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MINIWORKSHOP ON "*FRONTIERS IN MATERIALS SCIENCE*"
15 - 18 May 2001

301/1311-4

"High-Temperature Thermally-Insulative Coatings"

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Please note: These are preliminary notes intended for internal distribution only.

High-Temperature Thermally-Insulative Coatings

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Presented at the

ICTP/UCSB/TWAS Workshop on

"Frontiers in Materials Science"

Trieste, Italy, May 15-18, 2001

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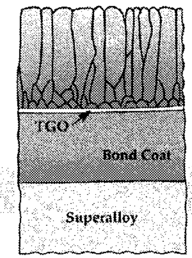

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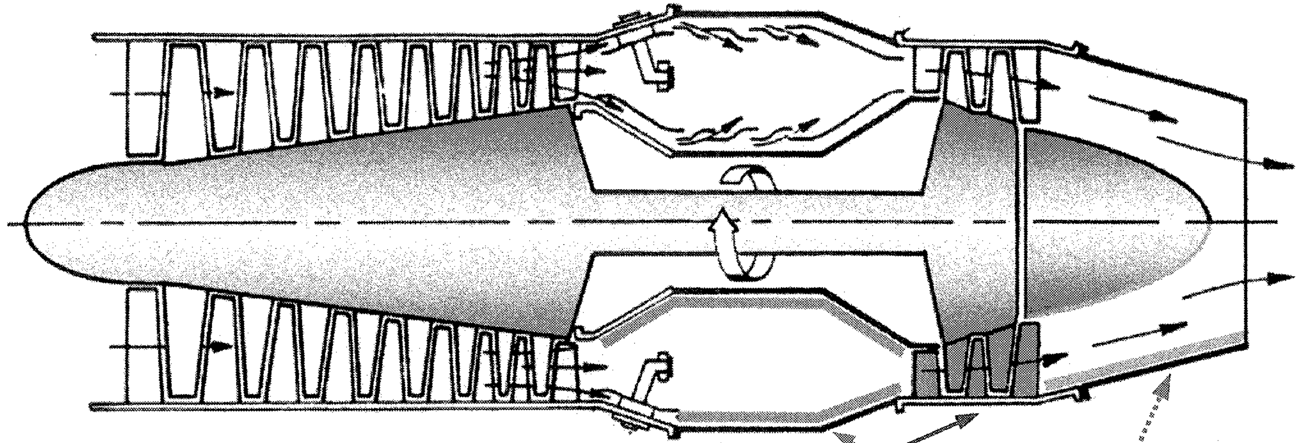
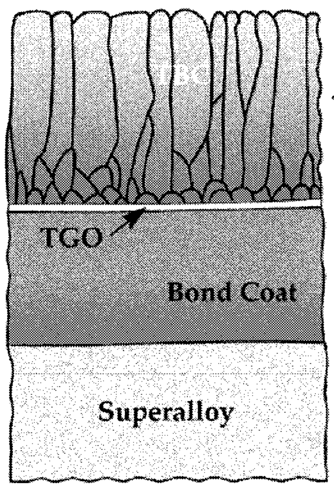
Advanced Thermostructural Materials

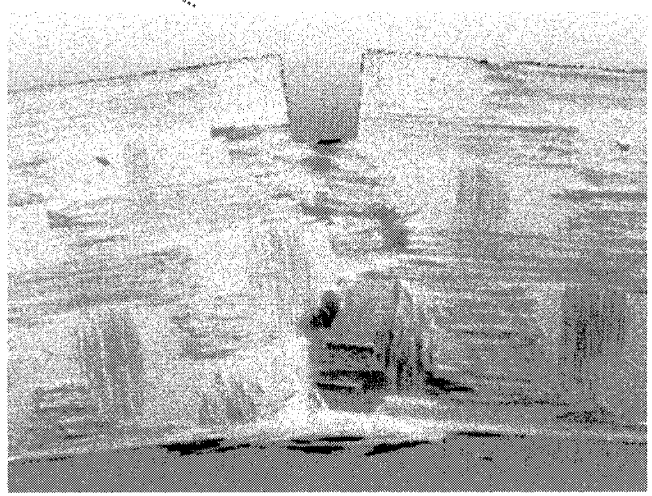


Research at UCSB

EB-PVD Thermal Barrier Coatings



All-Oxide Porous Matrix CFCCs



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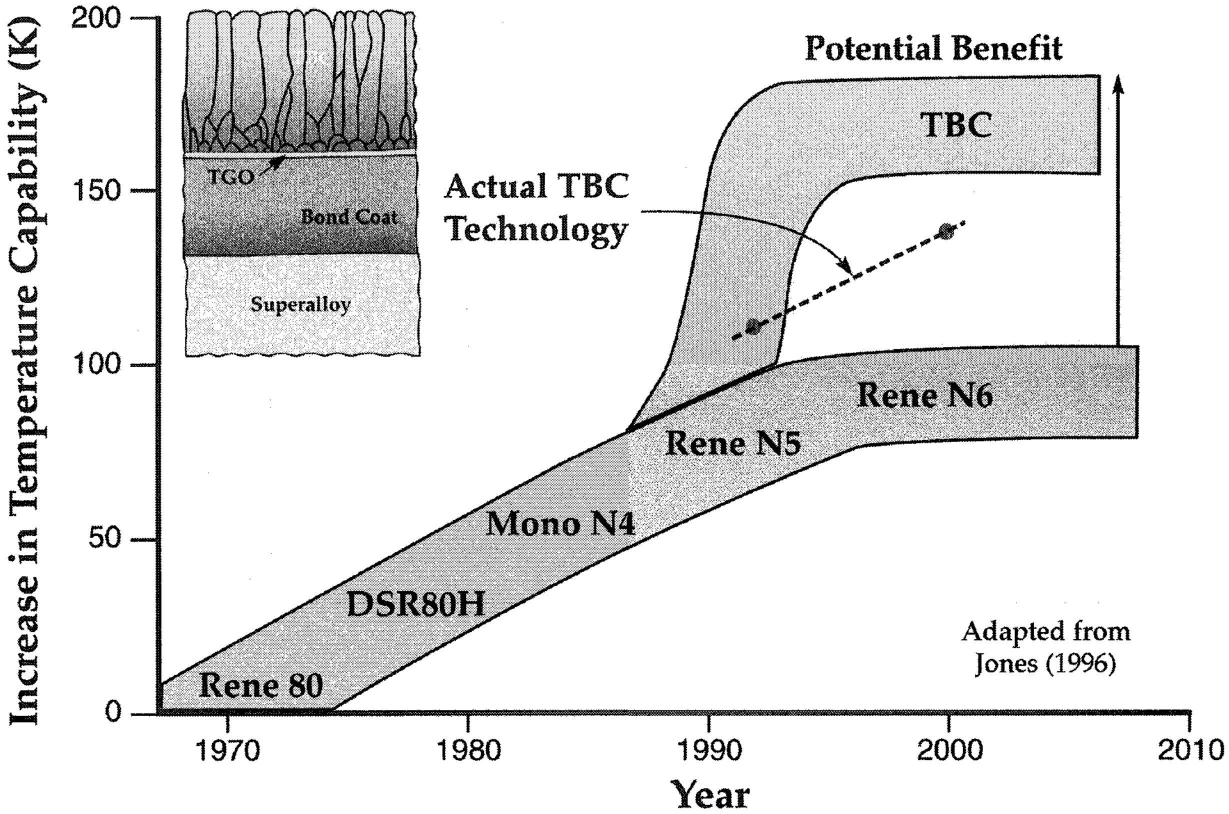
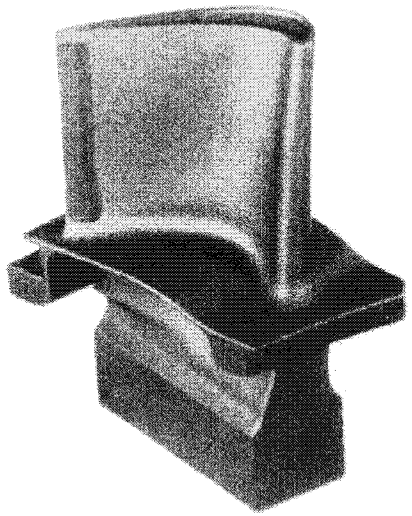
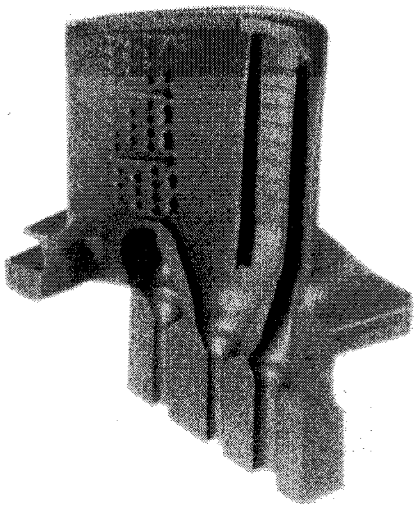
Benefits of Thermal Barrier Coatings

- Increase temperature capability of component
- Extend life and/or reduce cooling air







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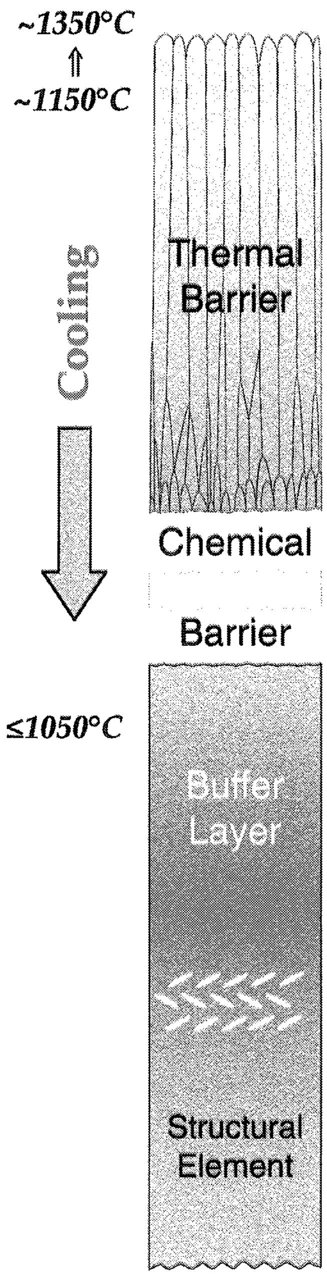


Anatomy of a TBC System

The Thermal Barrier: 7YSZ

- Low conductivity ($k \leq 1$ W/mK)
- Strain Tolerant
- Morphologically stable
- Erosion and Corrosion Resistant

The Chemical Barrier: Alumina (TGO)

- Low growth/diffusion kinetics
- Corrosion resistant
- Adherent over life of coating

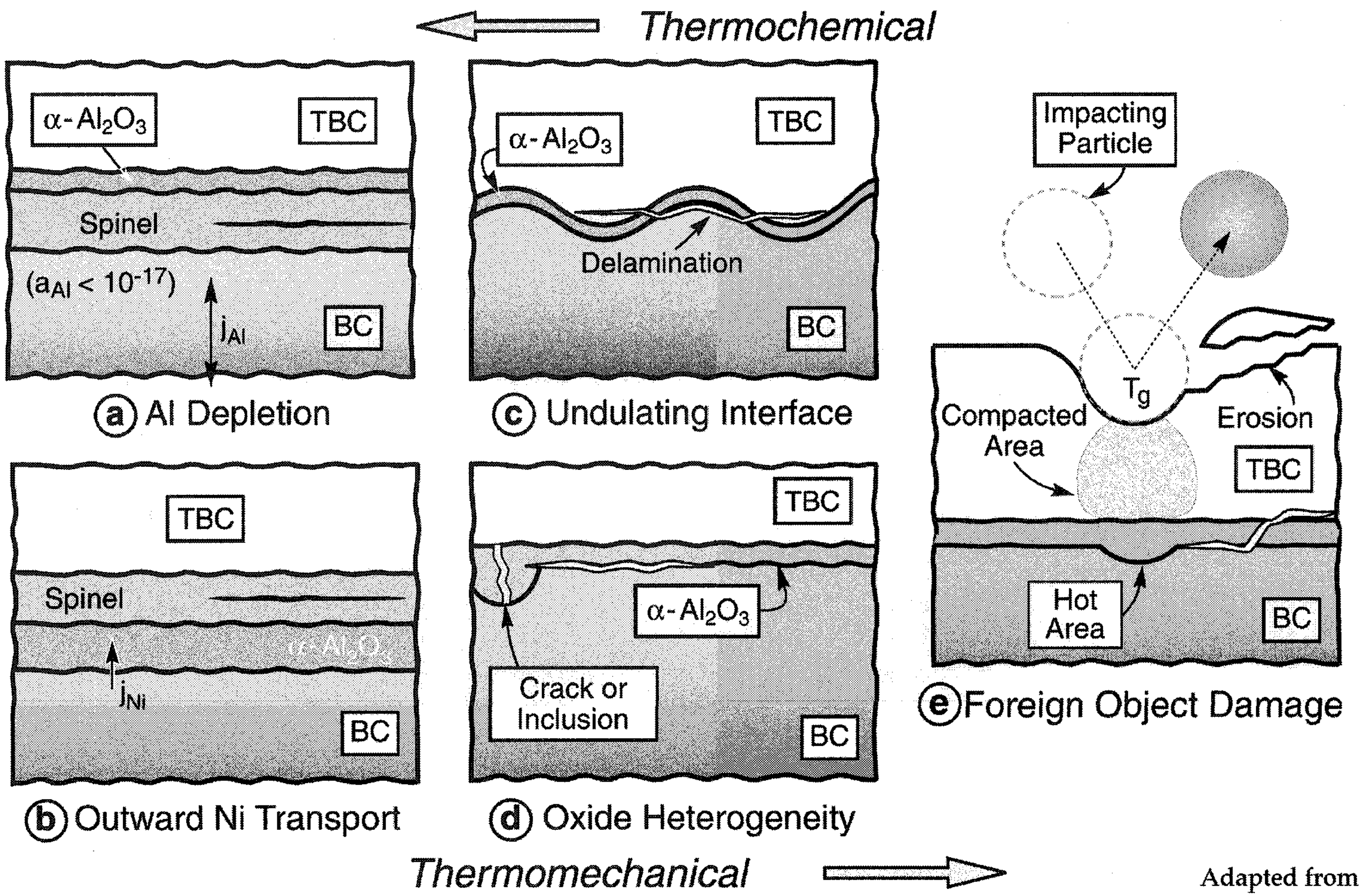
The Buffer Layer: Aluminide

- Sufficient Al to maintain stable TGO
- Microstructurally stable
- Adequate creep/yield strength
- Adequate toughness

The Structural Element: Superalloy

- Optimal mechanical properties
- Internally cooled

Partial Menu of Mechanisms leading to TBC Spallation



Adapted from A.G. Evans

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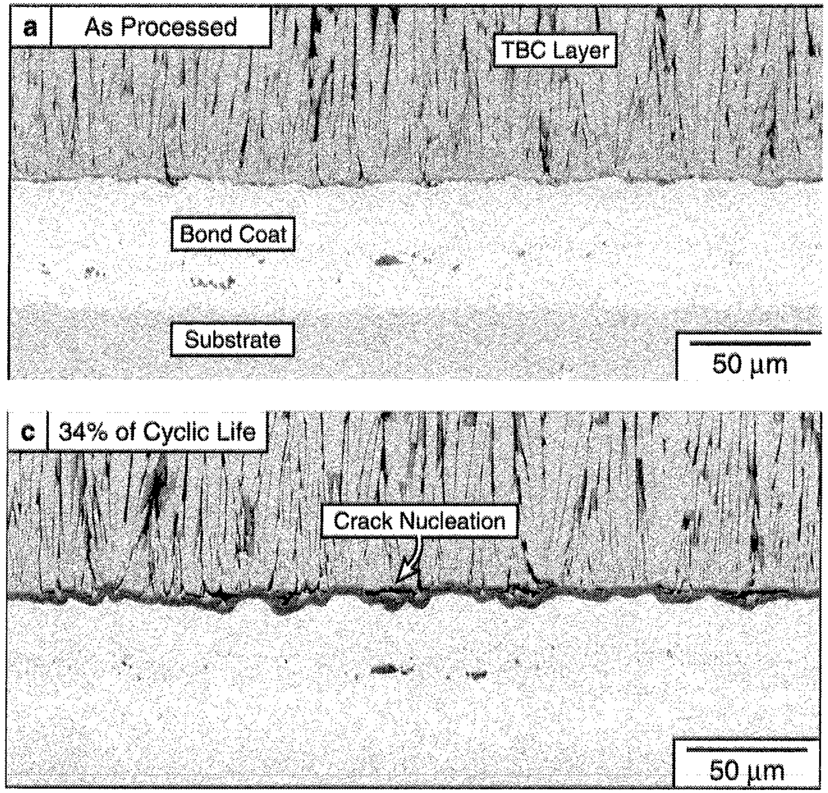
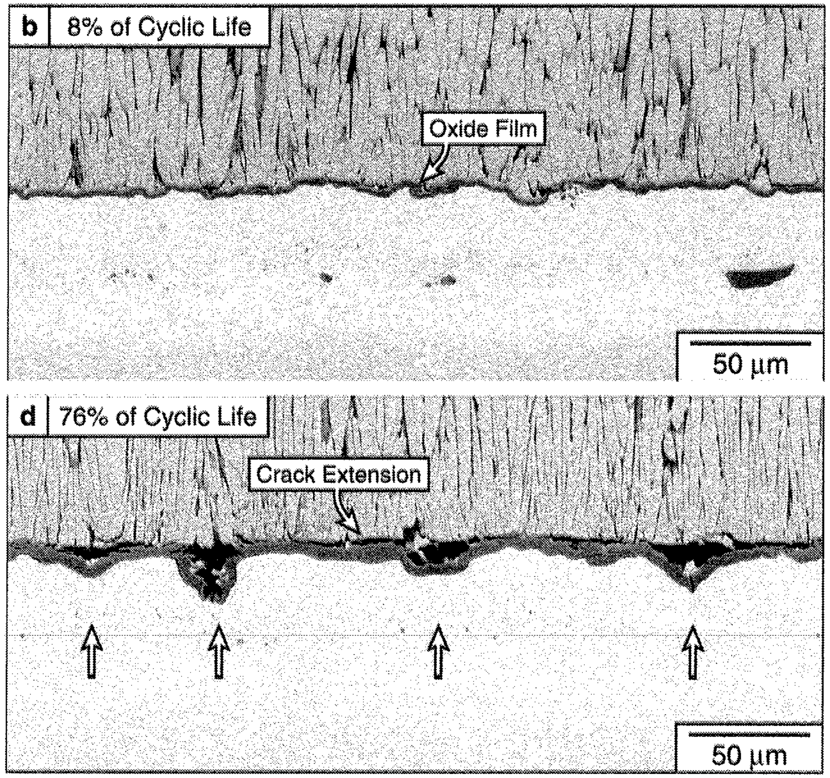
Evolution of Interface Morphology under Cyclic Oxidation

