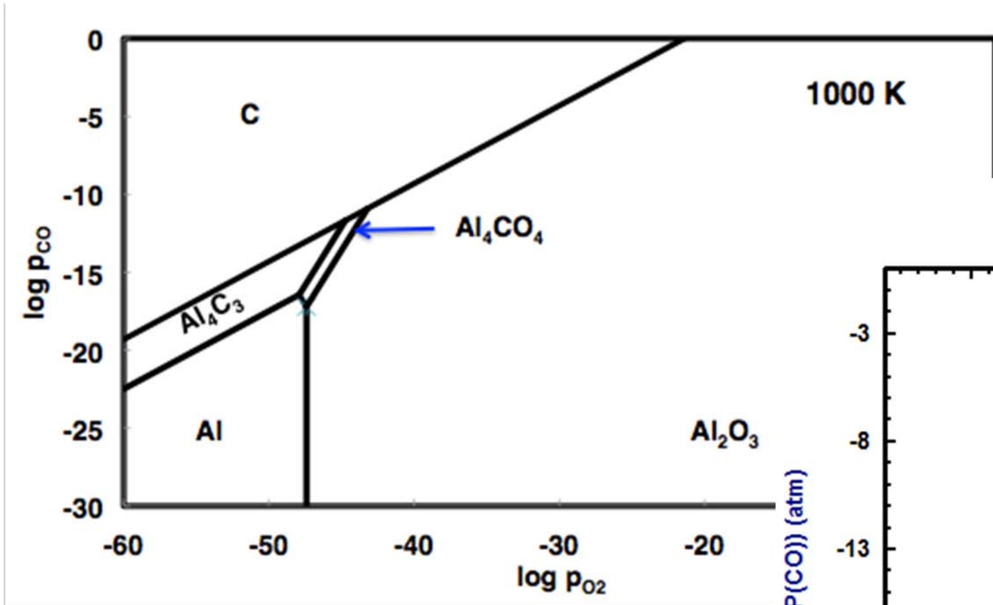


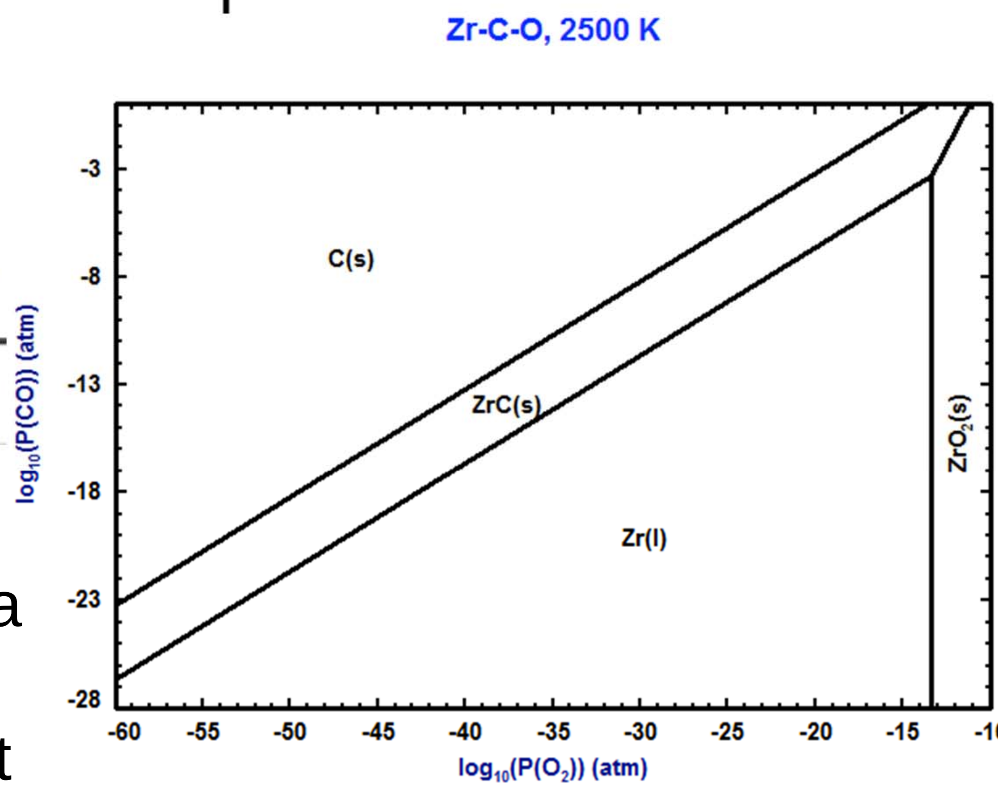
Configuration of Zr alloy/B_4C reaction system

