Stability Issues in Thermal Barrier Coatings

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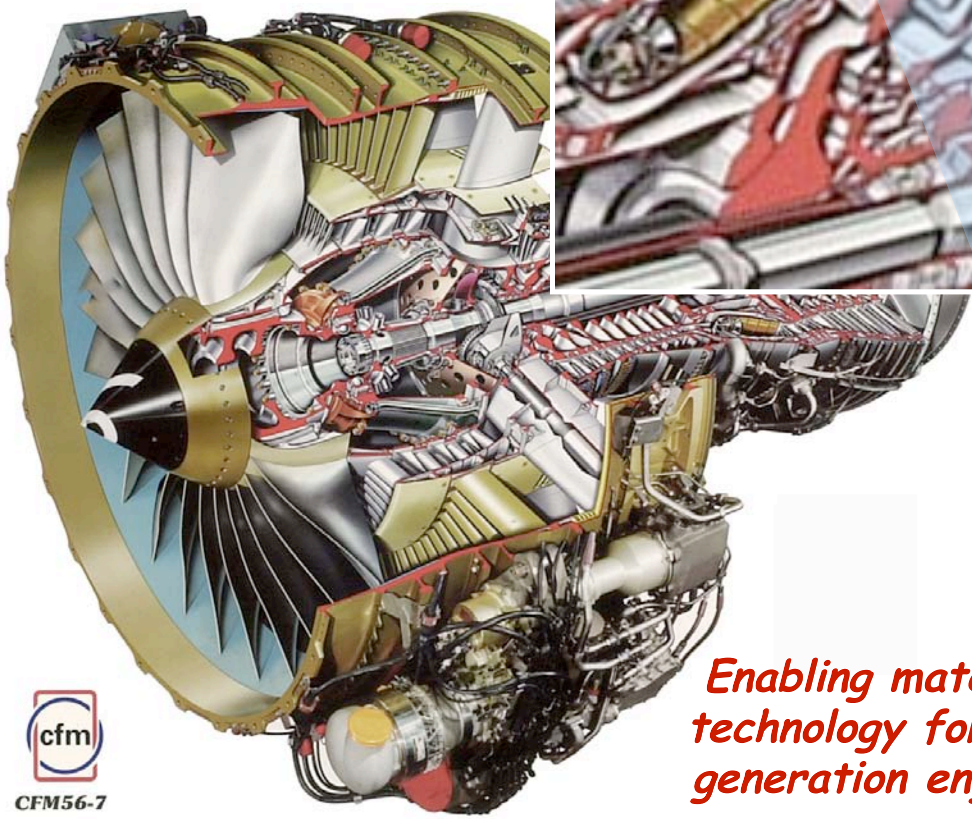
Thermal Barrier Coatings

Extend the limits and durability of high performance alloys in gas turbines



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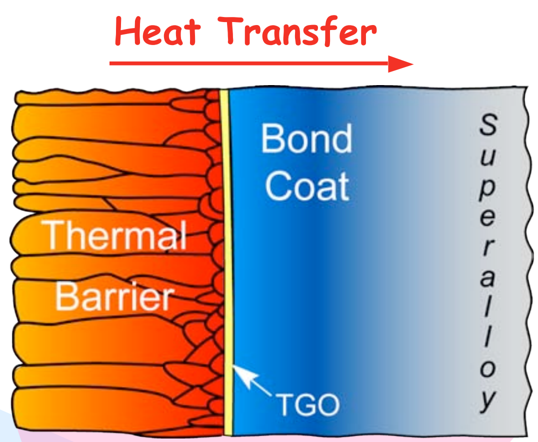
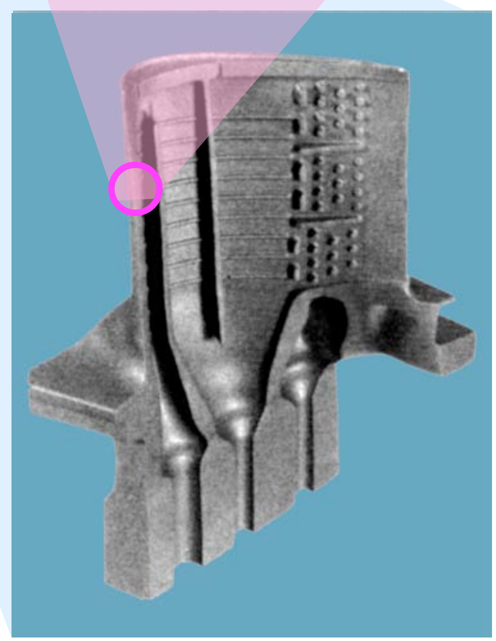




Enabling materials technology for next generation engines.

Mechanisms Limiting Durability in TBCs

Adapted from A.G. Evans

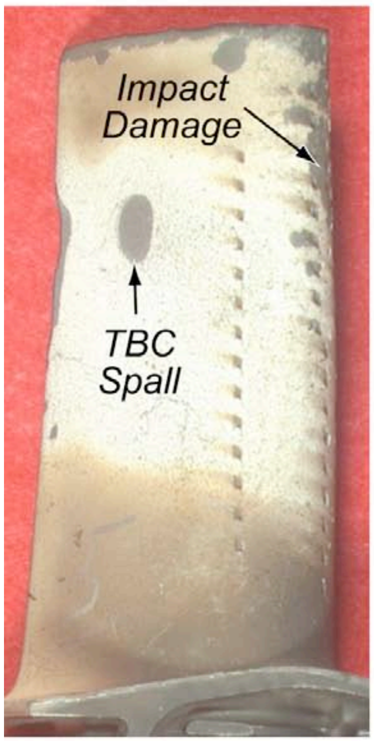
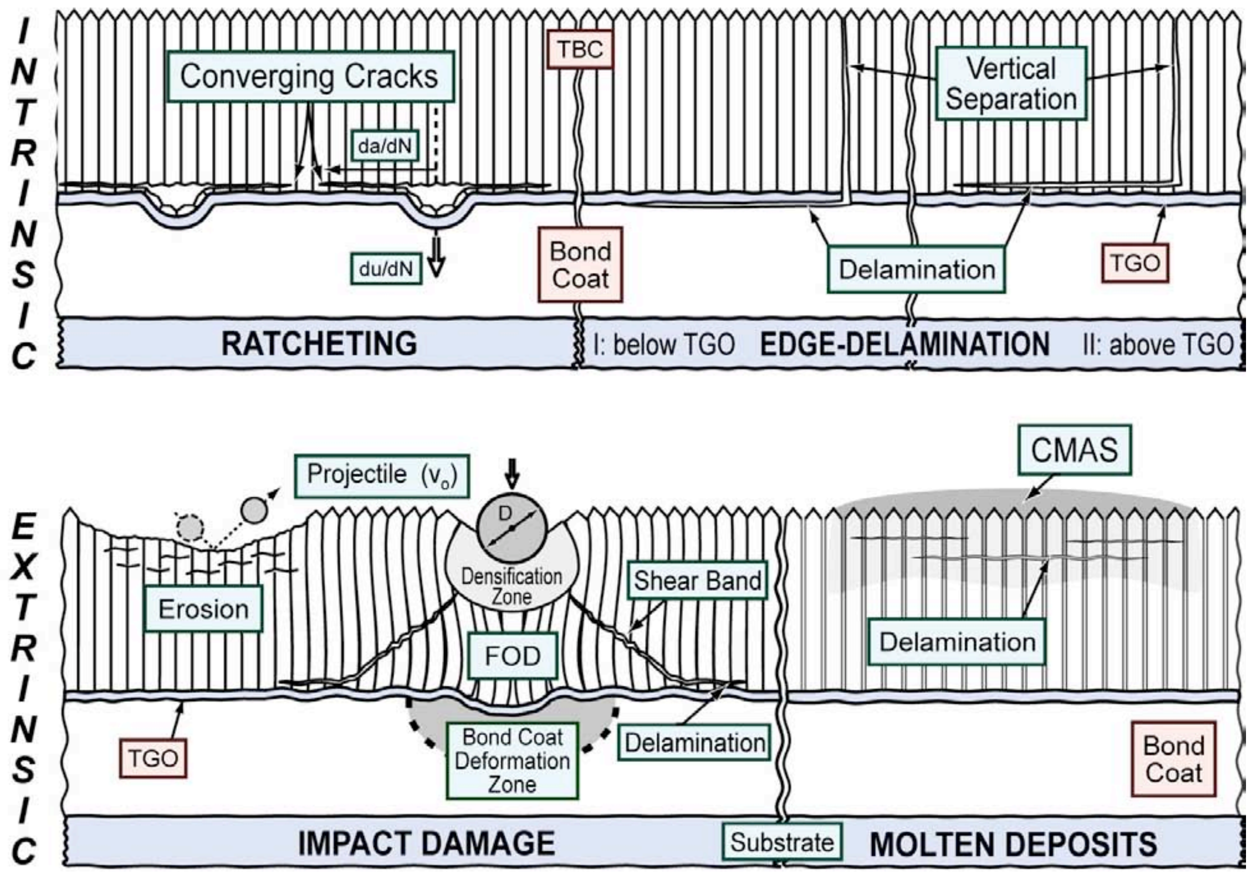


Image courtesy of R. Darolia (GE)

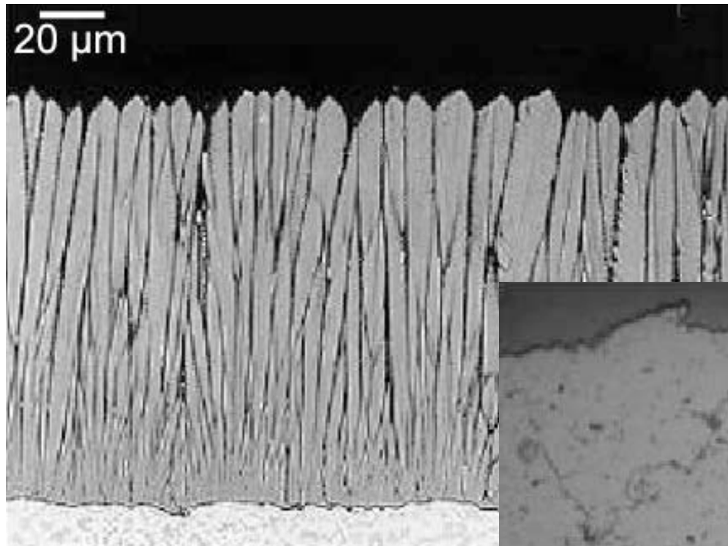


TBCs are "live" systems, whose structure evolves over time. Predictive models must incorporate effects of evolution dynamics on damage/failure mechanisms

Historical Evolution of Thermal Barrier Coatings

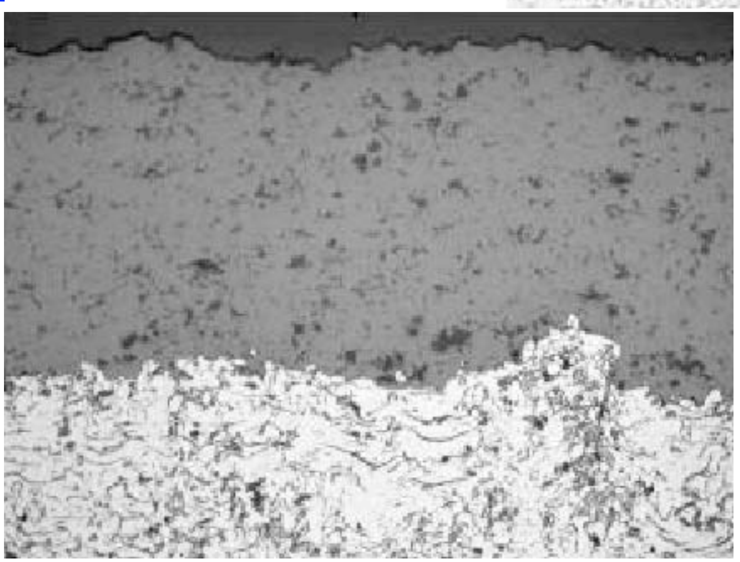
Adapted from C. Johnson
GE Global Research Center

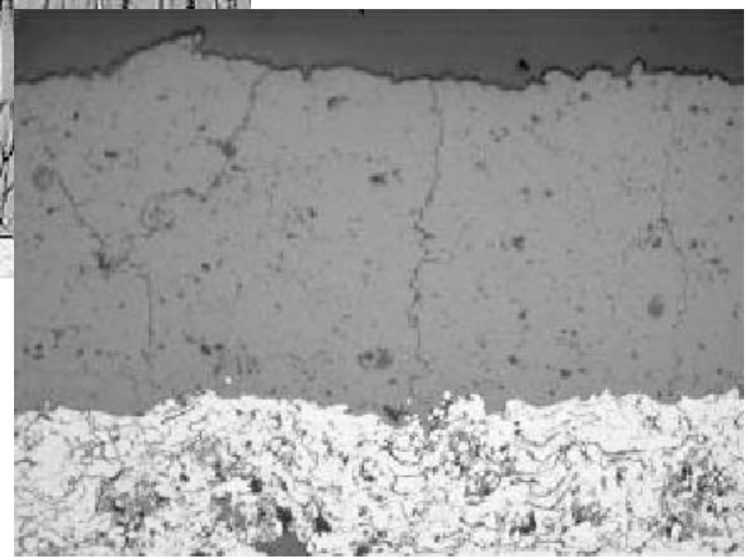
Performance



Electron Beam PVD
125-250 µm
High Performance
Aeroengine Airfoils

Air Plasma Spray
250-750 µm
Limited Performance
Combustors

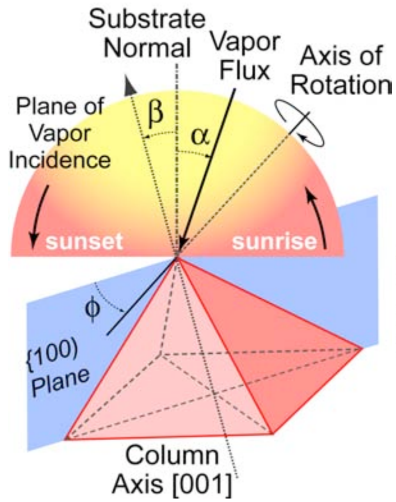


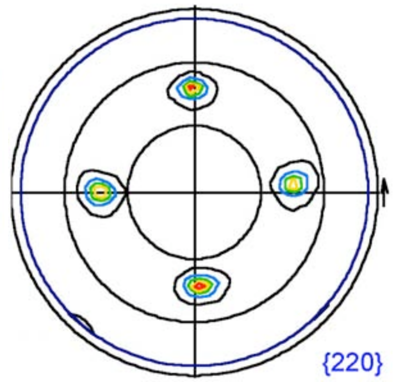


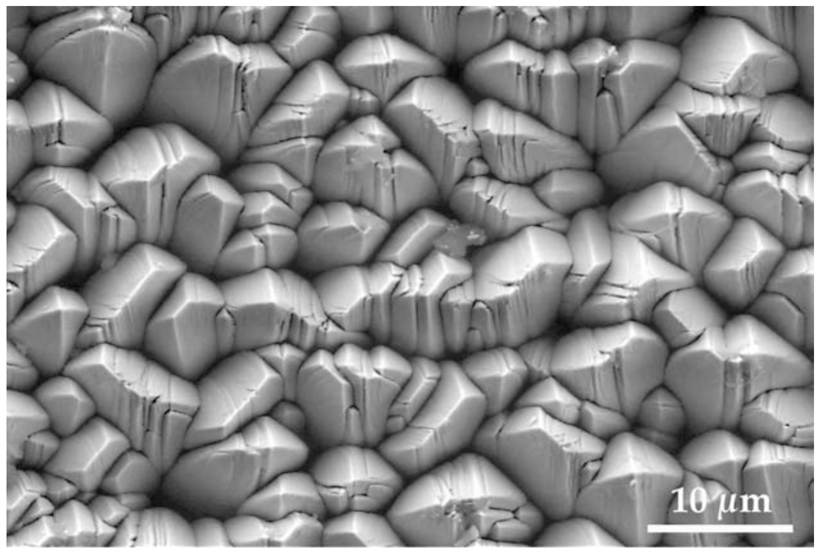
Dense Vertically Cracked APS
May be > 500 µm
Power Generation Turbine Airfoils

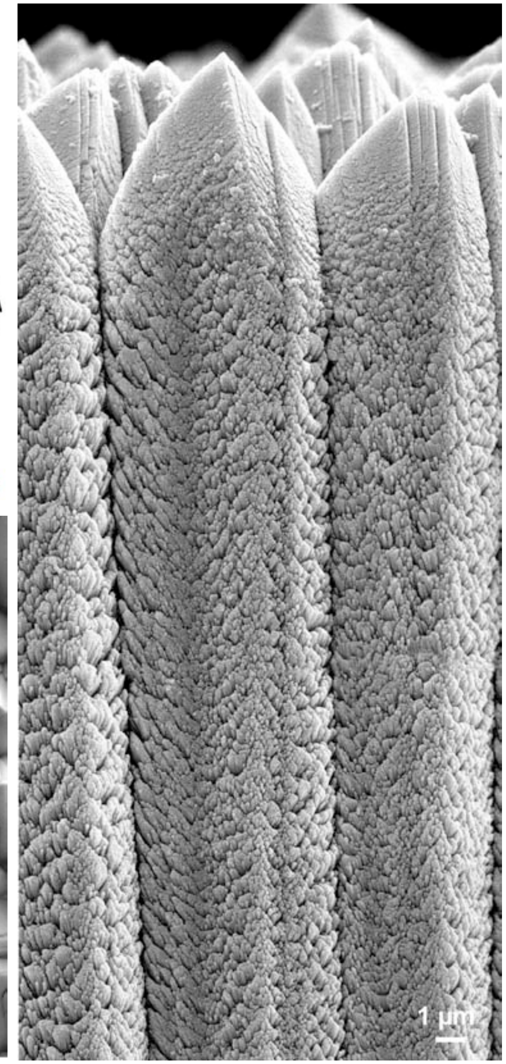
Time of introduction

EB-PVD Growth of TBCs



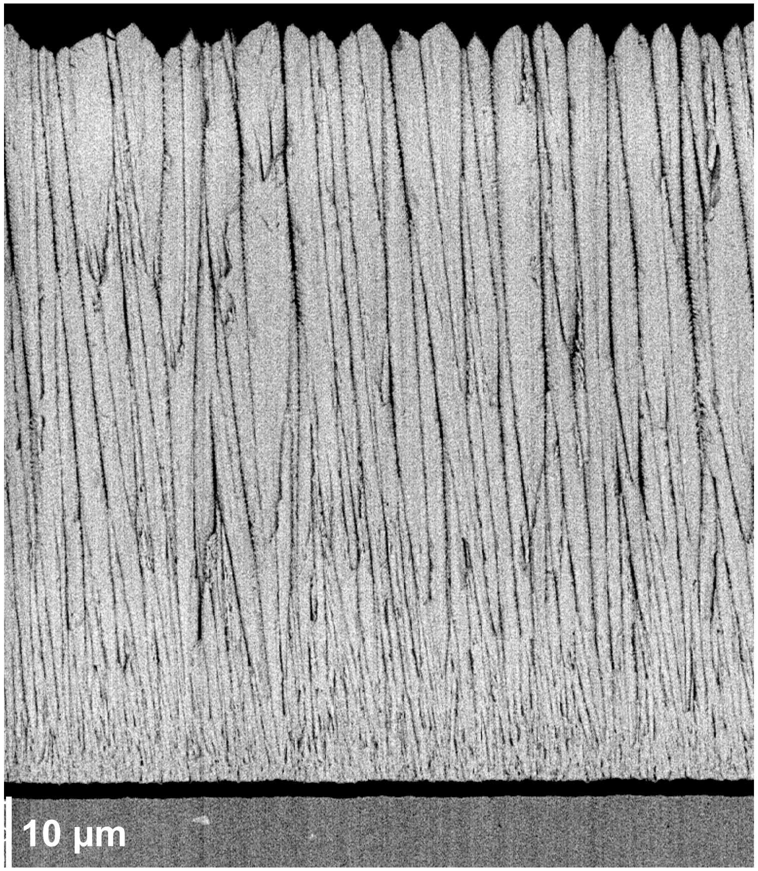


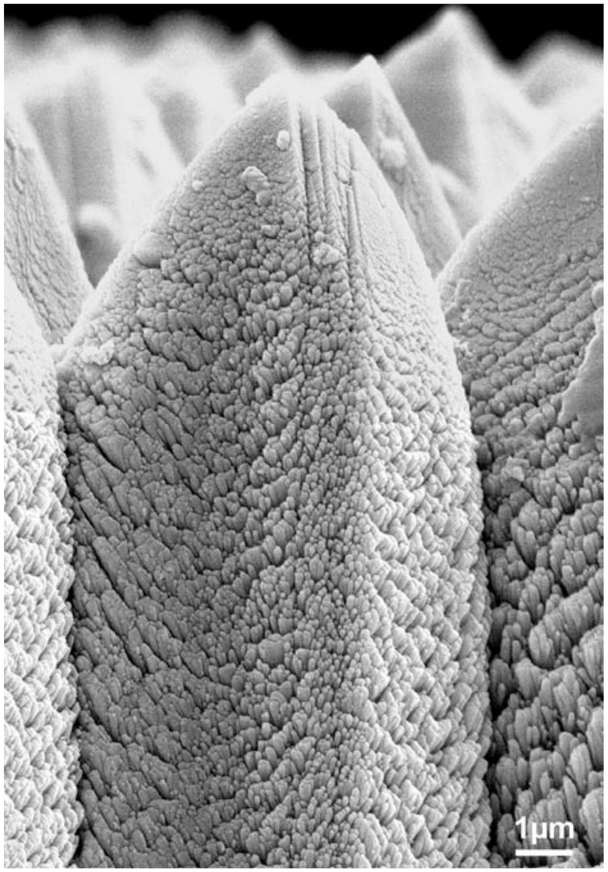




- Columnar structure with strong biaxial texture:
  - ➩ [100] out of plane
  - ➩ [001] in plane, ⊥ to rotation axis

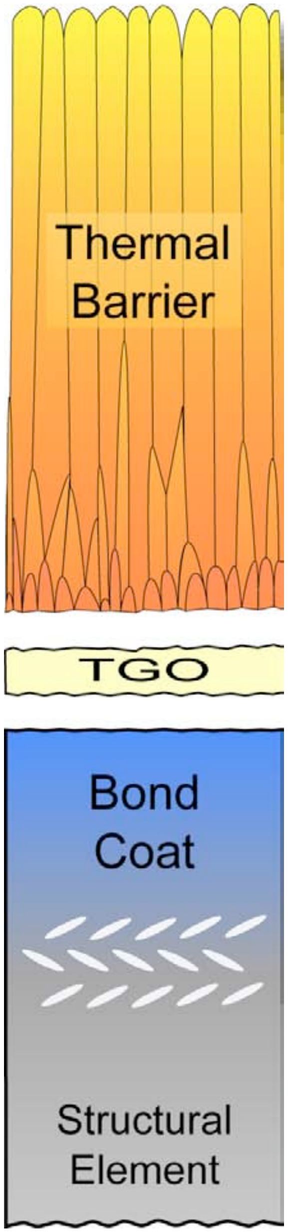
Porosity: A key to Performance and Durability





- *Through thickness segmentation enables accommodation of CTE mismatch during thermal cycling.*
- *Intra-columnar porosity further reduces intrinsically low thermal conductivity.*

Thermal Barrier Stability Issues



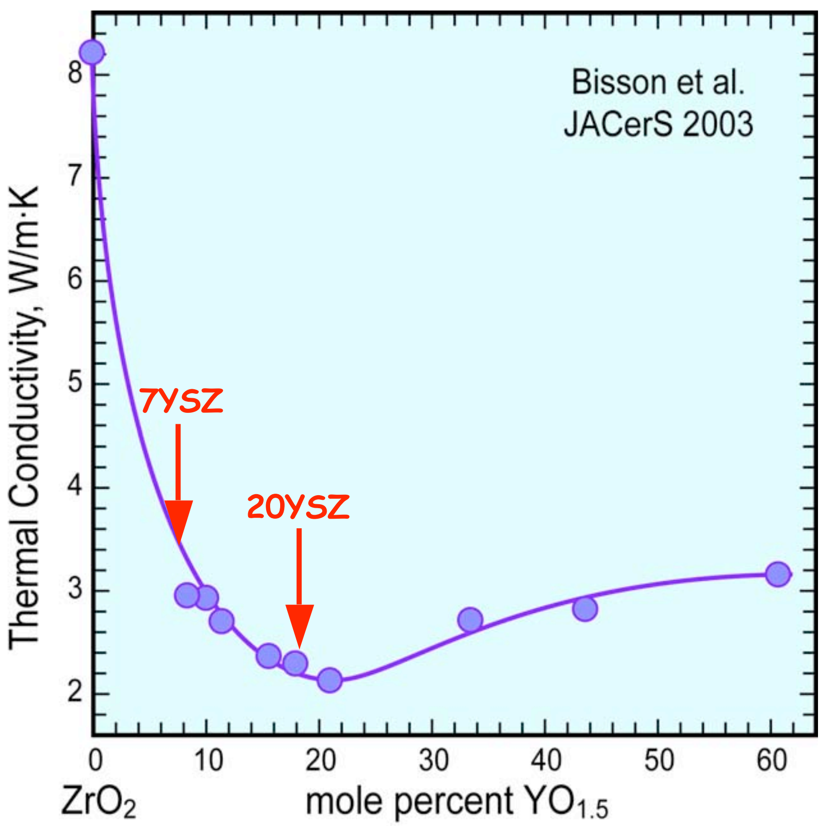
- *Evolution of pore architecture*
  - ↳ *Degradation of insulating efficiency*
  - ↳ *Degradation of strain tolerance/erosion resistance (may be accelerated by molten deposit penetration)*
- *Evolution of phase constitution*
  - ↳ *t' (non-transformable) → t (transformable) + c*
  - ↳ *Accelerated by molten deposits (CMAS, S/V)*
- *Thermochemical interactions with TGO*

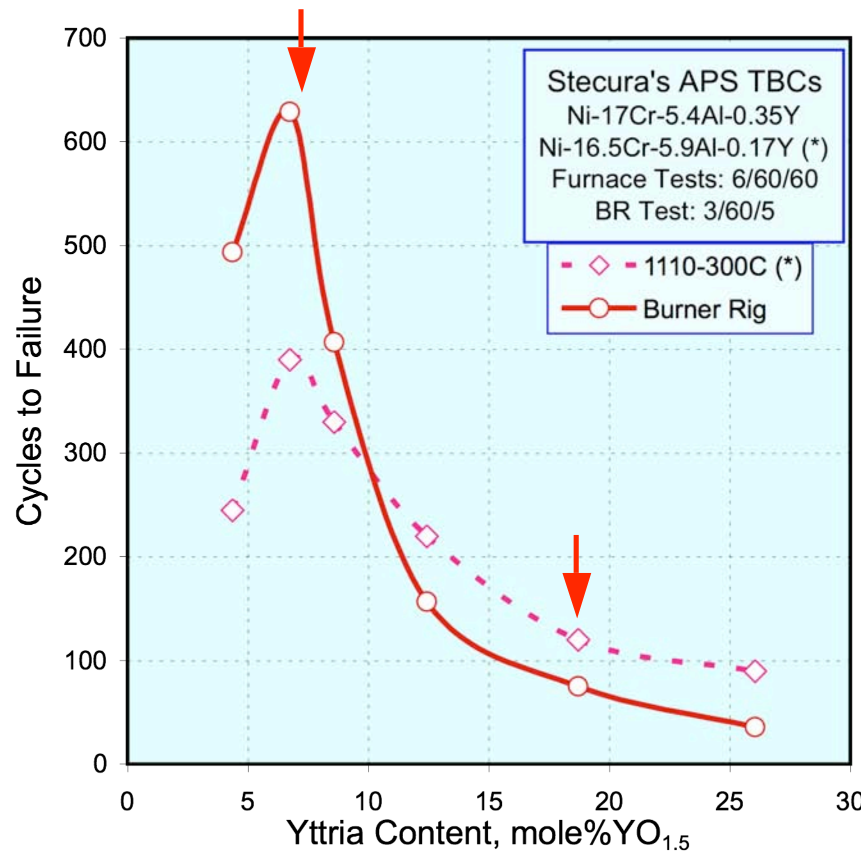
Two Broad Concerns:

- *Problems are exacerbated by demands for operation at higher T or in more aggressive environments*
- *Uncertainty about the effects of novel TBC compositions on the stability of the system*

Chemistry and Phase Constitution

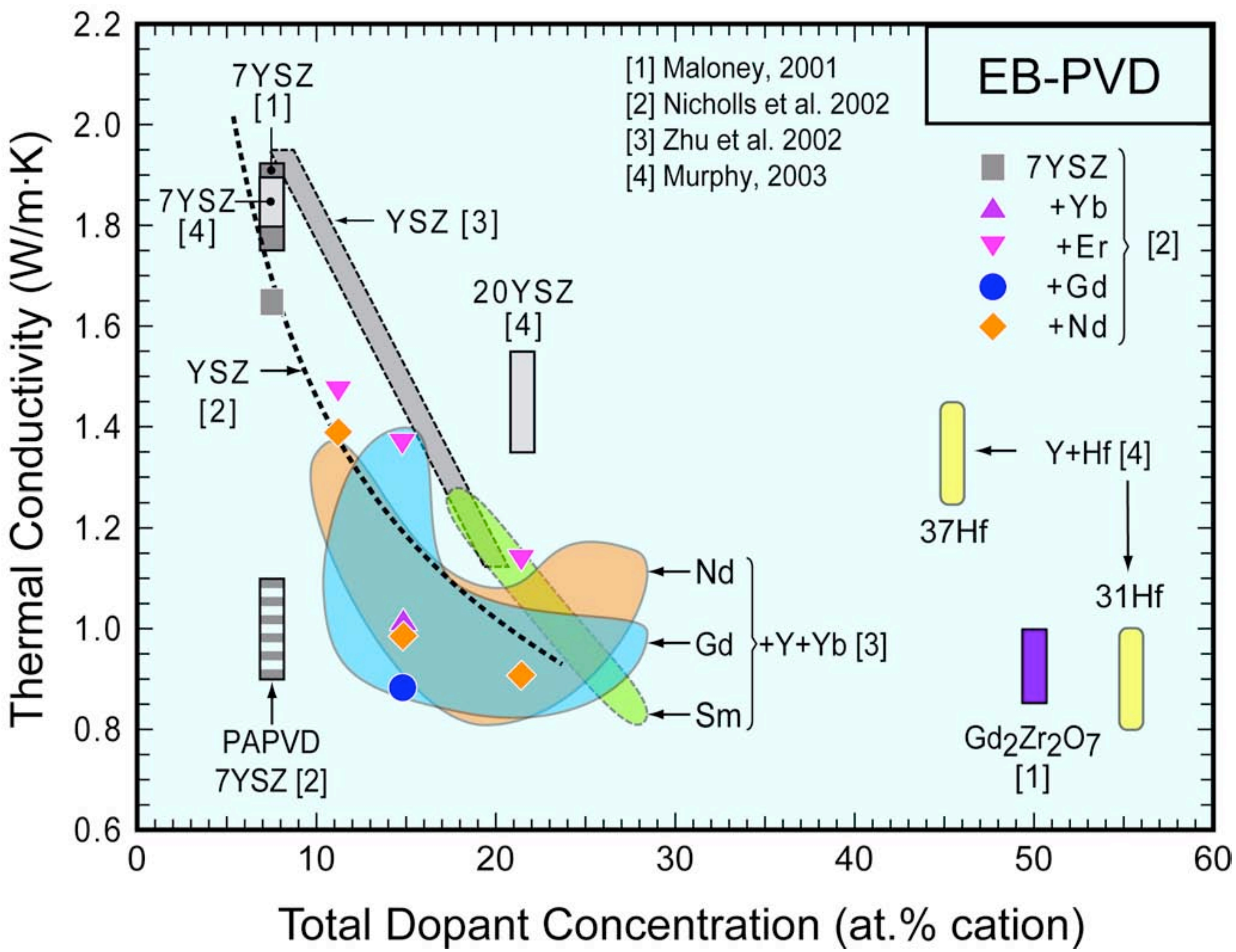
TBC Chemistry: Why "7"YSZ?