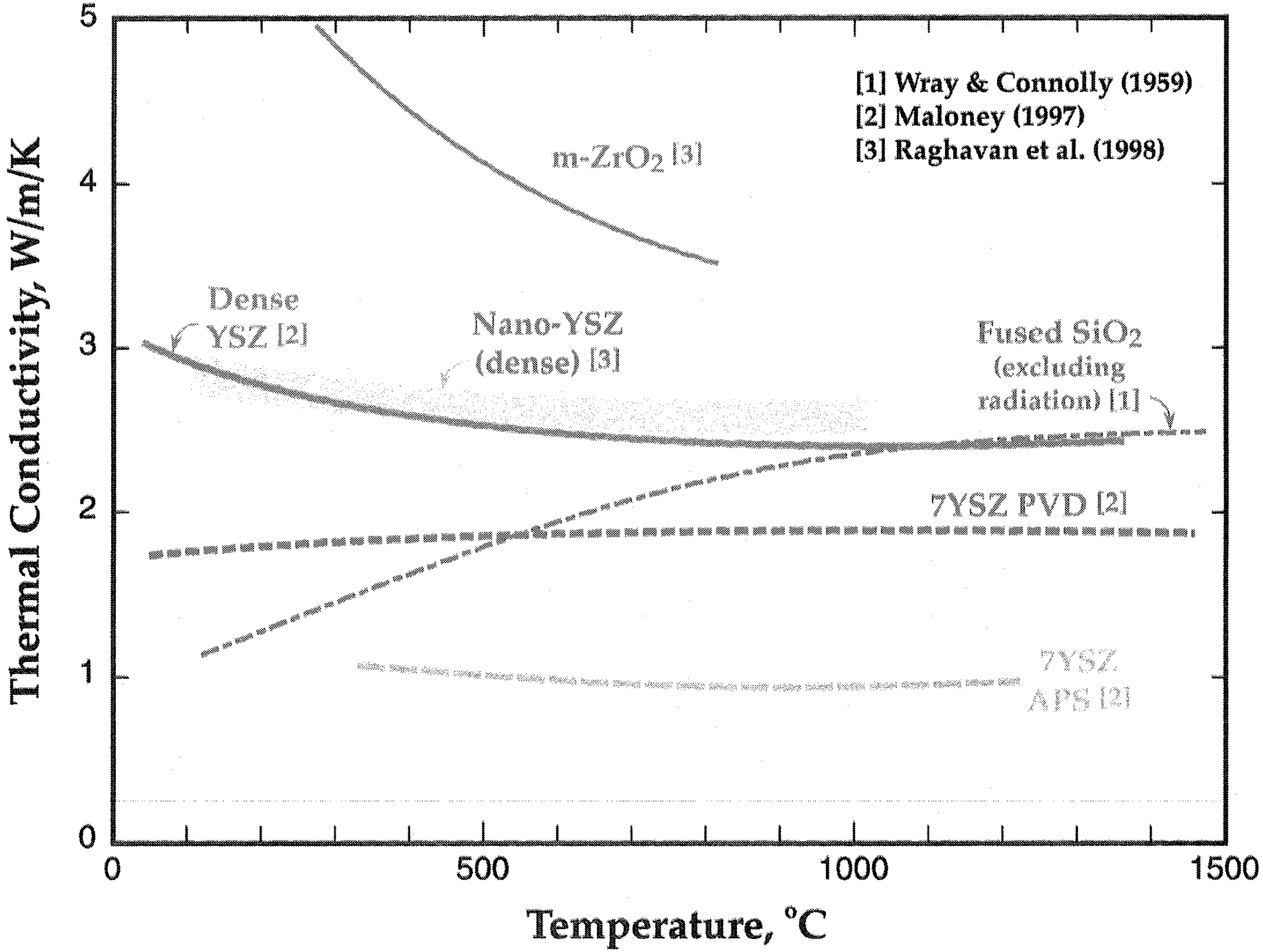


YSZ on (Ni,Pt) Al Bond Coat



Courtesy of D. Mumm
(Princeton University)

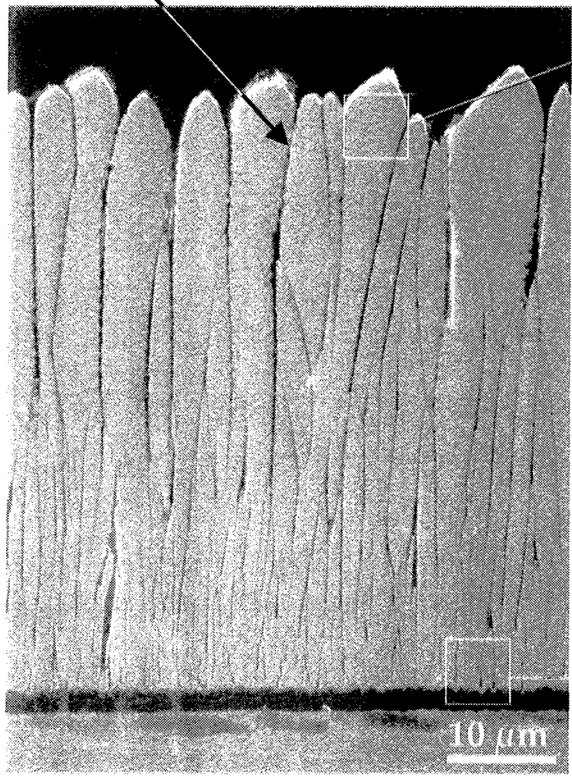
Thermal Conductivity of ZrO_2 and YSZ

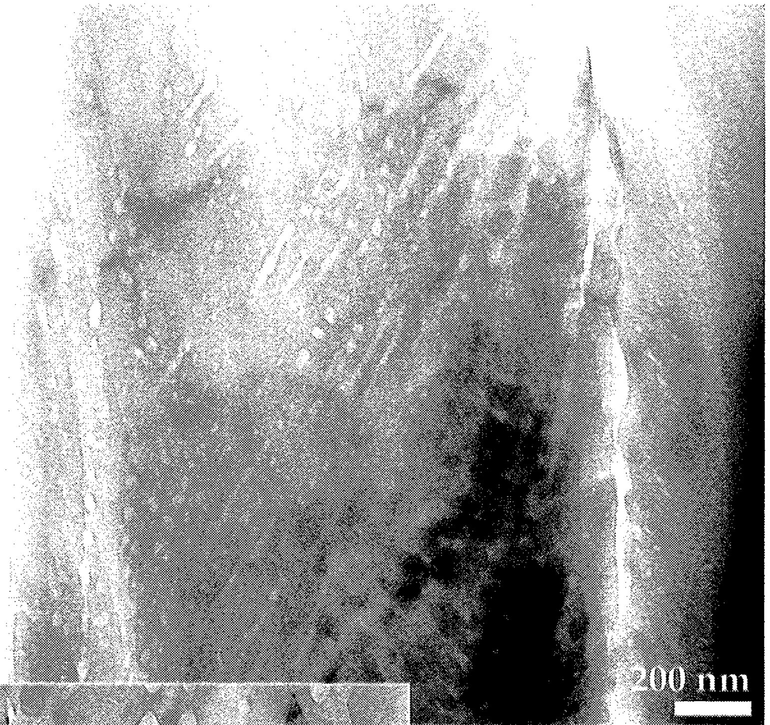


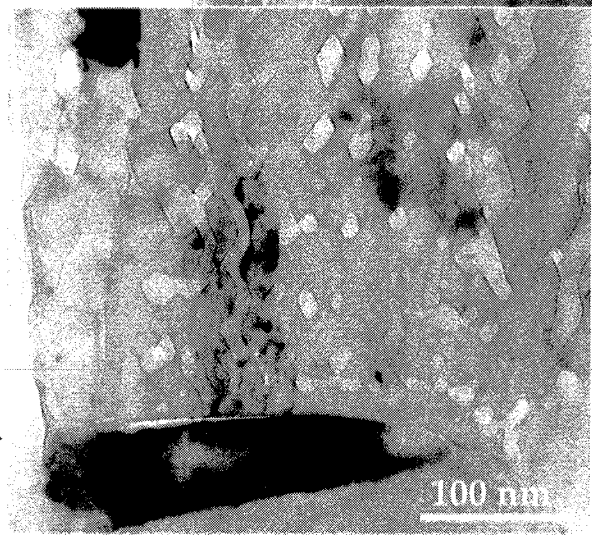
Porosity: key to TBC Performance

Intercolumnar
⇨ Compliance

Intracolumnar
⇨ Insulation





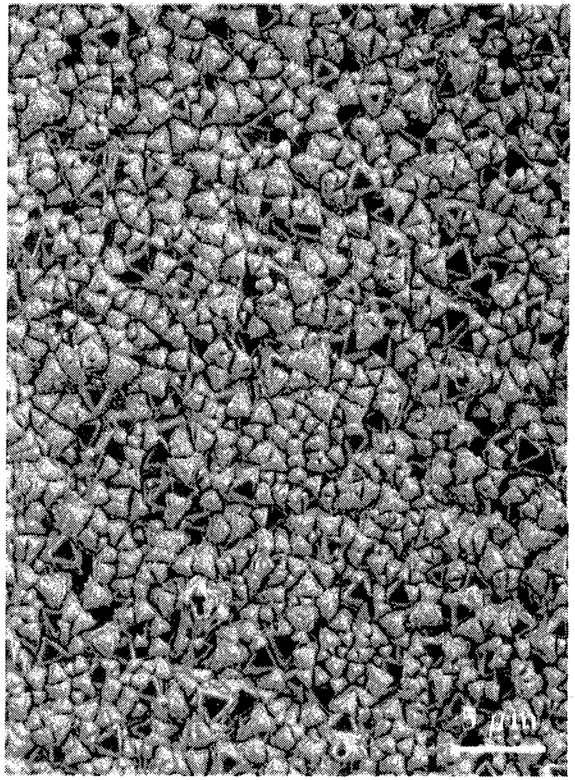


Different scales of shadowing

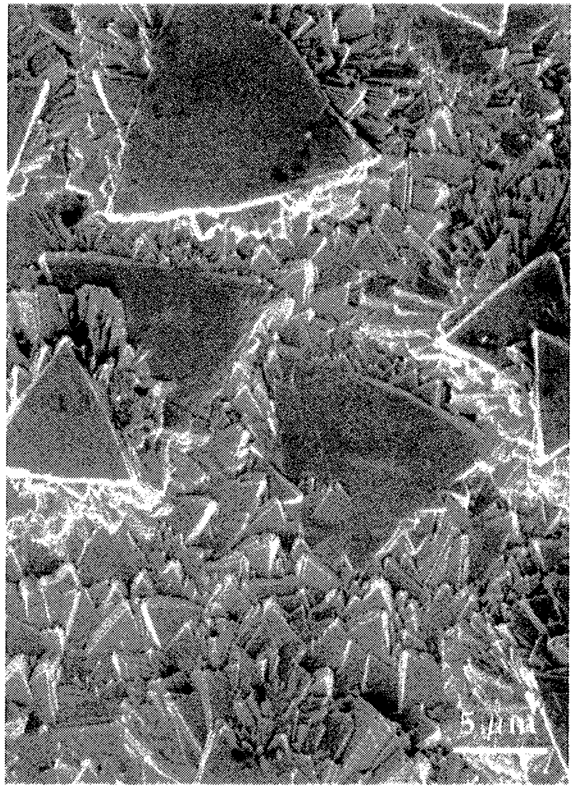
TEM on NiCrAlY
courtesy of E. Sommer
and M. Rühle
MPI-Stuttgart

Effect of Temperature on Surface Morphology and Texture

↓ Stationary Substrates



900°C: Dominant ⟨111⟩



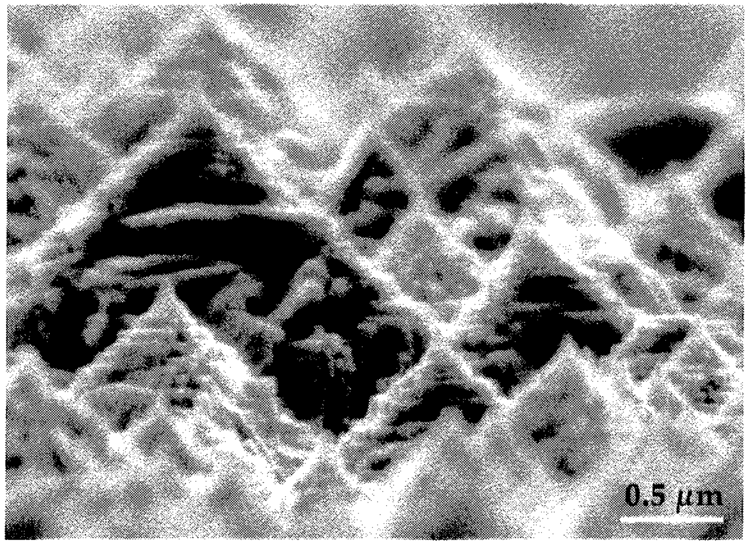
1000°C: ⟨111⟩ > ⟨220⟩

1100°C: ⟨220⟩>⟨311⟩>⟨111⟩

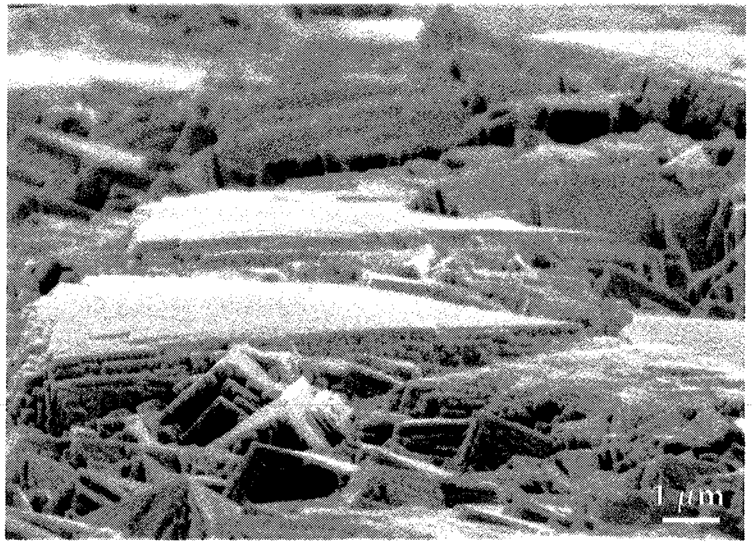
Normal Vapor Incidence
Pre-oxidized FeCrAlY Substrates

Effect of Temperature on Tip Morphology

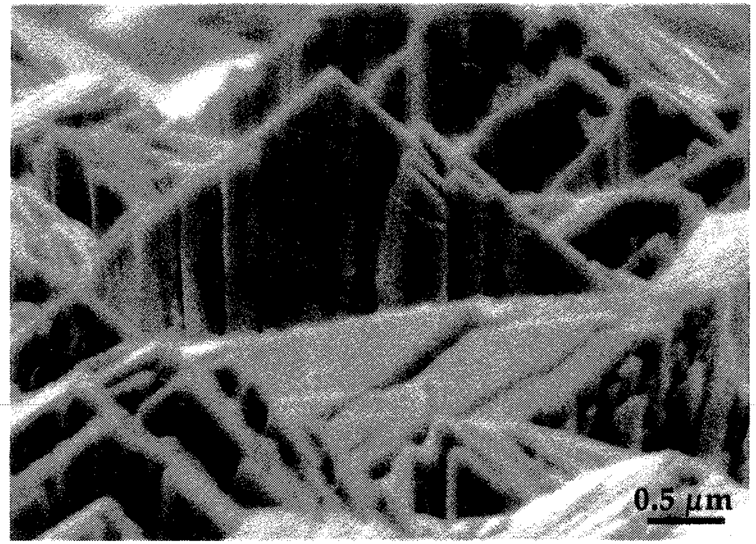
- Growth facets always {111}
- "111" columns grow with (111) facet normal to axis in two distinct morphologies
- Other column orientations grow with facets oblique to axis.



900°C: Dominant ⟨111⟩



1000°C: ⟨111⟩ > ⟨220⟩

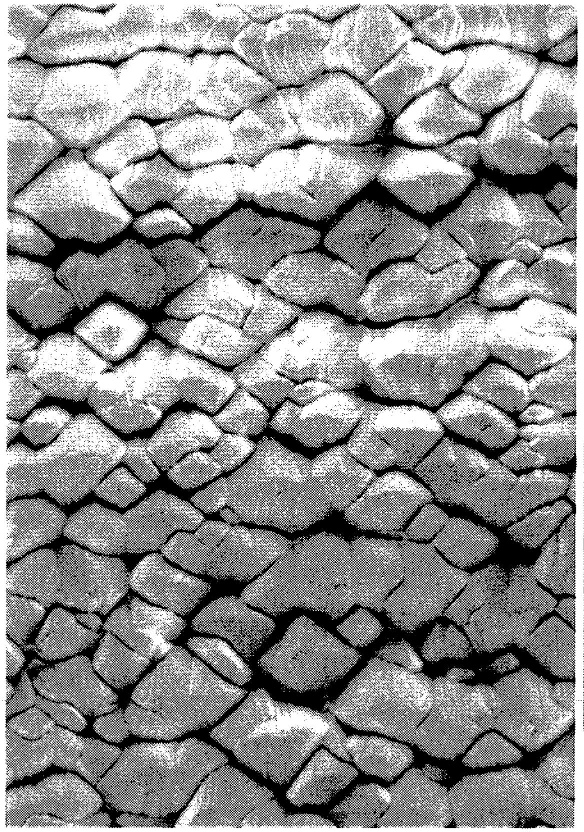


1100°C: ⟨220⟩>⟨311⟩>⟨111⟩

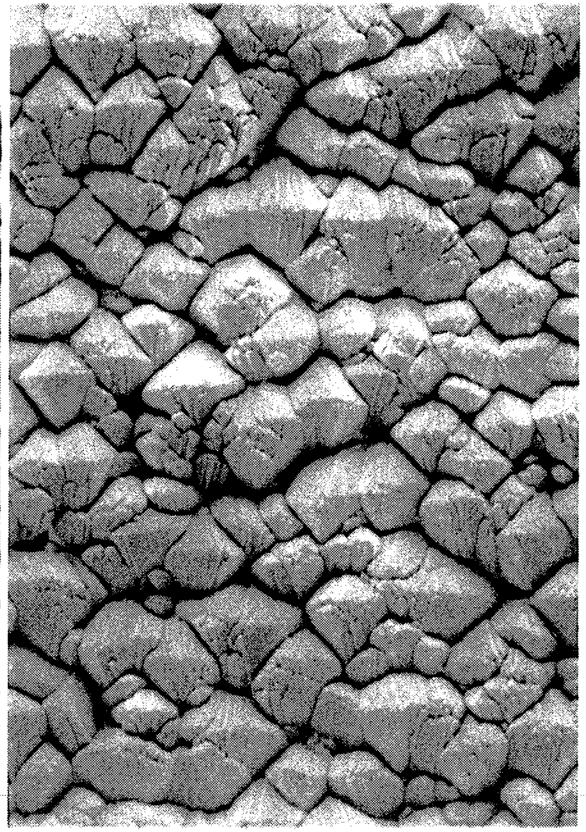
Levi-9/00

Effect of Temperature on Surface Morphology and Texture

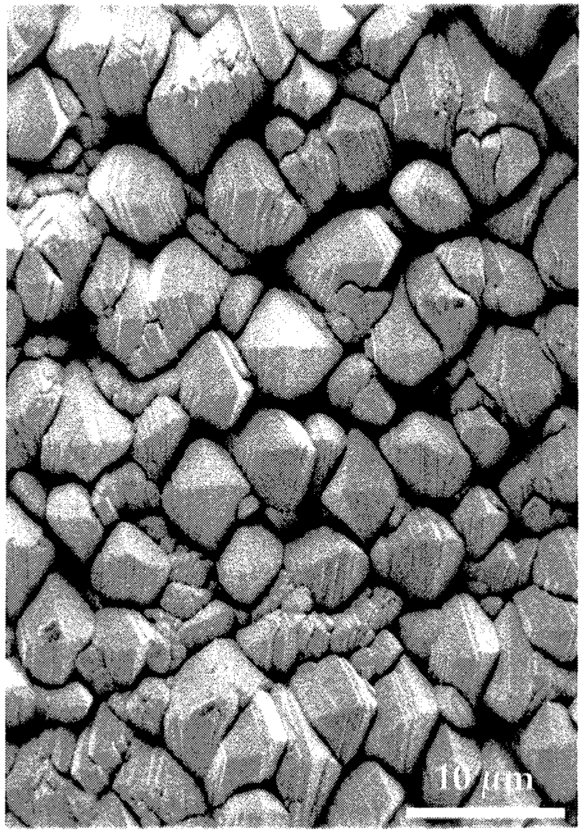
Rotating Substrates



900°C: ⟨200]