- Zr-Y-Ti alloy reacting with B_4C contained in graphite crucibles at 2000 K plus.
- 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

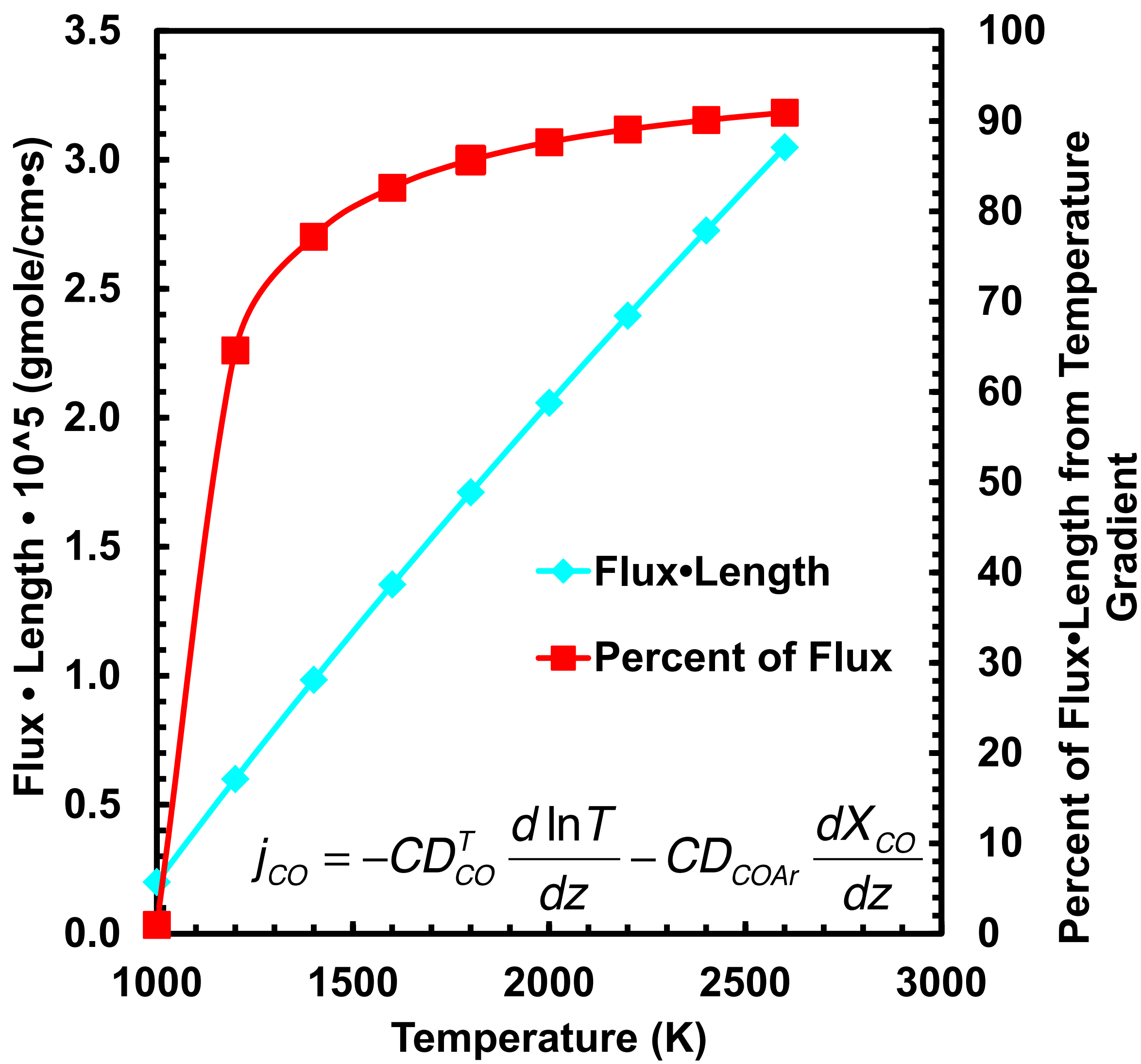




- $Al/Al_4CO_4/Al_2O_3$ estimated at 1000 K for a $p_{O2} = 10^{-47}$ atm
- Zr-Y-Ti alloy/B_4C react at > 2125 K