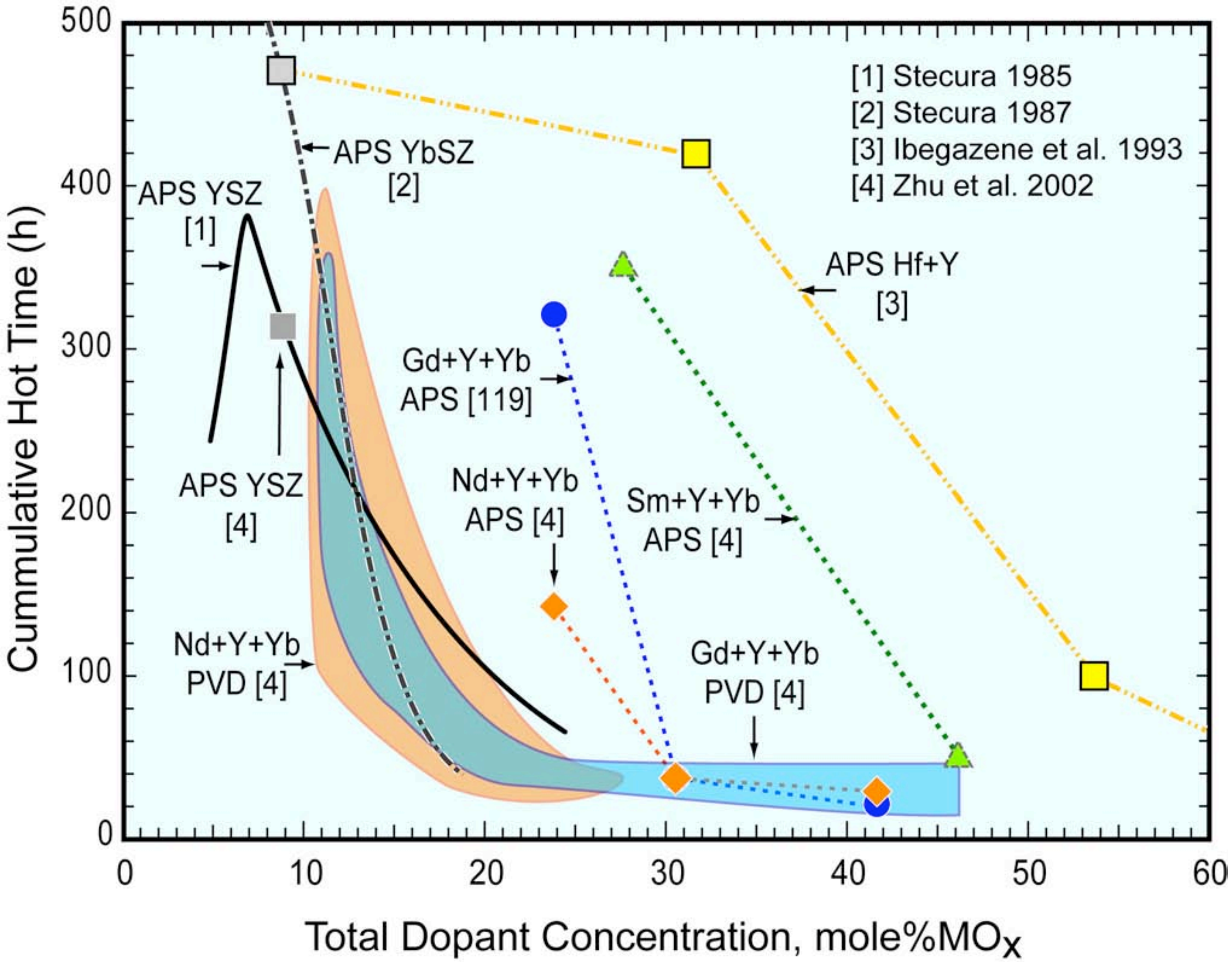
- *Not optimum in terms of thermal insulation efficiency*
- *Selection motivated by durability in cyclic tests*

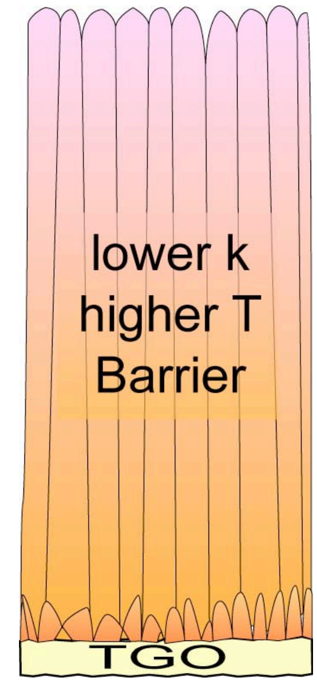
Thermal Conductivity of Some Emerging TBCs



- *A large variety of alternate compositions, mostly based on rare earth additions to ZrO_2 or YSZ, offer improved thermal insulation efficiency over 7YSZ. But…*

Cyclic Life v. Stabilizer Content



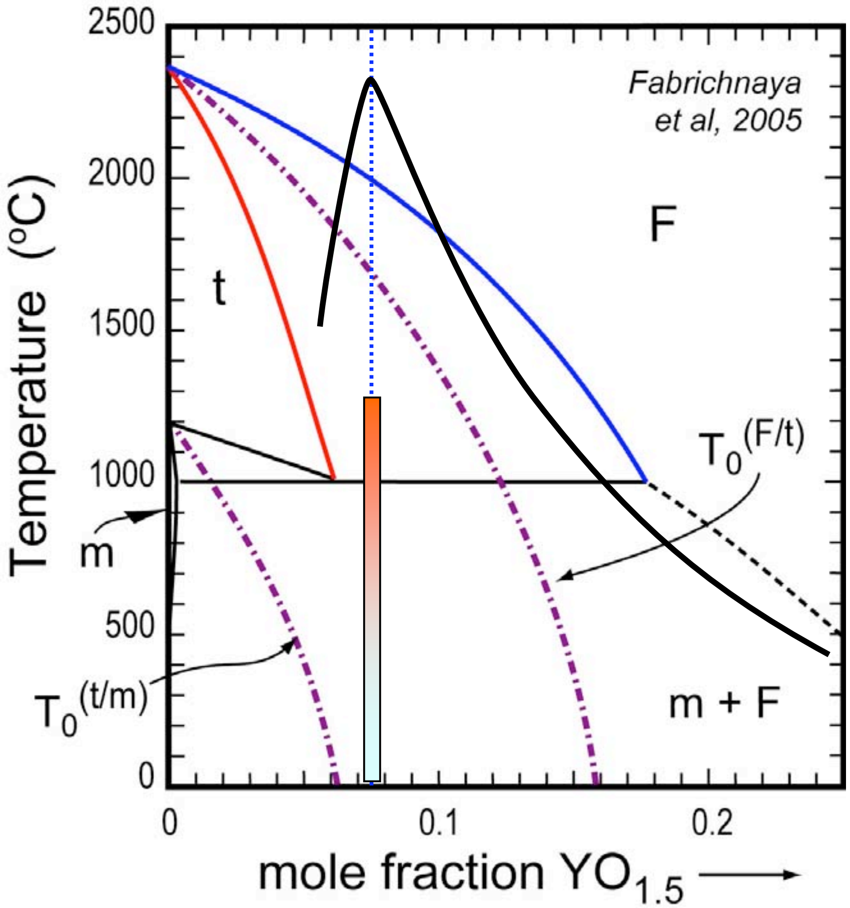


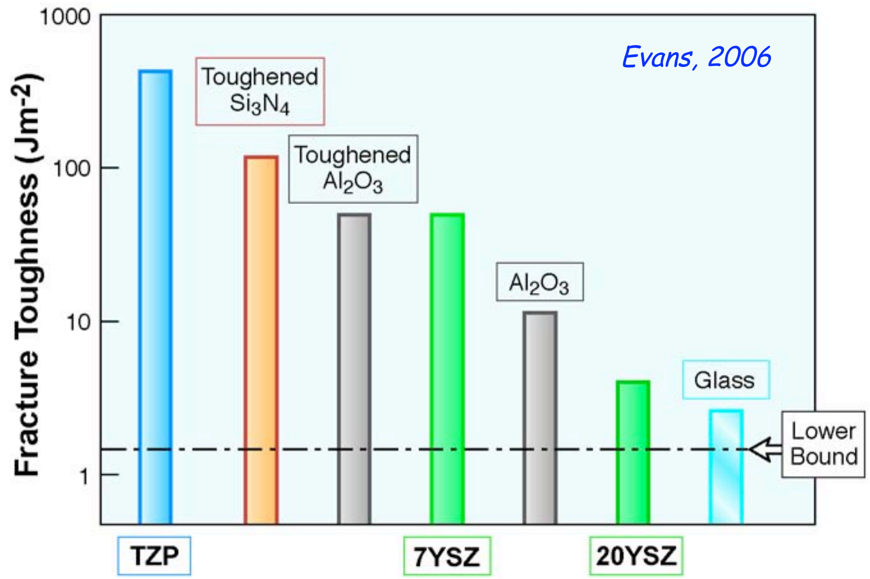
- *Cyclic life is compromised with increasing stabilizer content for singly- as well as co-doped ZrO_2.*

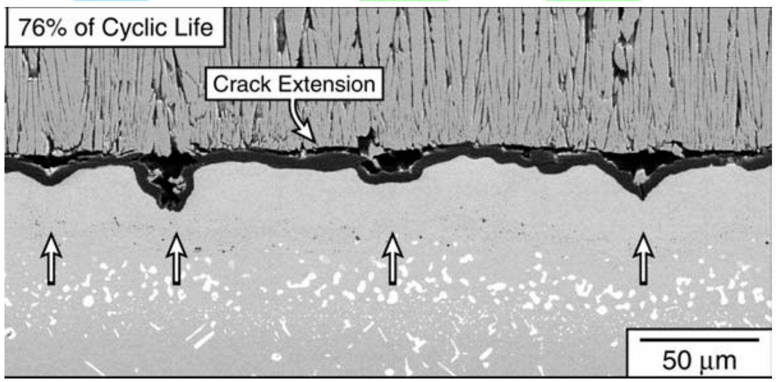
Levi, C.G.: *Current Opinion in Solid State and Materials Science*, 8 (2004) 77-91.

Phase Constitution and Implications

Image from Mumm &Evans



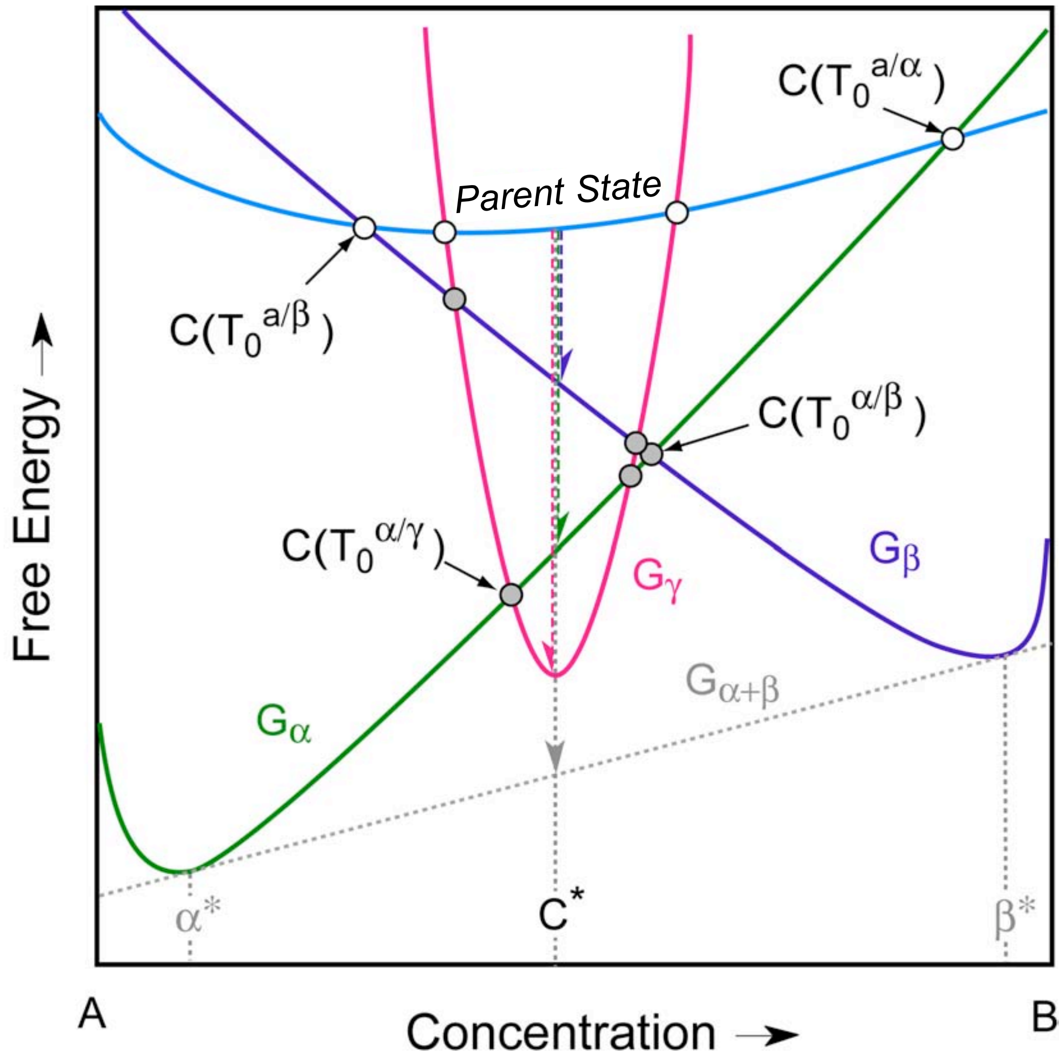




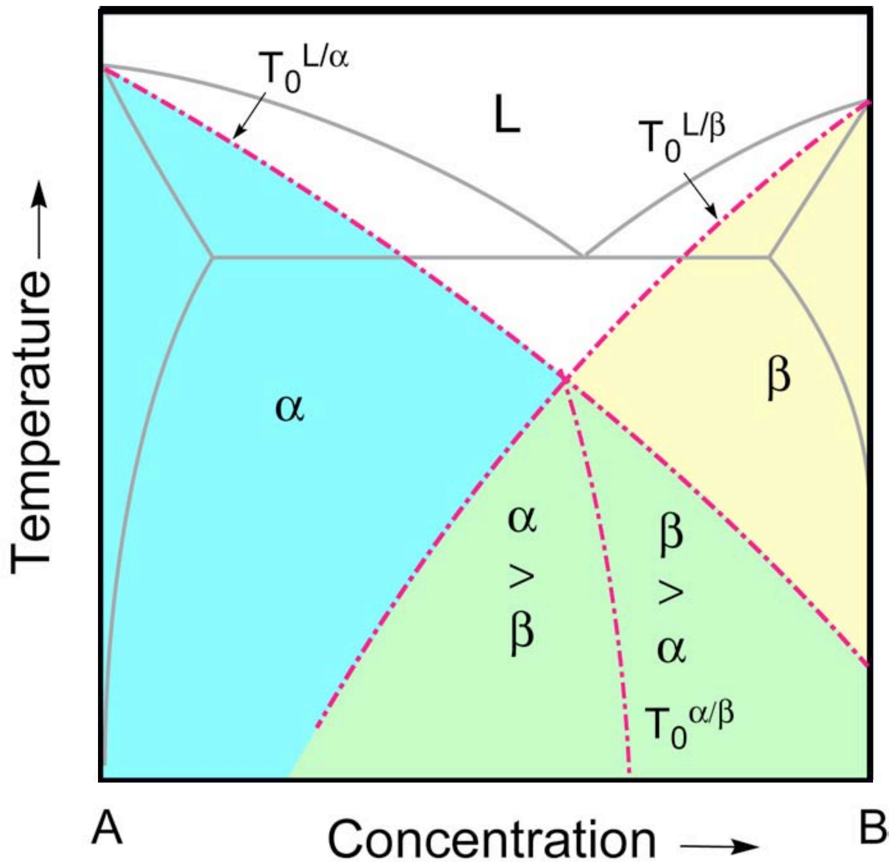
Durability limited by crack propagation through TBC: expected to depend on toughness, which depends on Y content, but why a peak?

Diffusionally Constrained Phase Selection

- How does one generate a tetragonal single phase beyond the solubility limit?
- Transformations requiring long range diffusion are constrained at low T/T_M. However, any single phase that yields a decrease in free energy relative to the parent phase can form.
- At any given T-X there is a menu of phases and a thermodynamic hierarchy.
- Menu and hierarchy change at intersection of the G-X curves ("T_0" points).



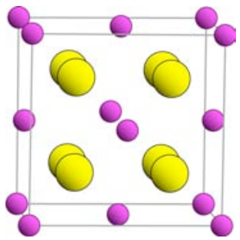
Mapping the Thermodynamic Possibilities



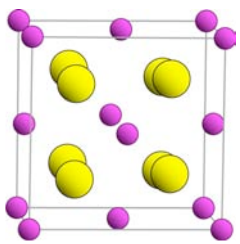
- *When all other solid phases are kinetically suppressed, the stability limit for a crystalline phase of a given composition is set by onset of partitionless melting (low kinetic barrier) i.e. $T_0^{L/s}$*
- *Phase fields and hierarchies are determined by the position of the relevant T_0 curves.*

Levi, C.G. : *Acta Materialia* **46** (3) 787-800, 1998.

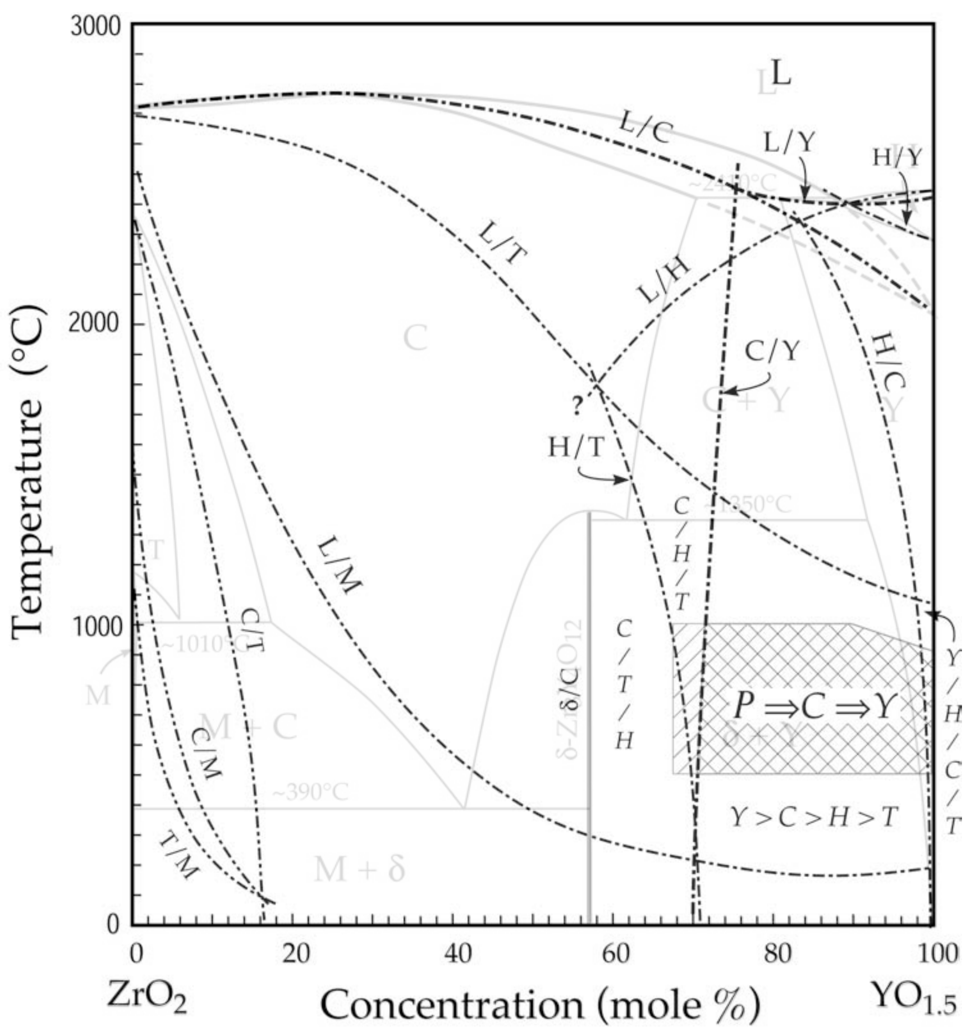
Phase Hierachies in ZrO_2-$YO_{1.5}$



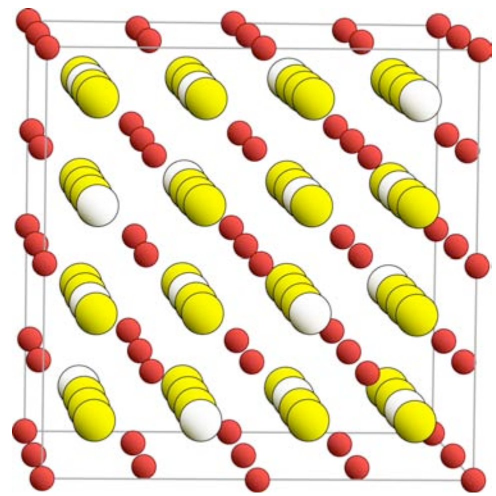
Fluorite (C)



Tetragonal Zirconia (t)

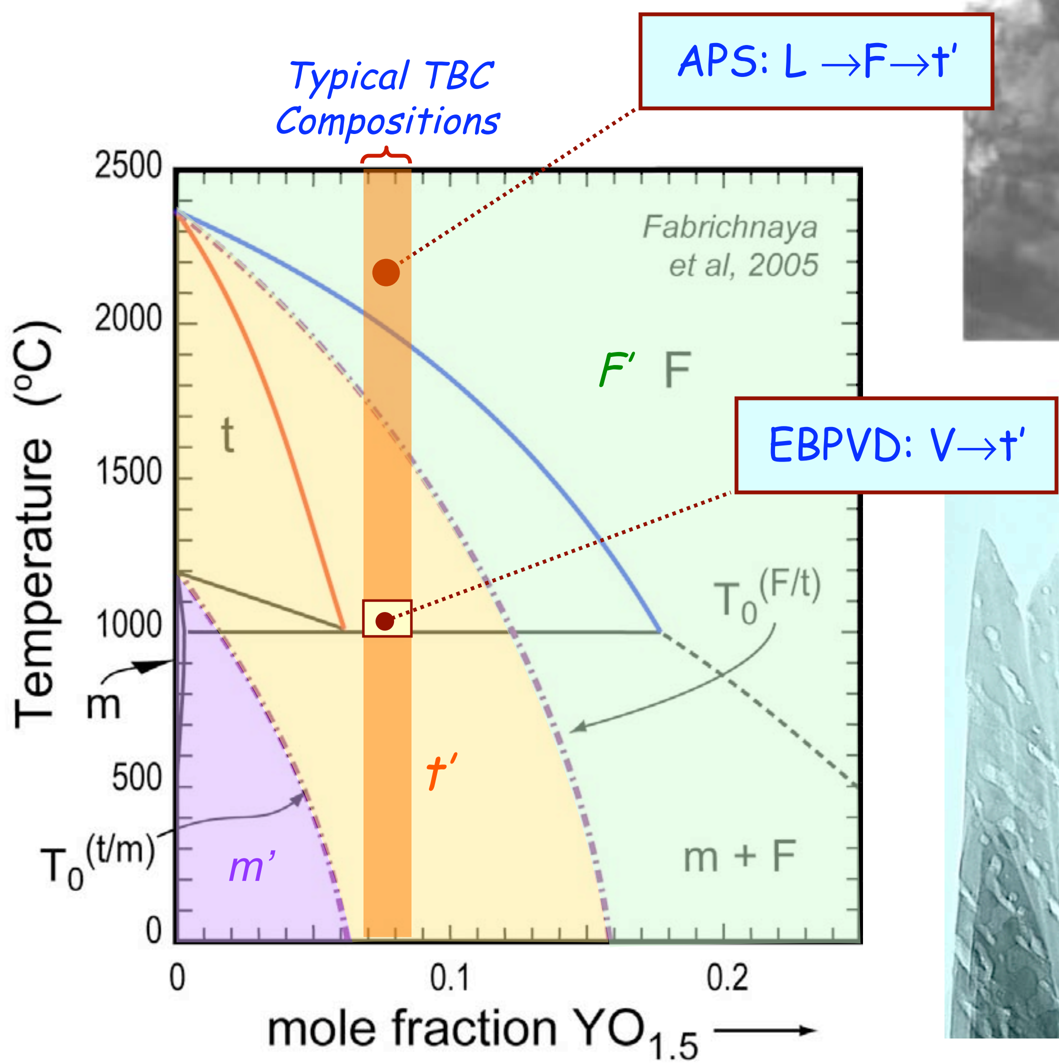


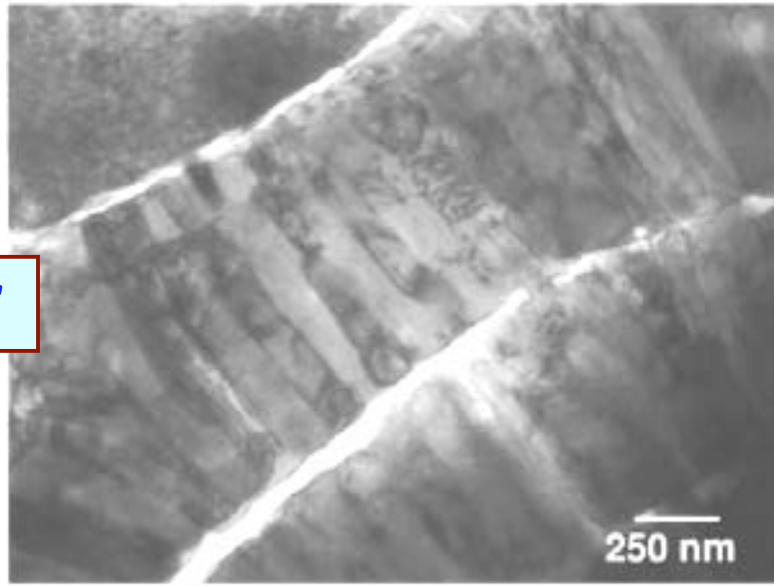
Levi, C.G. : *Acta Materialia* **46** (3) 787-800, 1998.