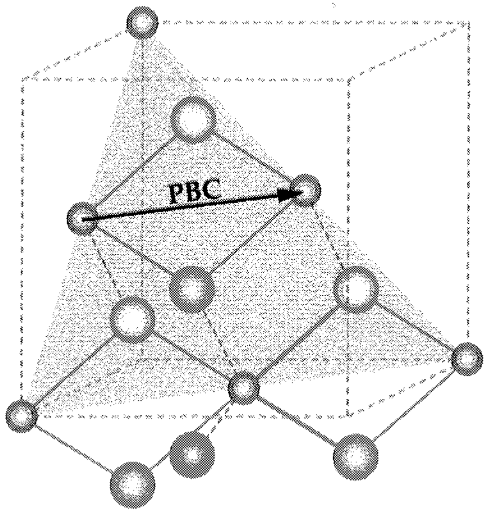
1000°C: ⟨200]



1100°C: [002} + ⟨200]

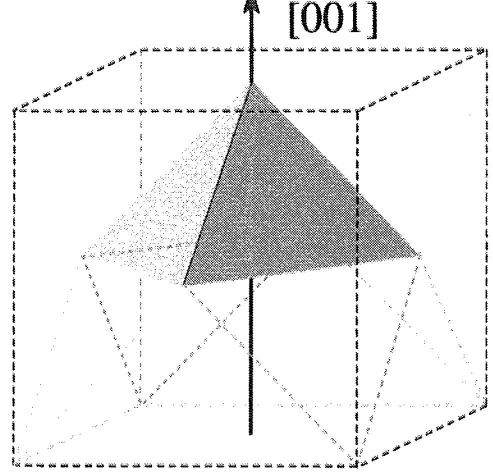
8 RPM, ~0.9 μm/min
(Flux ~ 3.2 μm/min)

Levi-9/00

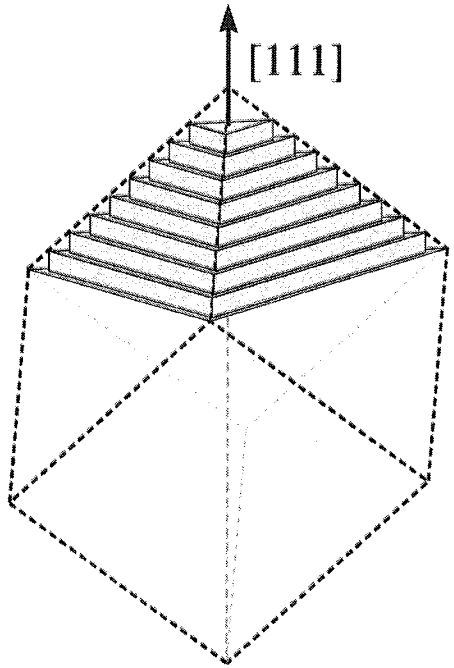


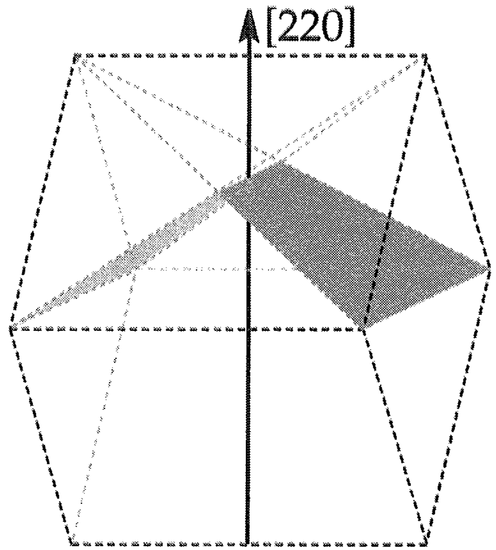
Texture and Tip Configurations

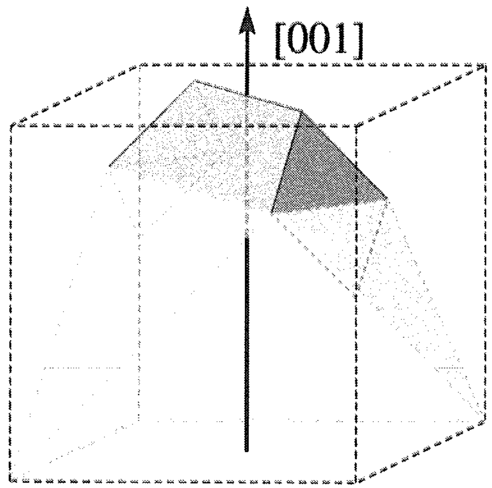
{111} active growth facets, independent of texture.
(Consistent with PBC analysis of fluorite, Hartman, 1972)



Rotating Substrates

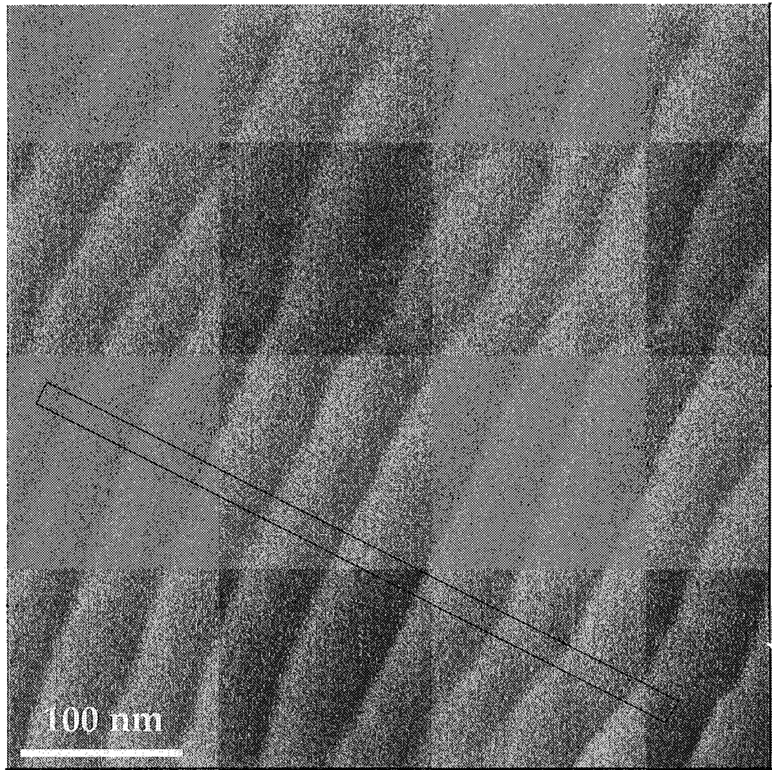


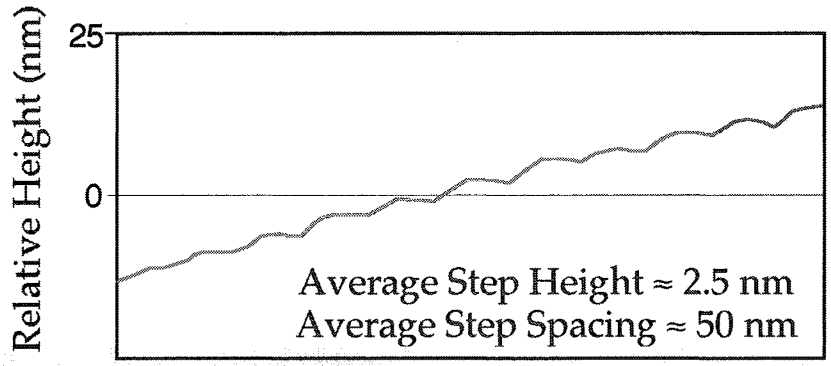


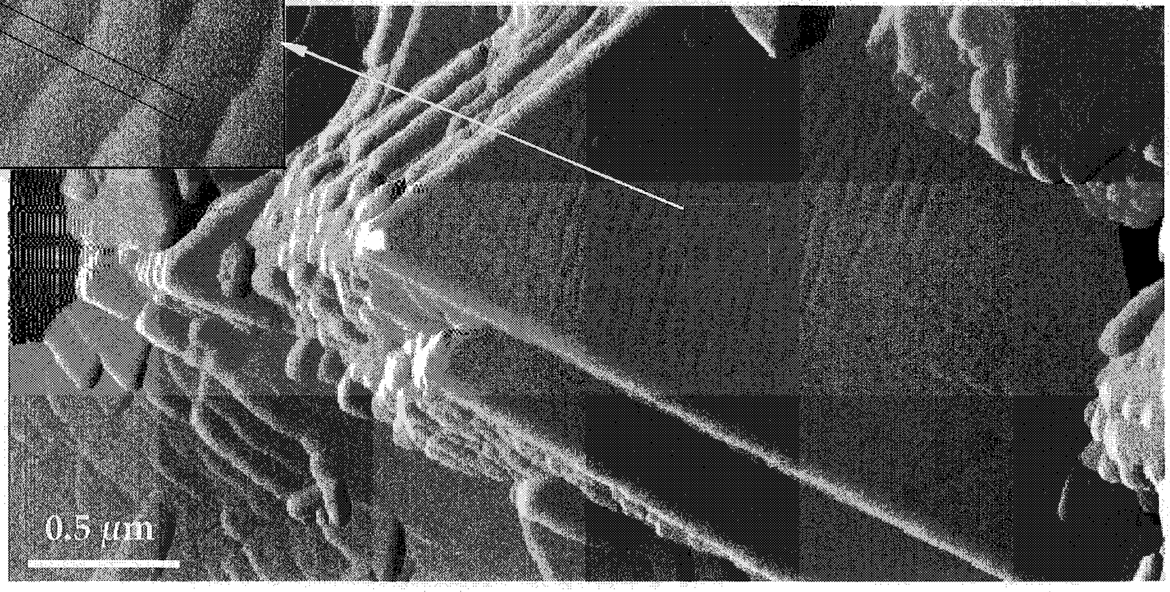


Stationary Substrates

Step Propagation on "Flat" (111) Facet

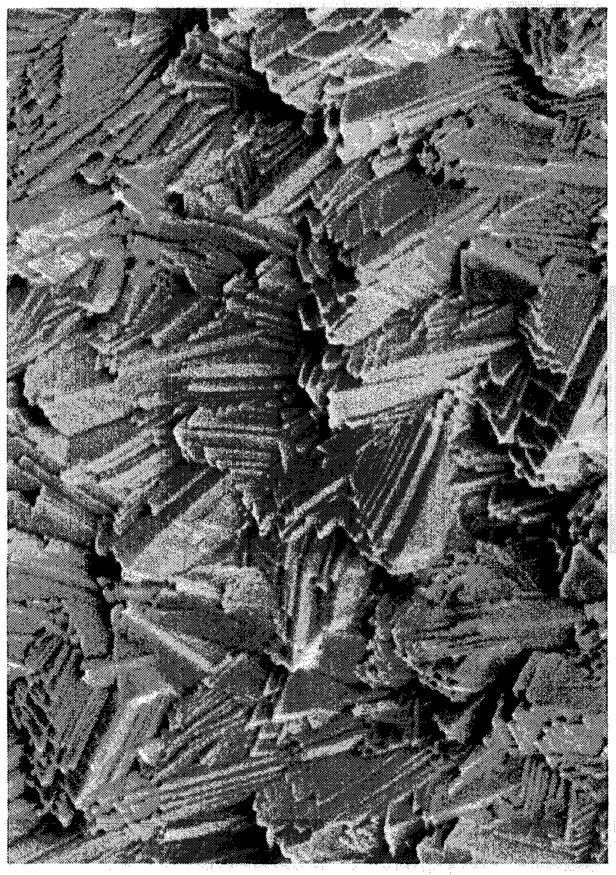




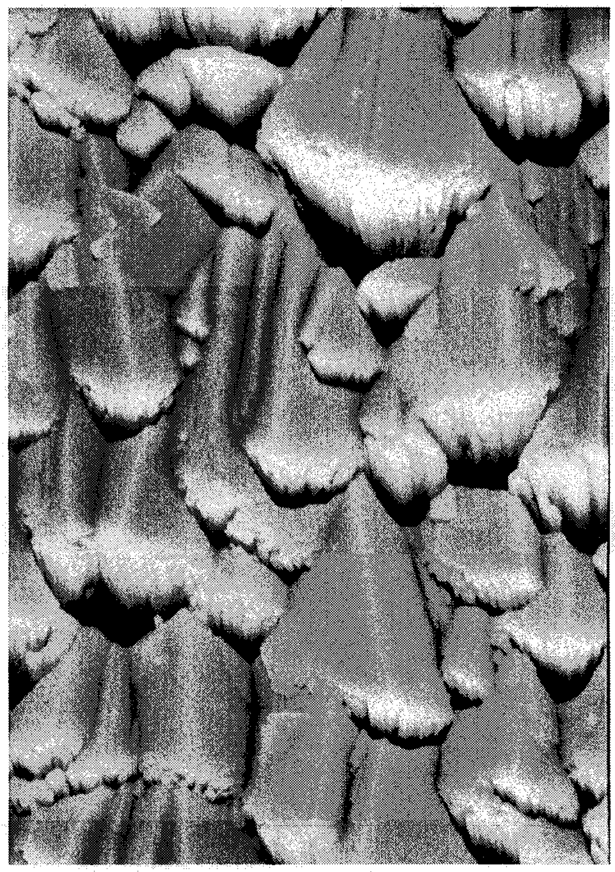


Stationary Deposition
Normal VIA
1000°C, 1.1 μm/min

In-Plane Texture Development Under Oblique Vapor Incidence



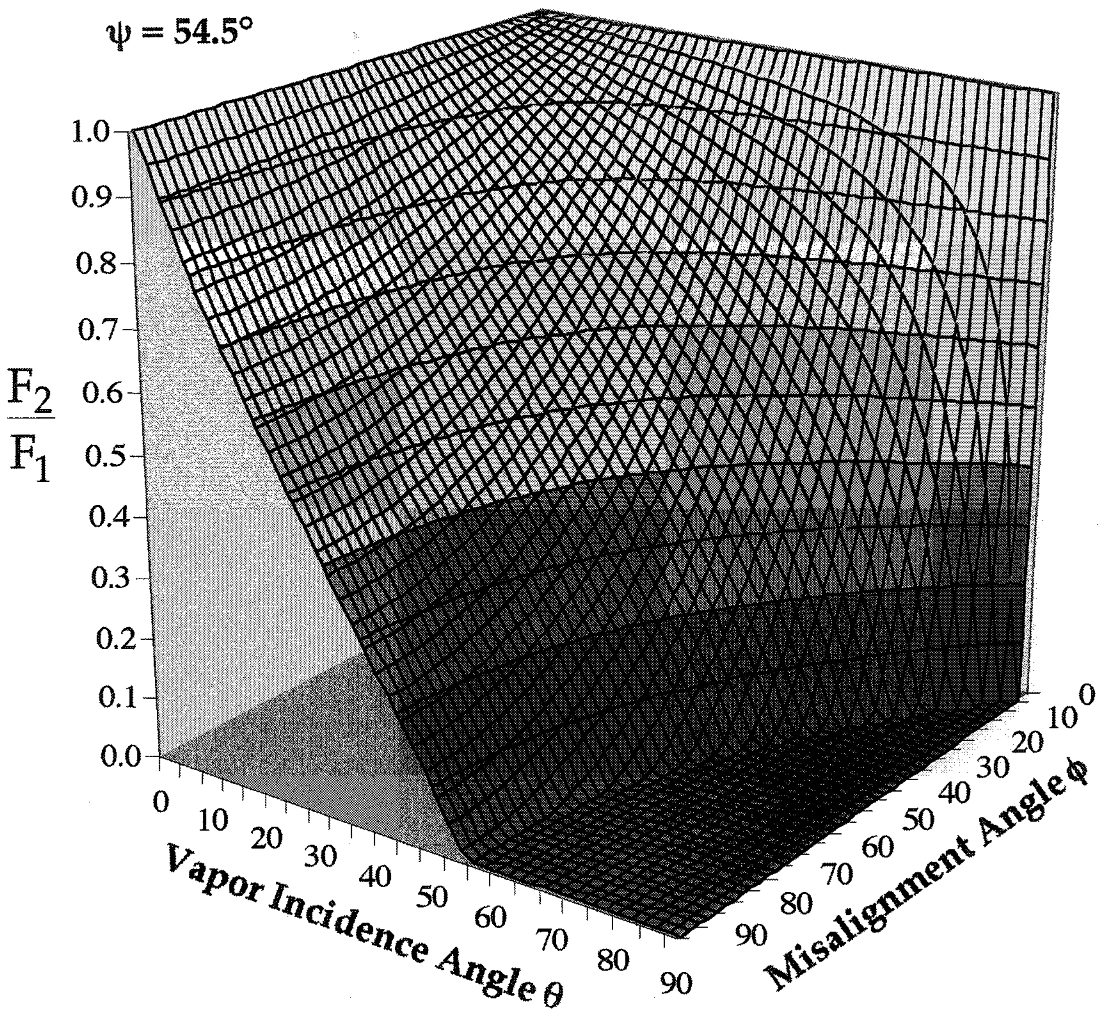
Normal VIA (0°)



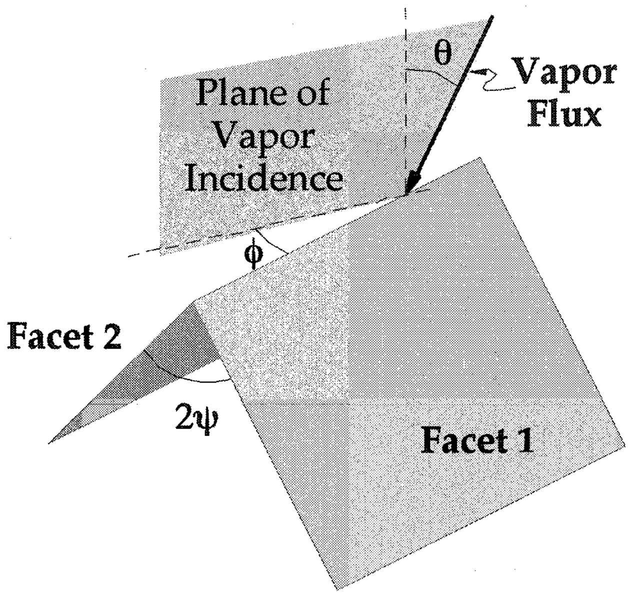
Oblique VIA (45°)

Stationary Deposition, 1100°C, ~1 μm/min

Geometric Argument for Evolution of In-Plane Texture



- Ridge misalignment under oblique vapor incidence results in asymmetric growth of rooftop column tip and eventual elimination.