Maheswaraiah, Sandate and Bronson - 2012

Diffusional Flux – Kinetics Issues



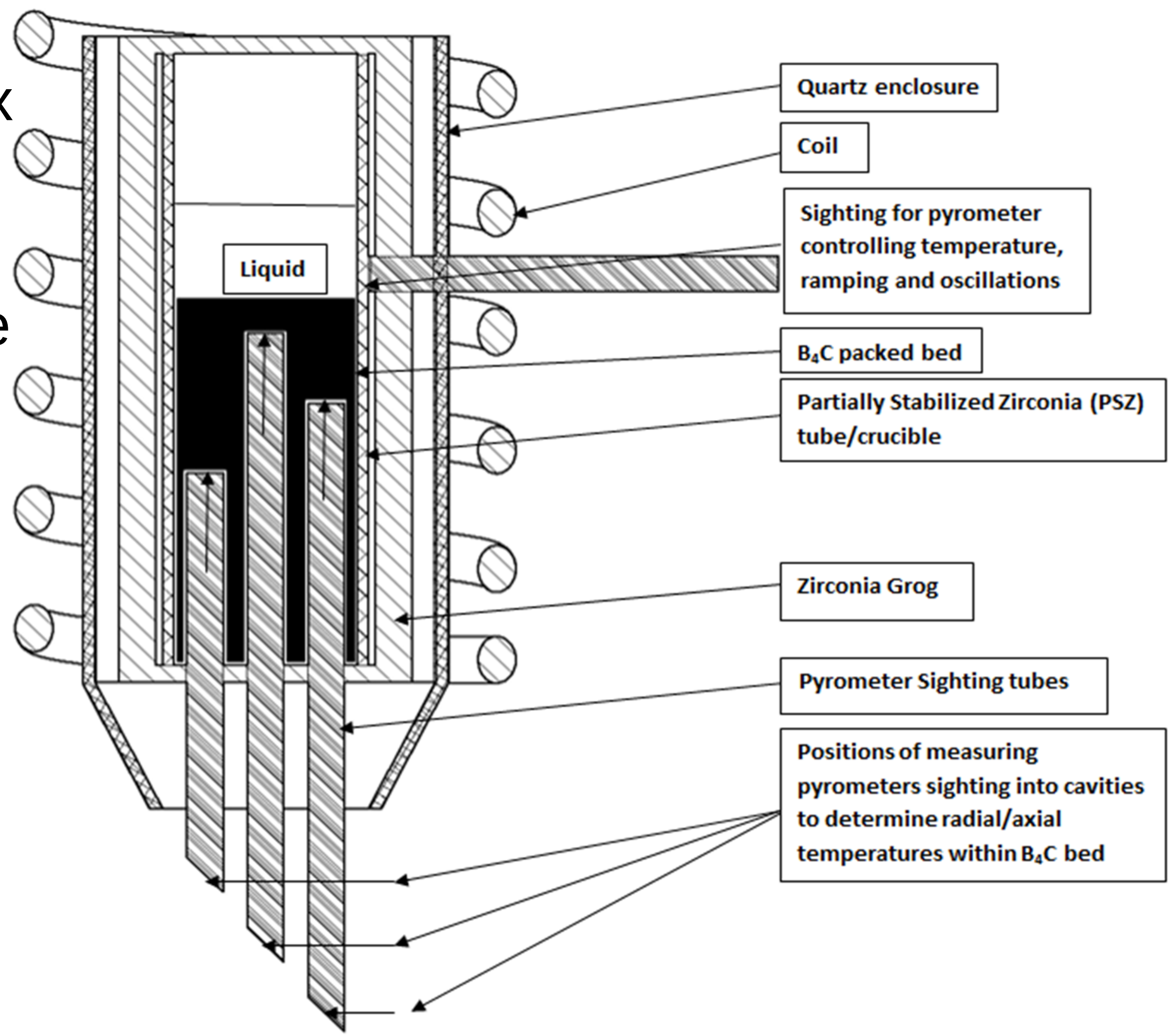
- D_{COAr} from Poirier-Geiger and checked with Chapman-Enskog Eq.
- Mean temperature