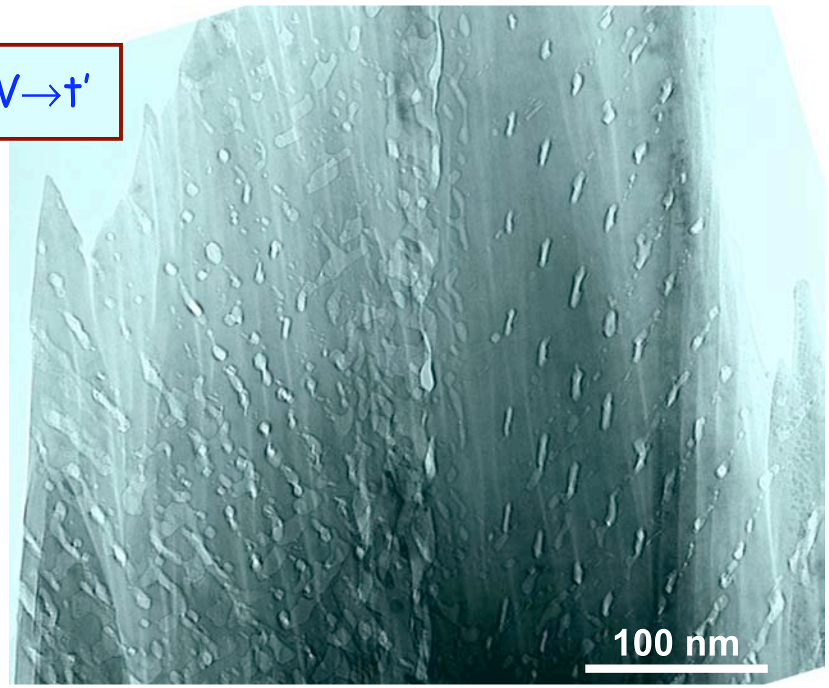


Bixbyite (Y)

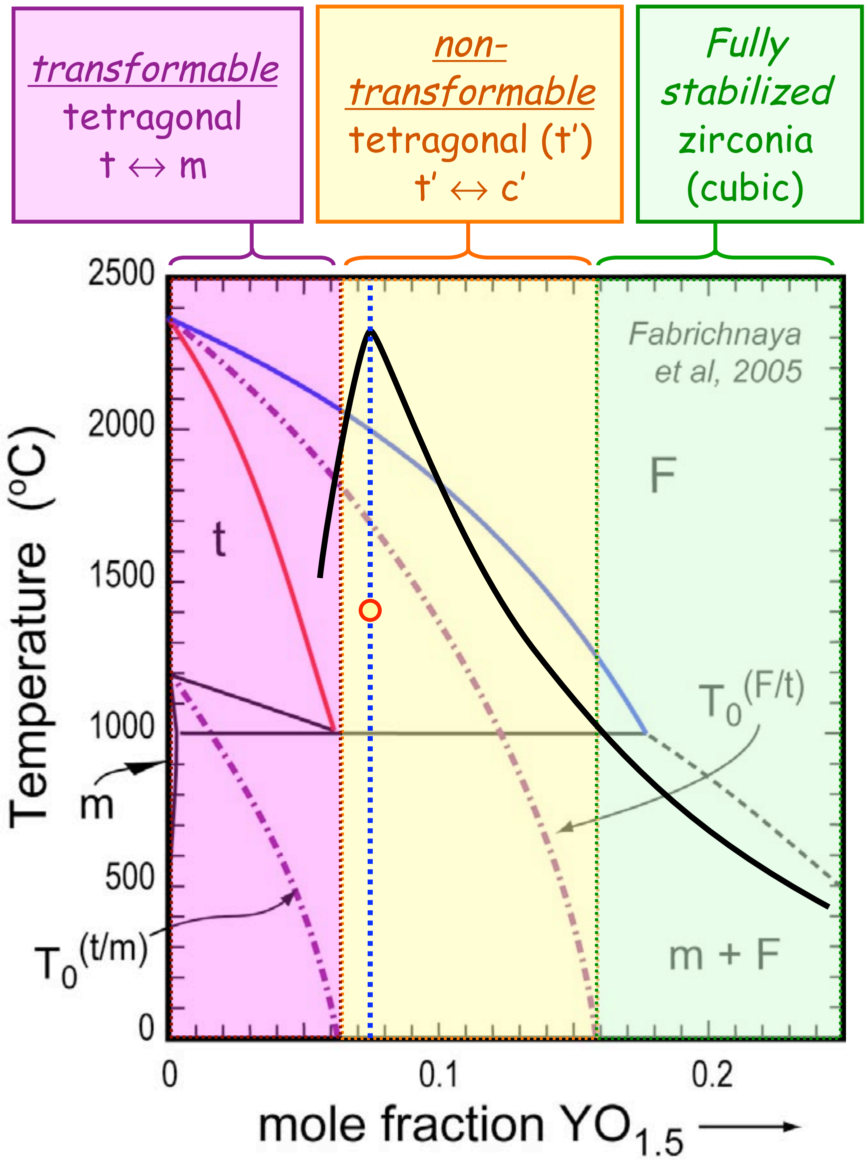
Processing effects on t' microstructure





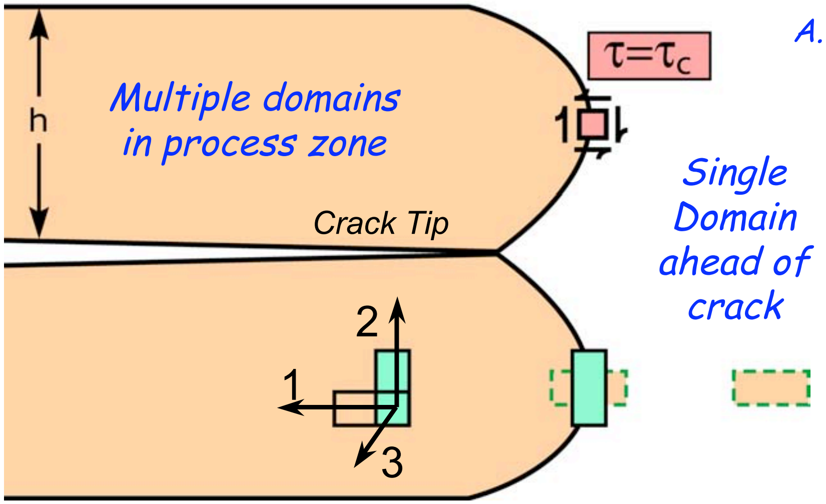


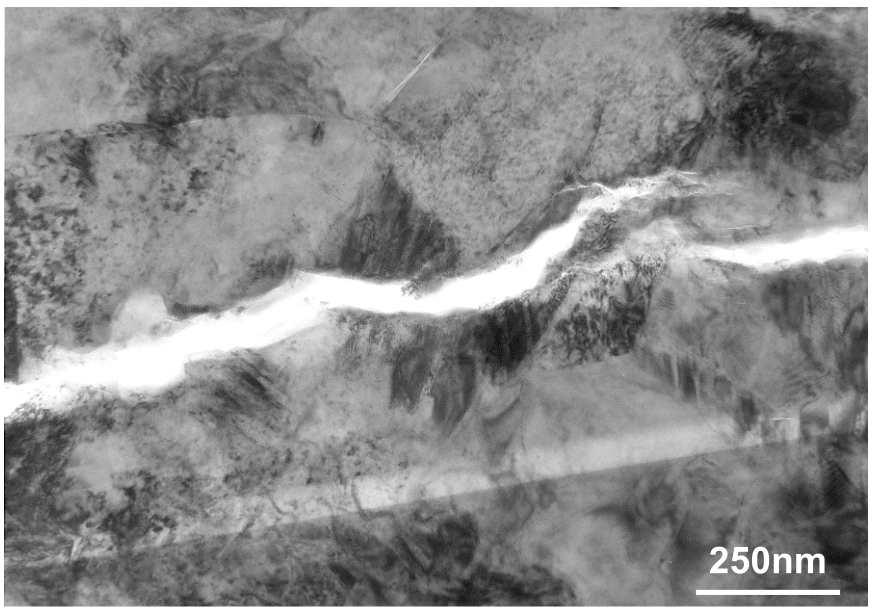
Toughness dependence on composition



- *Cubic zirconia (and pyrochlore) structures have generally low toughness. No significant toughening mechanisms available.*
- *Tetragonal compositions are much tougher. Substantial toughness available via controlled t→m transformation.*
- *Transformation toughening not operational at high temperature. "Transformability" not desirable under thermal cyclic conditions.*
- *Optimum TBC composition is tetragonal, single-phase, non-transformable ➪ t'.*

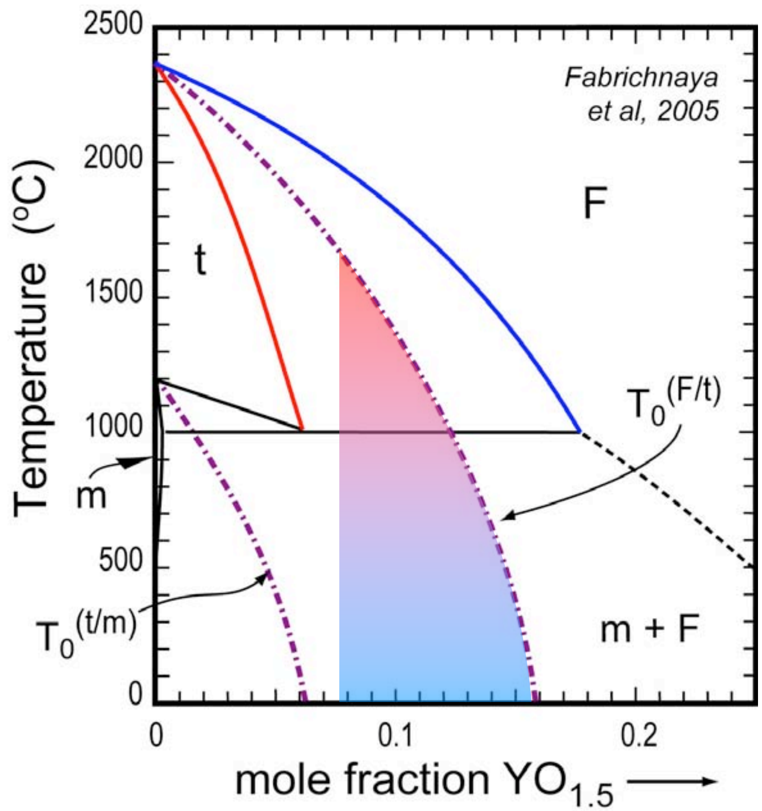
Ferroelastic Switching





Mercer et al. 2005

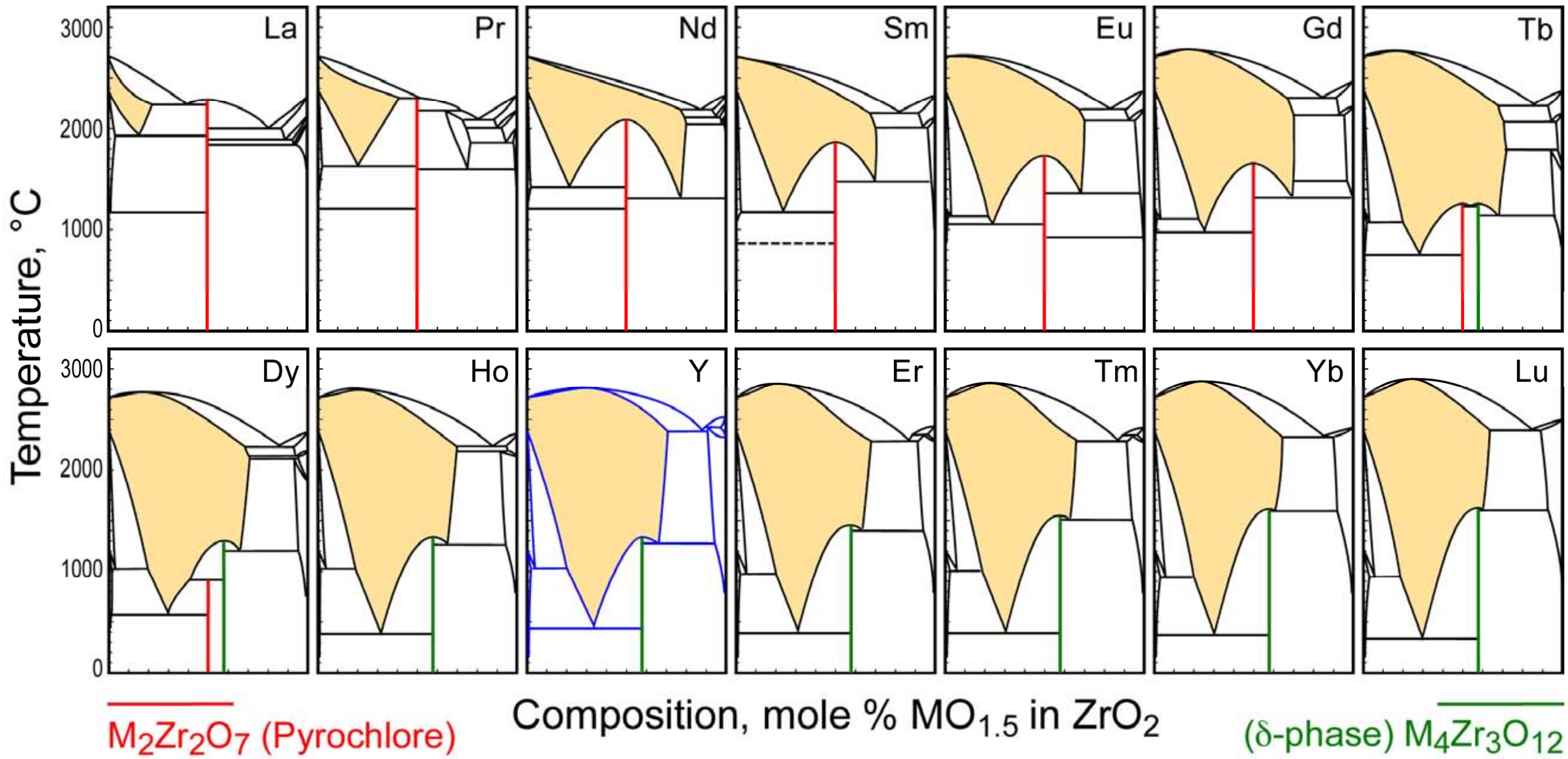
- *Proposed toughening mechanism relies on tetragonality, which vanishes as $(c, T) \Rightarrow T_0(F/t)$.*



Dopants of Interest in ZrO_2-based TBCs

Well behaved phase equilibria with increasing ionic size

Pyrochlore stability decreasing ⇒

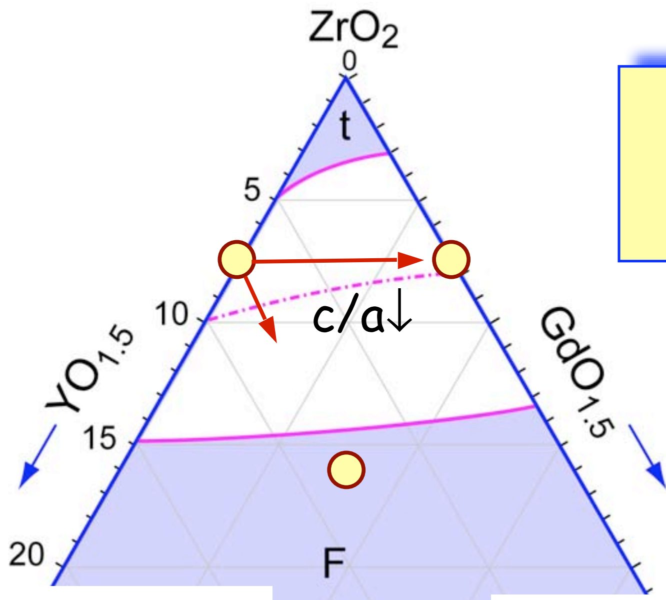


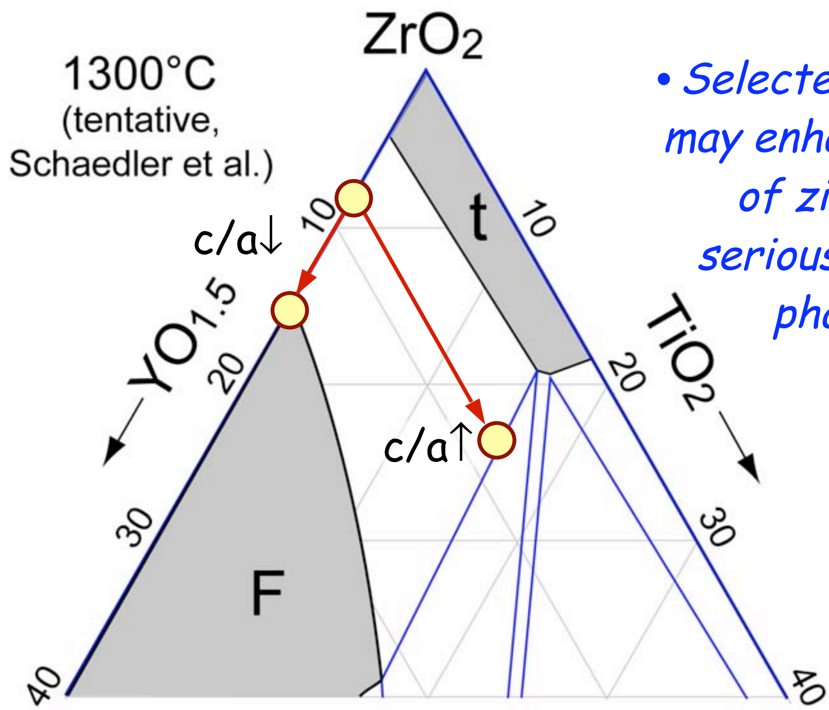
δ-phase stability increasing ⇒

Calculated diagrams, after Yokokawa et al.

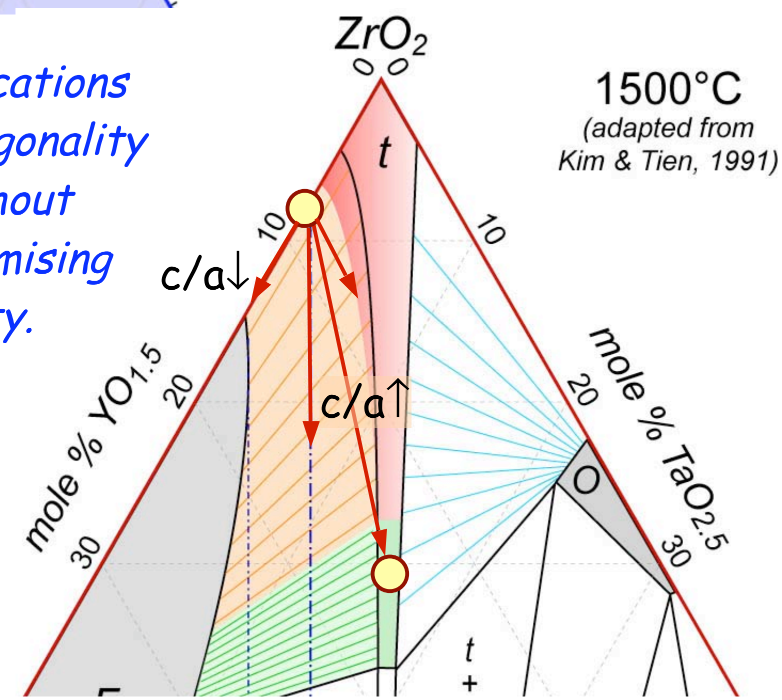
Looking for the right dopants

- *Co-doping 7YSZ with large RE cations decreases the tetragonality of the structure*



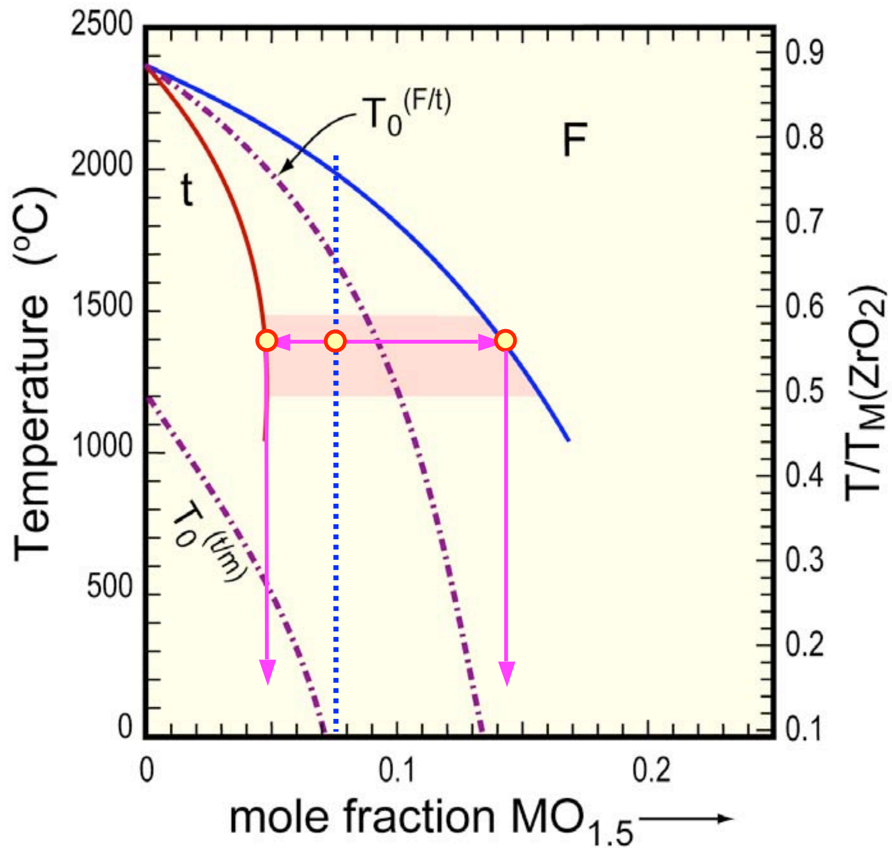


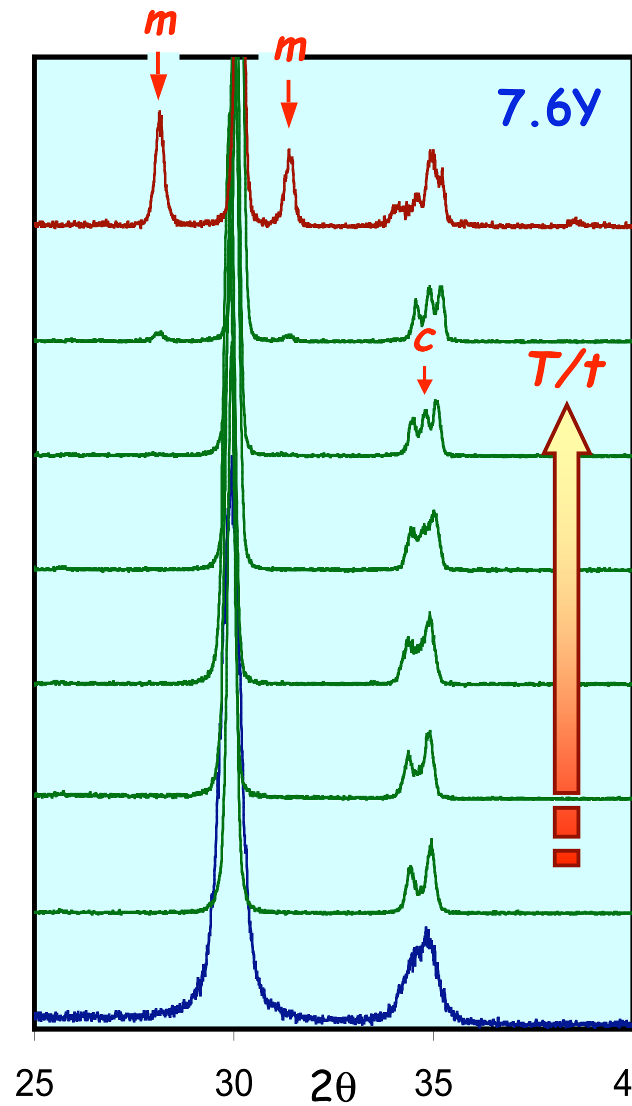
- *Selected smaller cations may enhance tetragonality of zirconia without seriously compromising phase stability.*



Phase Stability: Thermal Decomposition

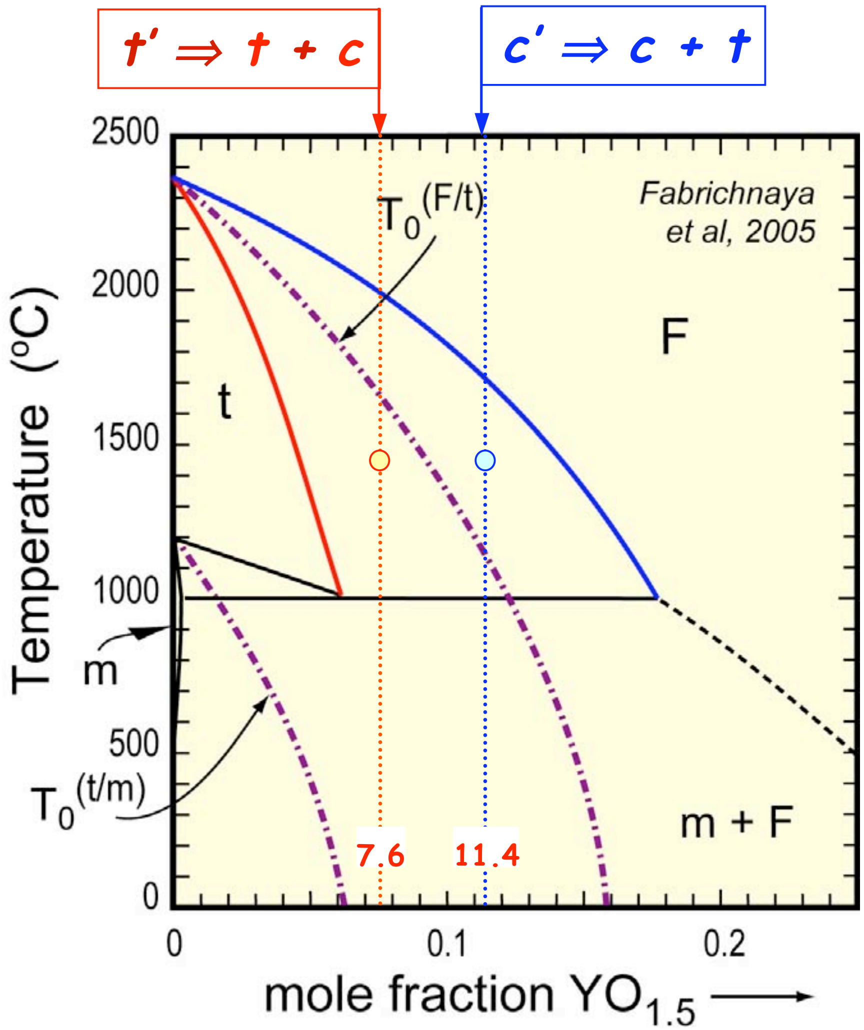
Phase (In)stability: the operating limit to t'

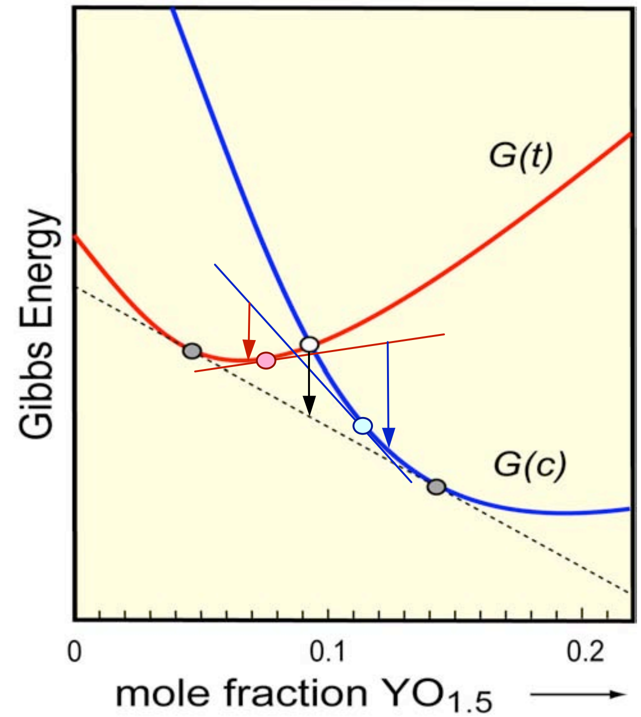




- t'-7YSZ falls in the equilibrium t + c field ➪ inherently metastable
- Increasing T activates partitioning kinetics: t' → t + c
- depleted t → m upon cooling

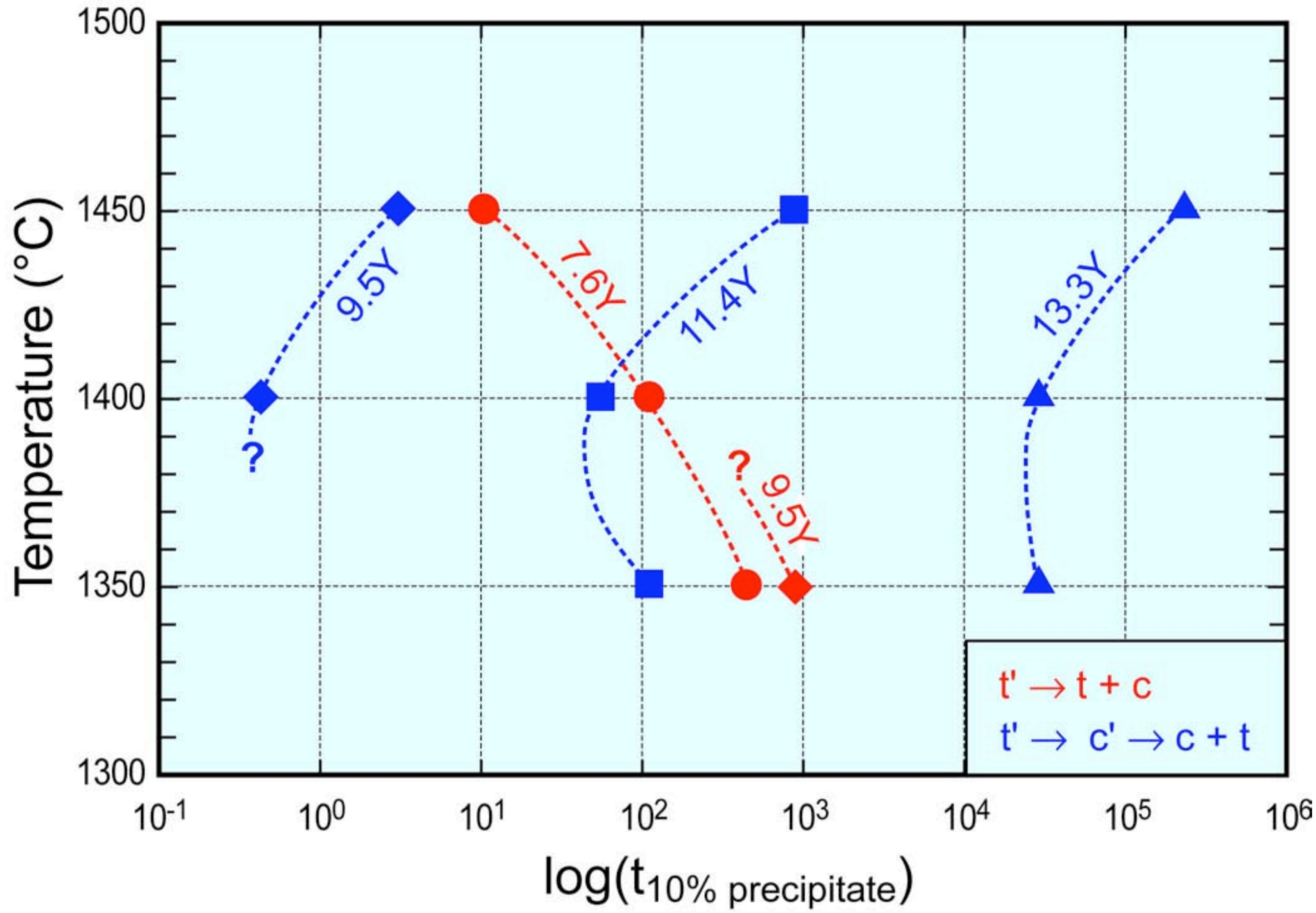
Effect of Composition on De-stabilization Path





- *Parent and precipitate phase switch with increasing %Y.*
- *Driving force scales with distance form equilibrium boundaries, peaks at $T_0(F/t)$*

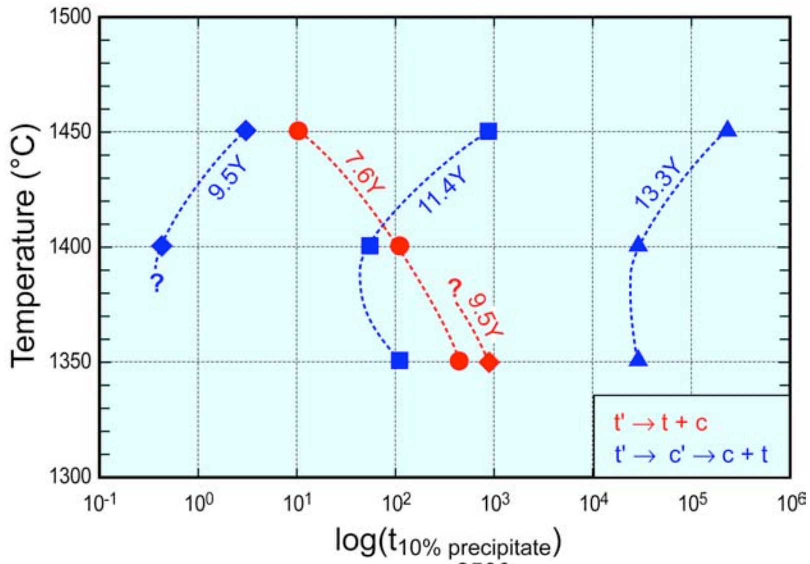
Effect of Y content on Kinetics



Precipitation follows approximately AJMK kinetics but significant differences observed depending on the decomposition path

Rebollo

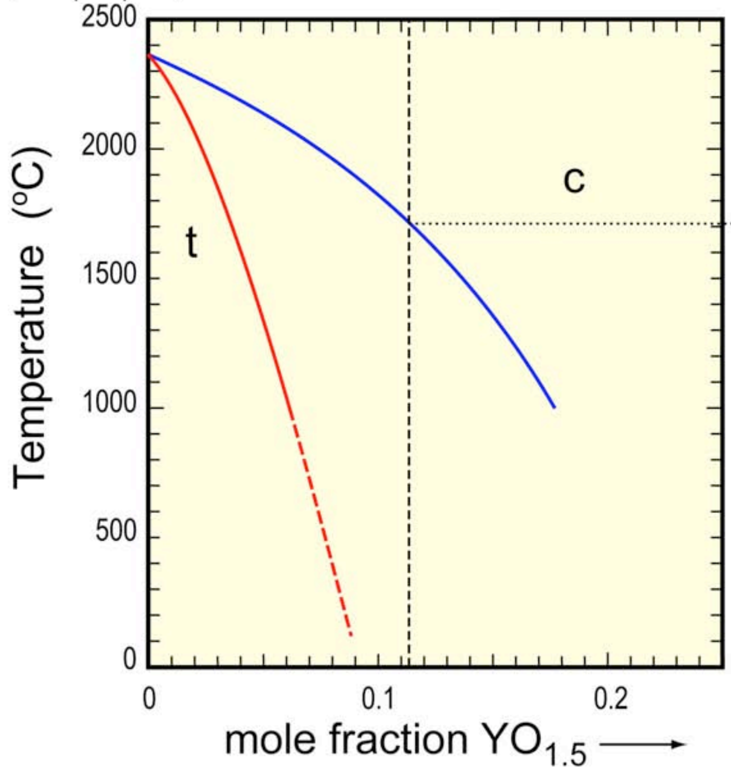
Understanding Partitioning Kinetics

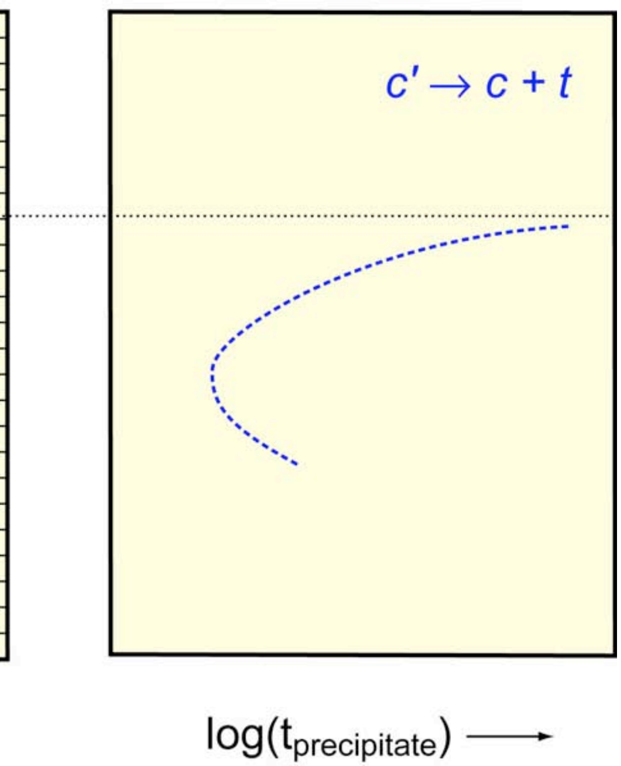


The classical case: driving force increases with decreasing temperature but diffusion becomes more sluggish, giving rise to "knee" in the TTT curve.