Facet Flux Ratio

$$\frac{F_2}{F_1} = \frac{\cos\theta \sin\psi - \sin\theta \sin\phi \cos\psi}{\cos\theta \sin\psi + \sin\theta \sin\phi \cos\psi}$$

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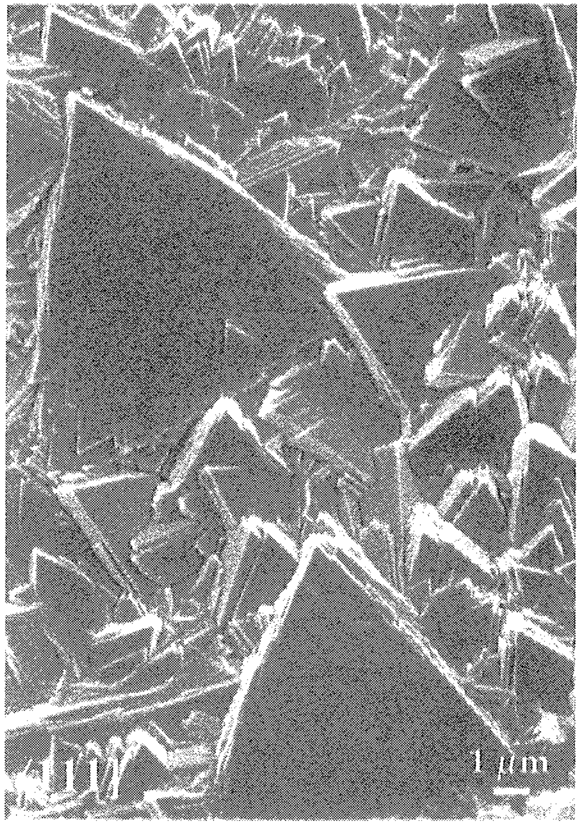
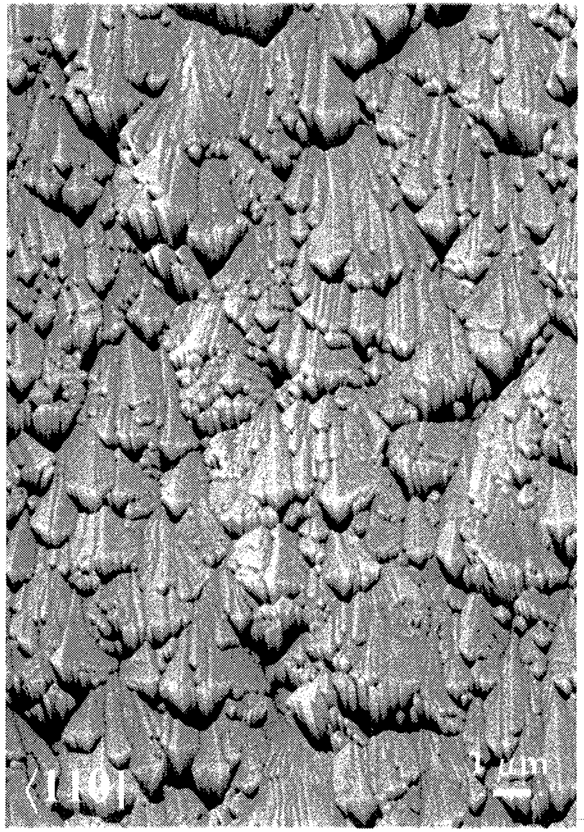
Effect of Vapor Incidence Pattern on Column Tip Morphology

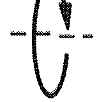


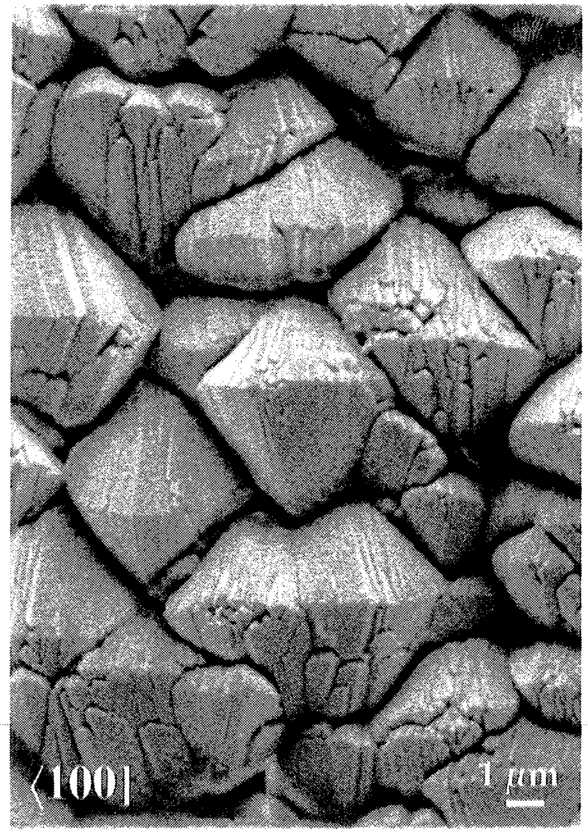
Stationary, Normal VIA

Deposition Temperature = 1000°C
Net Deposition Rate ≈ 1 μm/min



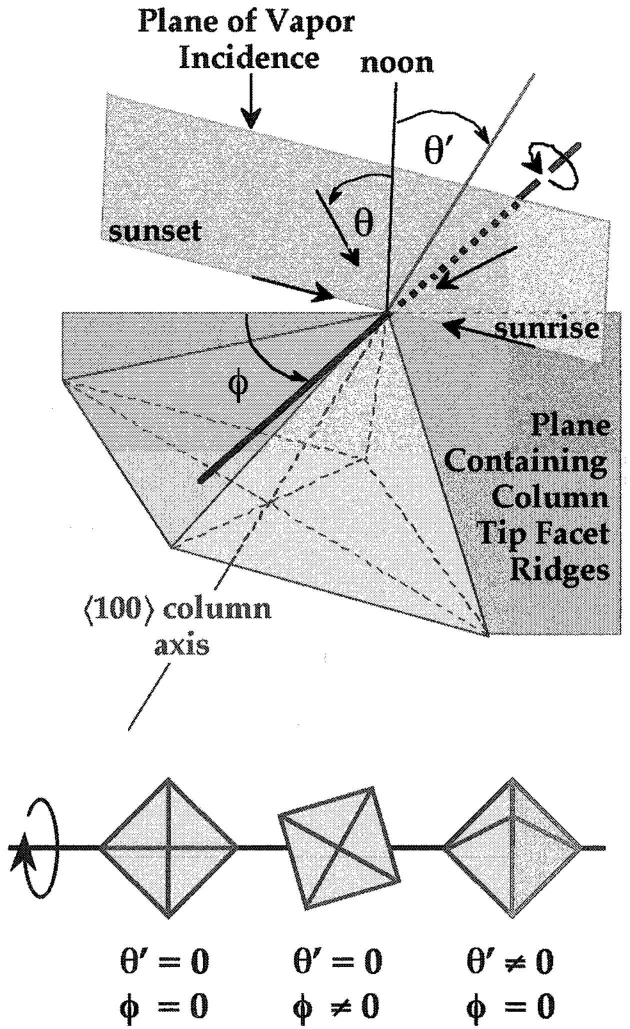
Stationary, 45° VIA

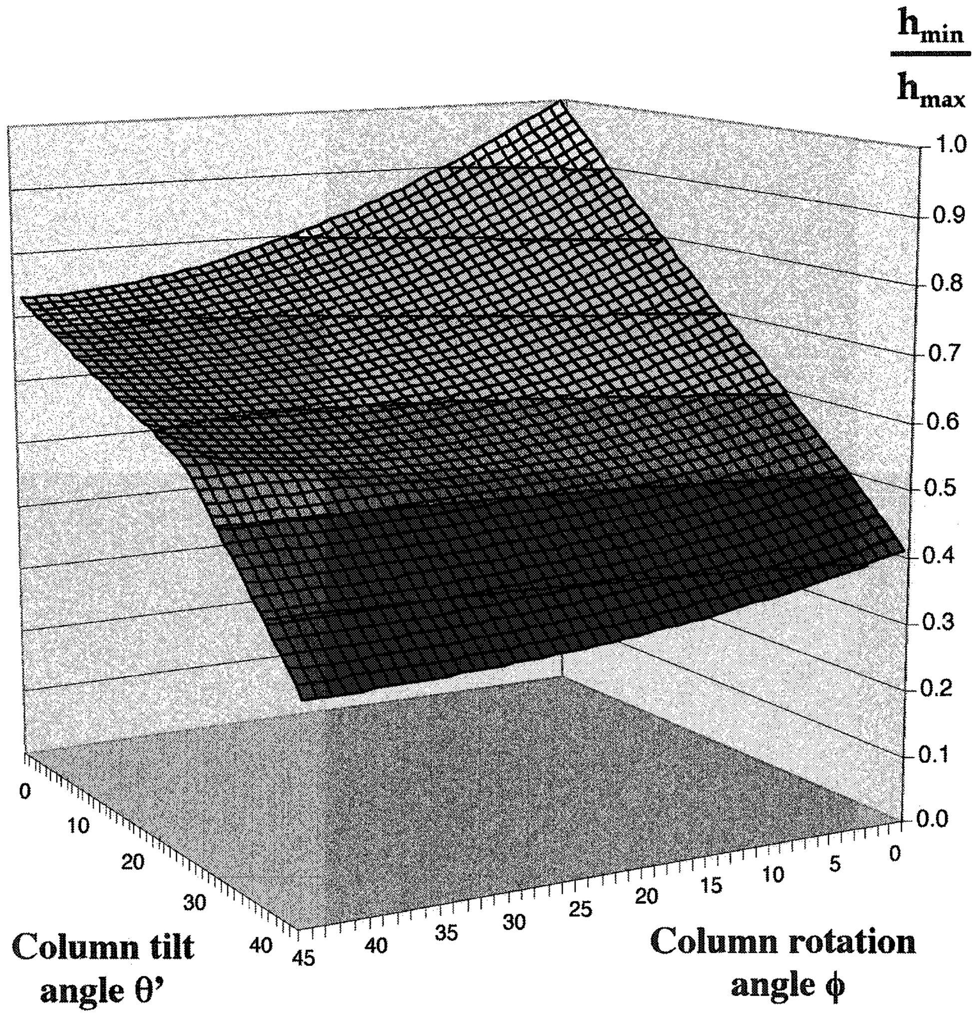




Rotating, 8 RPM

Selection of In-Plane Orientation upon Rotation



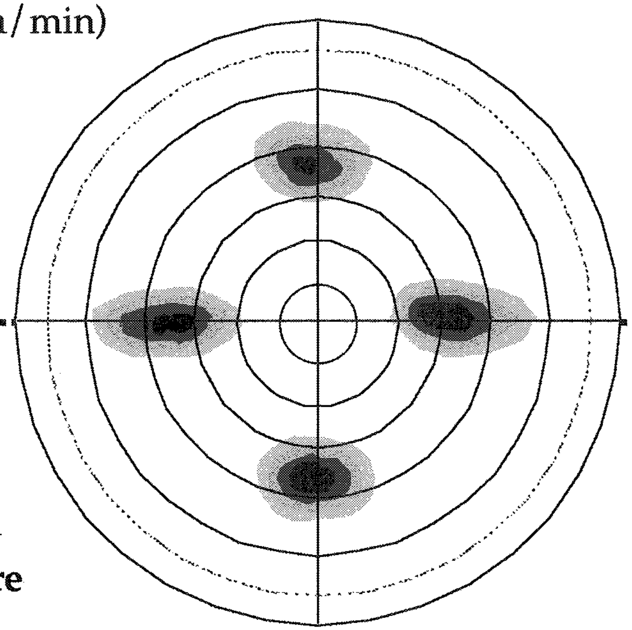


 Levi-9/00

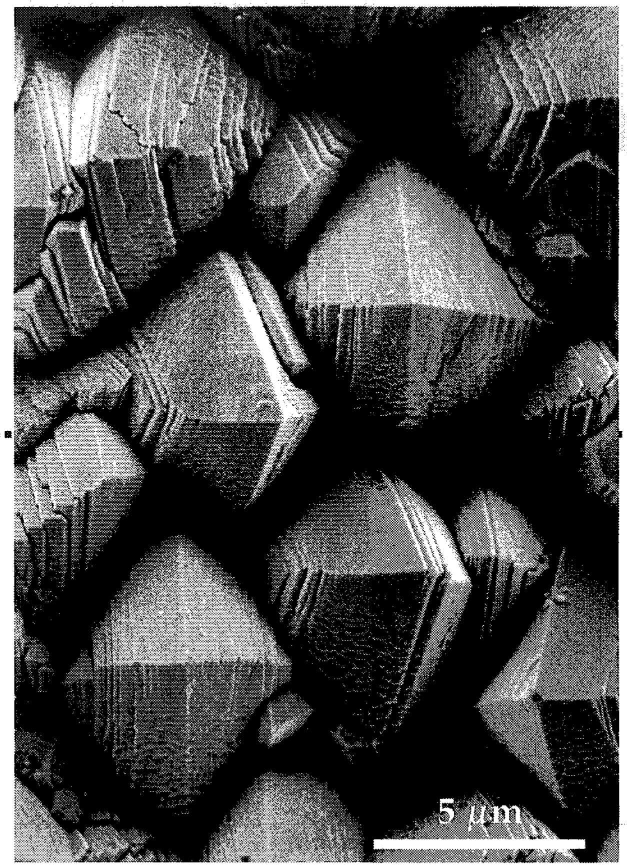
Deviations from Dominant Texture

1100°C, 8 RPM
~ 0.9 μm/min
(flux ~ 3.2 μm/min)

axis of
substrate
rotation



{220/202}
Pole figure

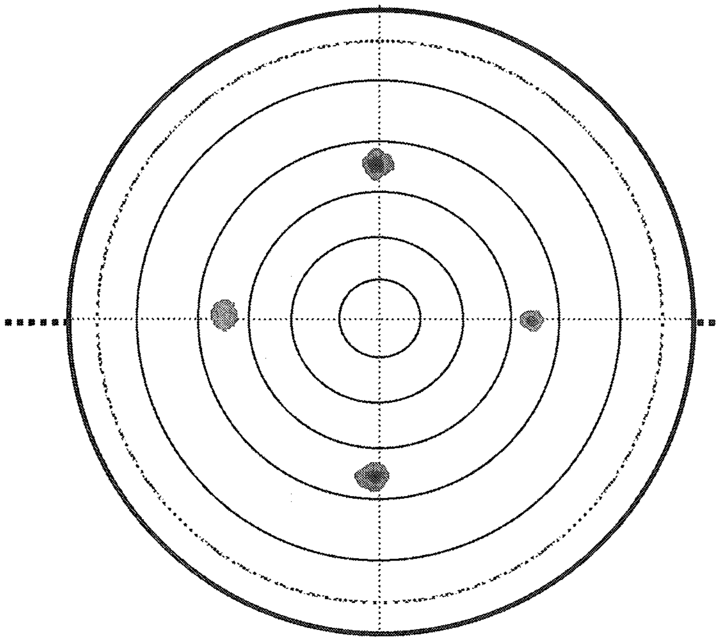


Larger column orientation scatter along plane parallel to the rotation axis

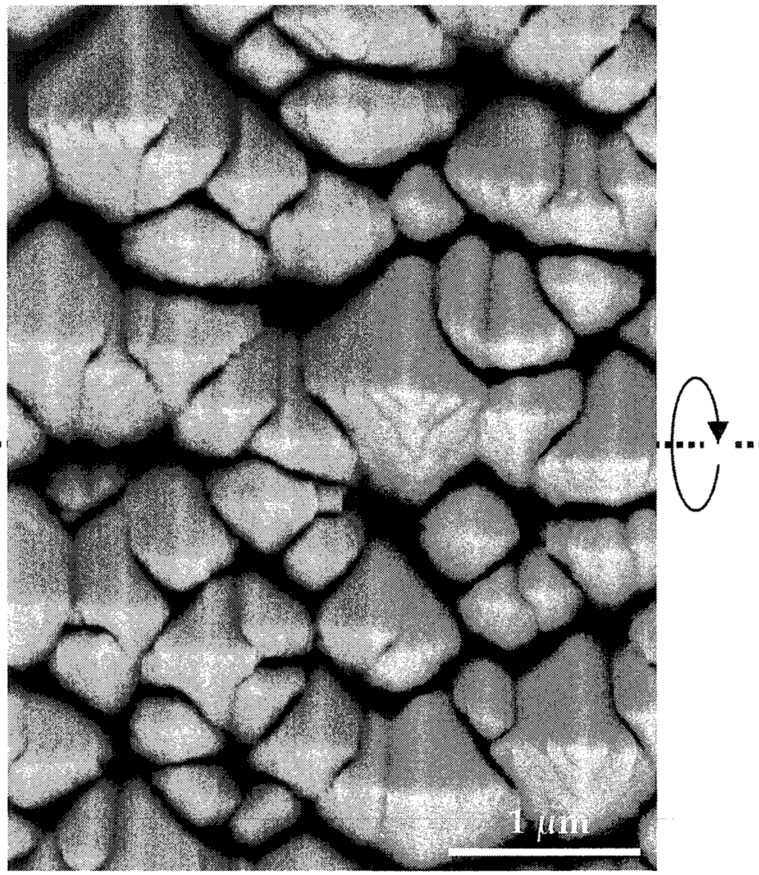
[002] + •200] Texture

Texture Dispersion on Flat Sapphire Substrate

1000°C, 8 RPM, ~ 0.3 μm/min
{220/202} Pole figure



axis of substrate rotation



Reduced scatter in column tip orientation and texture anisotropy

⟨200] Texture

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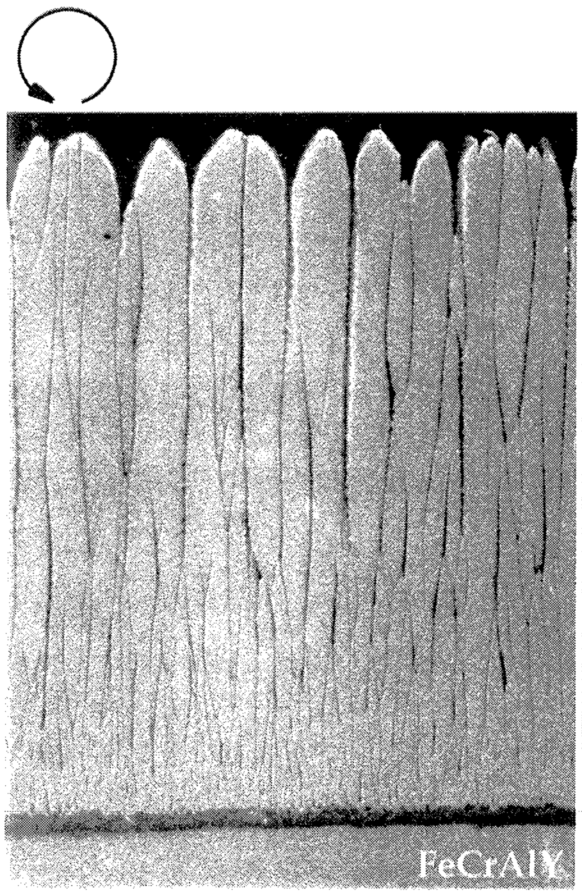
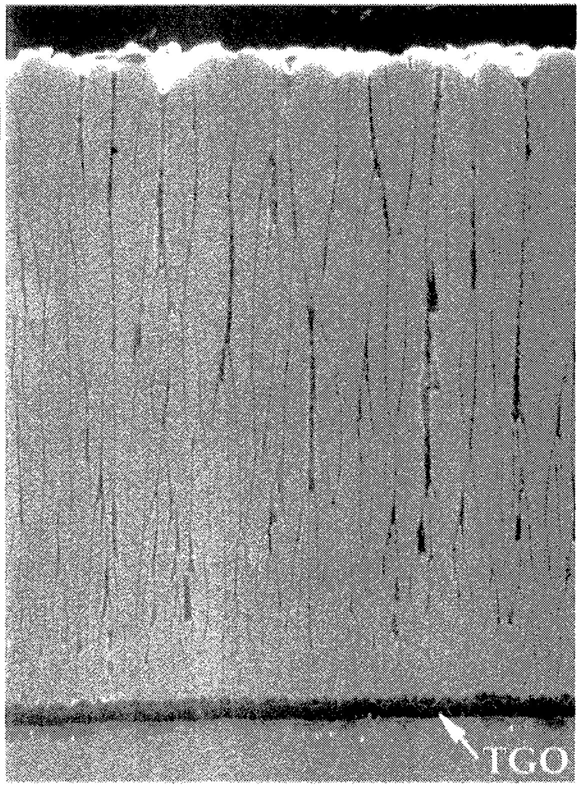
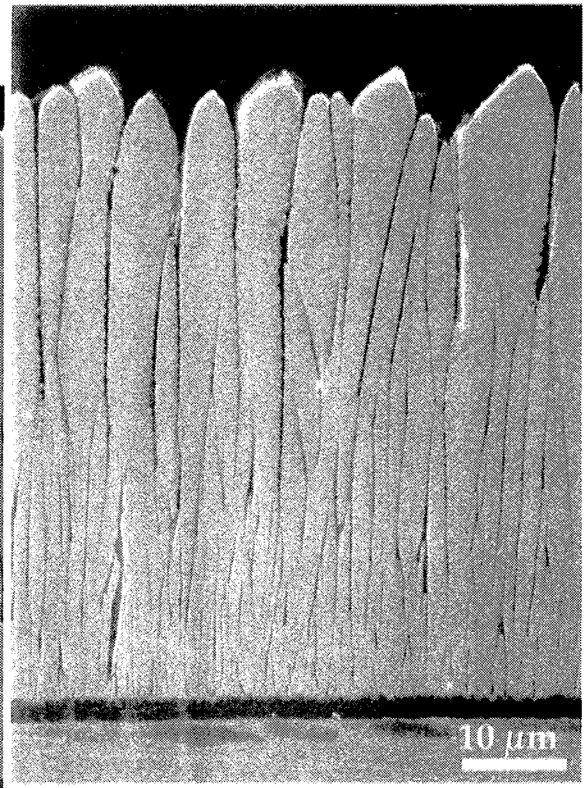
Columnar Microstructures for Deposition under Rotation