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

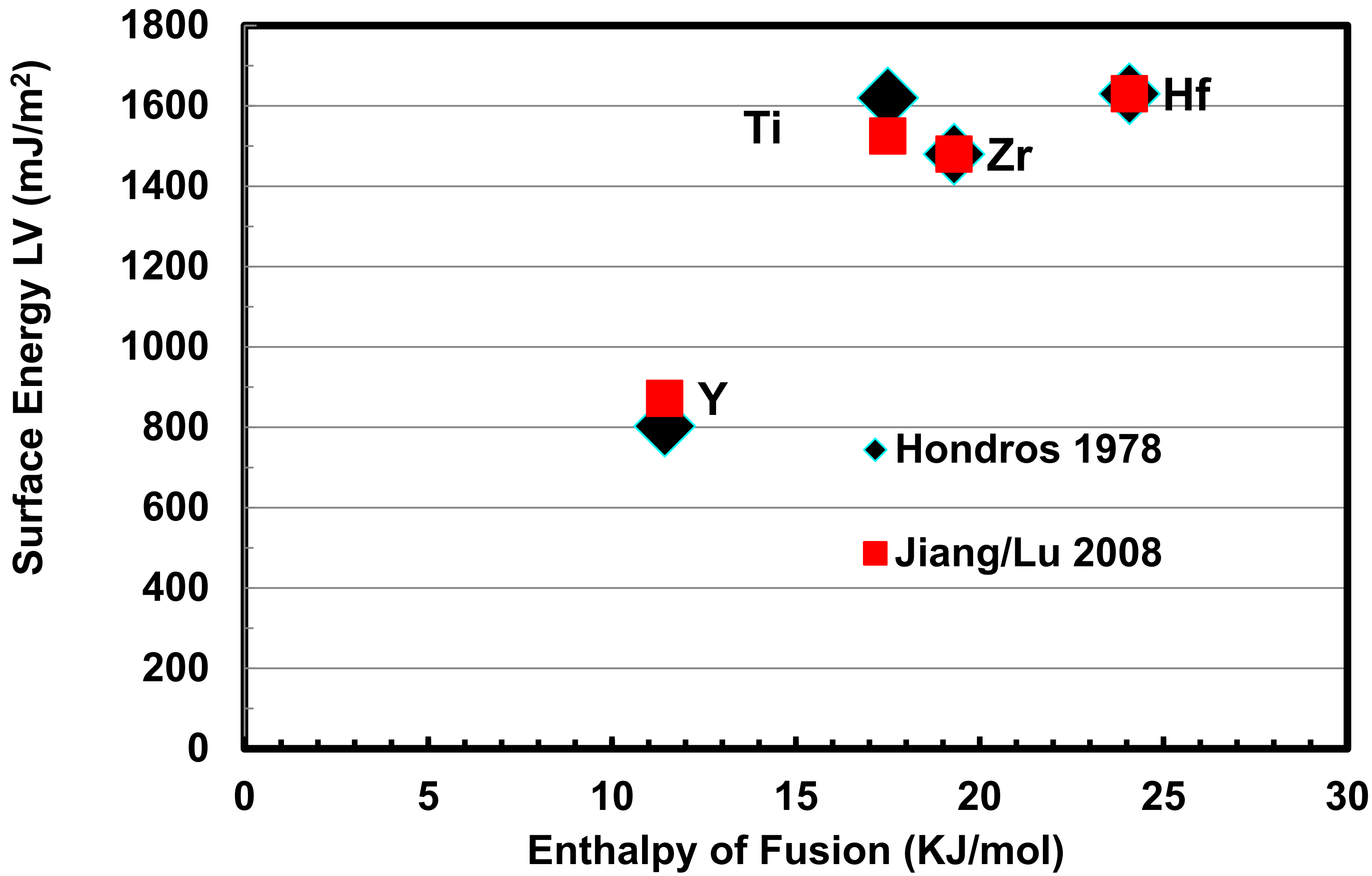
- $Al/Al_2O_3/Al_4CO_4$ reaction rate?