Compositions with "High" Y content: 11- and 13-YSZ

t' at ambient, transform diffusionlessly to c' at the heat treating temperature.





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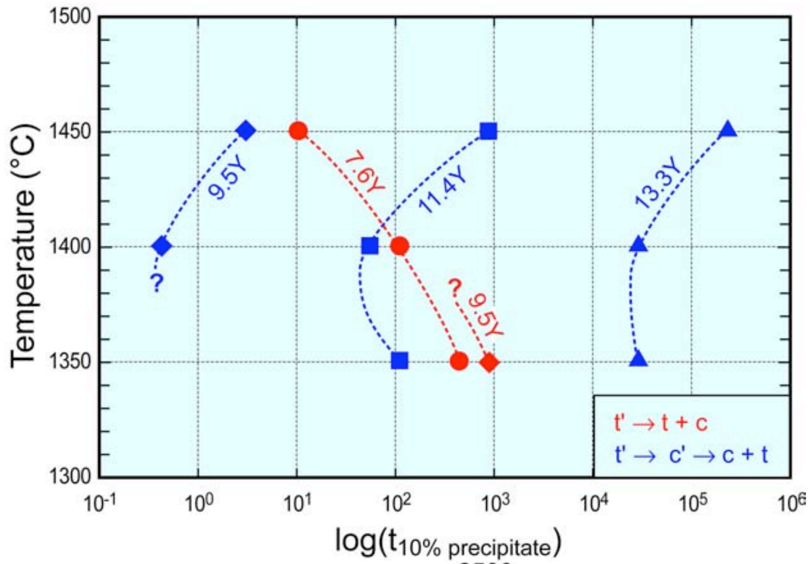
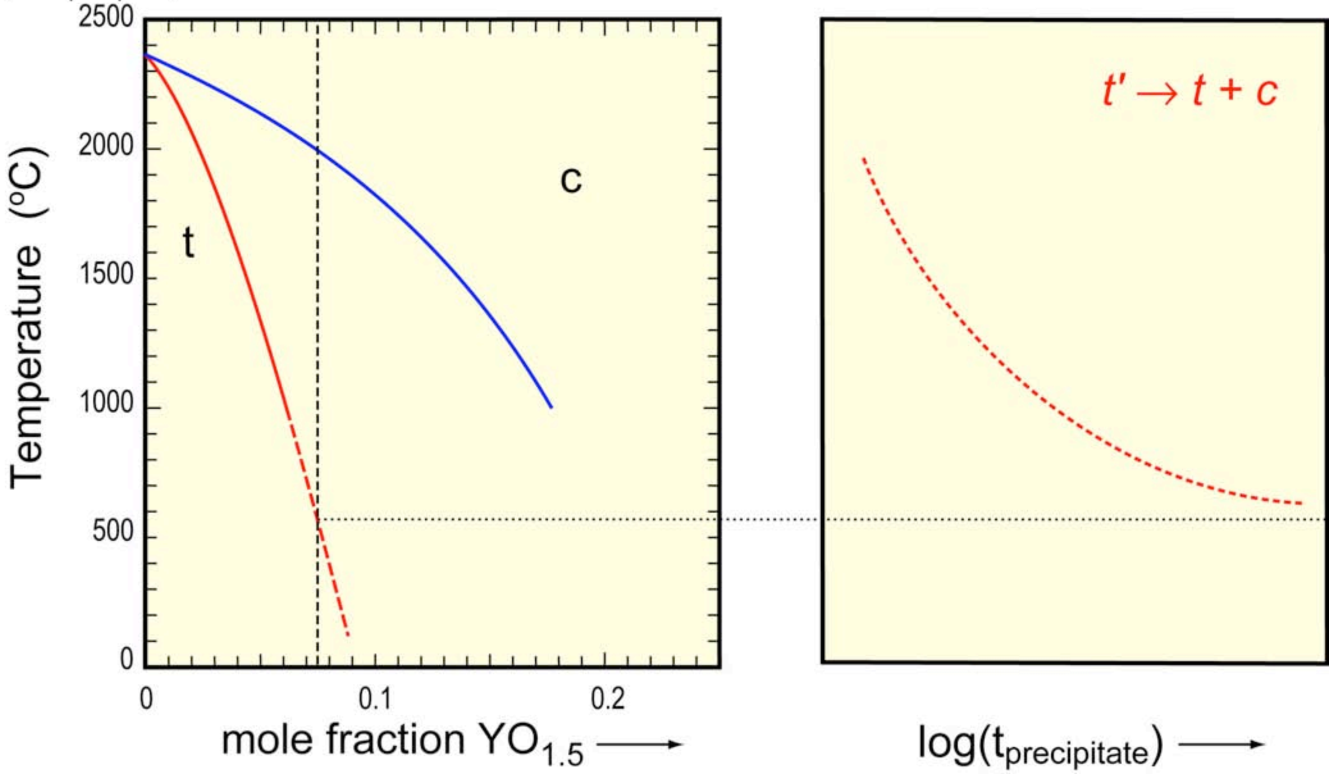


Understanding Partitioning Kinetics

The non-classical case: both driving force and diffusion kinetics increase with increasing temperature - no "knee".

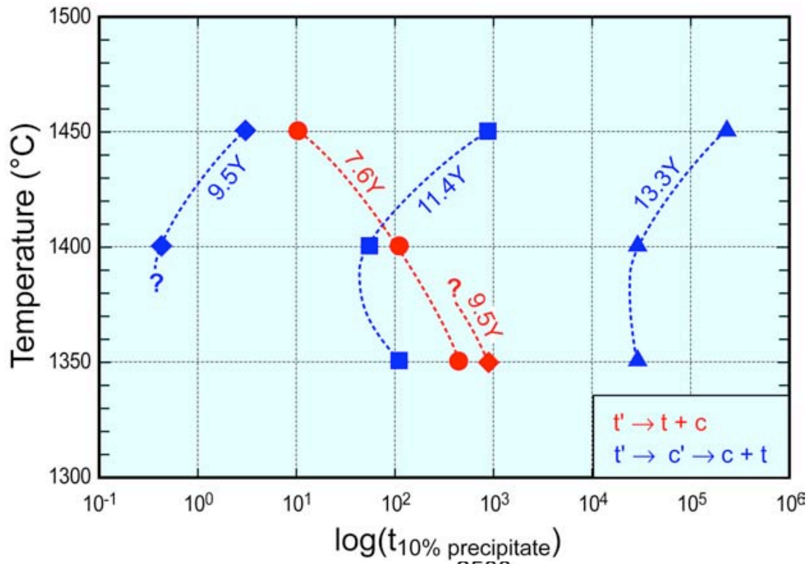
Composition with "Low" Y content: 7YSZ

t' at ambient as well as at the heat treating temperature.



Rebollo

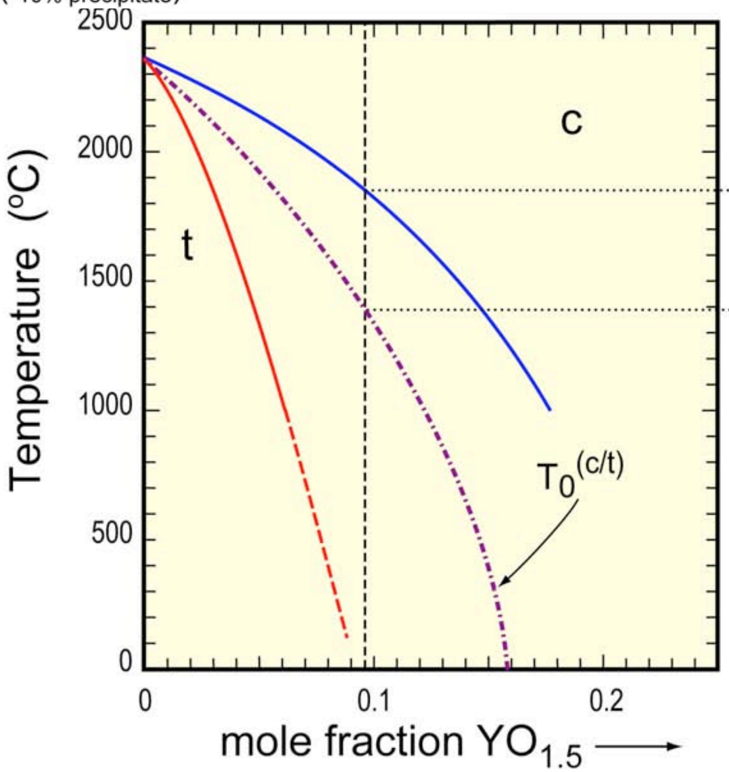
Understanding Partitioning Kinetics

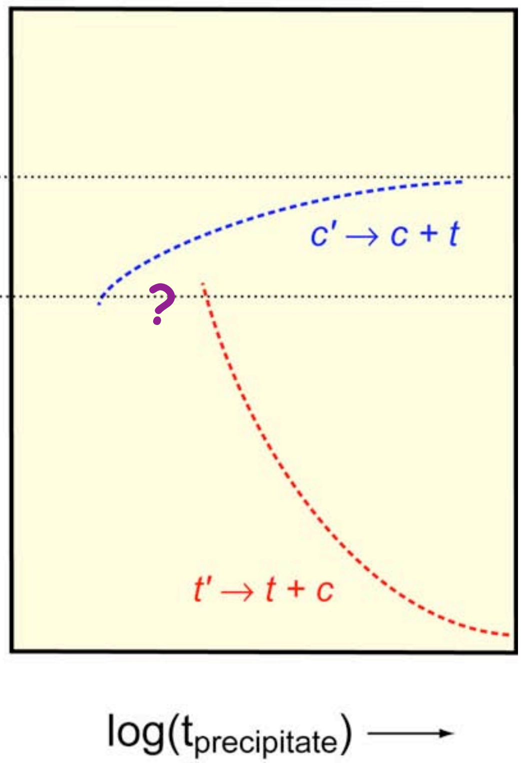


The special case: $T_0(c/t)$ is within range of heat treatment. It follows the "classical" case at $T > T_0(c/t)$ and the "non-classical at $T < T_0(c/t)$.

Composition with "Intermediate" Y content: 9YSZ

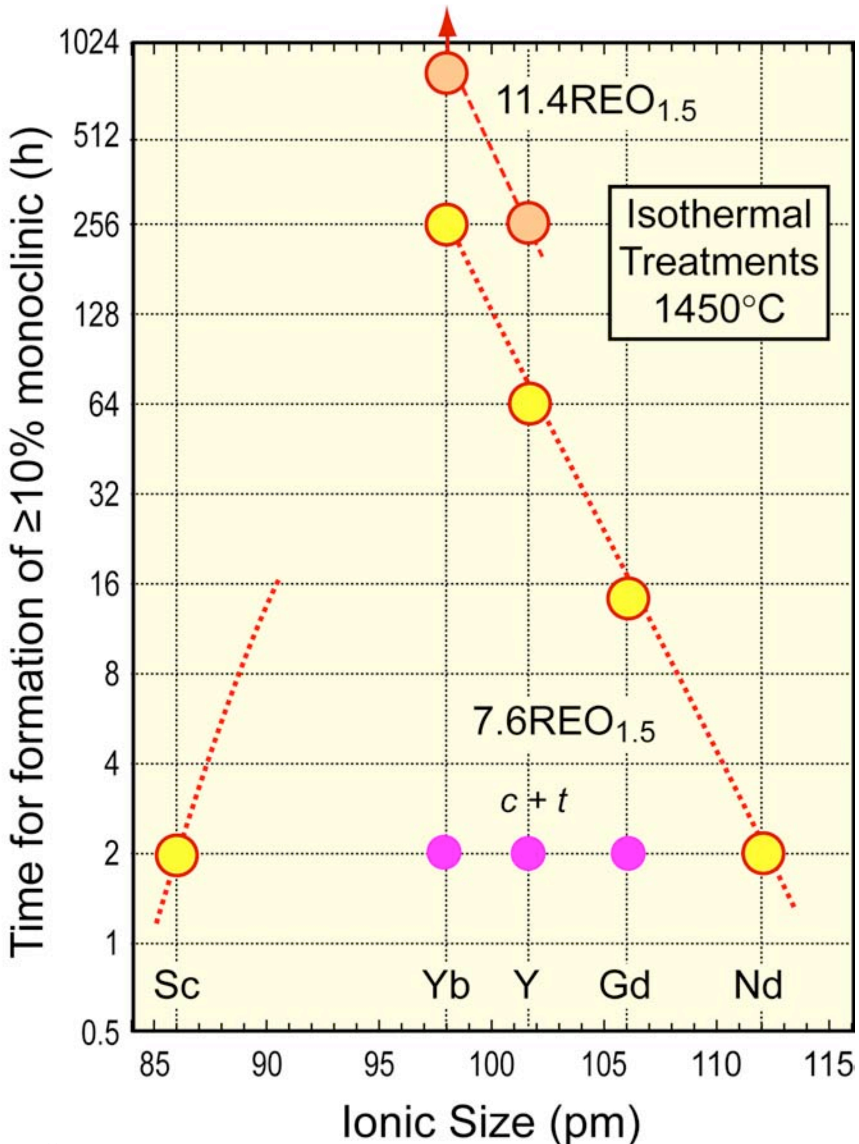
t′ below $T_0(c/t)$
c′ above $T_0(c/t)$
Possibility that both mechanisms operate in the vicinity of $T_0(c/t)$





Rebollo

Effect of Cation Substitution

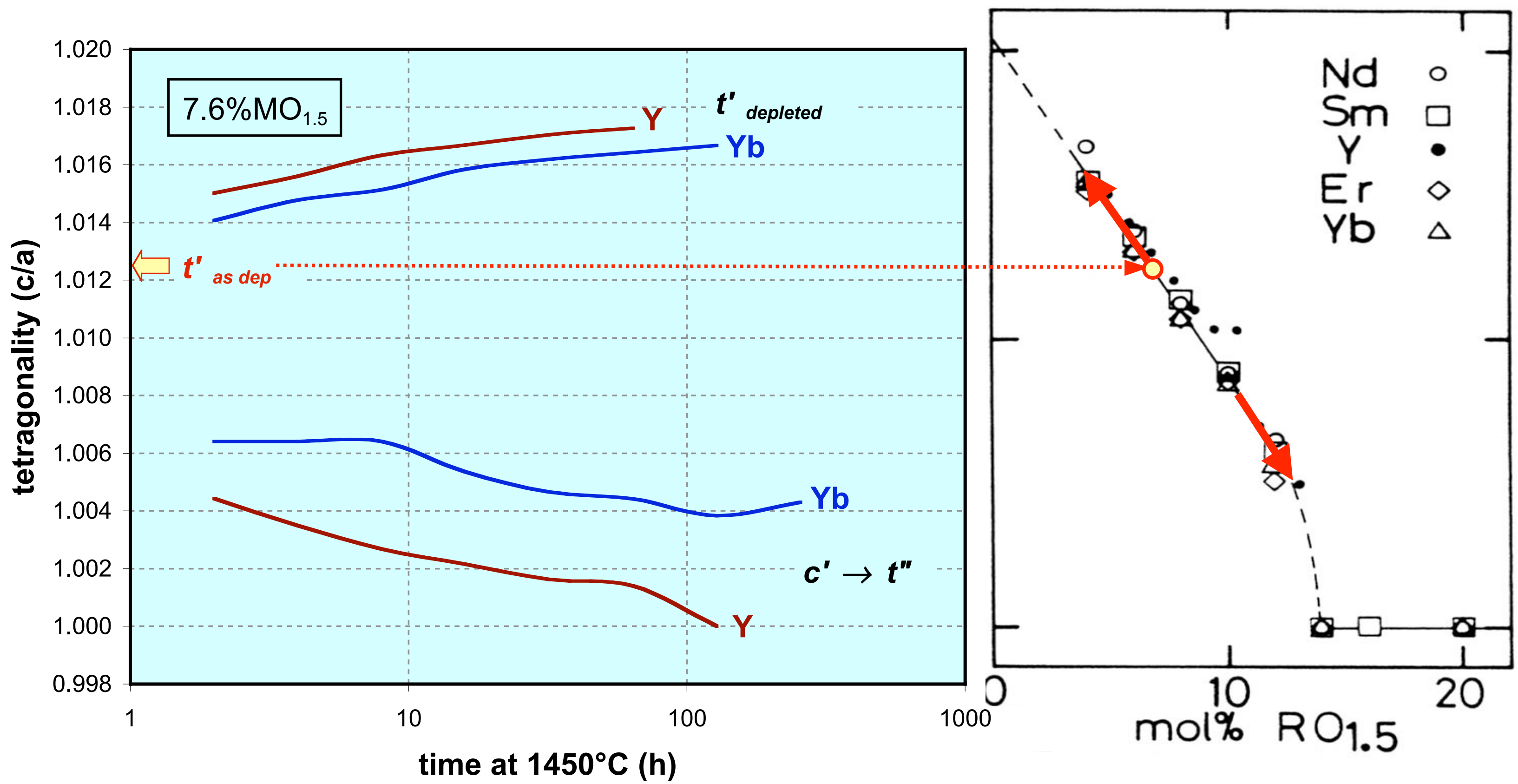


Rebollo

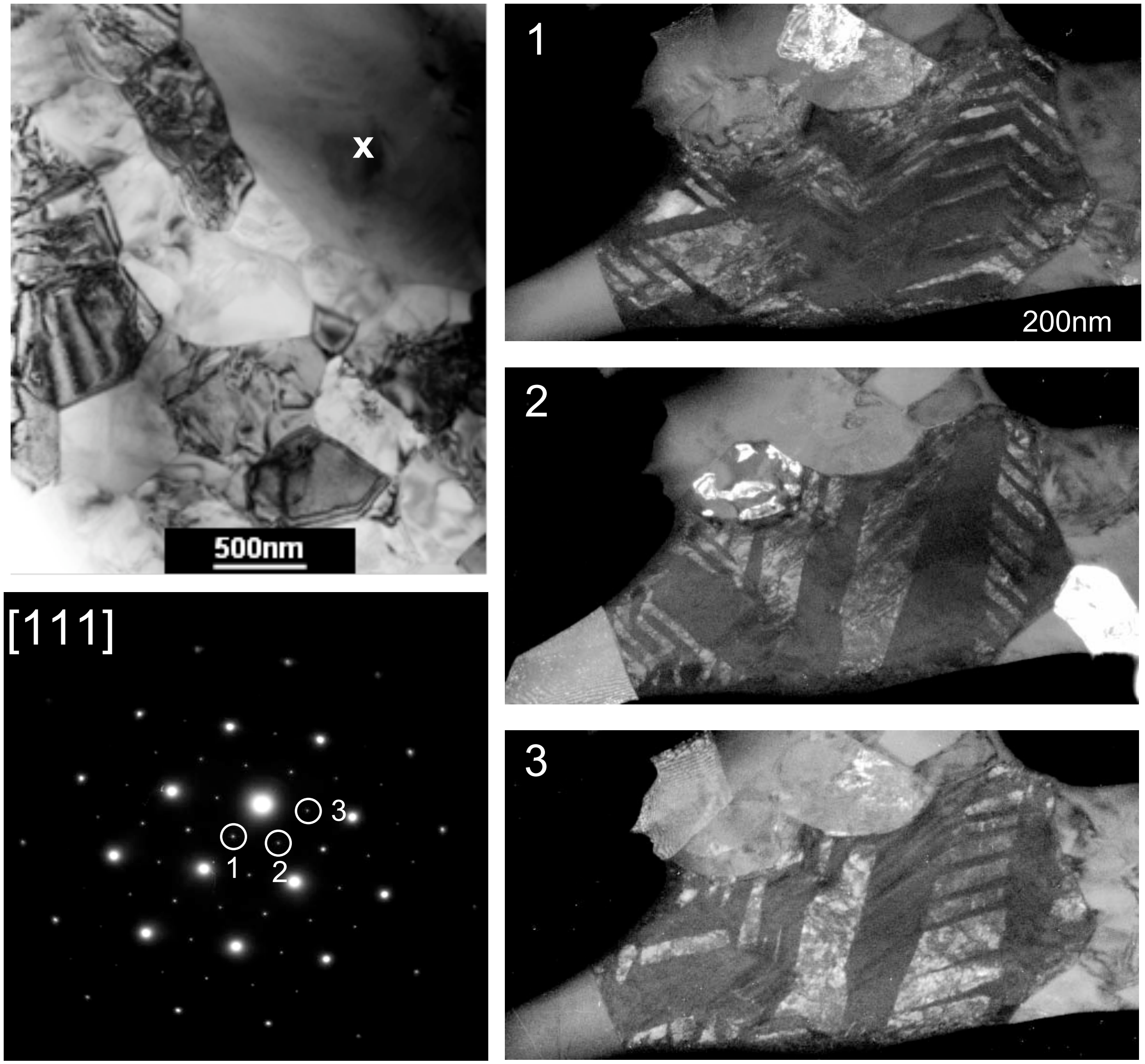
- *Comparative kinetic study using isothermal treatments at 1350, 1400 and 1450°C.*
- *Well behaved trend showing substantial effects of ionic size and concentration.*
- *t′ can exhibit early partial decomposition but remain "non-transformable" for much longer periods of time.*
- *Monoclinic can further evolve isothermally at ambient temperature (cf. Lughi and Clarke).*

Evolution of Phase Compositions

- *Gradual depletion from t′ or c′*
- *Precipitate composition evolves over time*



Rebollo, Gandhi

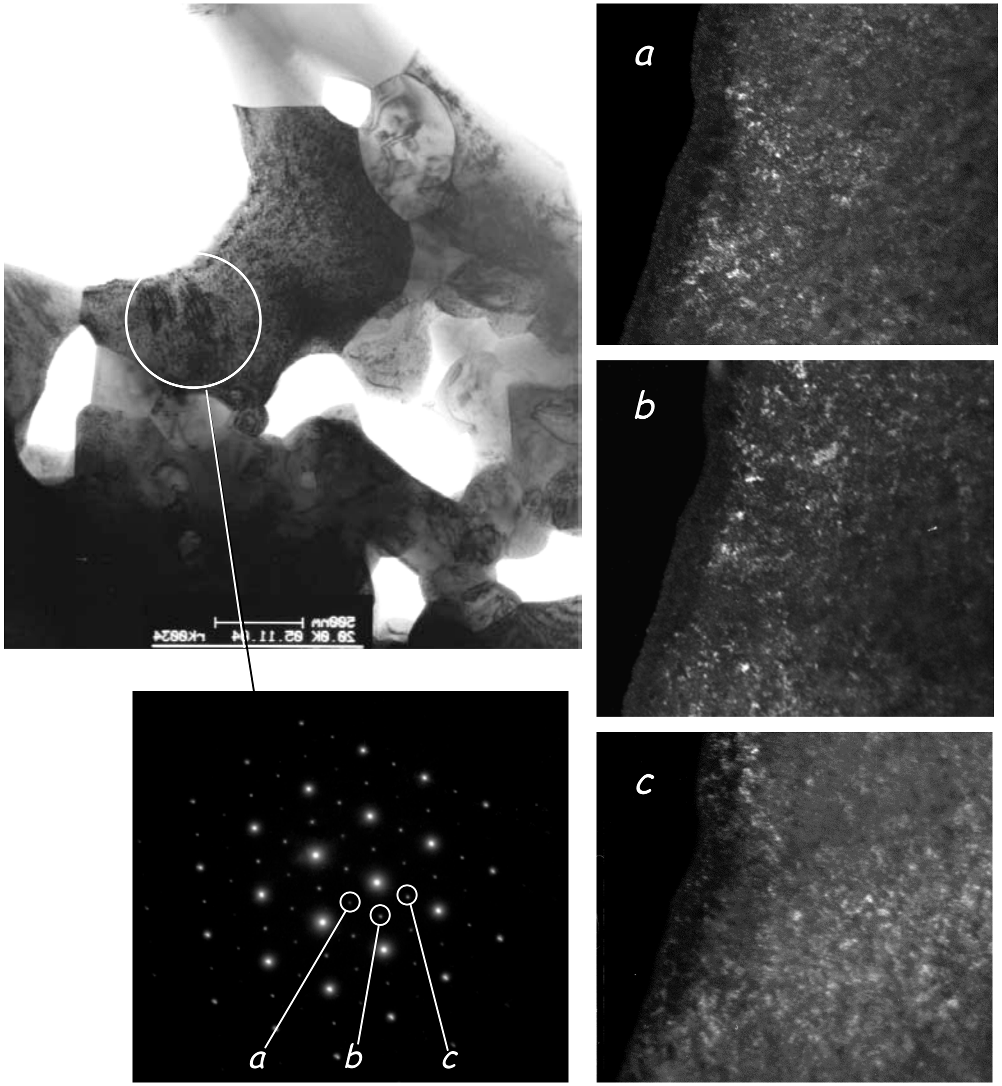


Displacive Transformation in 7YbSZ after 32h at 1450°C

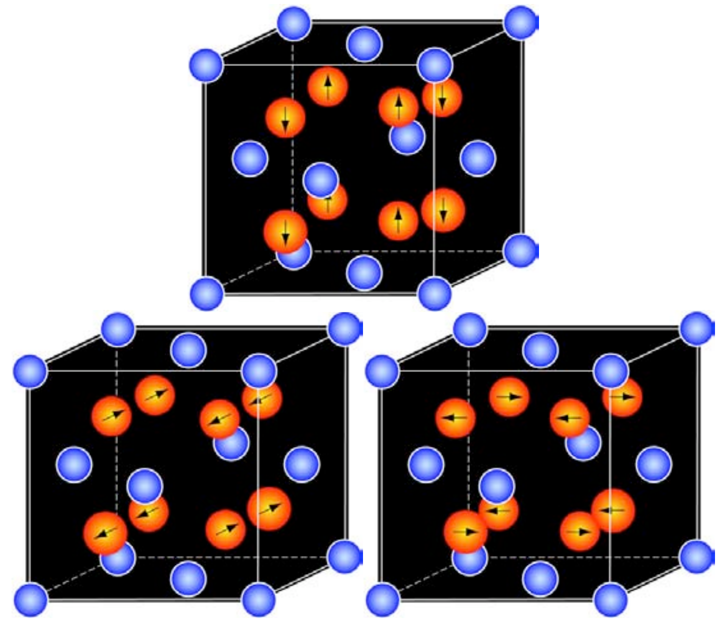
Tetragonal variants result from shear transformation along equivalent crystallographic planes in the parent cubic structure

Cairney and Rebollo, 2004

7.6Y after 16h at 1450°C



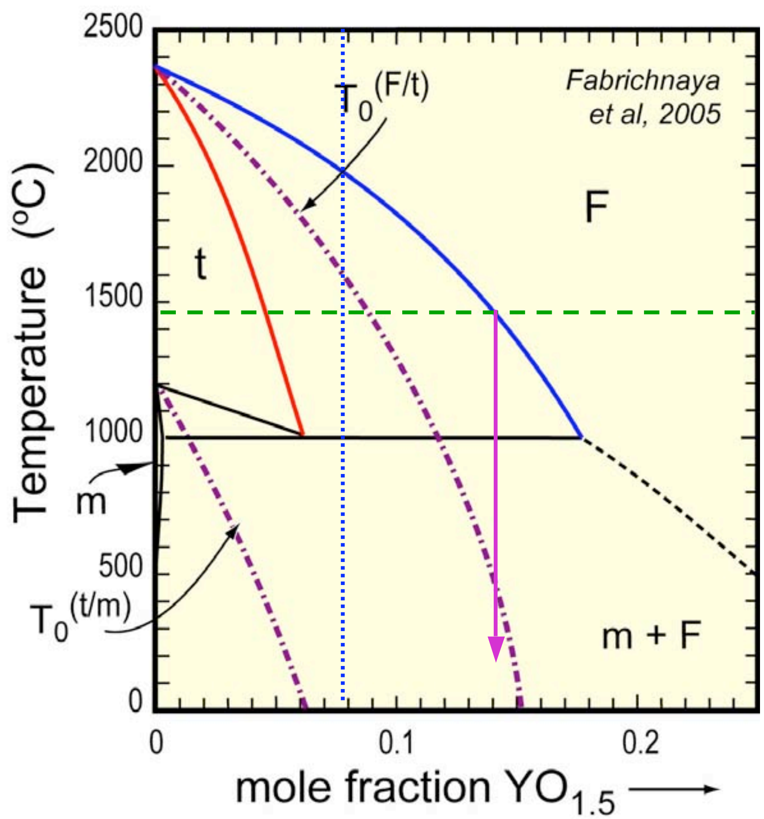
Transformation of grains that are cubic (Y-rich) at high temperature yields 3 tetragonal variants