900°C: Dominant ⟨200]



1000°C: Dominant ⟨200]



1100°C: [002} + ⟨200]

8 RPM, ~0.9 μm/min
(Flux ~ 3.2 μm/min)

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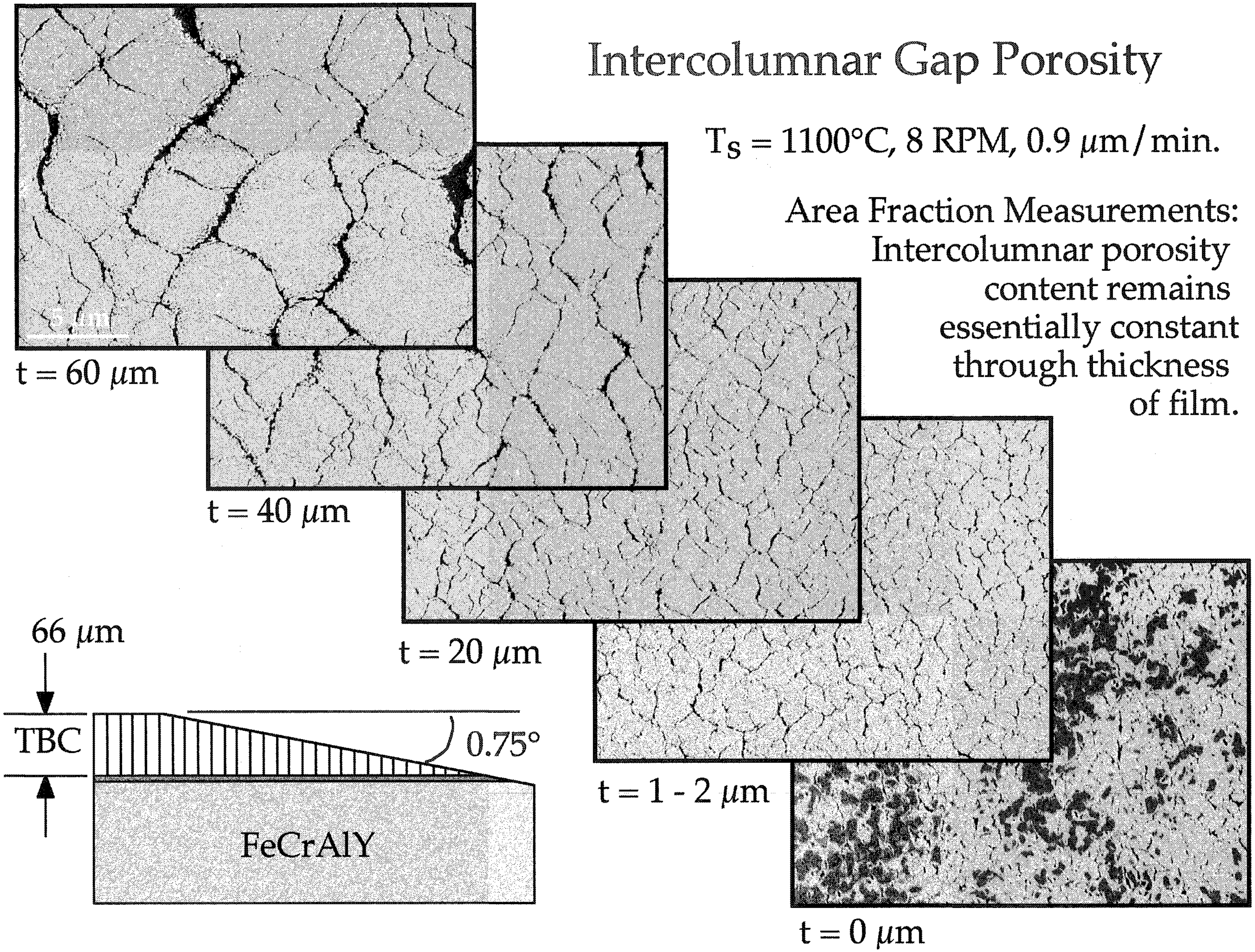
Intercolumnar Gap Porosity

T_S = 1100°C, 8 RPM, 0.9 μm/min.

Area Fraction Measurements:
Intercolumnar porosity content remains essentially constant through thickness of film.



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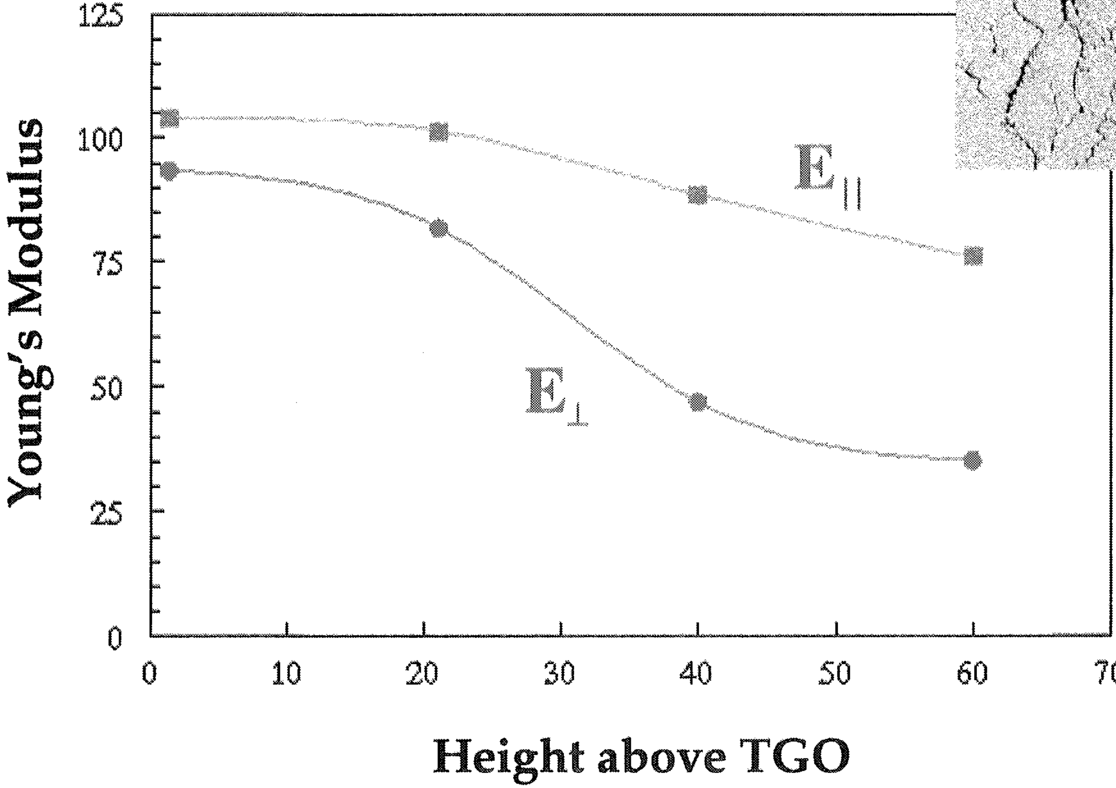
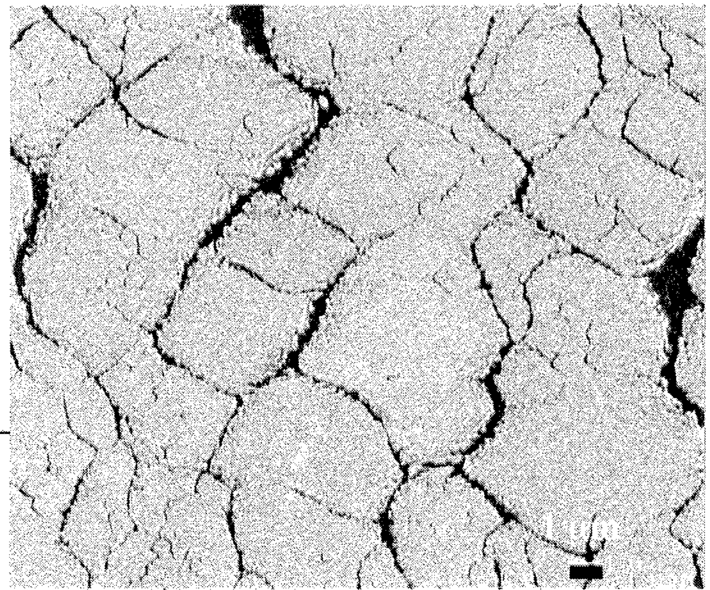
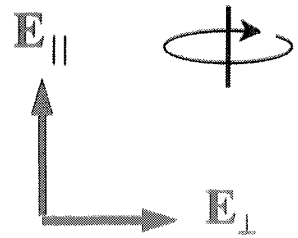
Calculated In-Plane Modulus Anisotropy

(Courtesy of Ed Fuller, NIST)





60 μm above TGO



Graph assumes 60% reduction due to intra-columnar porosity

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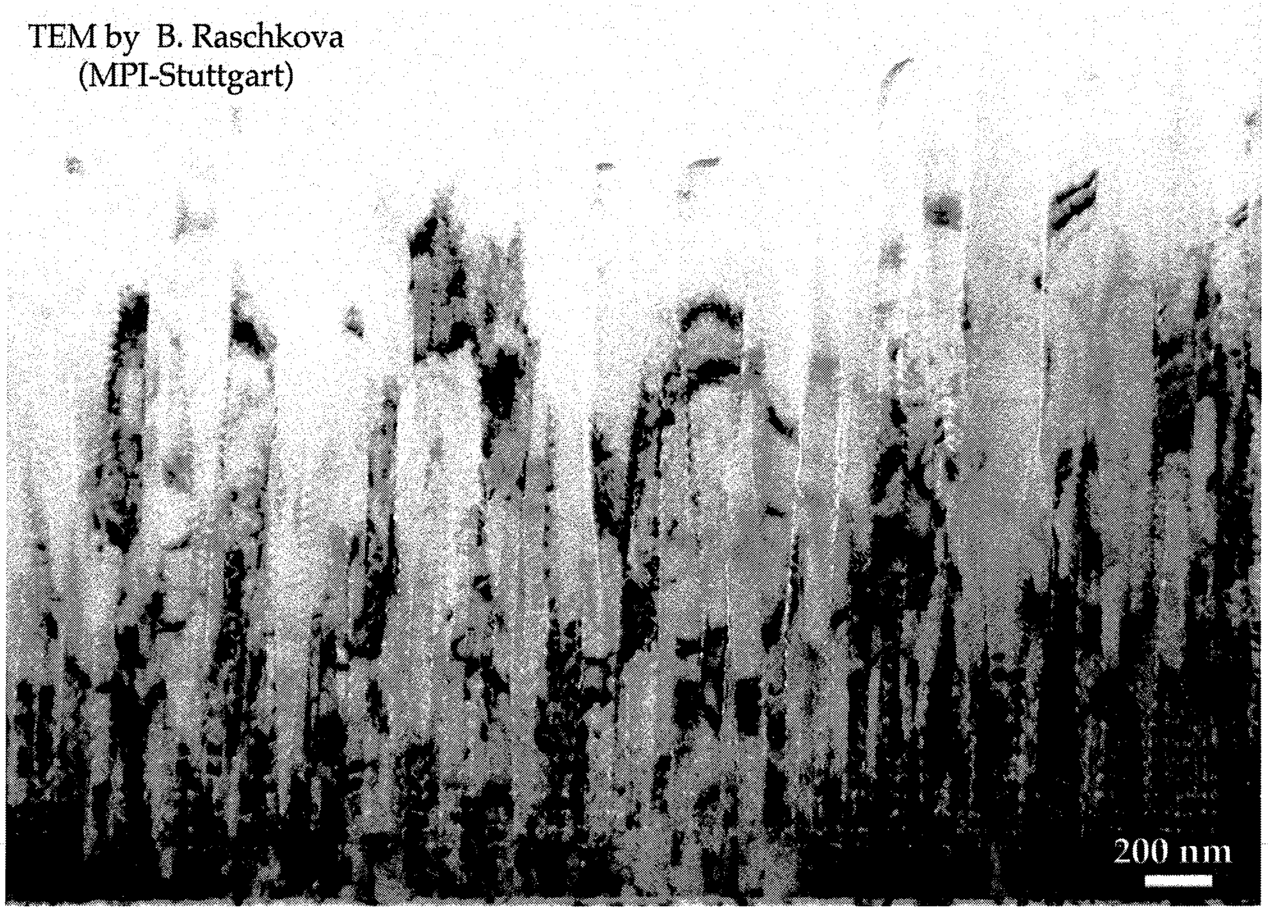
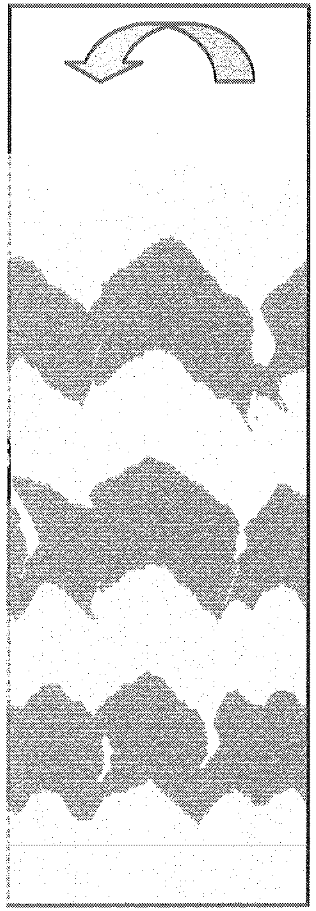
Near-Substrate Pore Structure

TEM by B. Raschkova
(MPI-Stuttgart)



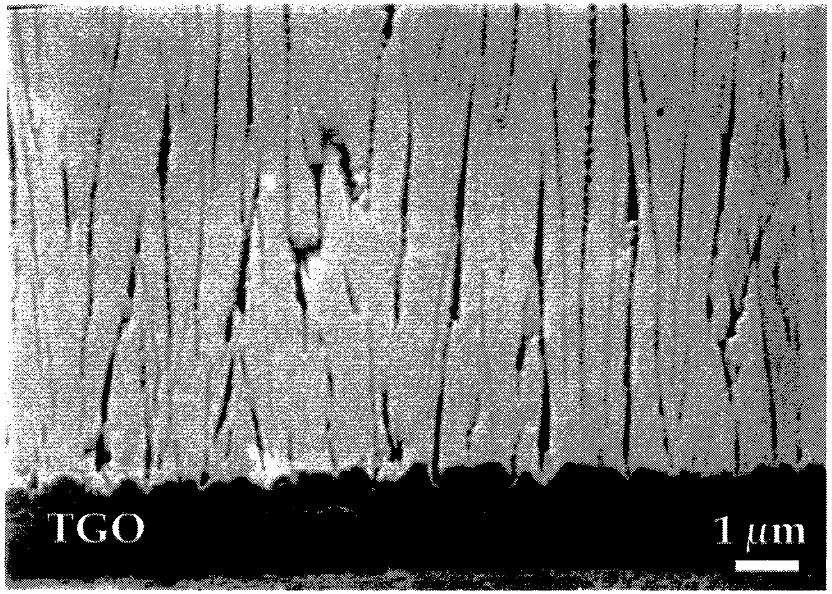
YSZ Grown on Sapphire. Pore Spacing Equivalent to Thickness Deposited per Revolution (~35 nm)



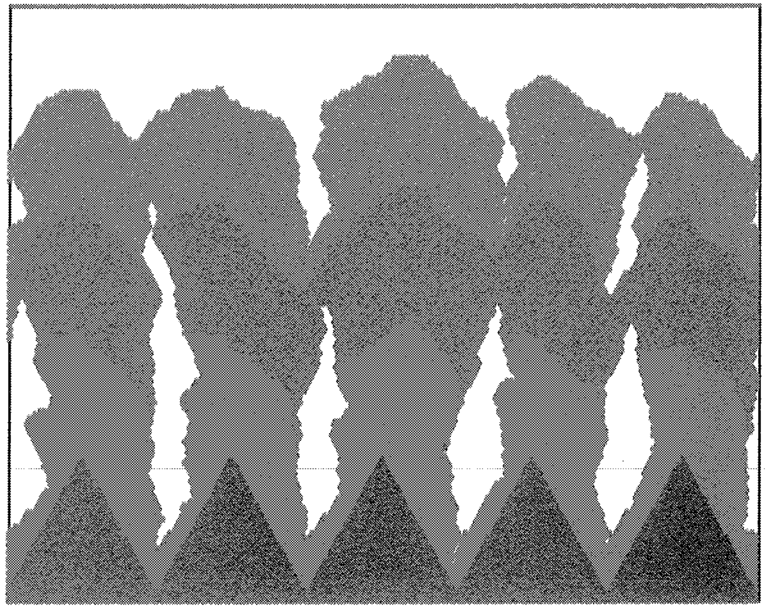
2D Kinetic MC
(~40000 atoms)

Levi-9/00

Intercolumnar Gap Initiation by Shadowing from TGO Roughness

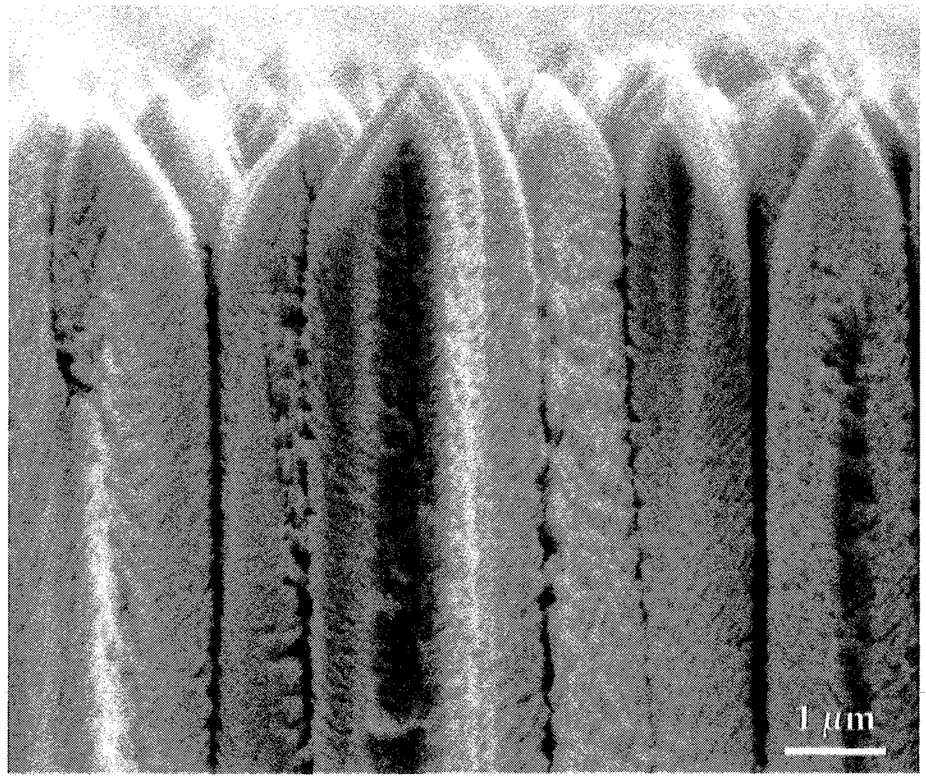


Root of Columns in TBC
Deposited on Pre-Oxidized
FeCrAlY Substrate
(1100°C, 8 RPM, ~0.9 μm/min)