Temperature Measurement of Hf Melt Reacting with B_4C Packed Bed > 2600 °

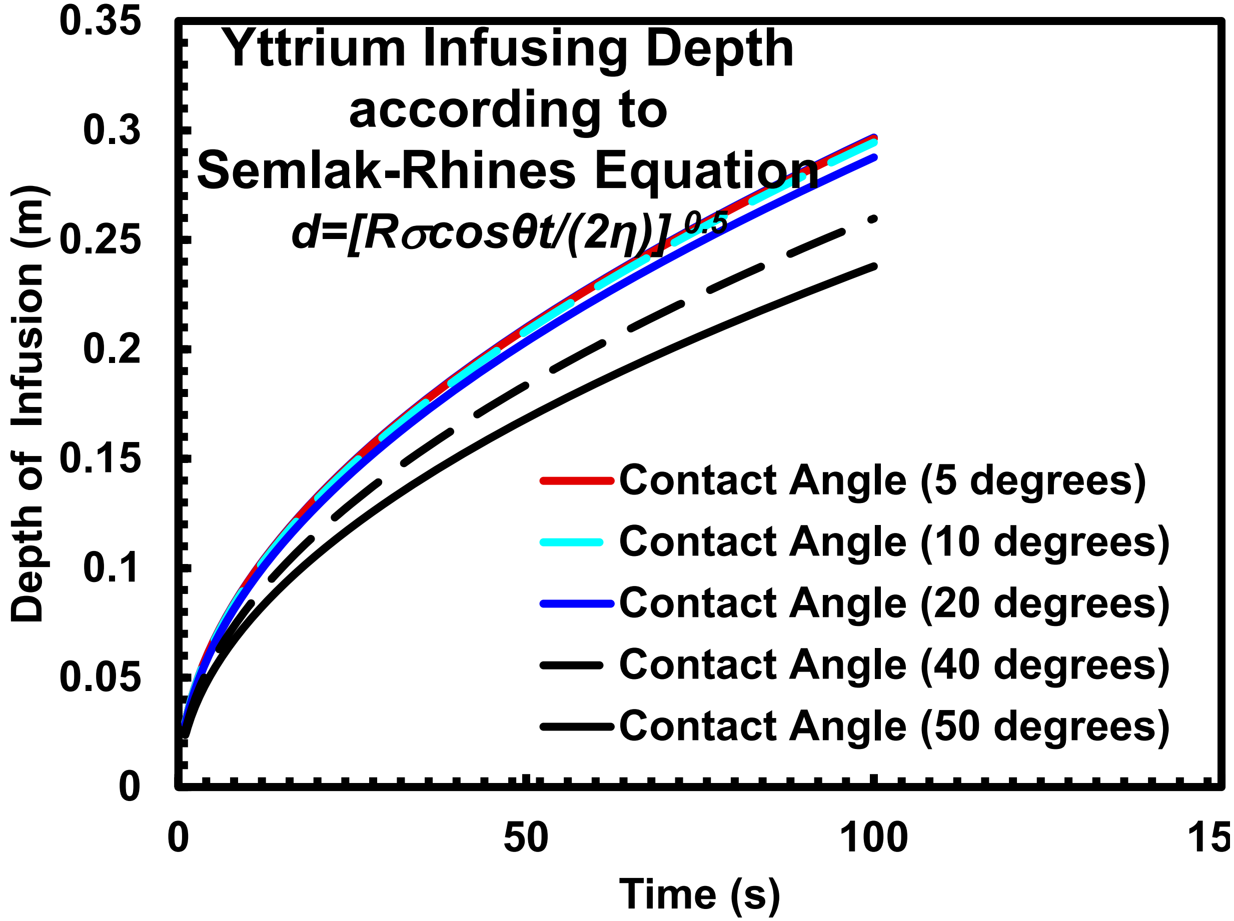
- Determine effect of dT/dx on infusion (i.e., σ_{LV})
- Determine the effect of ΔT spike on infusion
- Determine dT/dx on metastable phase formations.



Surface Energies for Hf Alloy Melts Determined from Elements



Depth of Infusion into Packed Bed Driven by Surface Energies



- Expand dσ/dx (e.g.,

$$\eta \frac{\partial u_x}{\partial y} = \frac{\partial \sigma}{\partial T}\frac{\partial T}{\partial x}$$

- Use Fluent to model computational fluid dynamics.
- Determine alloying effects (e.g., Hf-Y-Ti)

$$\Gamma_i^{Hf} = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \ln p_{O_2}}\right)_{T,i\neq k}$$

- Determine σ with:
  - Butler equation (Yeum, Speiser and Poirier-1989)
  - Multicomponent ΔG incorporating σ using FactSage

Densification of ZrB_2-TiC-Y_2O_3 (with and without Ta) Composites Using Spark-Plasma Sintering at University of Arizona

Dr. Erica L. Corral[1]
Luke S. Walker
Victoria R. Marotto

Dr. Arturo Bronson[2]
Brenda Mota, Carlos E. Castillo
David Pham, Alvaro Sandate

ZrB_2-TiC-Y_2O_3-Ta would react to form ZrO_2-Y_2O_3-TiO_2-Ta_2O_5 determining TiO_2-Ta_2O_5 glassy phase.