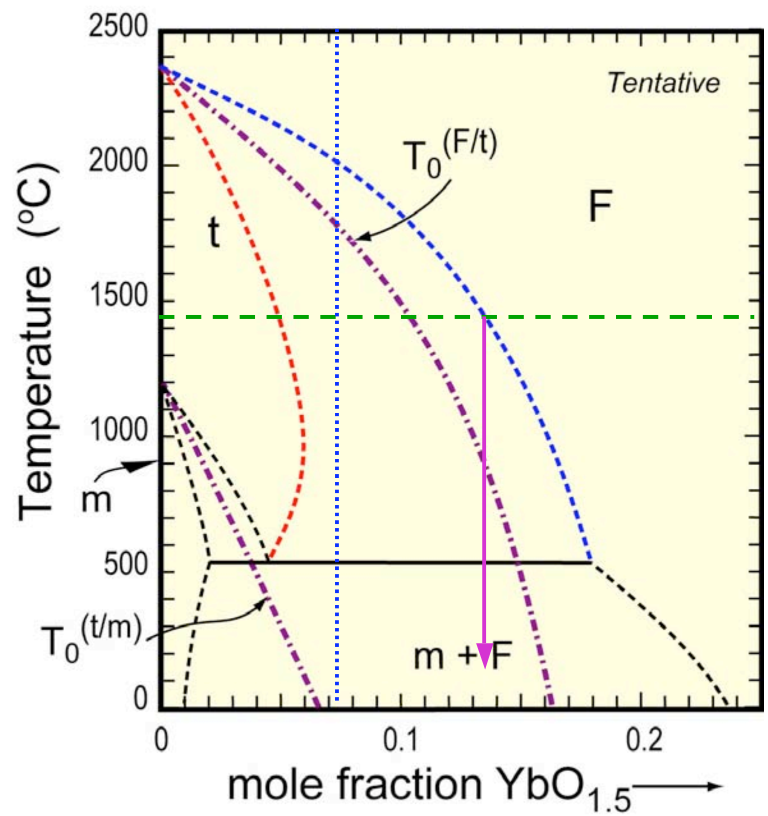


Postulate: Variants result from ordering of anion displacements in the characteristic tetragonal pattern along each of the 3 cubic directions ⇨ t″

Cairney and Rebollo, 2004

Thermodynamic Effects: Y v. Yb





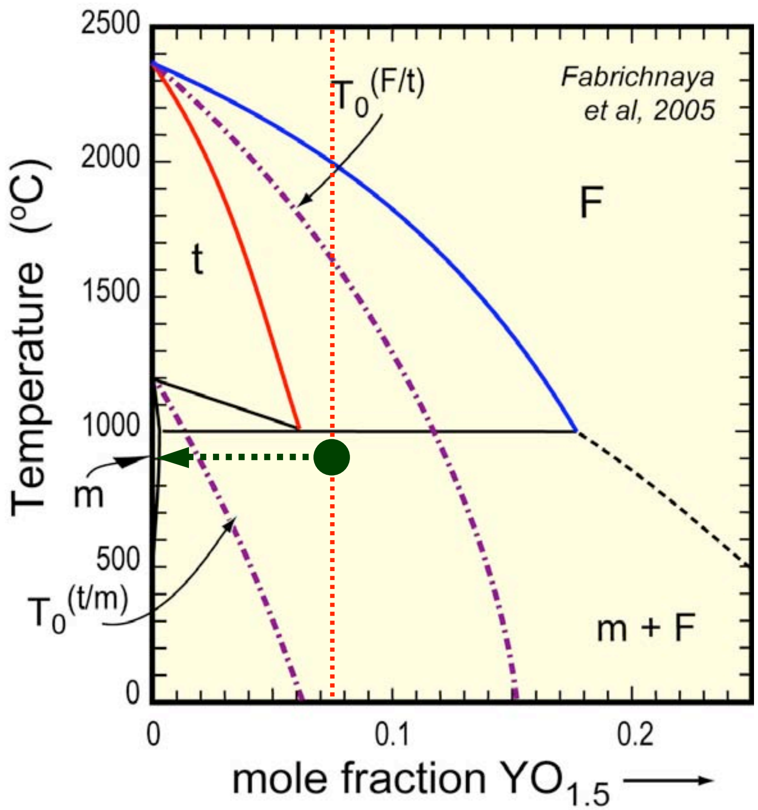
- *Evolution of twinned t′ microstructures in Yb but not in Y*
  ↪ *suggests higher $T_0(T/F)$ for Yb compared with Y.*

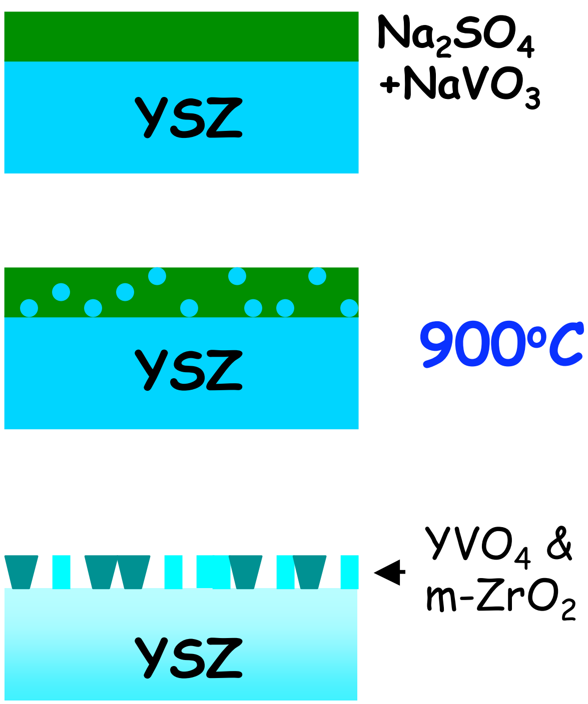
Rebollo

Chemically assisted de-stabilization of t'

Low Temperature De-stabilization of t' by S/V

$$t'\text{-}(Zr_{1-x}Y_x)O_{2-x/2} + (x/2)V_2O_5(\text{melt}) \Rightarrow xYVO_4 + (1-x)m\text{-}ZrO_2$$



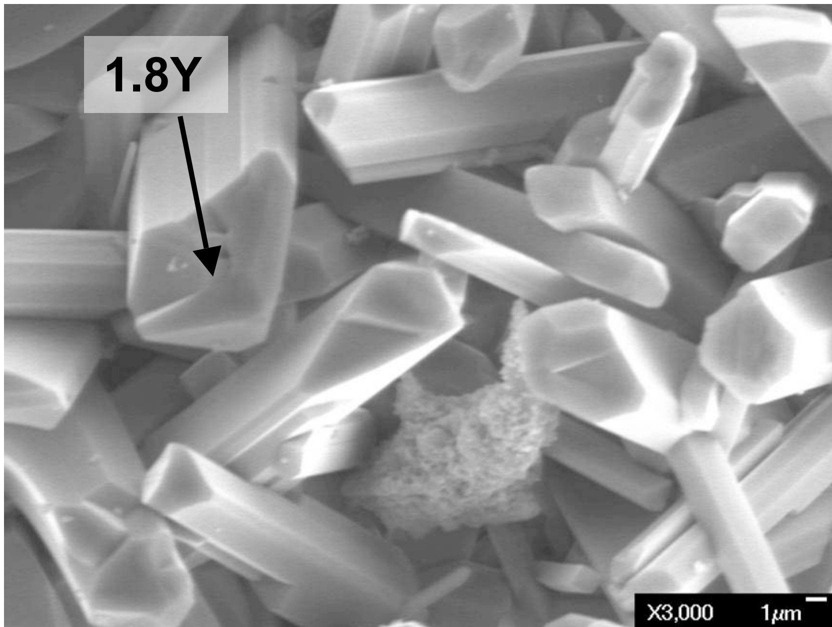


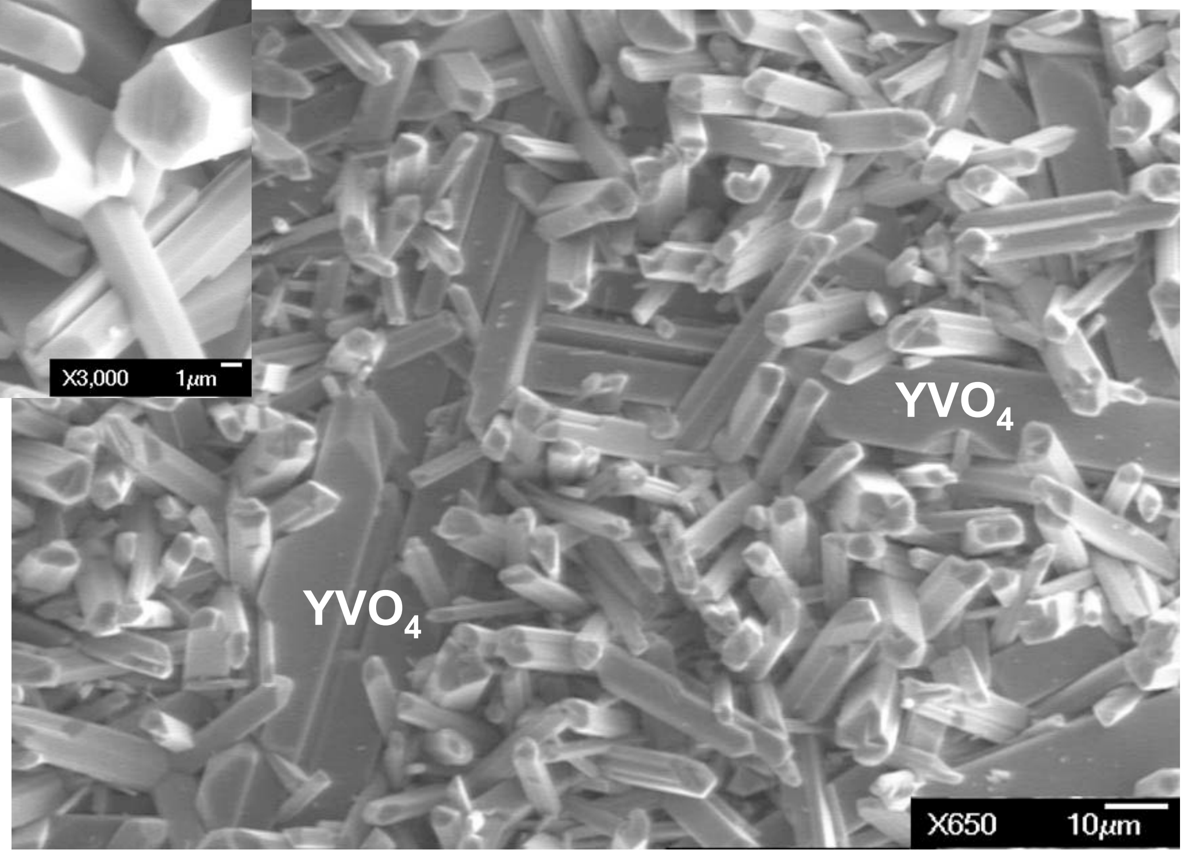
YVO_4 and monoclinic ZrO_2 precipitate directly from the melt.

F. Pitek

Vanadate attack on 7YSZ

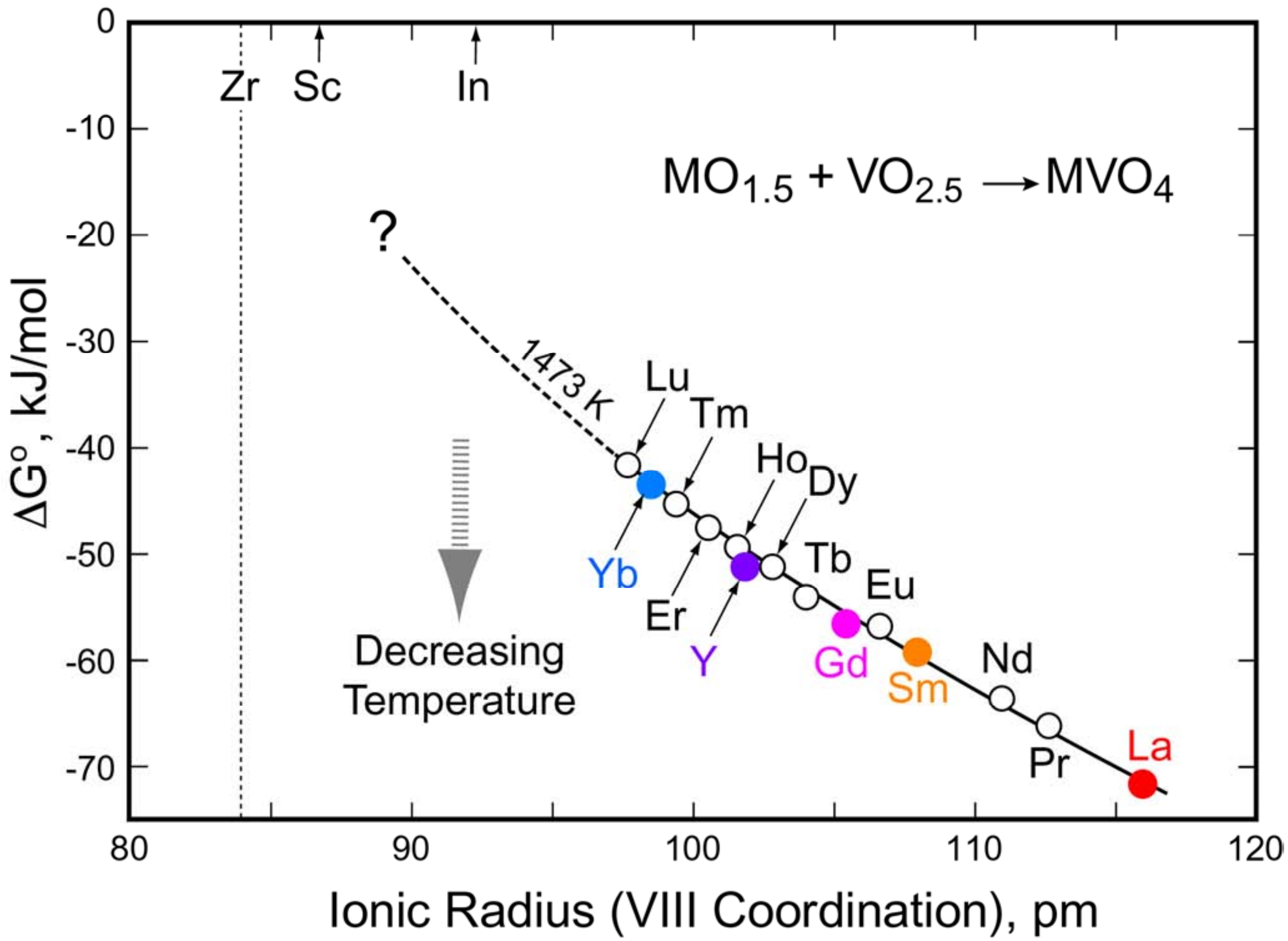
Molten 70:30 Sulfate:Vanadate
25-35mg/cm^2, 100 h at 900°C in Air
25 h cycles with salt replenishment





- *Precipitation of YVO_4 and m-ZrO_2 crystals on the surface.*
- *Extensive spallation after 100 h.*

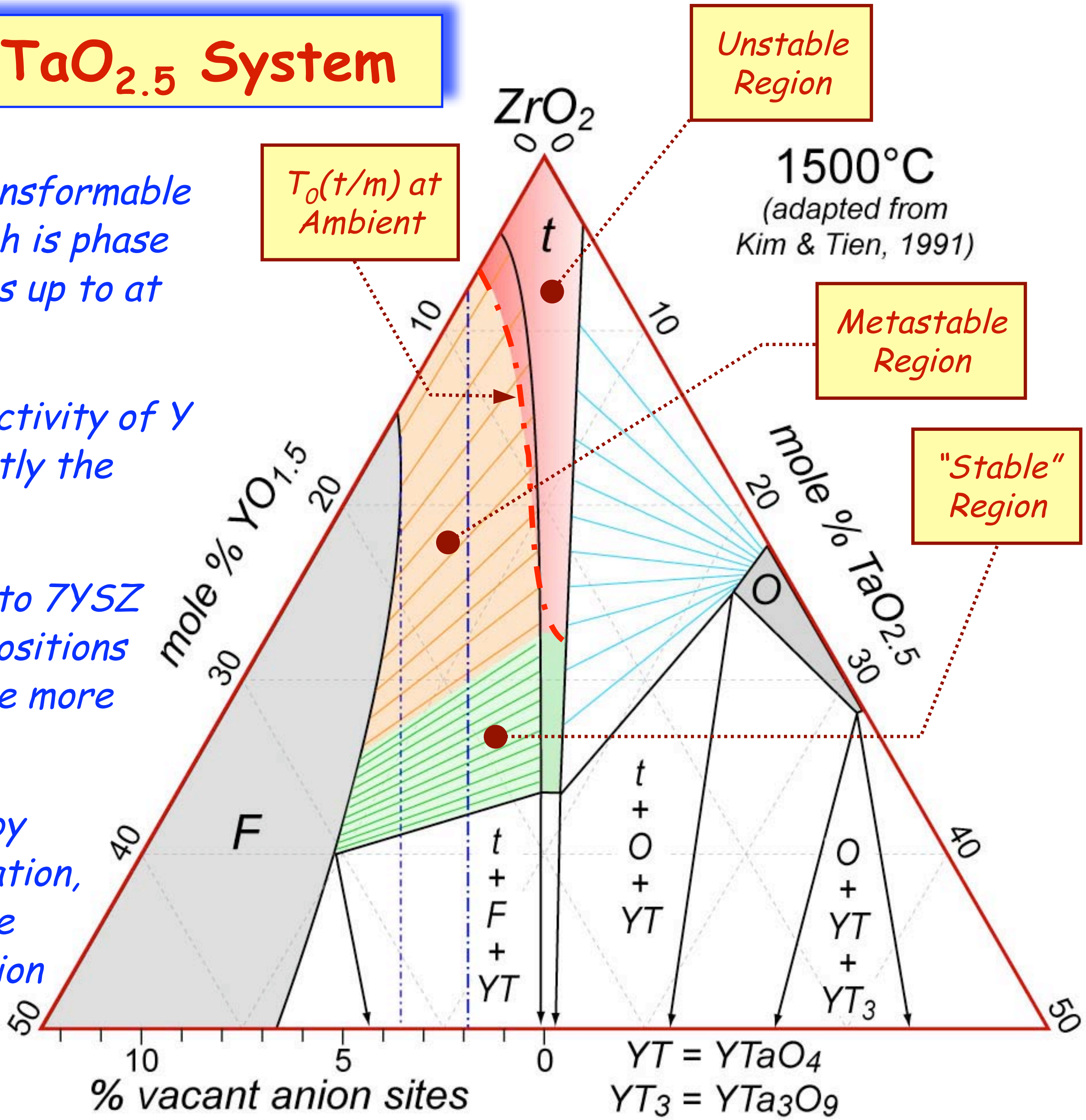
Vanadate formation with REOs



- *All rare earth oxides of interest as dopants/stabilizers in novel TBCs susceptible to attack by vanadate-bearing molten deposits.*

ZrO_2-$YO_{1.5}$-$TaO_{2.5}$ System

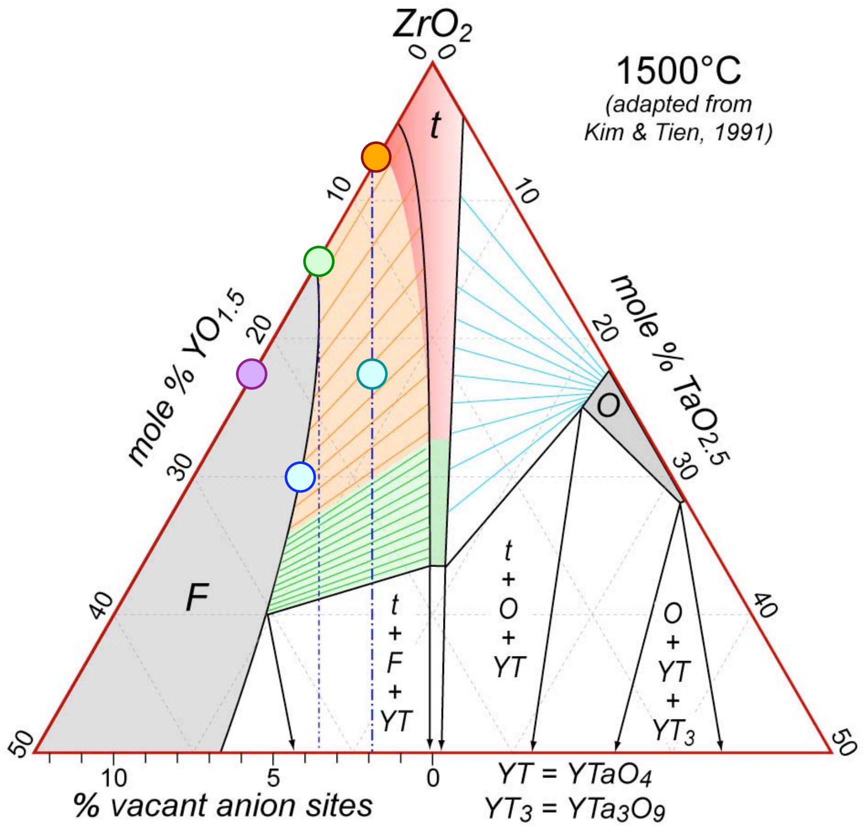
- System with a non-transformable tetragonal region which is phase stable at temperatures up to at least 1500°C .
- Ta would reduce the activity of Y in YSZ, and consequently the reaction rate.
- Simple addition of Ta to 7YSZ de-stabilizes t'. Compositions in the "safe" region are more desirable.
- If mechanism occurs by dissolution-reprecipitation, what is the path of the evolving TBC composition over time?

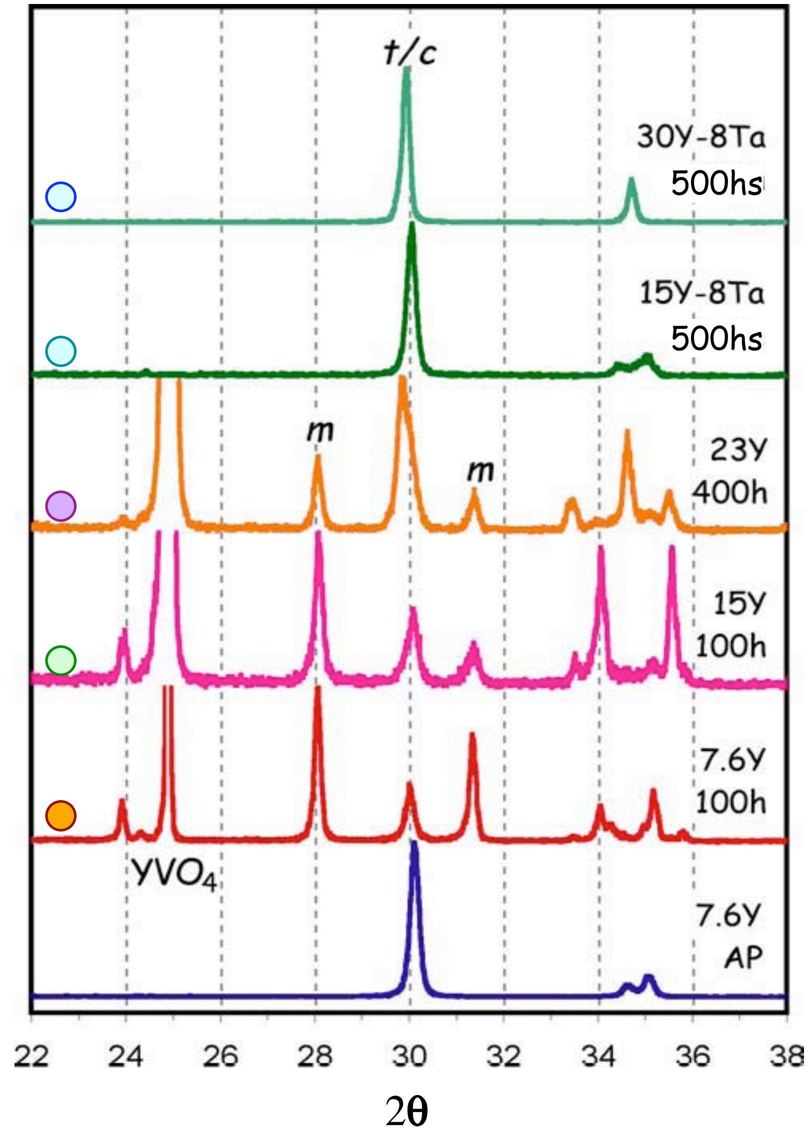


Corrosion Studies

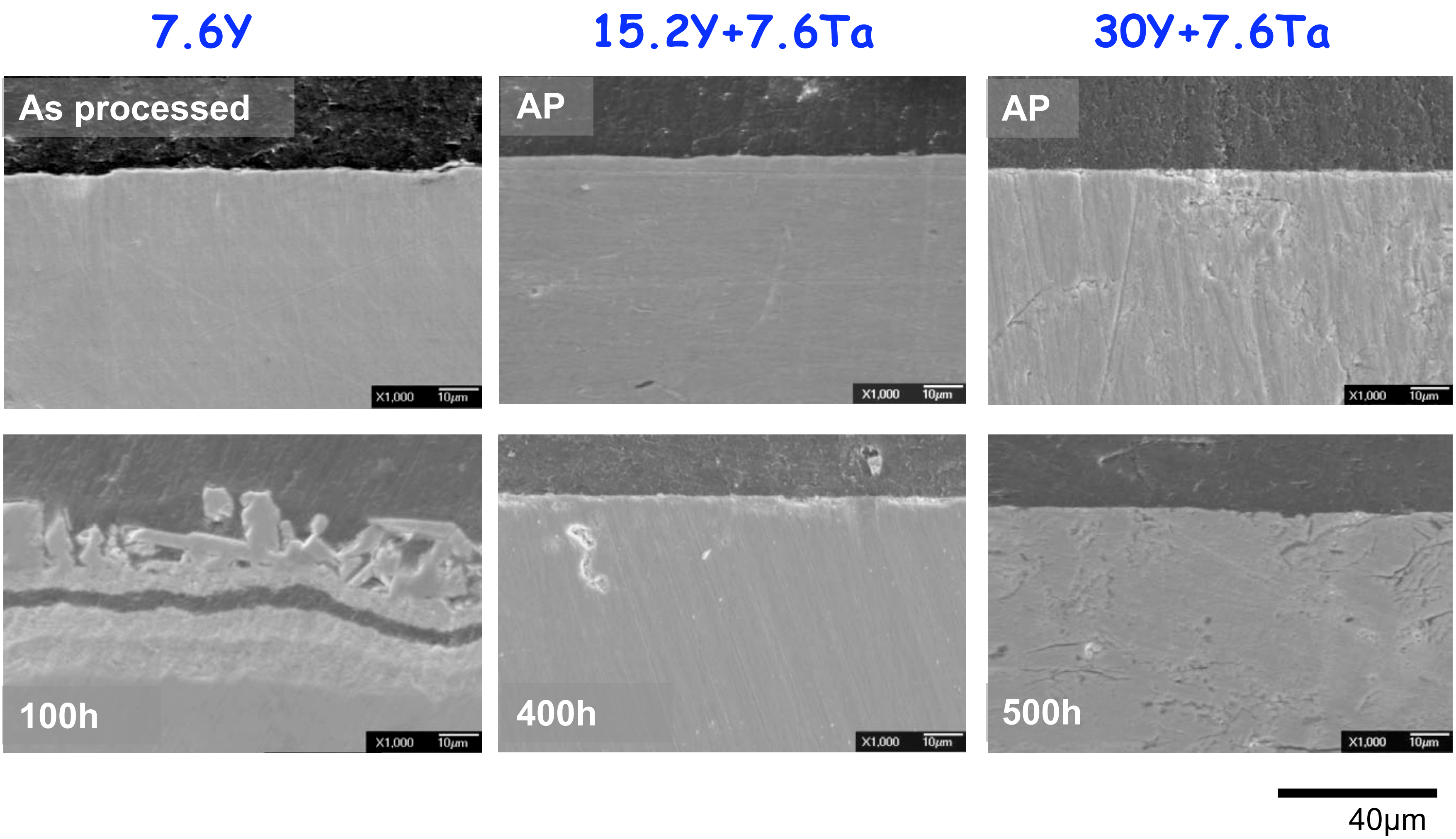
900C, 70S:30V
30±5 mg/cm^2

- *All Y compositions showed sign of de-stabilization, whereas the Ta co-doped materials revealed no evidence of attack.*





Comparison of Cross Sections

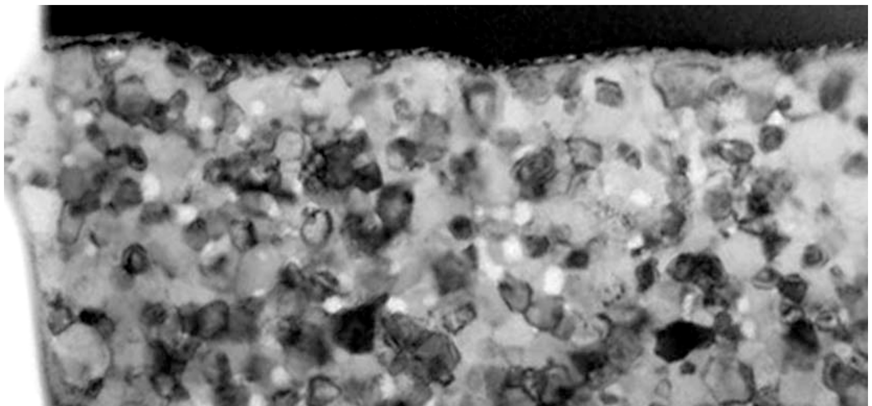


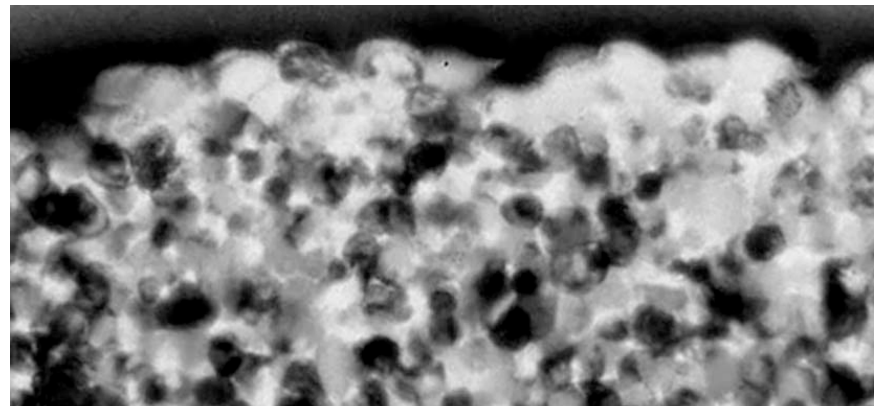
Pitek and Gilbert

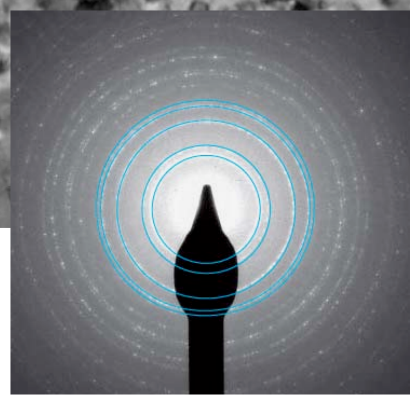
TEM Analysis of 30Y-7.6Ta Surfaces

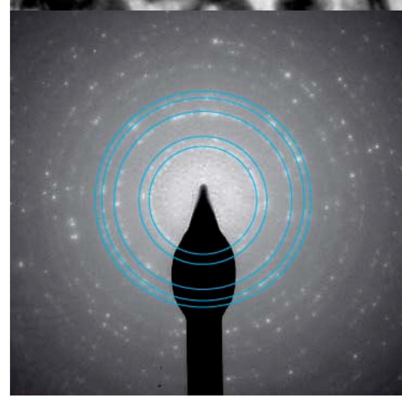
As processed (cubic)

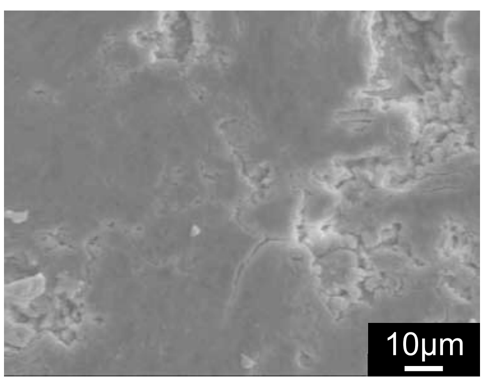
After 500h/900C, 30±5 mg/cm² 70S:30V



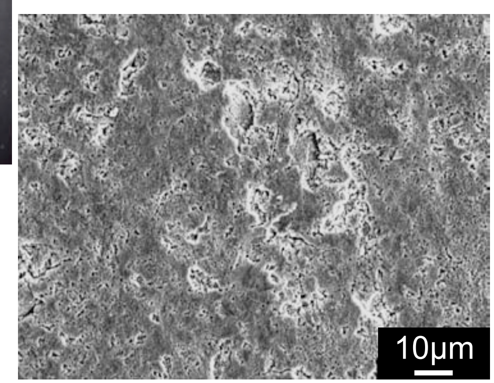








No detectable structural changes on surface after 500 h exposure, only small depletion of Y.