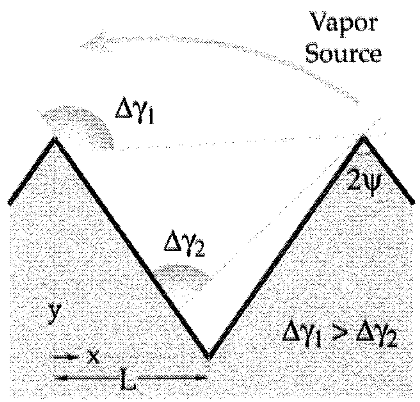


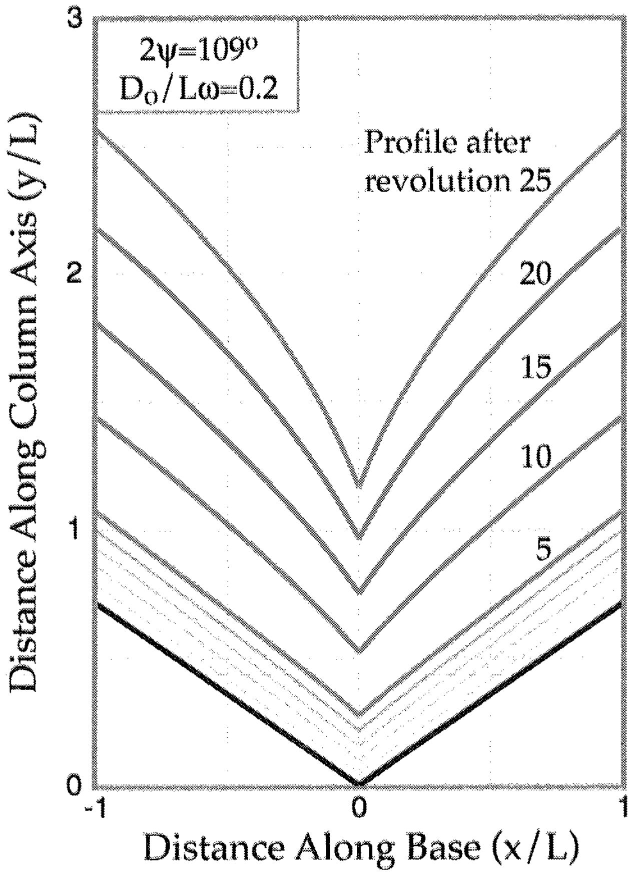
ABD Simulation
on Substrate with
Periodic Roughness

Evolution of Intercolumnar Gap



TBC Grown on FeCrAlY Substrate, 950°C, 8RPM





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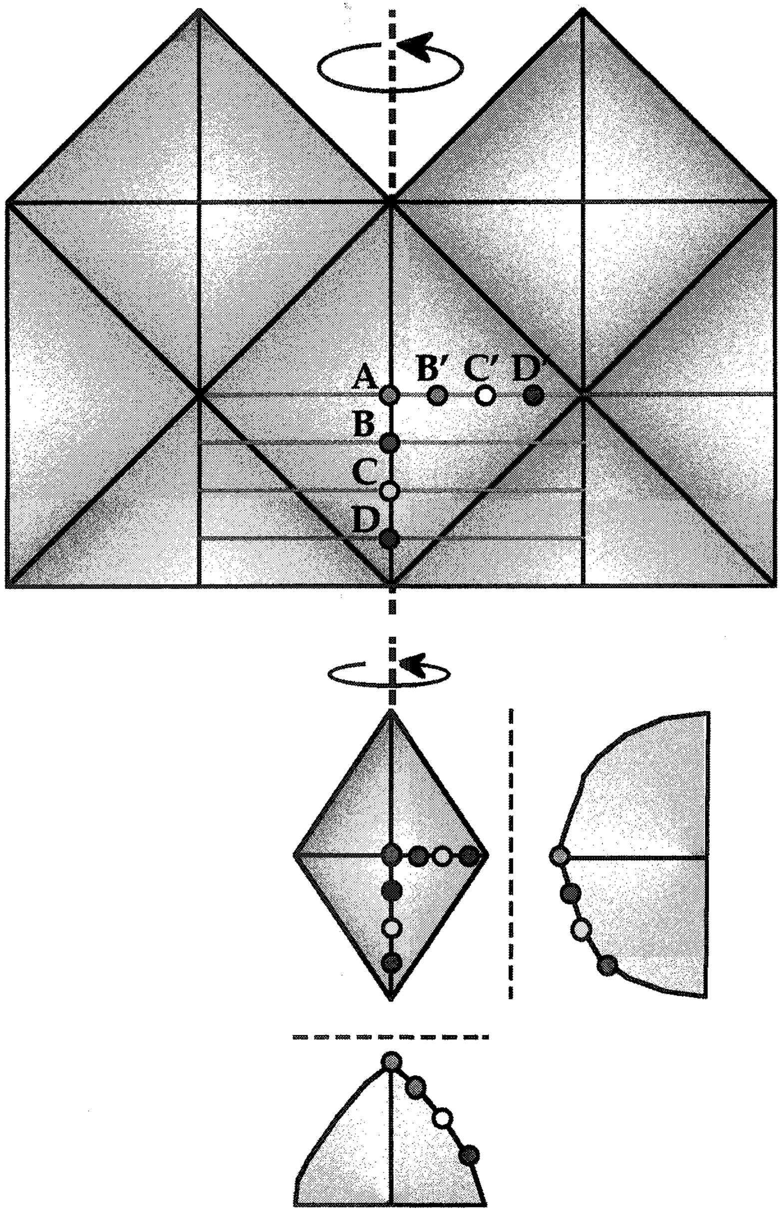
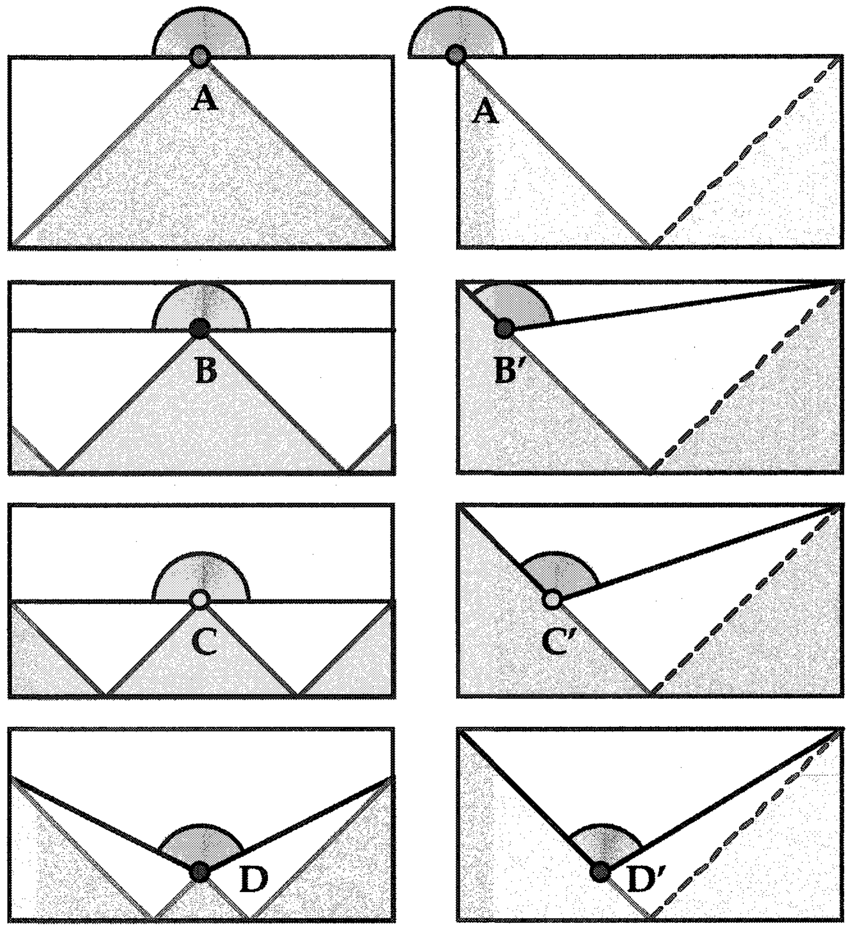
Column Anisotropy from Tip Shadowing





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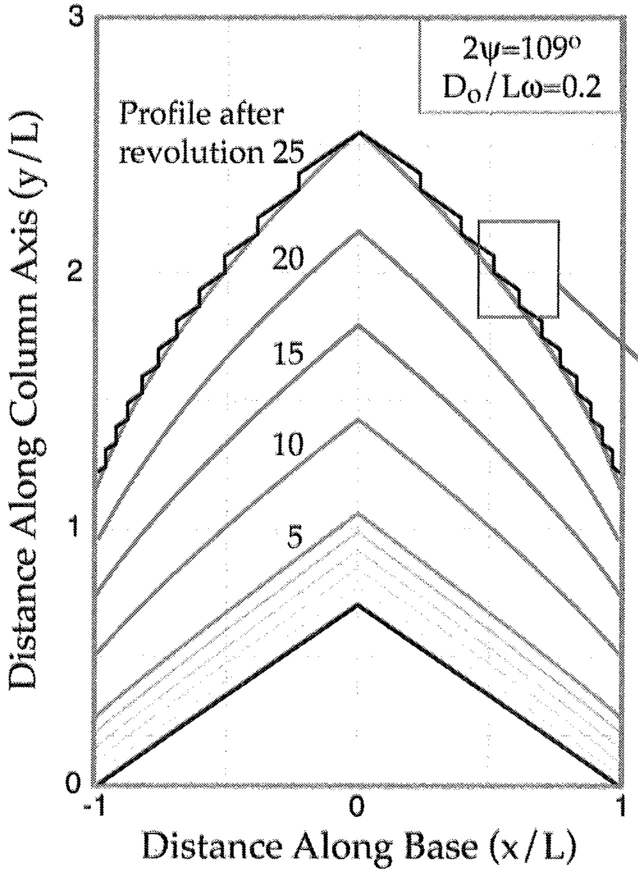
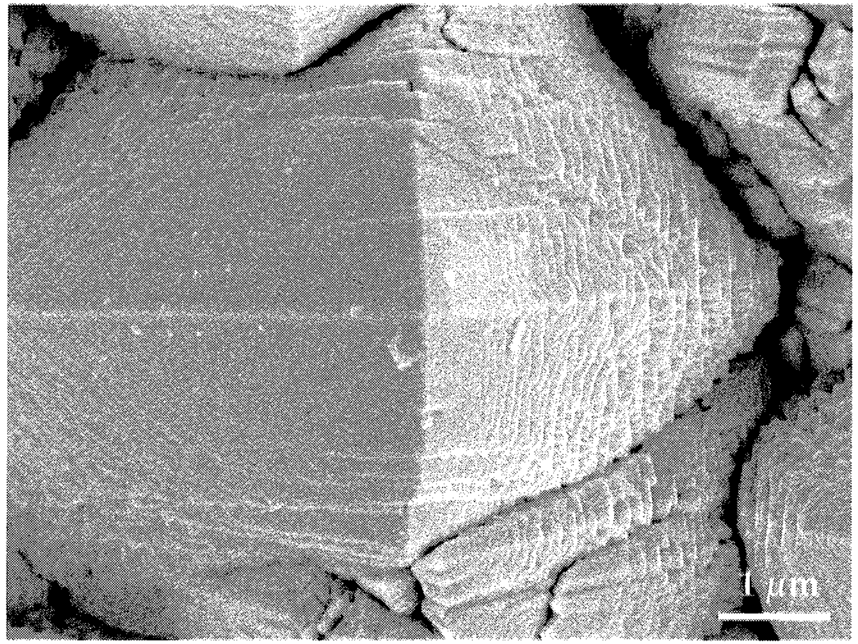
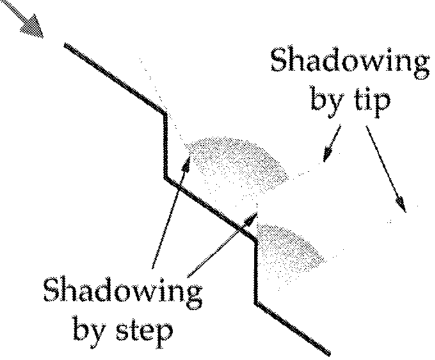
Shadowing by Tip Roughness



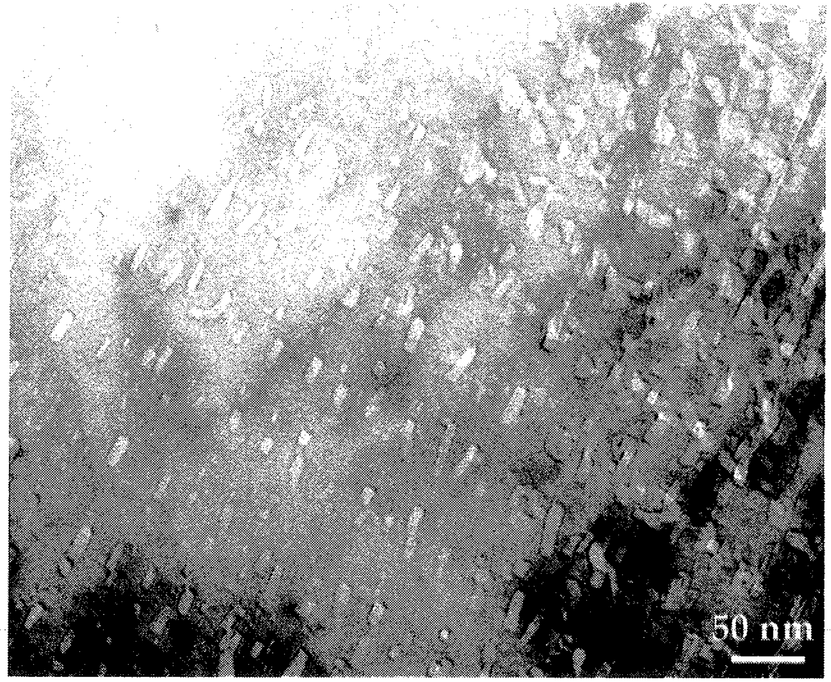




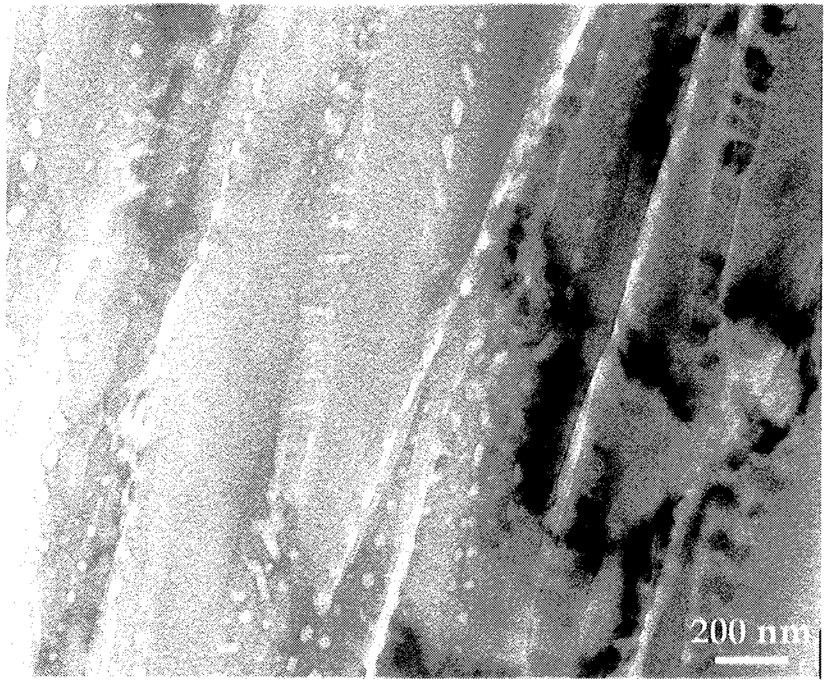
Shadowing enhanced by crystallographic "steps" which become accentuated toward the "valley".