[1] Department of Materials Science and Engineering, Arizona Materials Lab, The University of Arizona, Tucson, AZ
[2] Mechanical Engineering Department, The University of Texas at El Paso, El Paso, TX

Joint Work Between the Corral Lab and UTEP in Preparing ZrB_2-based ceramics with additions of Yttria and Ta for Improved Oxidation Resistance Through the Formation of Complex Oxide Scales

Material	Composition (wt%)								
	1	2	3	4	5	6	7	8	9
ZrB_2	79.3	62.0	37.8	33	29	26	30	23	18
TiC	10.3	12.5	15.6	27	36	42	13	19	23
Y_2O_3	10.4	25.5	46.6	40	40	32	37	28	23
Ta*	-	-	-	-	-	-	20	30	36
Temperature (°C)	1600 1650 1700ᵗ 1750	1500 1700 1750	1500 1700 1750	1700	1700	1700	1700	1750	1800

Sample volumes of 1.5 cm^3 from a 20mm die.

* – Ta foil was finely cut and dispersed in the powder

t – 3 samples of this composition produced

Compositions for ZrO_2-Y_2O_3-TiO_2-Ta_2O_5 scales

- In t-ZrO_2/c-ZrO_2 region
- Near c-ZrO_2/t-ZrO_2/$TiO_{2,L}$ region
- Near c-ZrO_2/$Y_2Ti_2O_7$ region
- Ta added for Ta_2O_5-TiO_2 eutectic scale

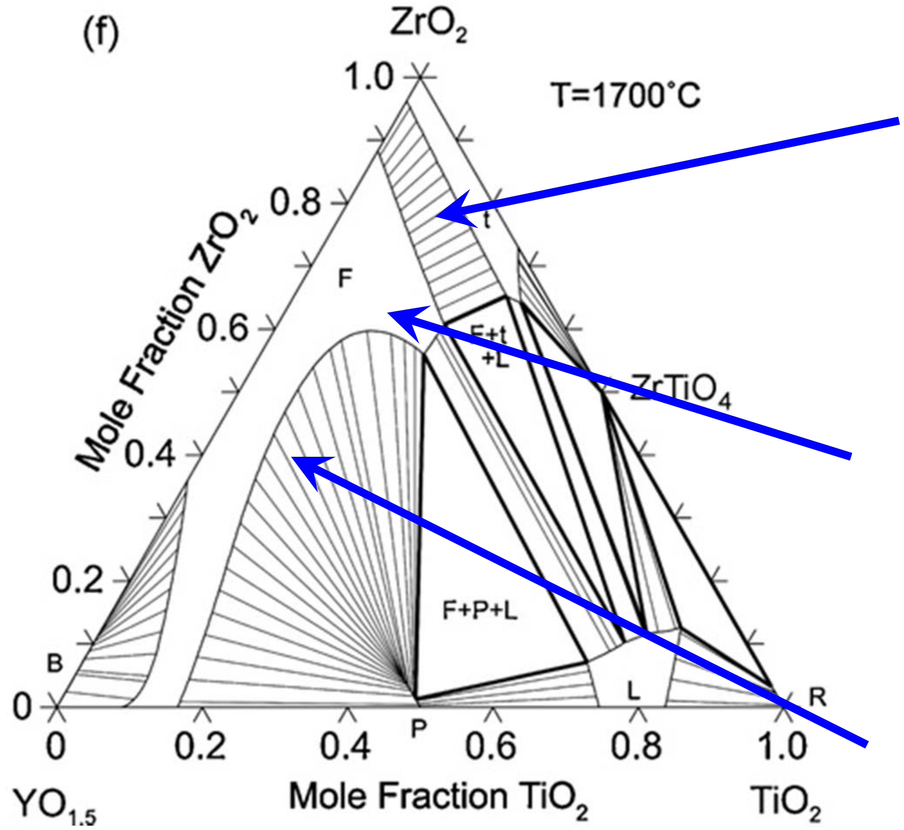


Diagram from Schaedler, Fabrichnaya and Levi -- 2008

12 TiO_2
10 Y_2O_3
78 ZrO_2

15 TiO_2
23 Y_2O_3
62 ZrO_2

15 TiO_2
45 Y_2O_3
40 ZrO_2