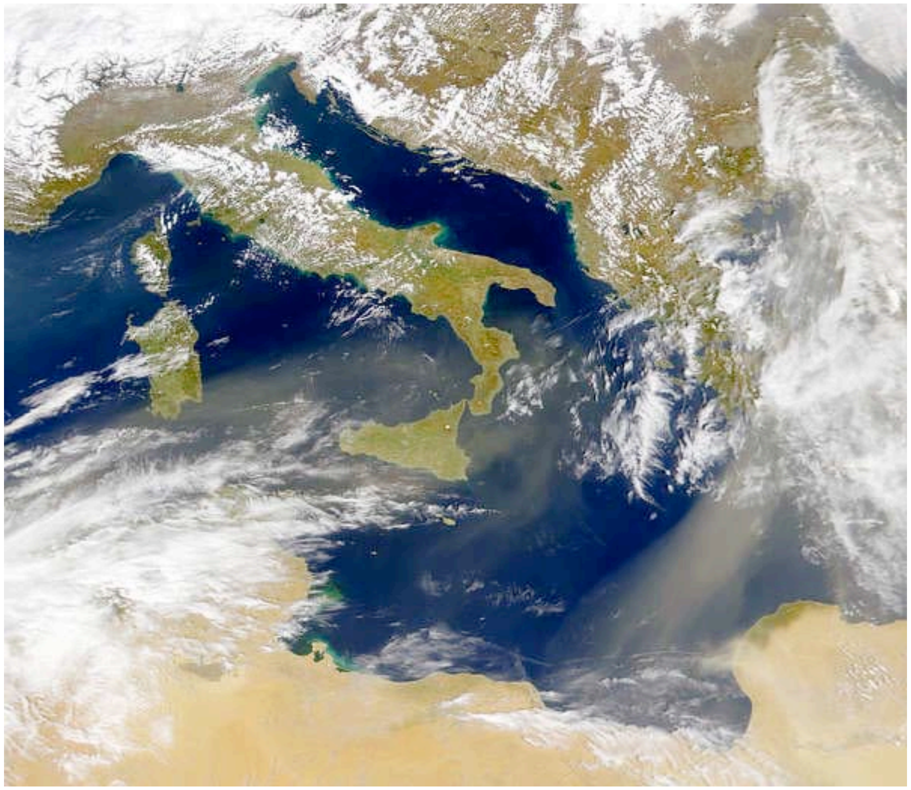


Pitek and Krämer

CMAS Degradation of TBCs:
The Price Paid for Higher Temperature Operation

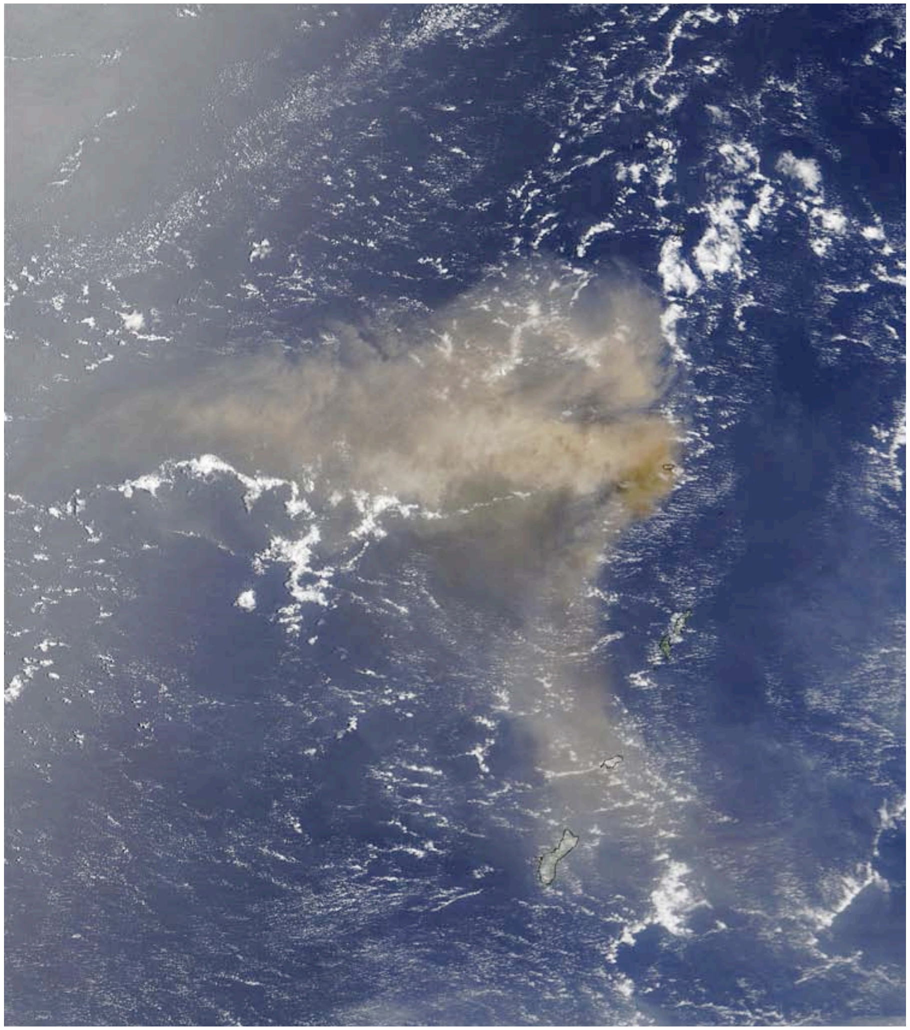
Photo Courtesy of R. Kowalik, US Navy

Sources of Airborne Siliceous Debris



Saharan dust blowing over the Mediterranean

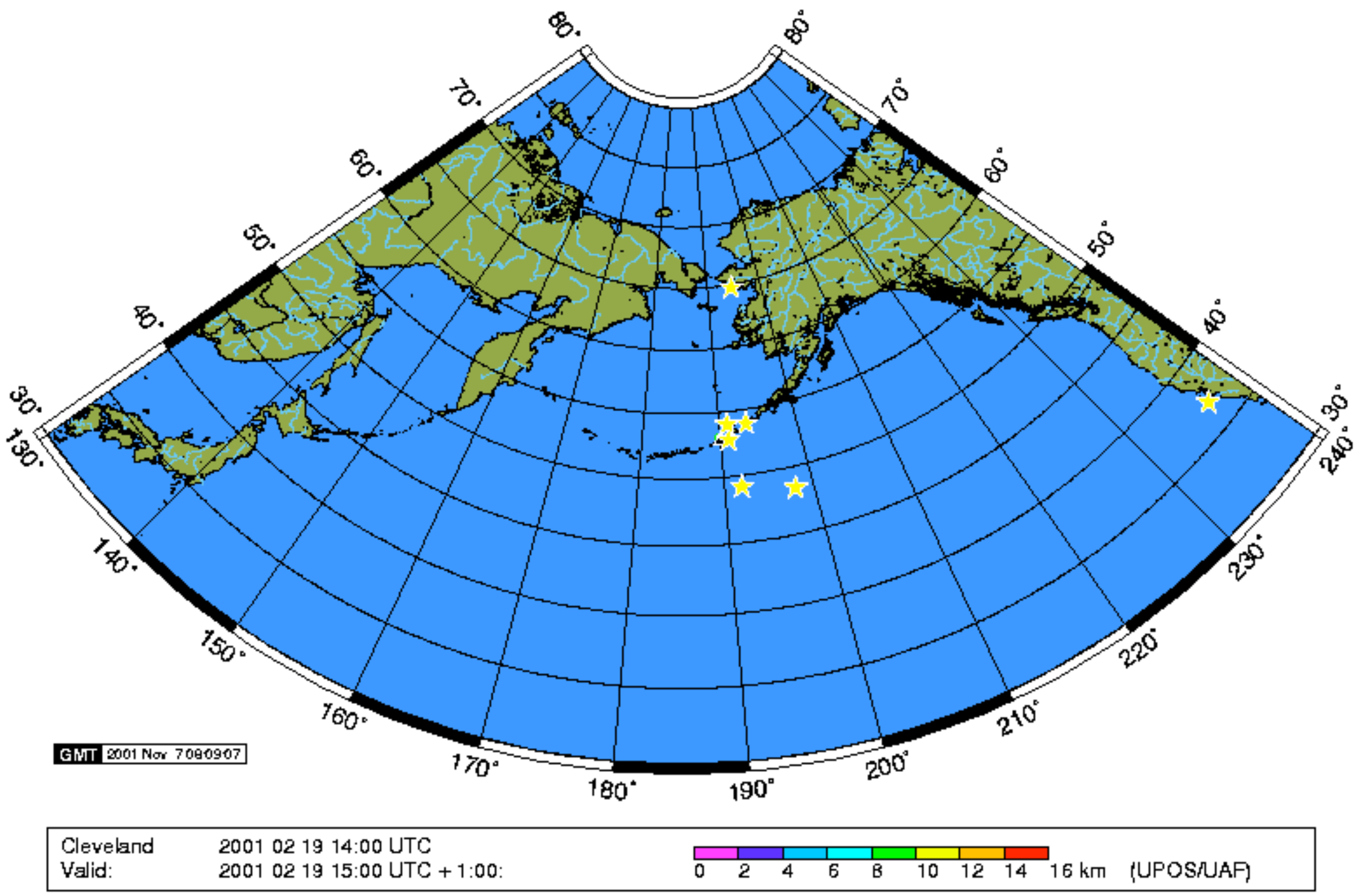
http://visibleearth.nasa.gov/view_rec.php?id=2197



Eruption of Anatahan Volcano Northern Mariana Islands

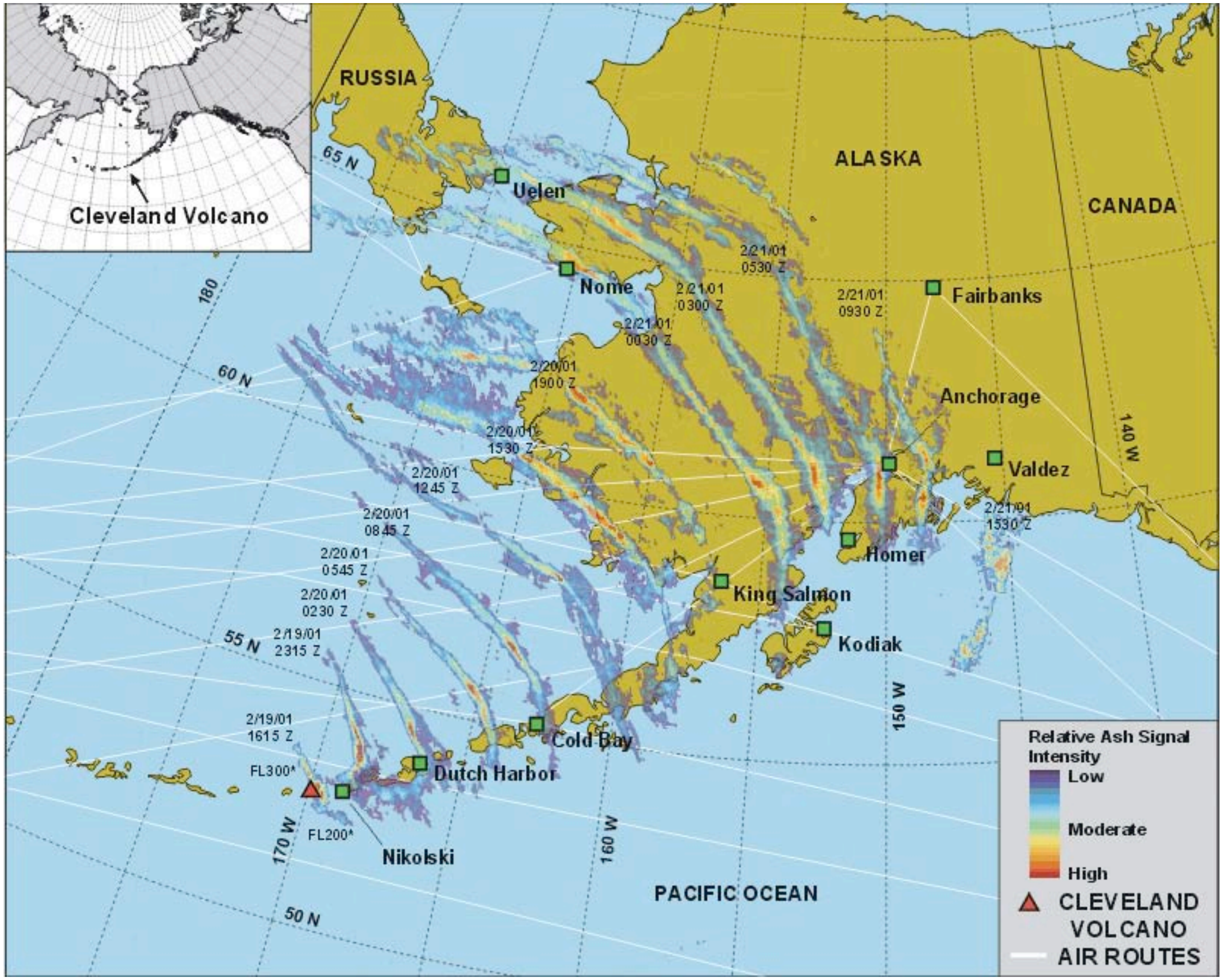
http://visibleearth.nasa.gov/view_rec.php?id=5257

Spread of Volcanic Ash Cloud



http://puff.images.alaska.edu/satimg.shtml

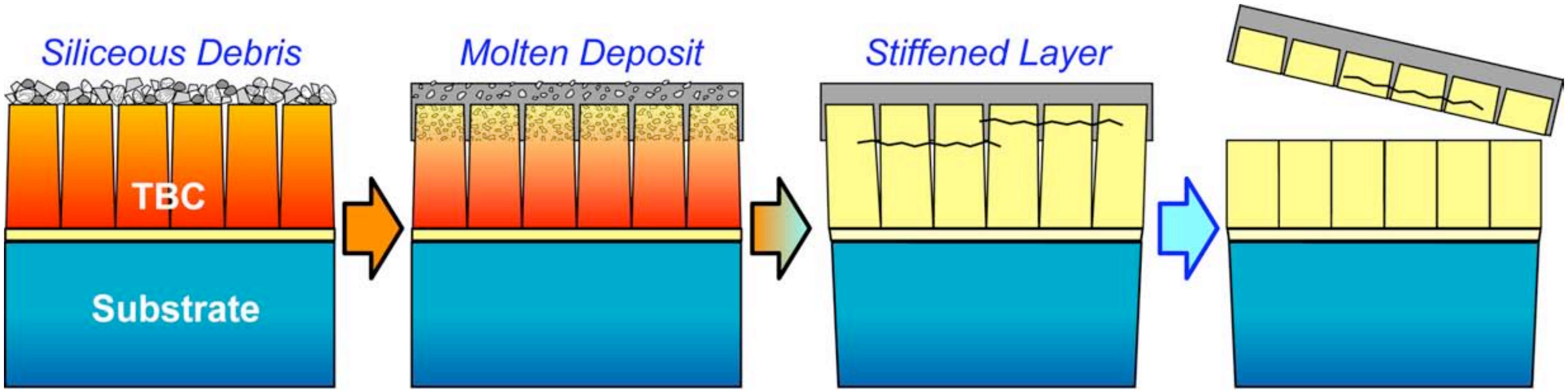
Spread of Volcanic Ash Cloud



http://puff.images.alaska.edu/satimg.shtml

CMAS Induced Damage in TBCs

Adapted from C. Johnson (GE-GRC)

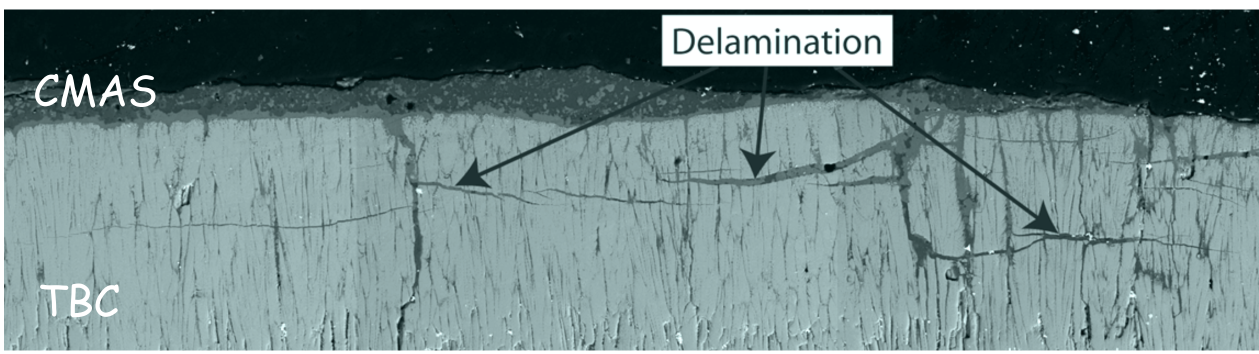


Solid Contaminants Deposit on TBC Intercolumnar gaps (cracks in PS) open

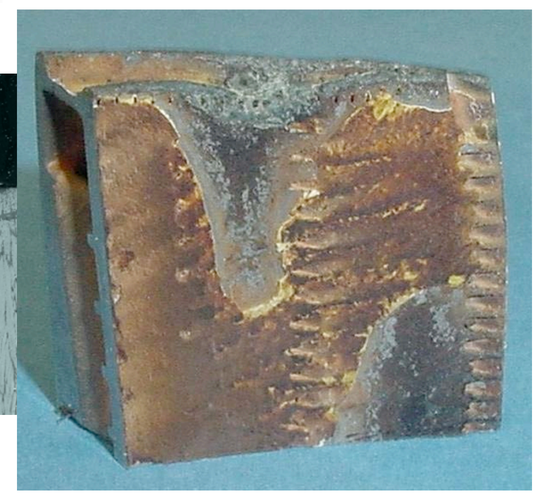
"Eutectic" Melt forms, infiltrates gaps (limited by thermal gradient) and attacks TBC

CMAS solidifies on cooling; degrades strain tolerance. Delaminations form.

Thermally induced stresses exfoliate infiltrated TBC layer

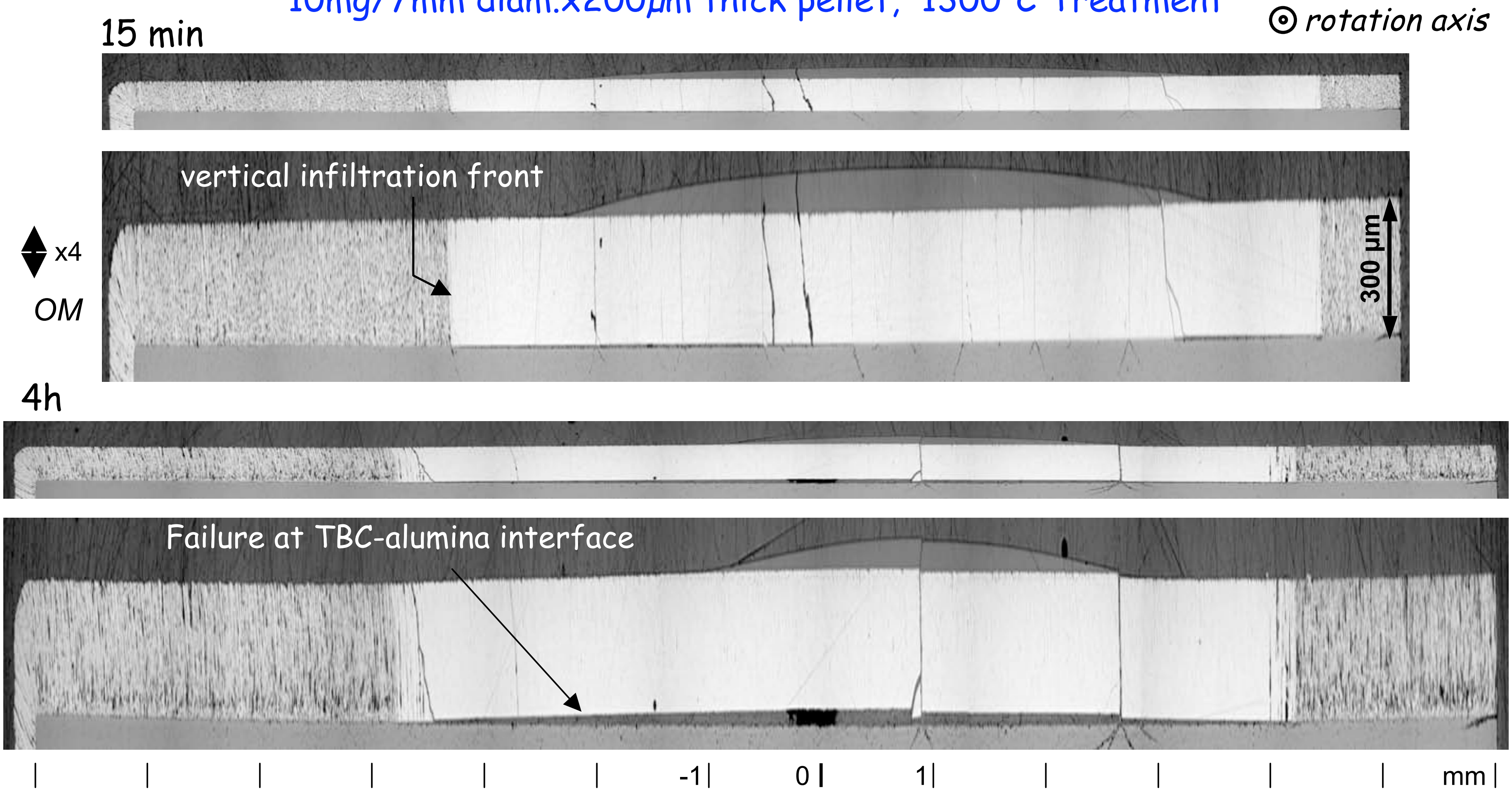


Mercer, Faulhaber, Evans, Darolia, 2005



Isothermal Infiltration into EB-PVD TBCs

Model CMAS: 33Ca-9Mg-13Al-45Si (T_M ~ 1235°C)
10mg/7mm diam.x200μm thick pellet, 1300°C Treatment



Infiltration into Capillary Channels

$$\frac{dL}{dt} \approx \underbrace{\frac{4}{k_t}\left(\frac{\omega}{1-\omega}\right)^2\left[\frac{D_c}{L}\right]}_{\text{Microstructure (porosity)}}\frac{\sigma_{LV}\cos\theta}{\eta}$$

Driving force

Kinetic hindrance

$$\sigma_{LV}\left(mJ/m^2\right) = 271.2 + 1.96\left[MgO\right] + 3.34\left[CaO\right] + 2.68\left[FeO\right] + 3.47\left[Al_2O_3\right]$$

dL/dt = rate of infiltration into small channel under capillary pressure alone

k_t = tortuosity factor (~2-5)

ω = volume fraction porosity (~0.1 for intercolumnar gaps)

D_c = diameter of capillary (~0.1-1µm)

L = length of penetration (0-250µm)

σ_{LV} = liquid surface tension (~0.5J/m^2)

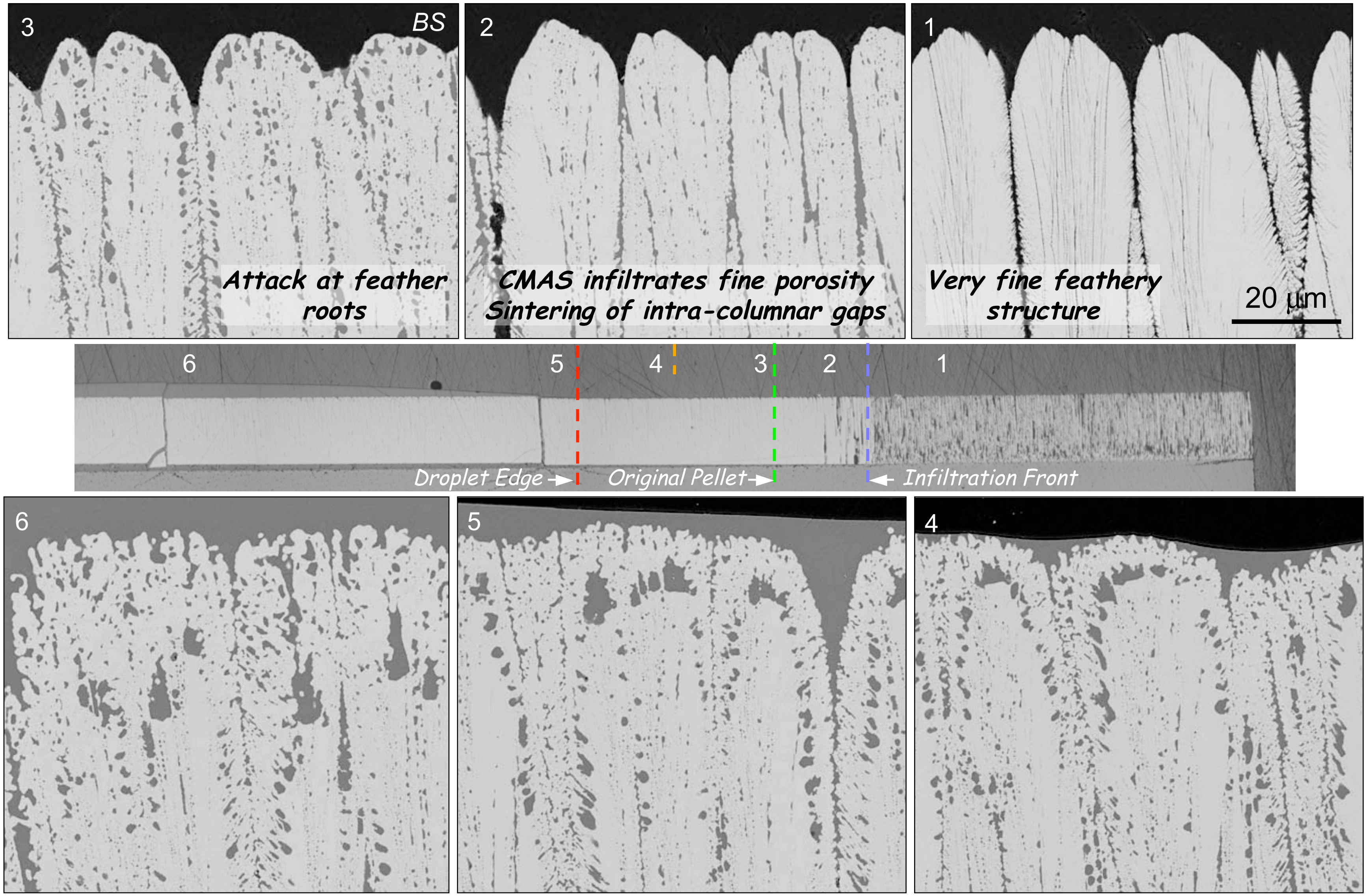
θ = contact angle ($\rightarrow$0 for highly wetting liquids)

η = viscosity ([O]10p at 1400°C for model CMAS)