Intra-columnar Porosity in Rotated Specimens

Cross Sections Parallel to Column Axis



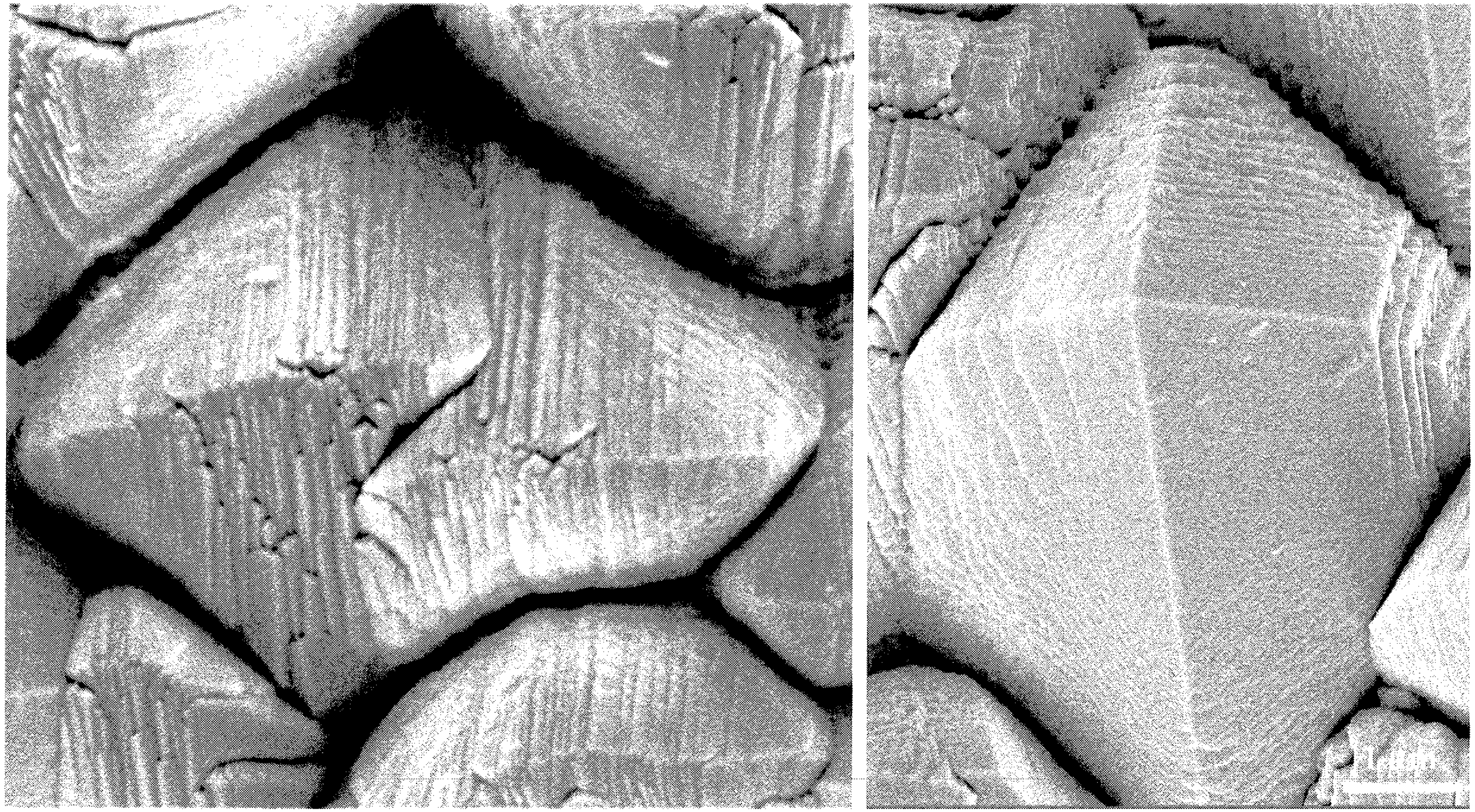
900°C k = 1.1 W/mK



1100°C k = 1.5 W/mK

Rotation rate = 8 RPM
Deposition rate ~0.9 μm/min
Flux ~ 3.2 μm/min

Facet Configurations on Column Tips

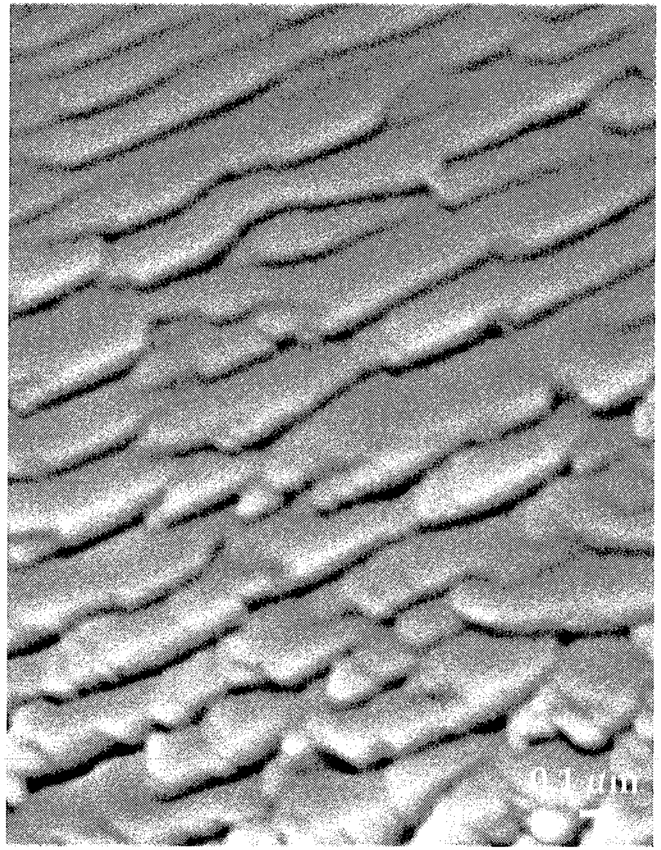


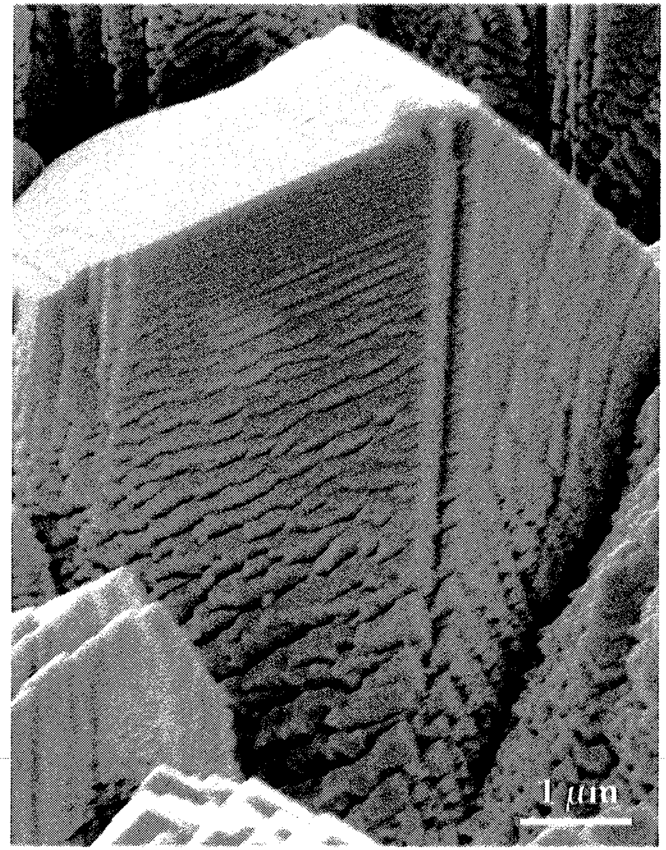
900°C **1100°C**

Rotation rate = 8 RPM
Deposition rate ~0.9 μm/min
Flux ~ 3.2 μm/min

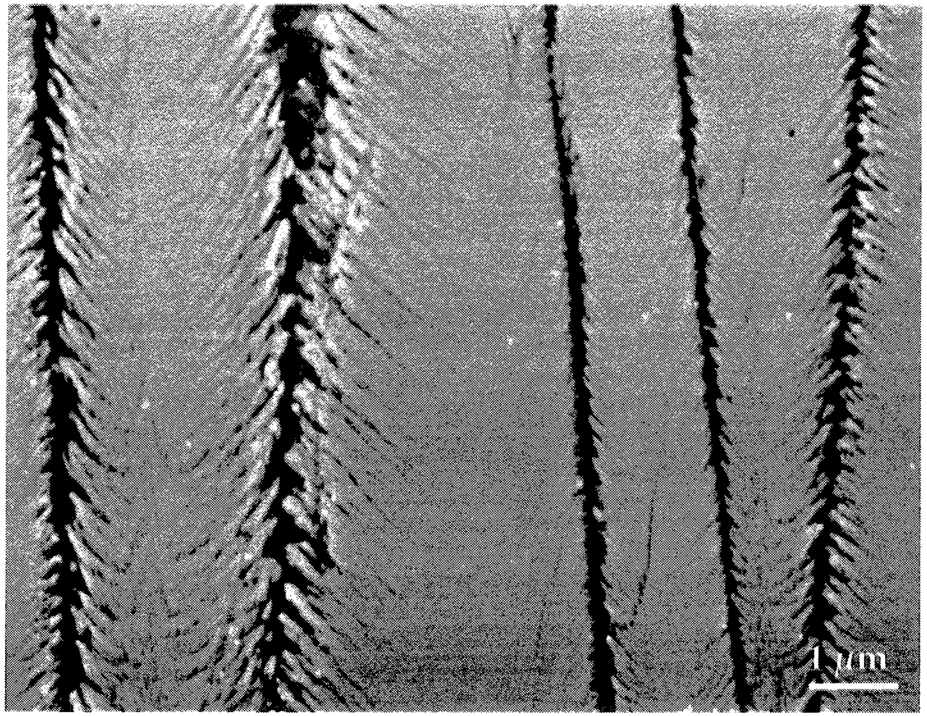
Levi-5/00

Evolution of Porosity at Steps on the Growth Surface

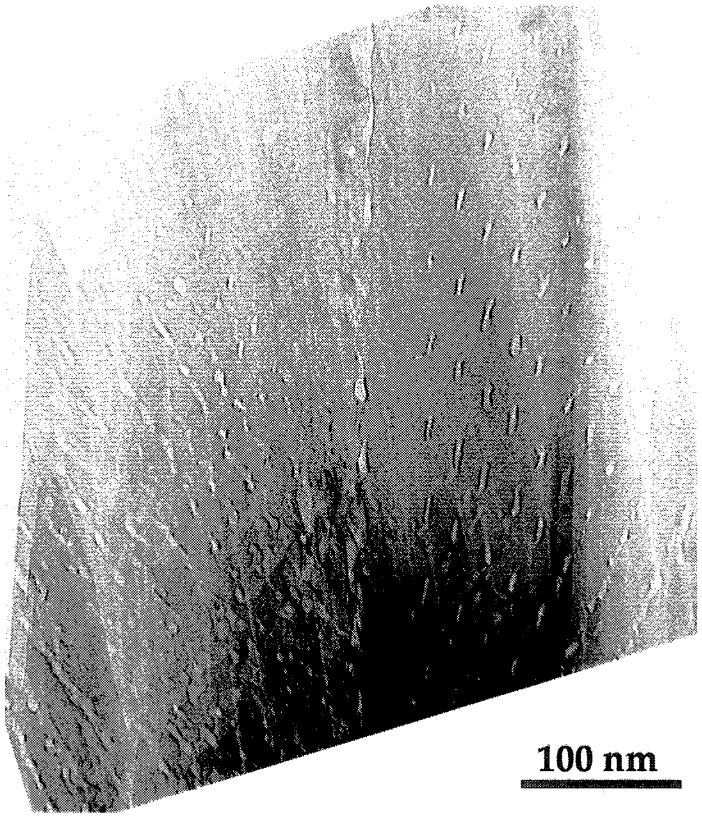




Origin of Feathery Structure



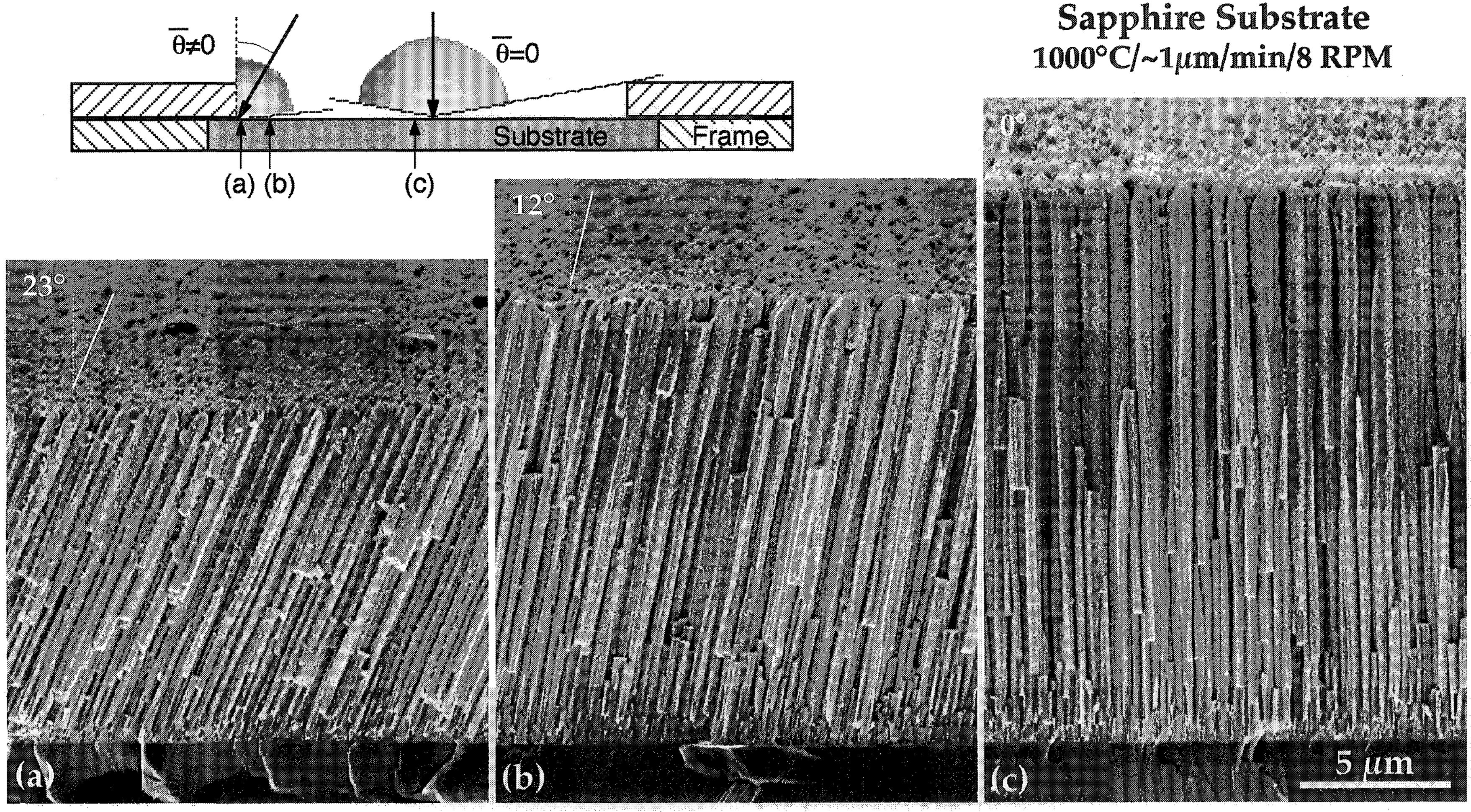
900°C



- Shadowing pattern gives rise to pores at steps in the growth front.
- Features propagate outward from column axis. Net rate and direction depend on interplay of local flux with crystallography / surface diffusion.
- Subsequent morphological reconfiguration leads to discrete pores.

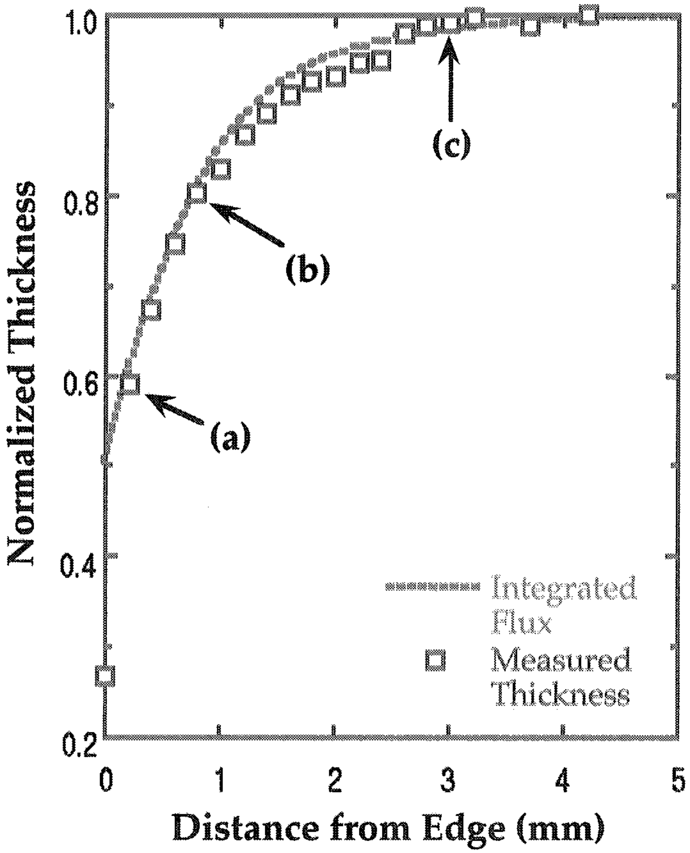
Effect of Macroscopic Shadowing on Structure

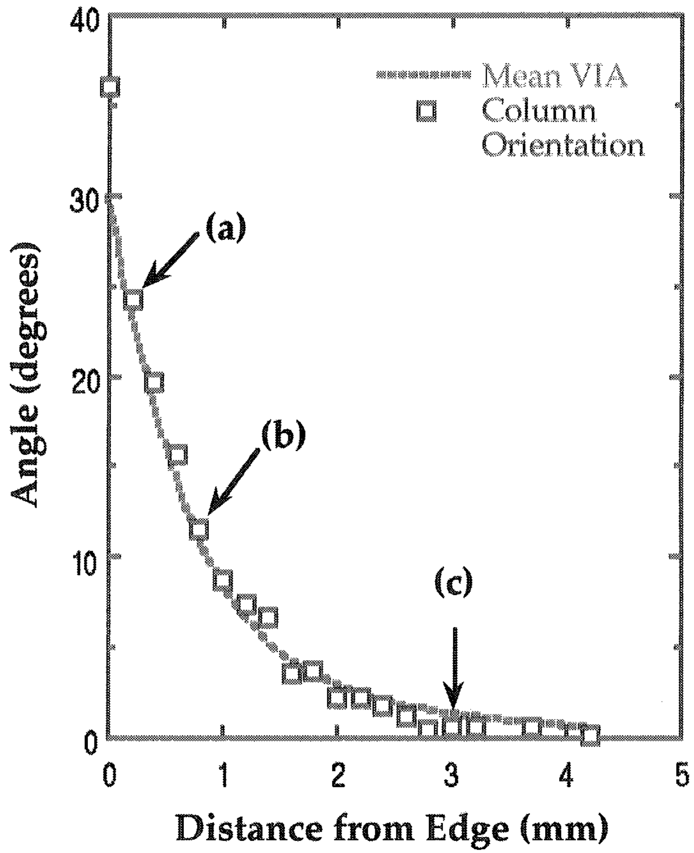
Sapphire Substrate
1000°C/~1μm/min/8 RPM



Levi-9/00

Macroscopic Shadowing Effects on Thickness and Column Orientation





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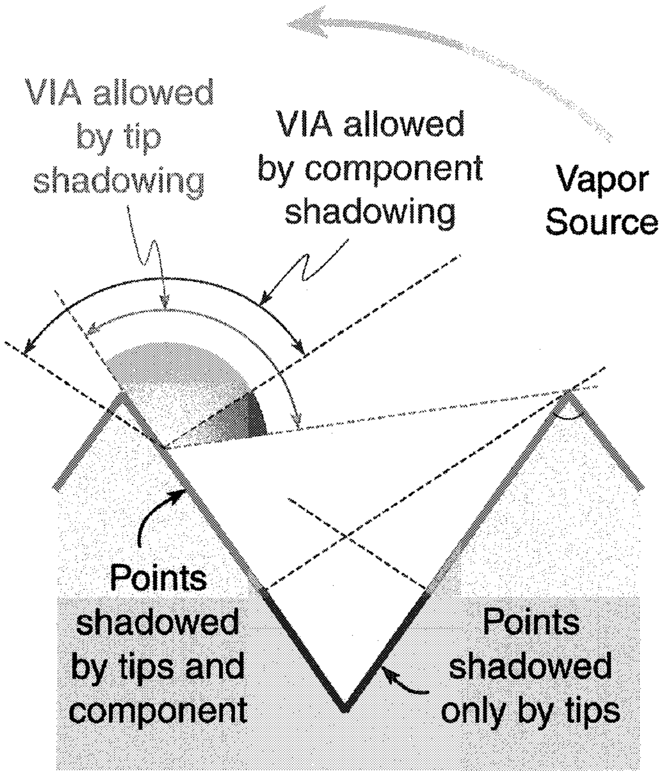
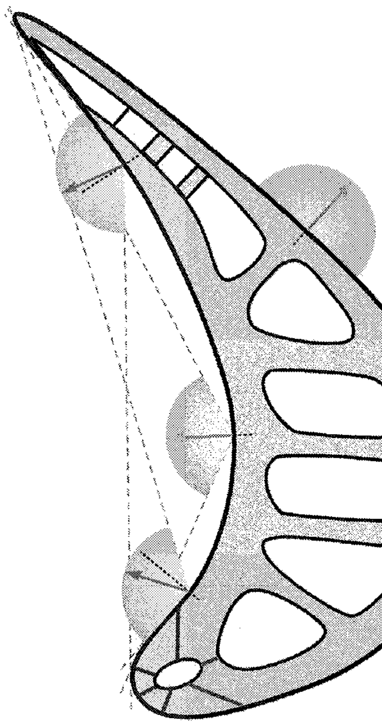
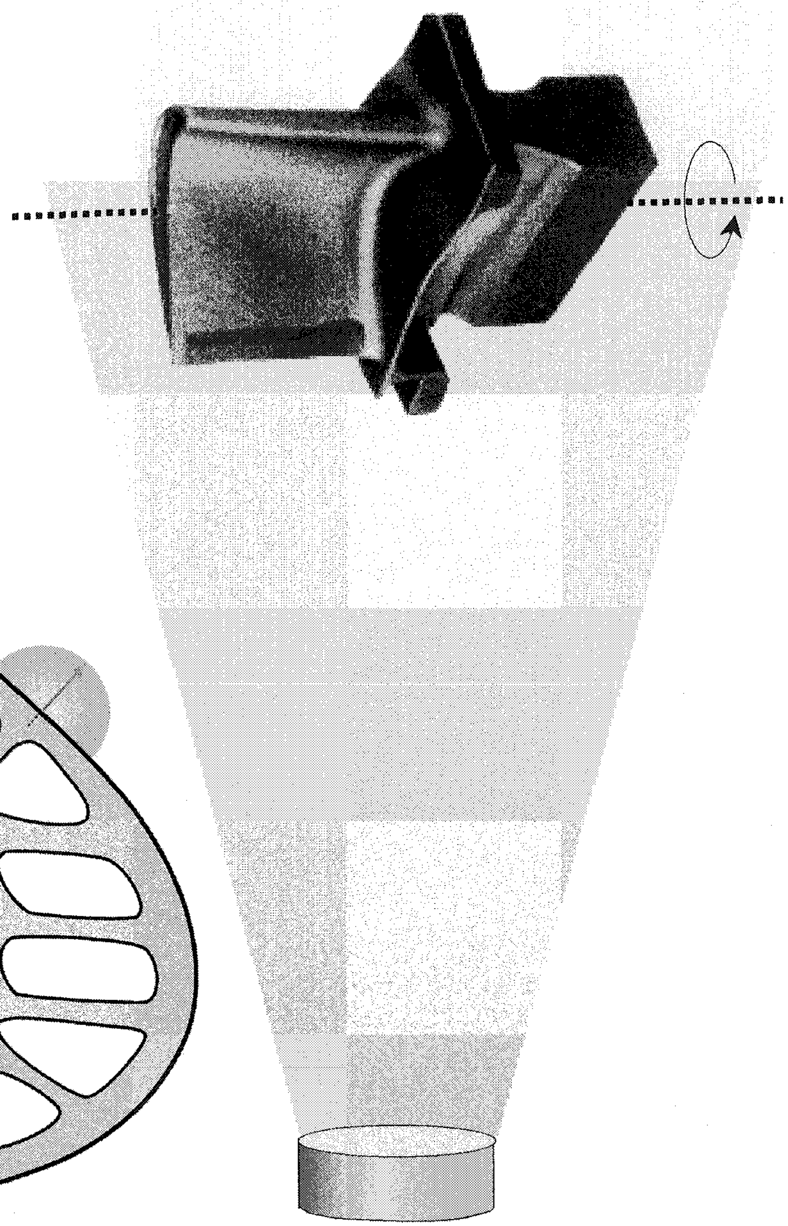
Shadowing by Vapor Interplay with Component Shape