Estimated infiltration times are of the order of 1 min

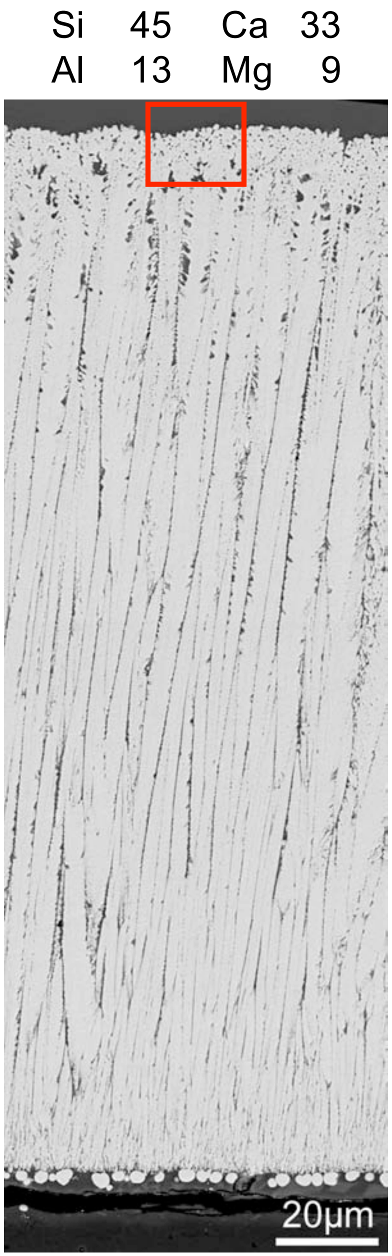
Progress of CMAS Attack on Column Tips

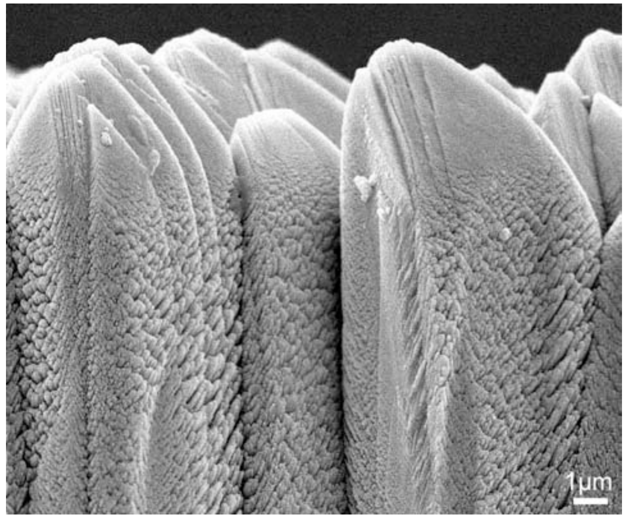
Krämer

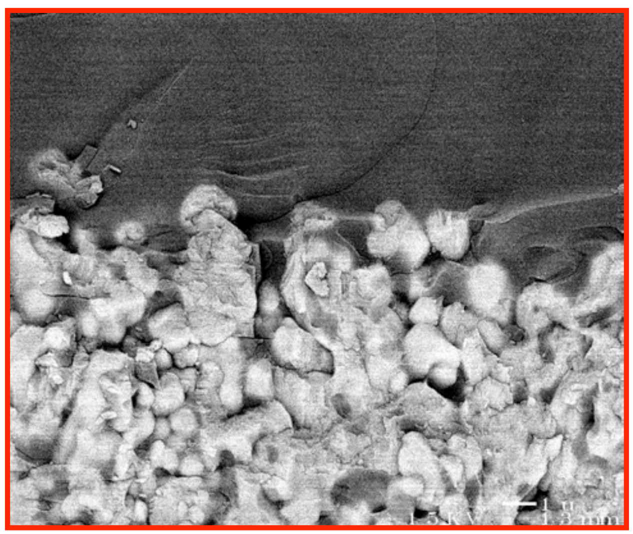


Increased size of attacked zone

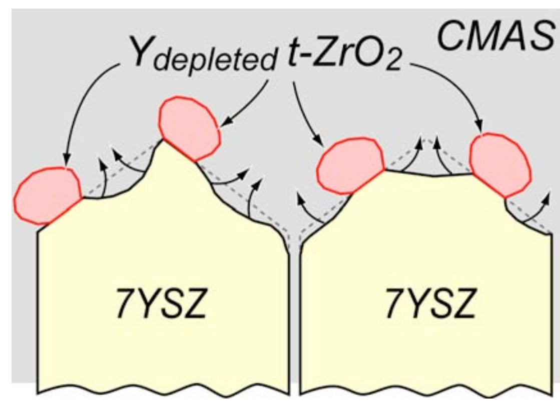
Corrosion Mechanism at Column Tips







- *t'-YSZ dissolves in CMAS and reprecipitates with a different Y concentration that depends on the local melt environment.*
- *Y-depleted Z at top ➪ unstable t ➪ monoclinic.*

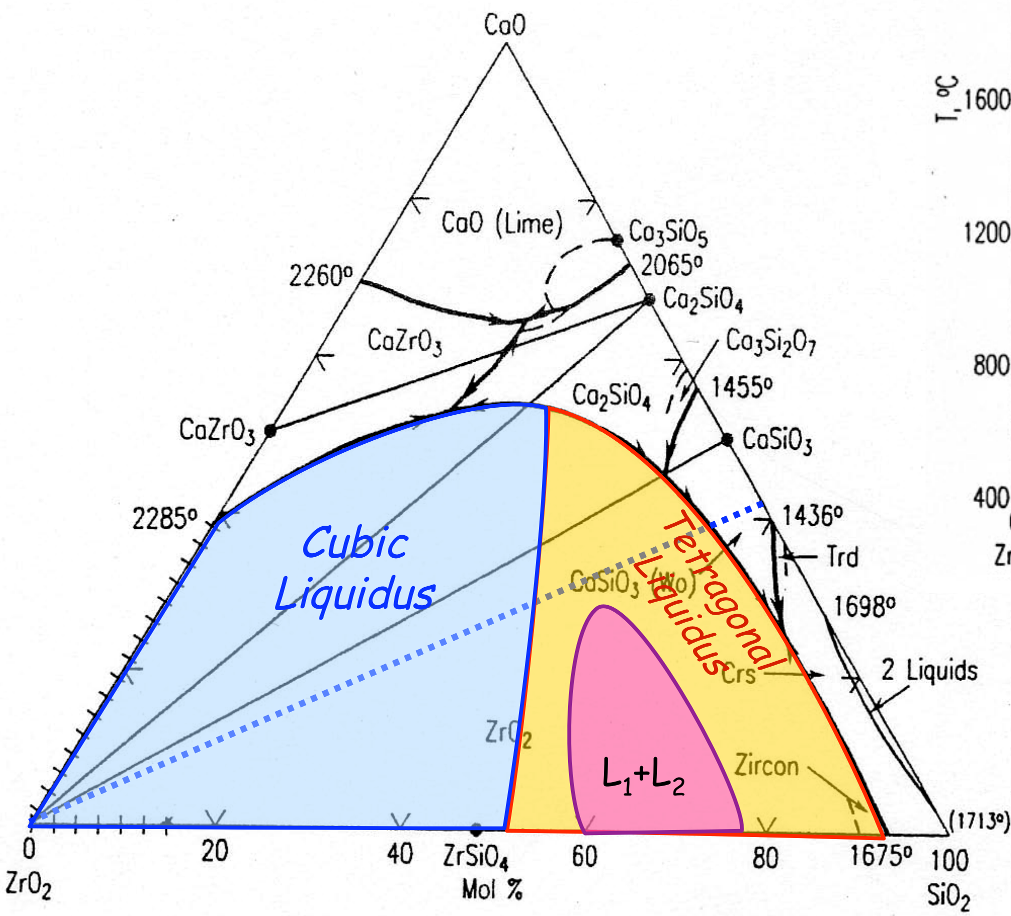


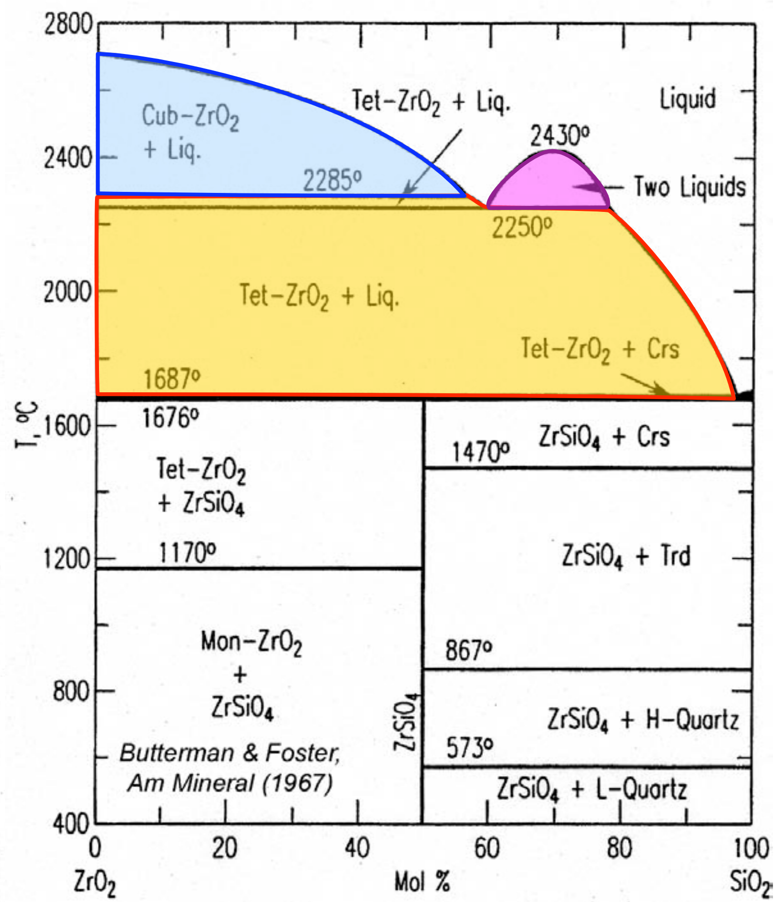
- *Column tip morphology completely obliterated.*

Krämer and Yang

ZrO_2-CS: A Model

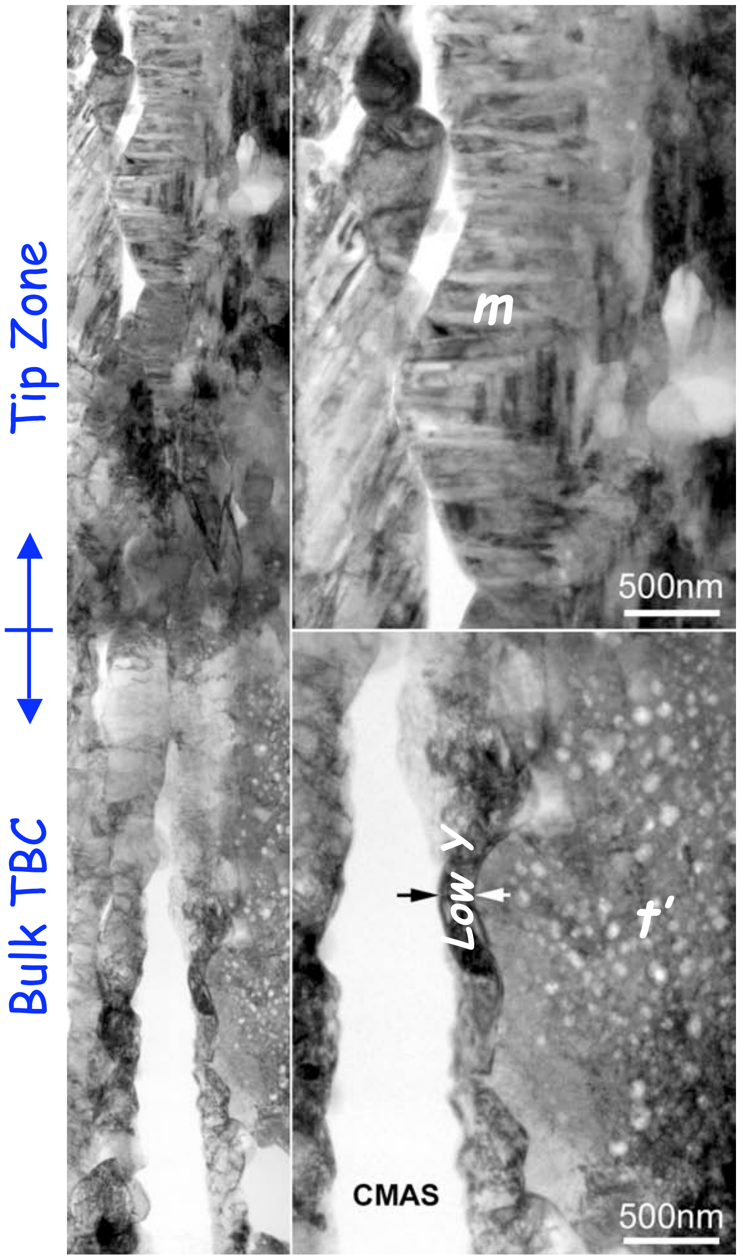
- Why does transformable tetragonal precipitate upon dissolution of t'?





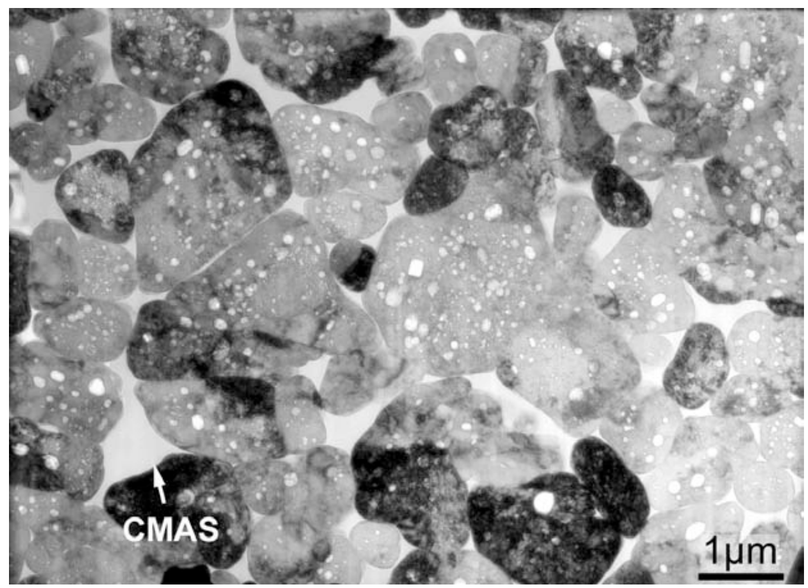
- "Current" phase diagram (1957) ignores tetragonal liquidus and miscibility gap emanating from Z-S binary.

Interaction within TBC bulk



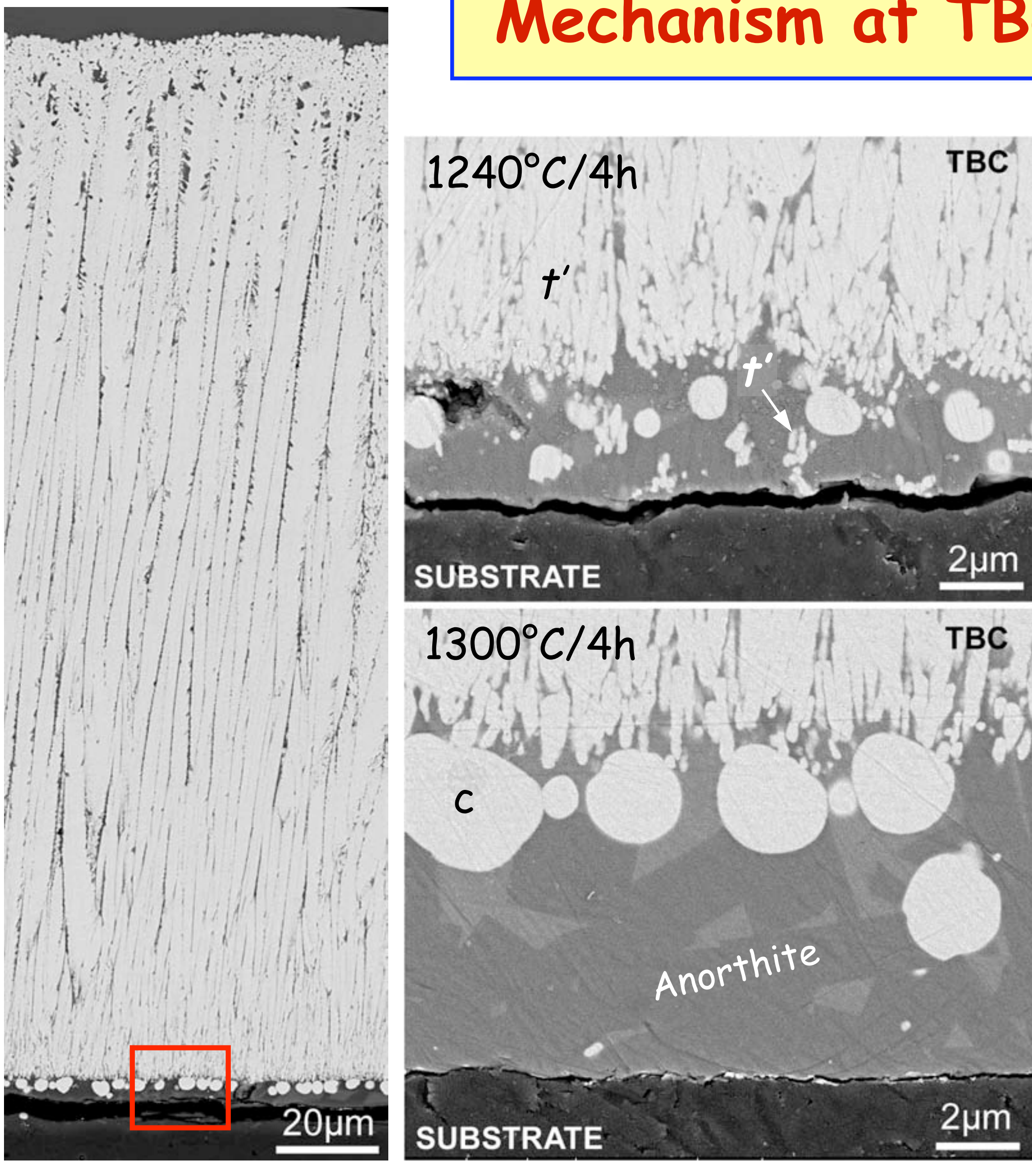
Krämer

- Except for near-tip zone, no evidence of reprecipitated phases and only minimal dissolution of 7YSZ within bulk of the TBC
  - Rapid saturation of CMAS melt (small CMAS:YSZ volume ratio).



Transverse view of columns near bottom

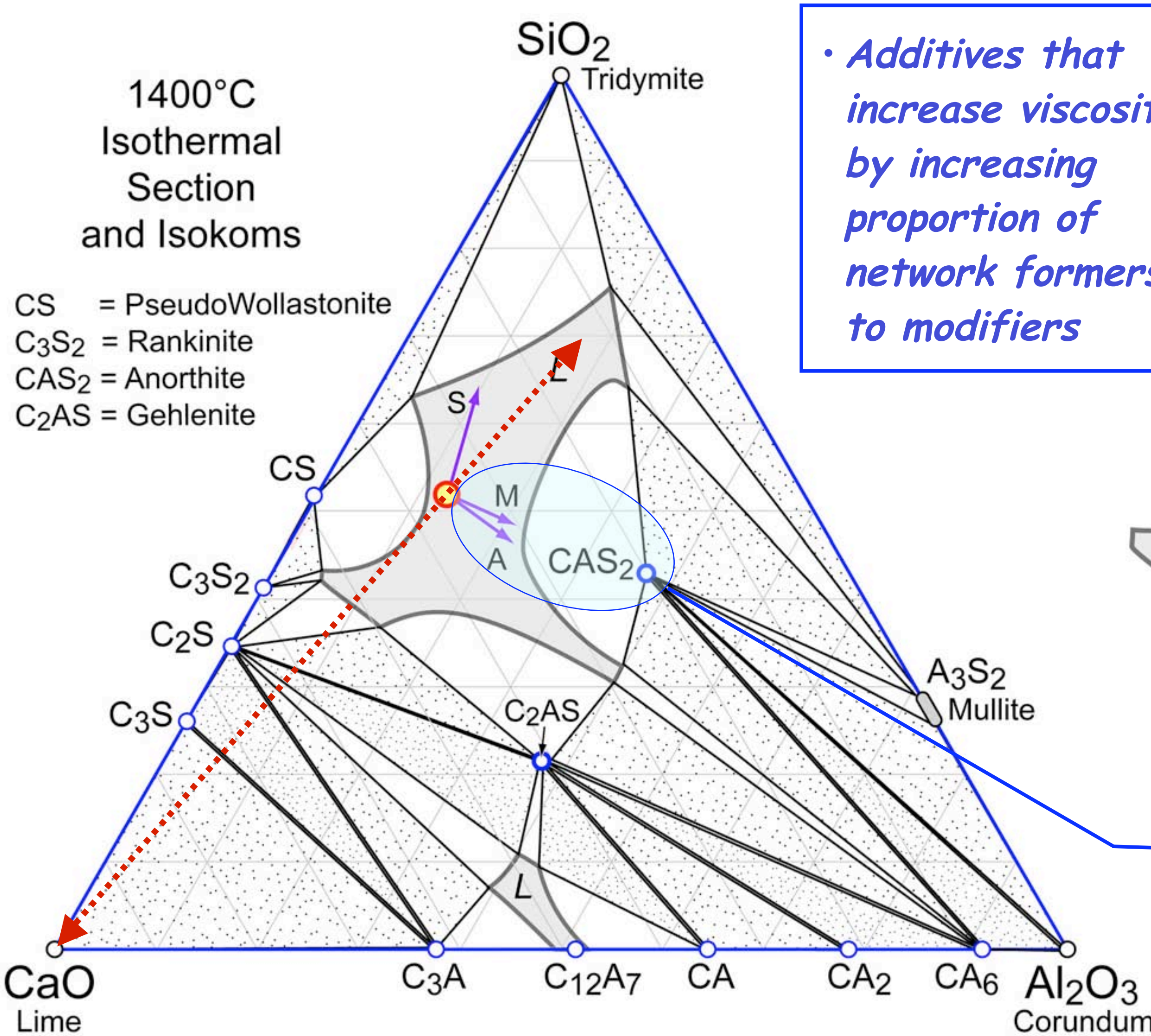
Mechanism at TBC/"TGO" Interface



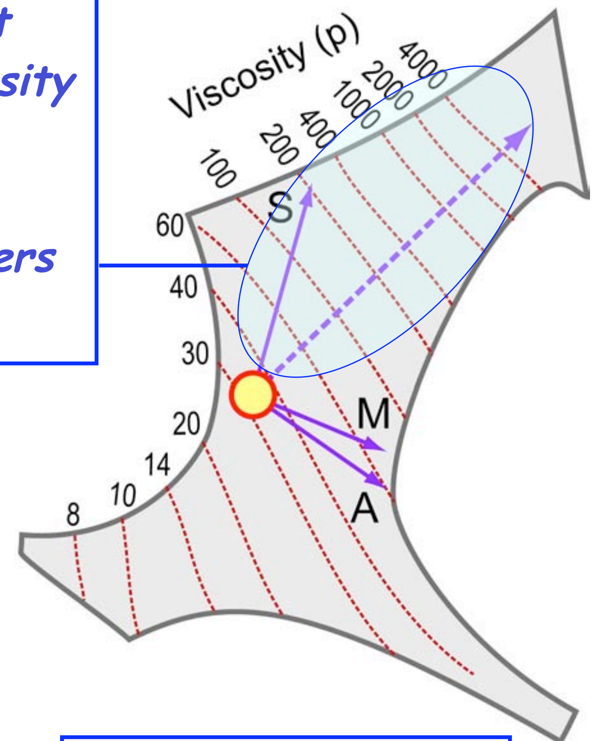
- *If CMAS reaches substrate (TGO) Al_2O_3 dissolves concurrently with ZrO_2*
  - *Reprecipitated ZrO_2 is now Y-enriched (cubic).*
  - *Al_2O_3 also reprecipitates as crystalline silicate, ~CA_2S_2 (Anorthite)*
- *Fine grains in "nucleation layer" detach from column roots and detach to feed growth of cubic globules.*
- *Extent of t′ dissolution much smaller than in the column tip region.*

Krämer and Yang

Earlier thoughts on Mitigation Strategies

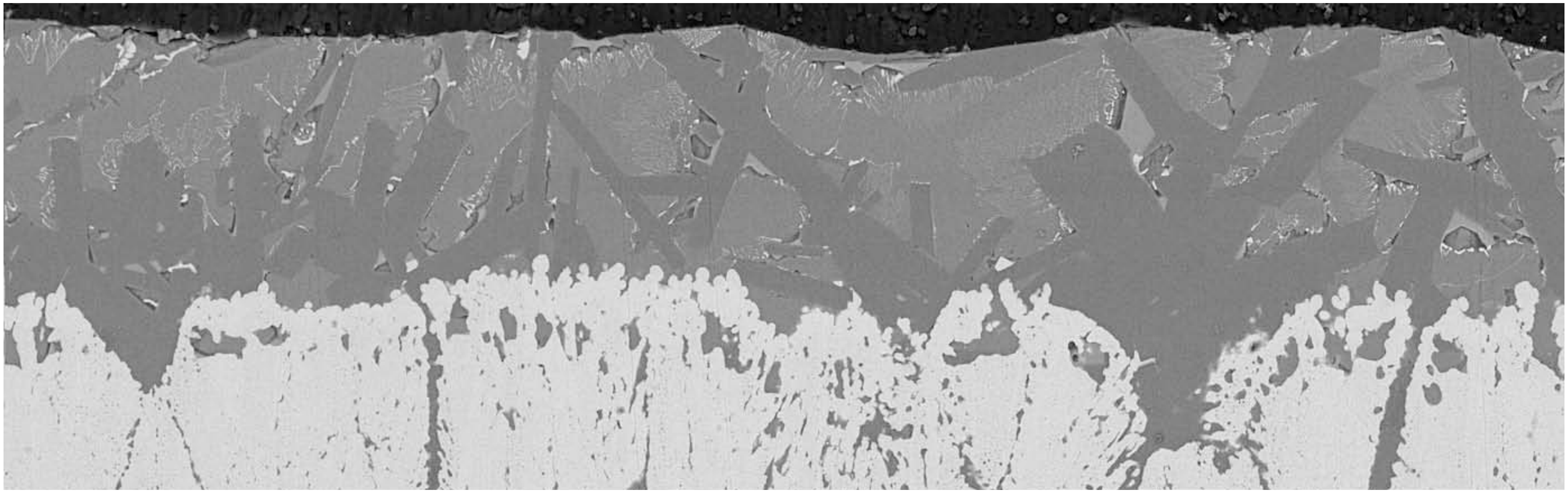


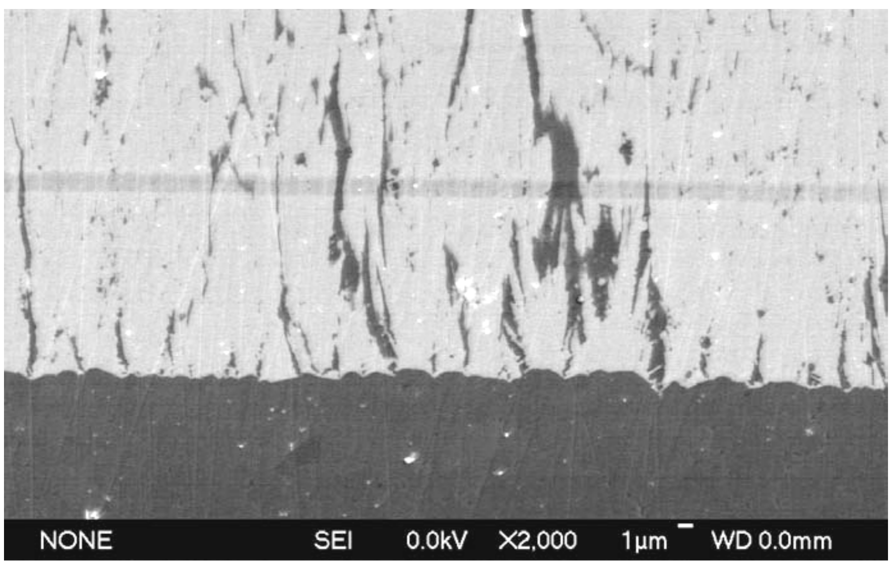
- *Additives that increase viscosity by increasing proportion of network formers to modifiers*



- *Additives that promote crystallization (alumina, mullite)*

CMAS on TBC pre-treated with Al_2O_3

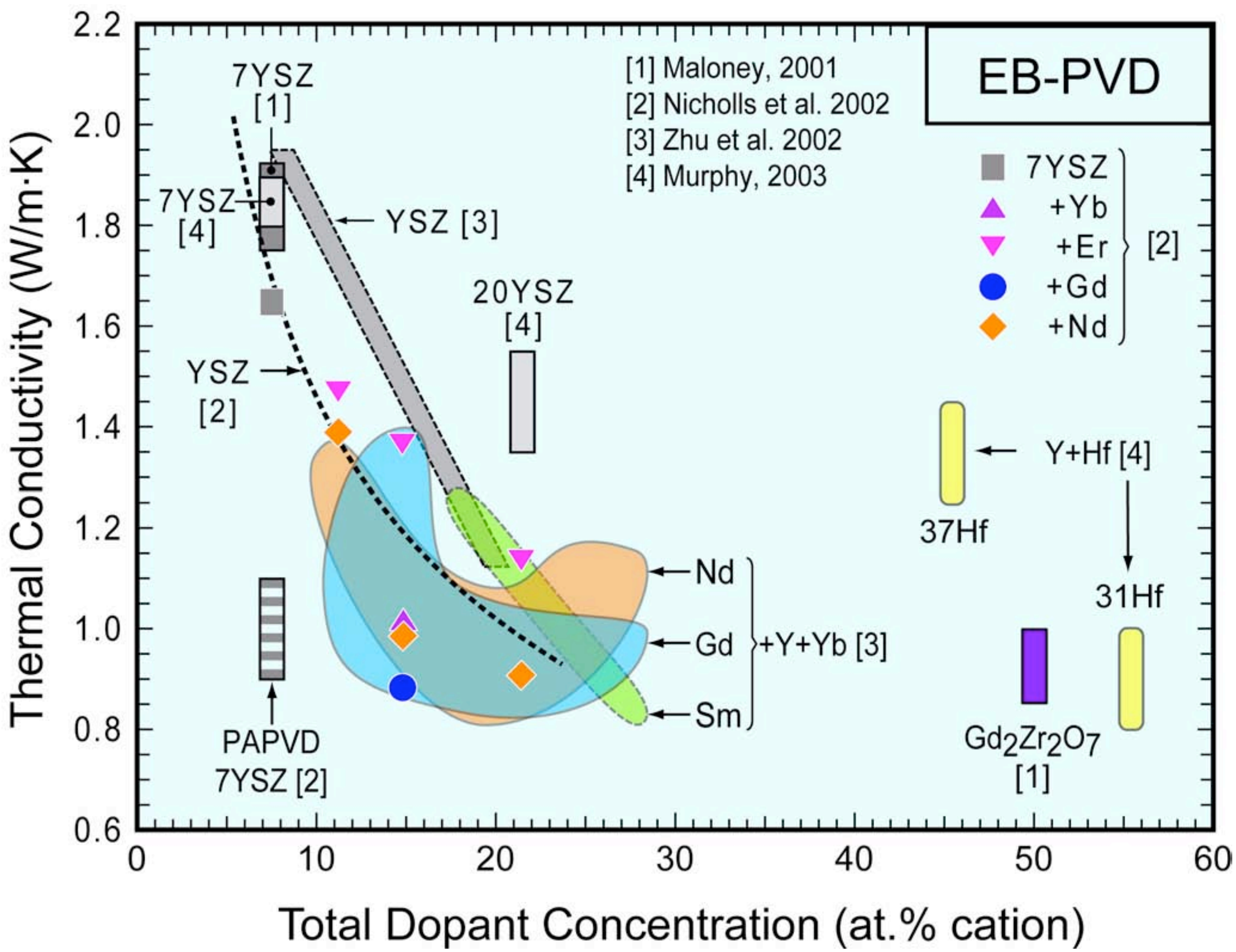




- *Pre-impregnation with Al_2O_3 does promote extensive crystallization (anorthite + spinel).*
- *Crystallization kinetics is not sufficiently rapid to compete with infiltration, presumably because of the isothermal condition and high treatment temperature.*

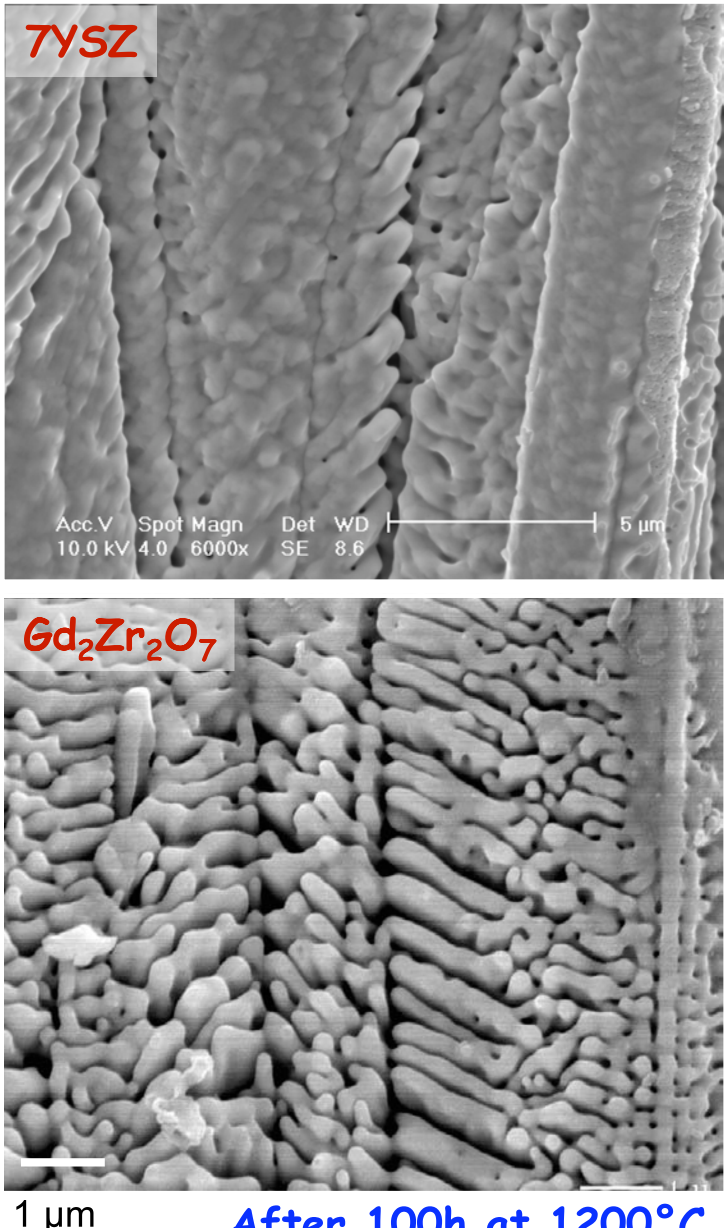
Advanced low-k TBCs:
Gd Zirconate

Thermal Conductivity of Some Emerging TBCs



- *A large variety of alternate compositions, mostly based on rare earth additions to ZrO_2 or YSZ, offer improved thermal insulation efficiency over 7YSZ. But…*

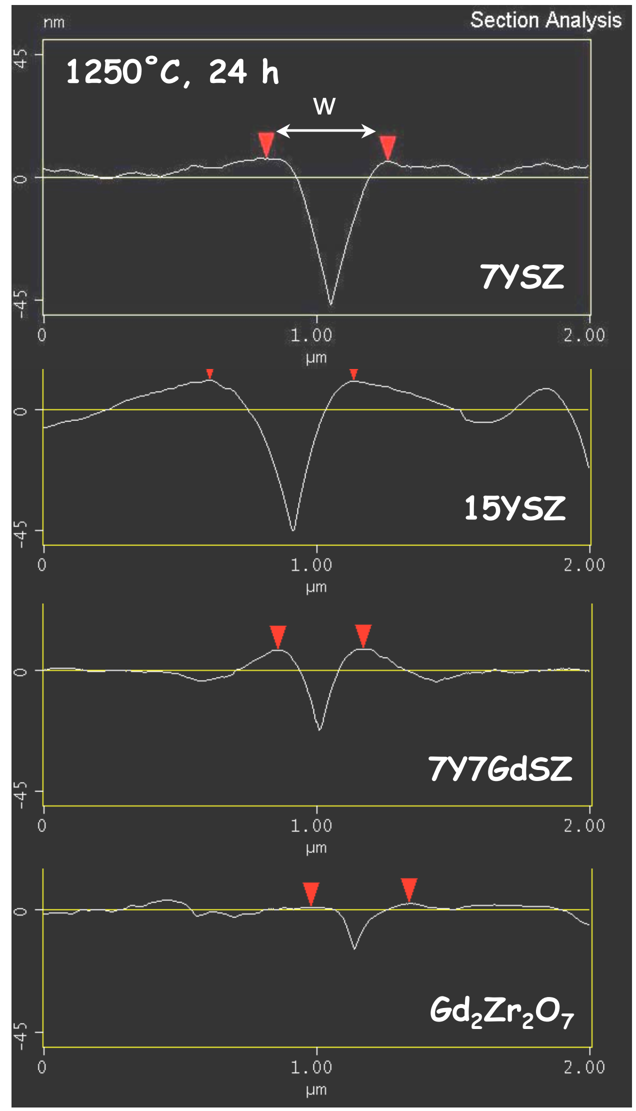
Leckie, Yang



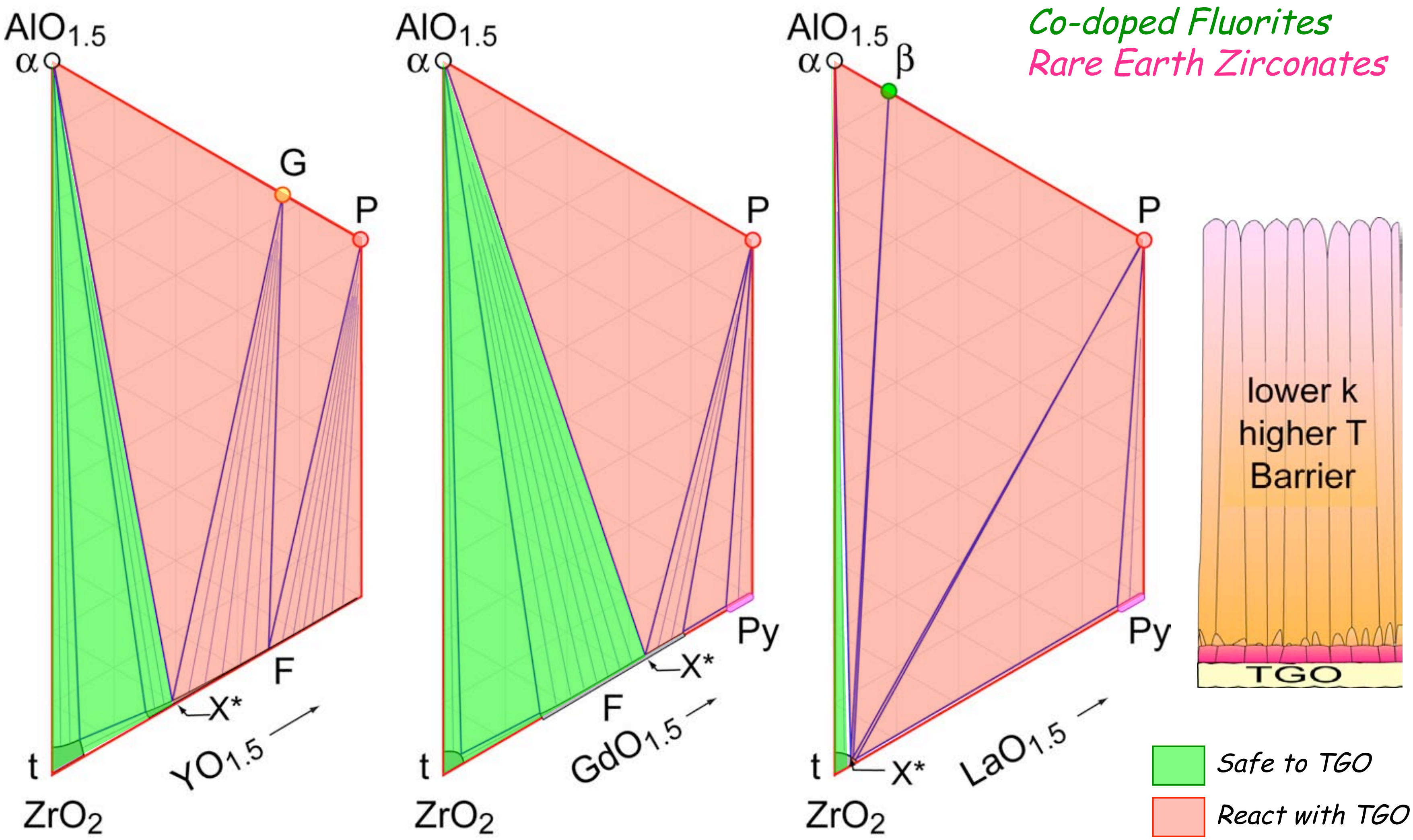
After 100h at 1200°C

Chemical Effects on Surface Diffusion

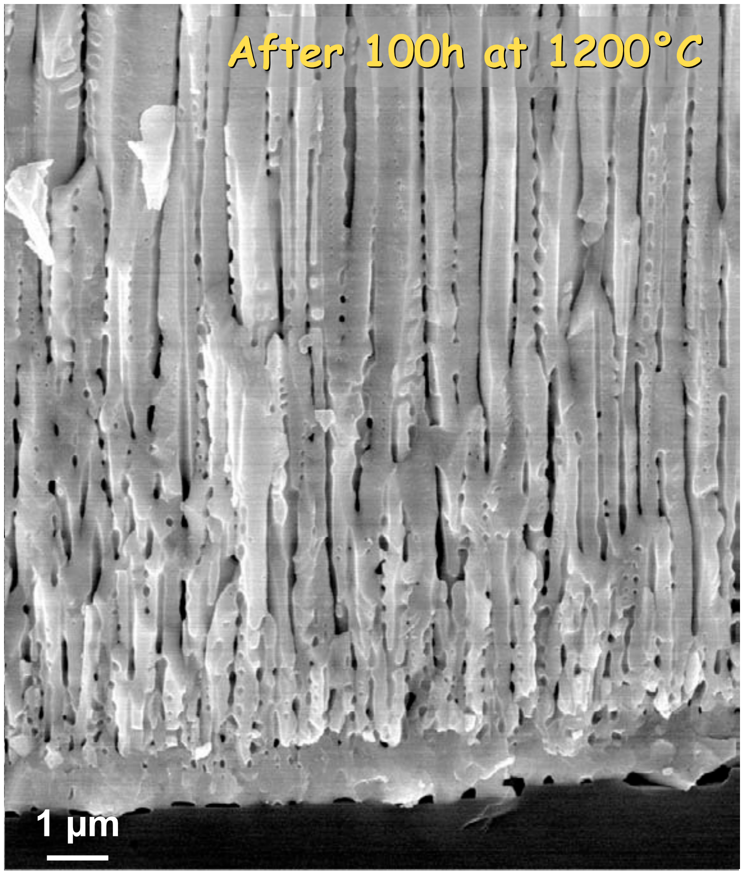
Significant benefits of Gd addition (and likely of other RE's) on improving the stability of the pore architecture, with concomitant benefits to the preservation of low k and strain tolerance.

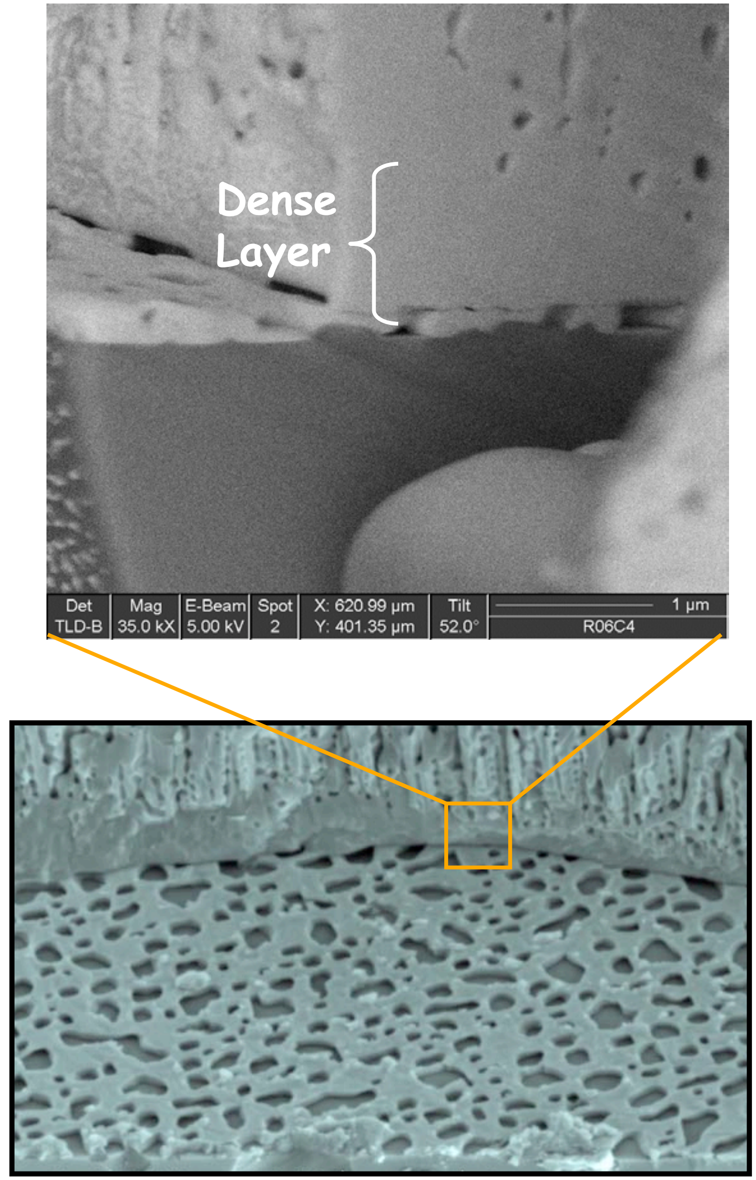


Thermochemical Compatibility Limits



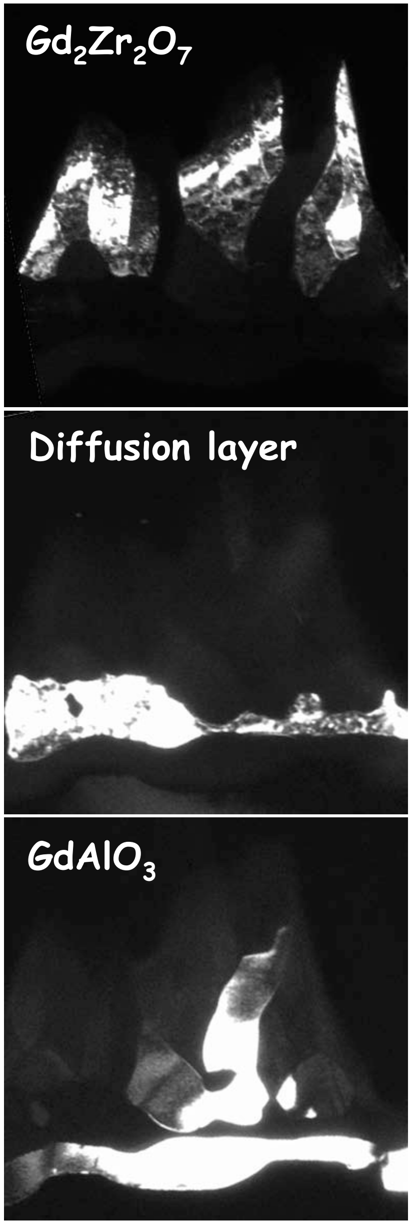
$Gd_2Zr_2O_7$/Alumina Interface Interaction

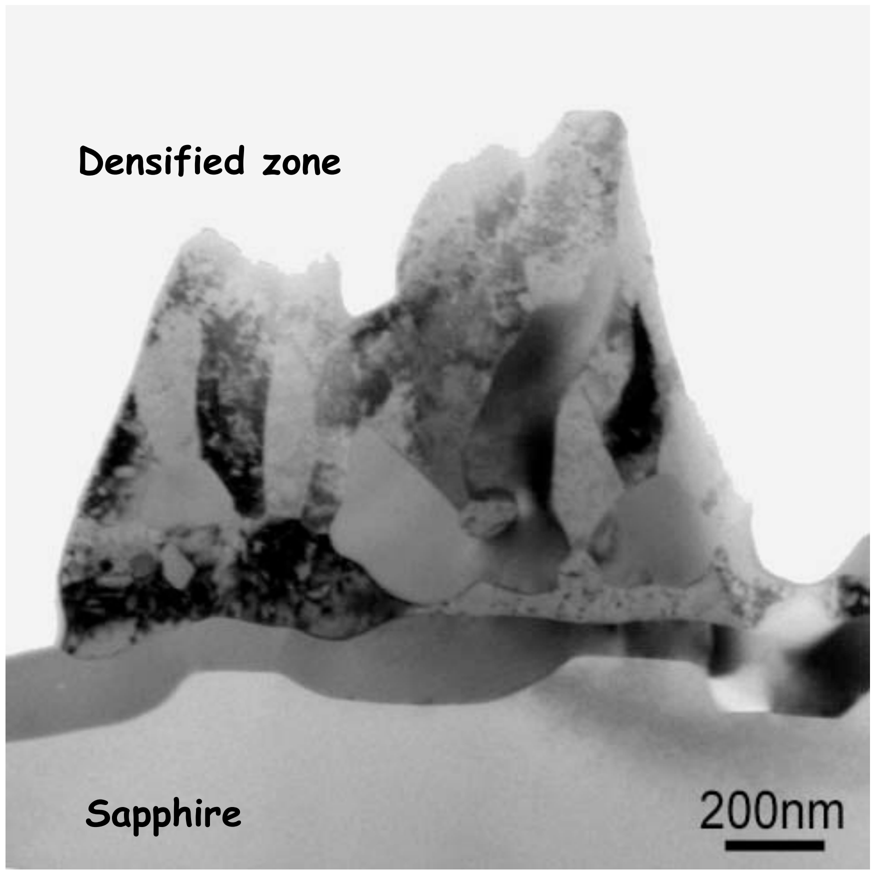




Leckie

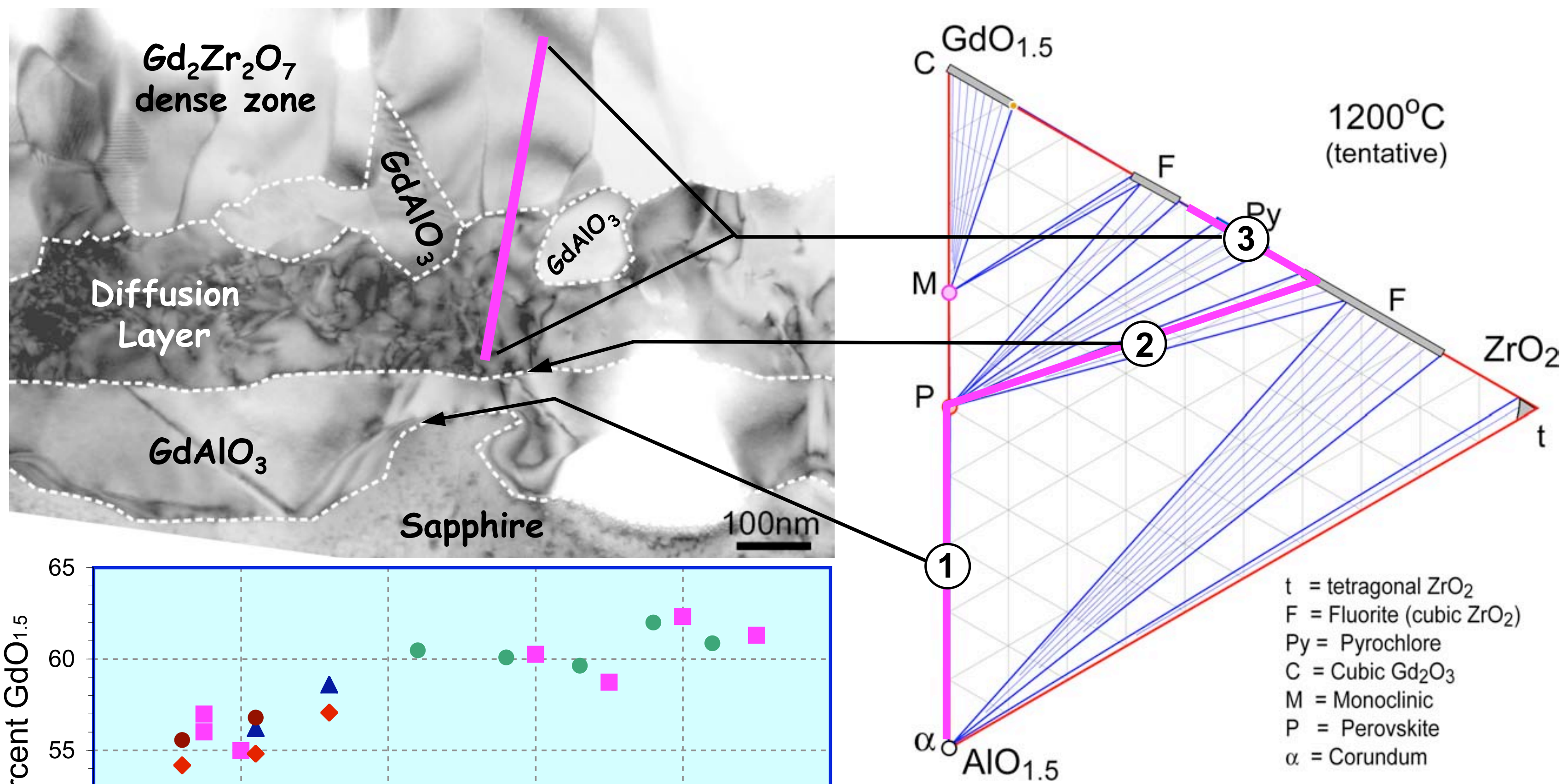
$Gd_2Zr_2O_7$/Sapphire Interaction Zone

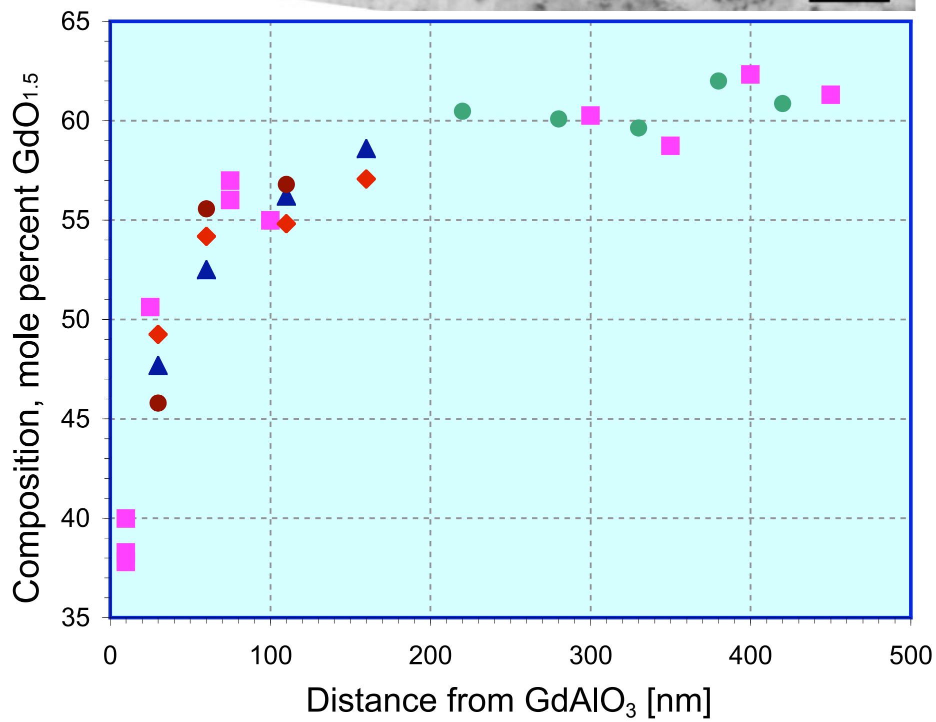




EB-PVD Film, 1200°C/100h

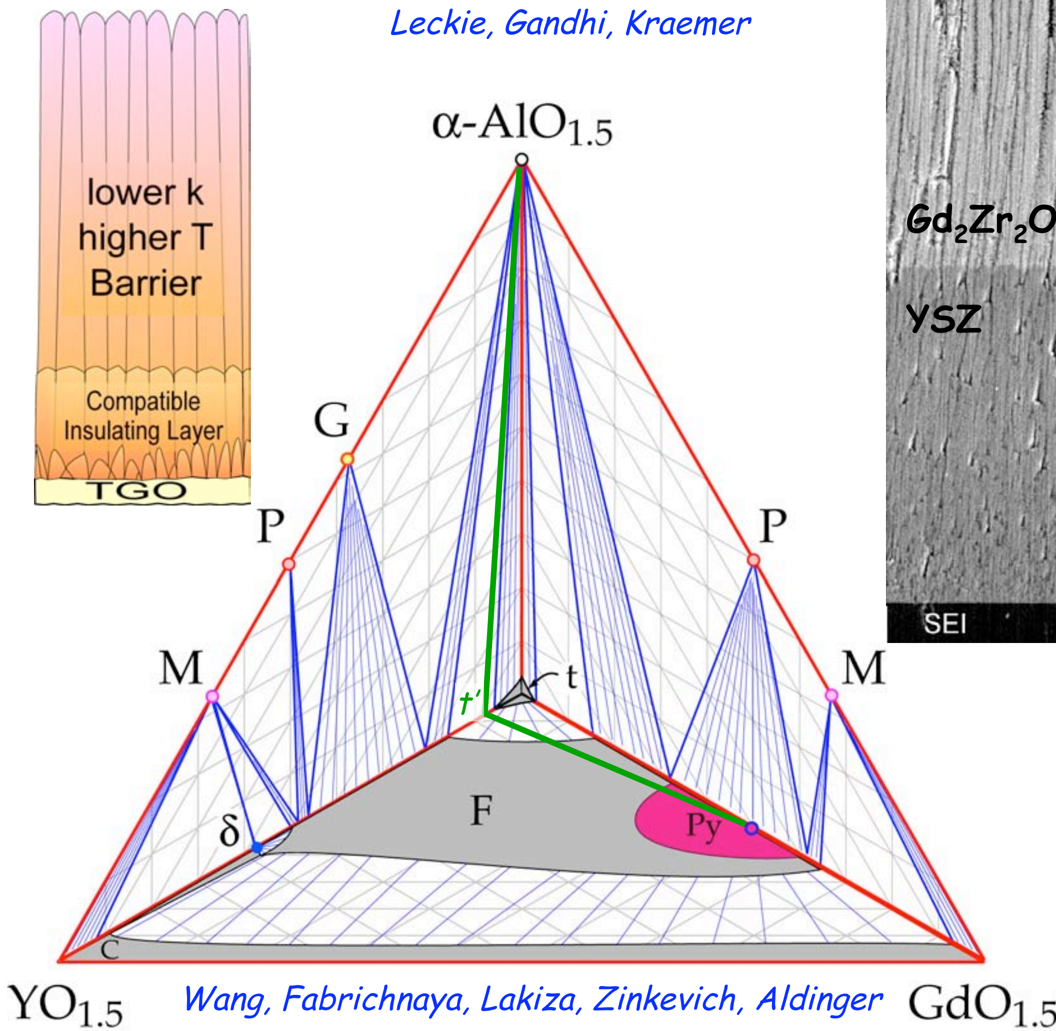
Krämer and Rühle





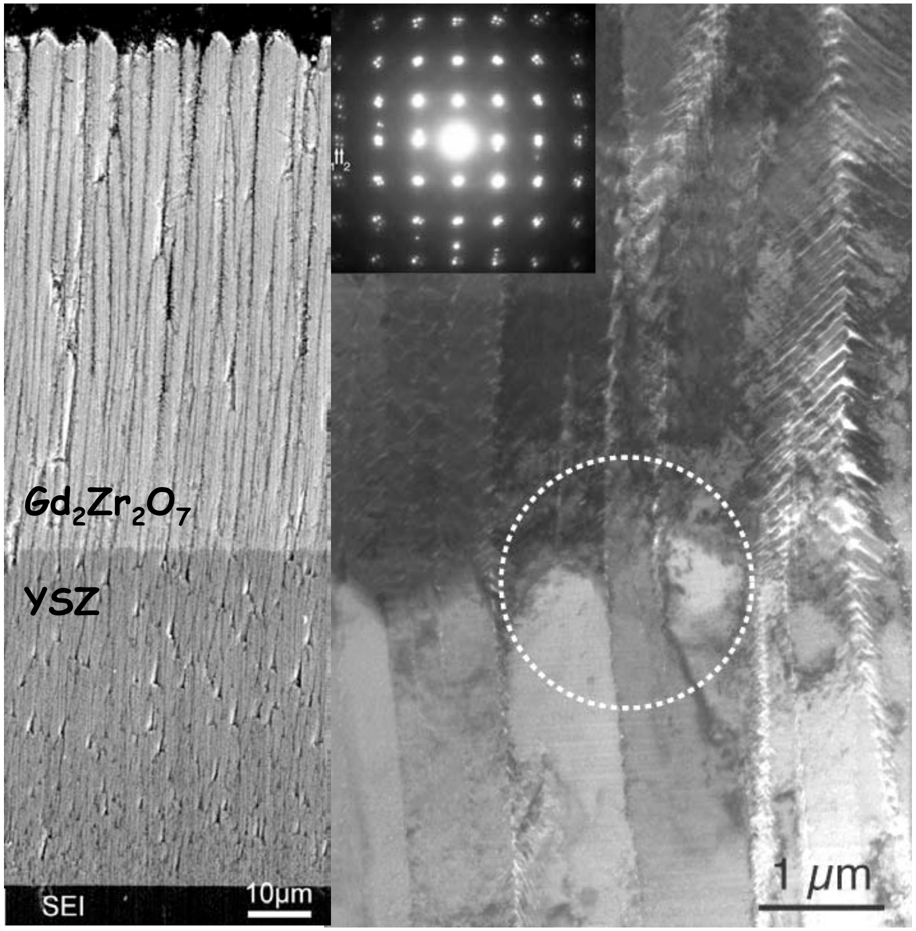
Diffusion Path

7YSZ Interlayer for Chemical Compatibility



Leckie, Gandhi, Kraemer

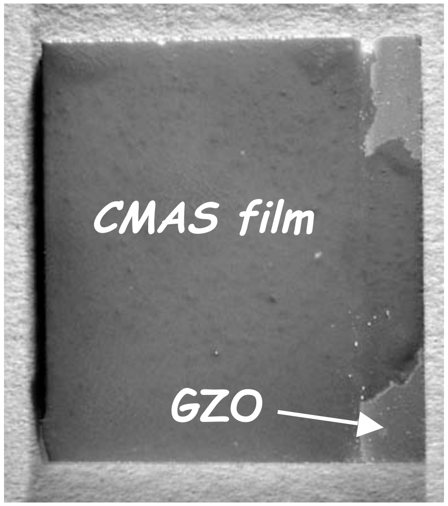
Wang, Fabrichnaya, Lakiza, Zinkevich, Aldinger



- YSZ is an effective barrier to minimize interaction between TGO and $Gd_2Zr_2O_7$.
- Epitaxial growth favors integrity of the interface.

CMAS Interaction: $Gd_2Zr_2O_7$ v. 7YSZ

Substantial difference in spreading behavior and reaction layer morphology



(4h/1300°C, Isothermal)