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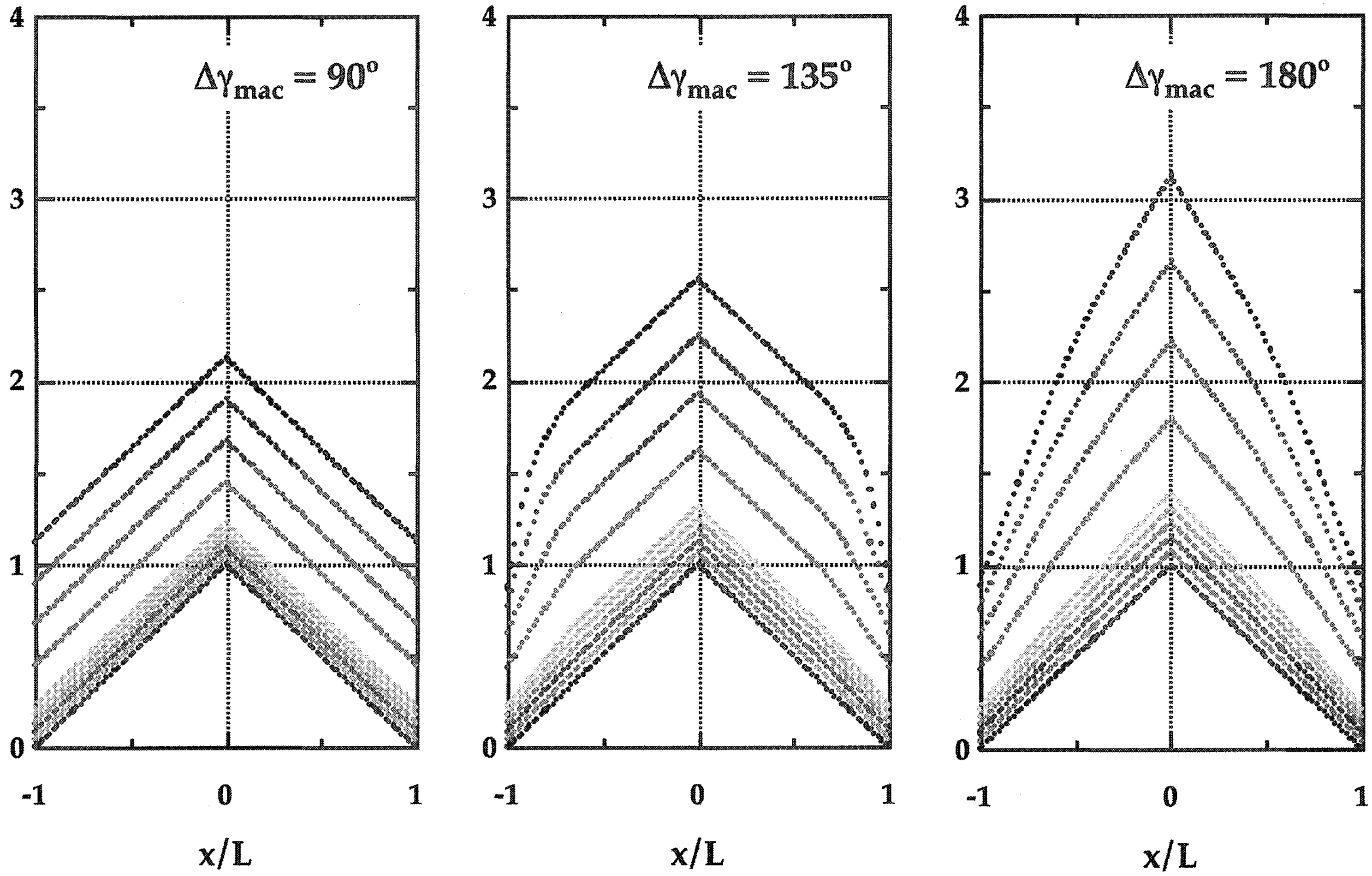
Influence of Macroscopic Shadowing on Tip Evolution



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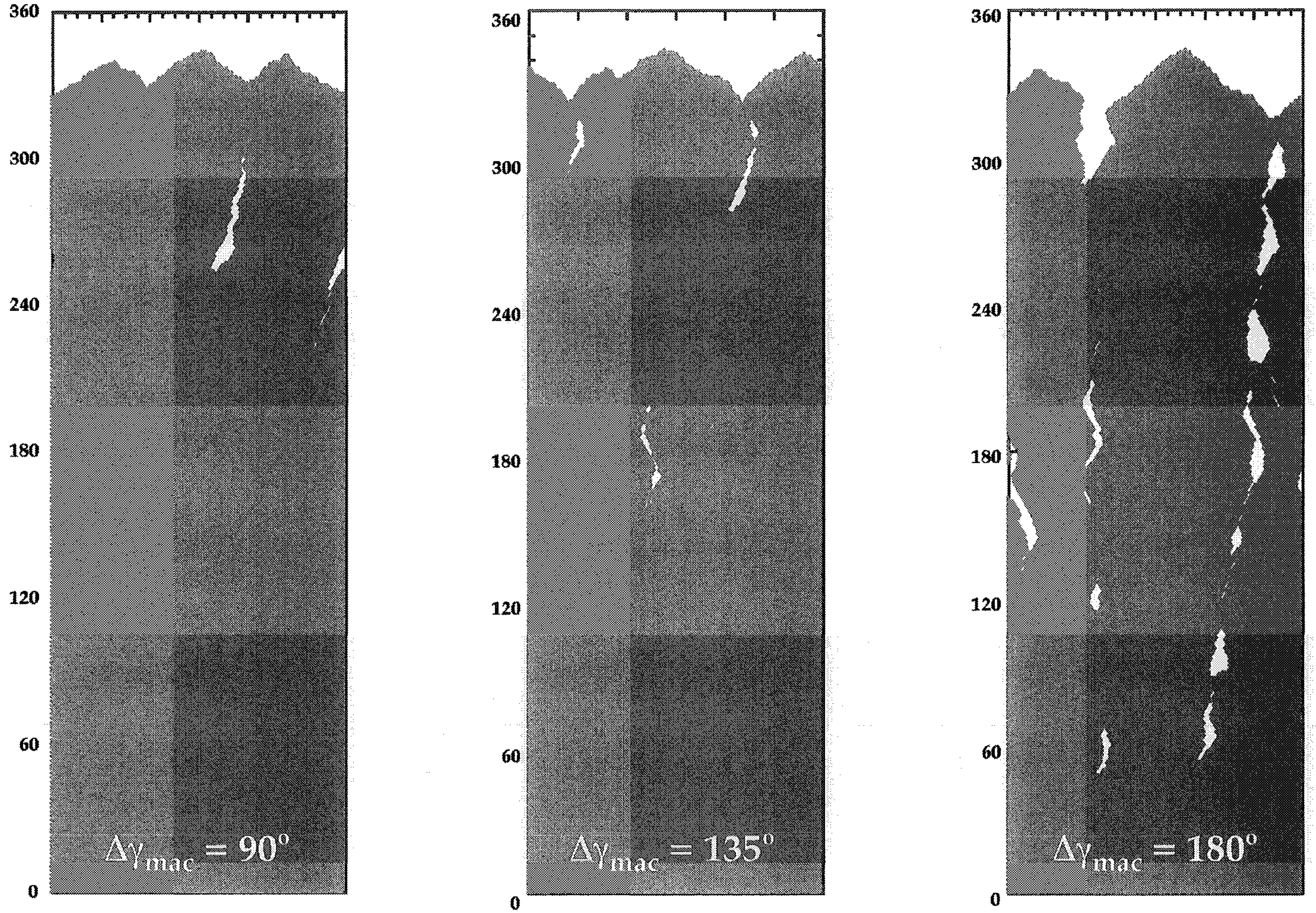
Influence of Macroscopic Shadowing on Intracolumnar Porosity



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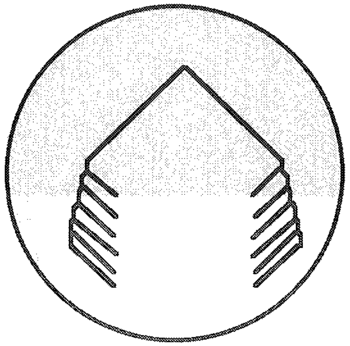
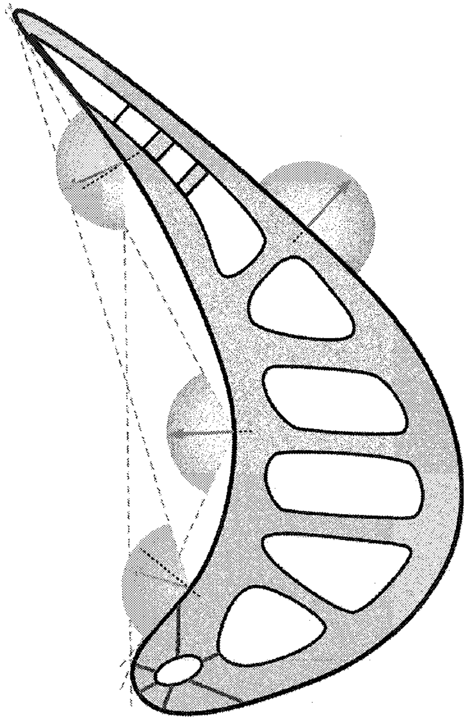
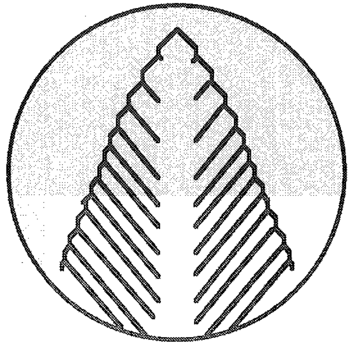
Expected Coating Variability from Macroscopic Shadowing Phenomena







Thinner

Less Insulating

Less Compliant

Thicker

More Insulating

More Compliant

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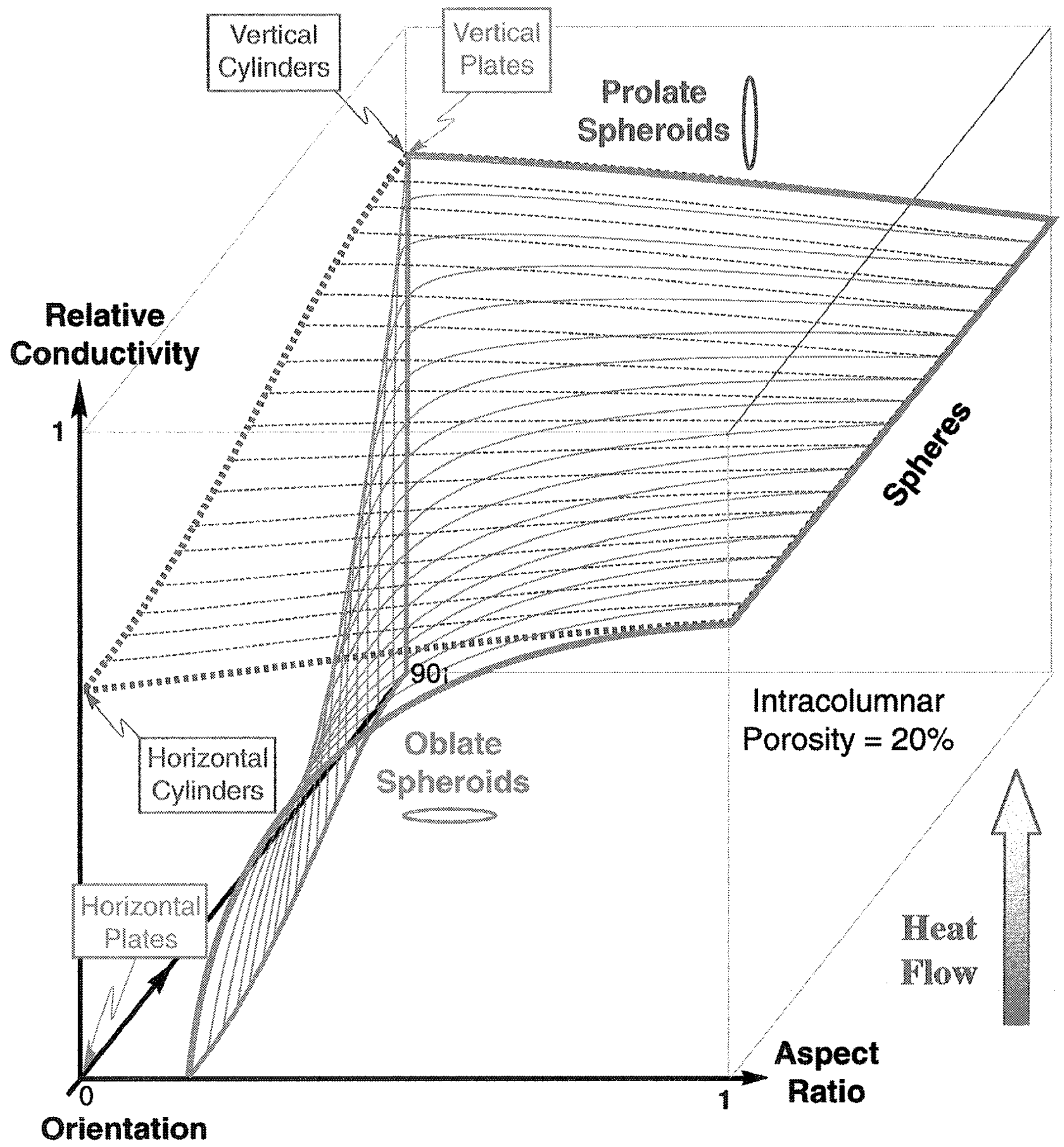
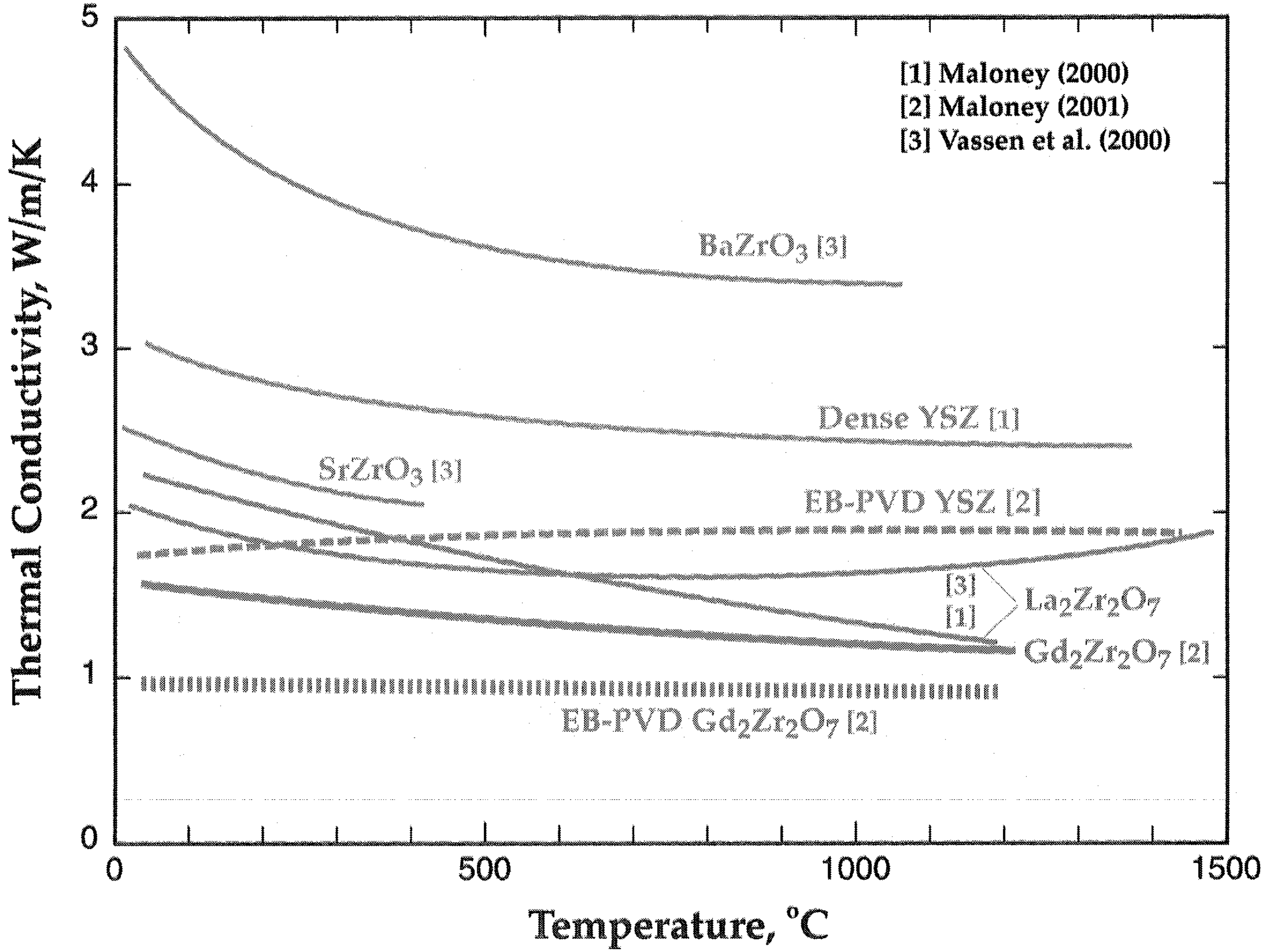
Effect of pore morphology on the thermal conductivity



Evolutionary breakdown and spheroidization of lamellar pores rapidly degrades insulating efficiency

Levi-4/01

Thermal Conductivity of Zirconates



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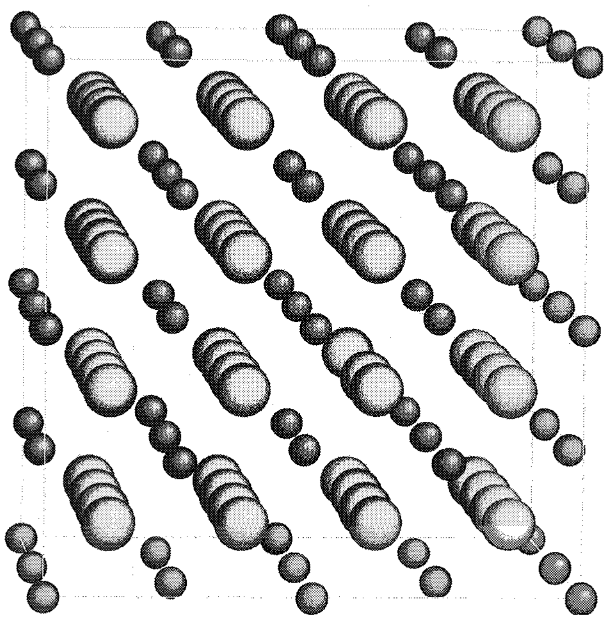
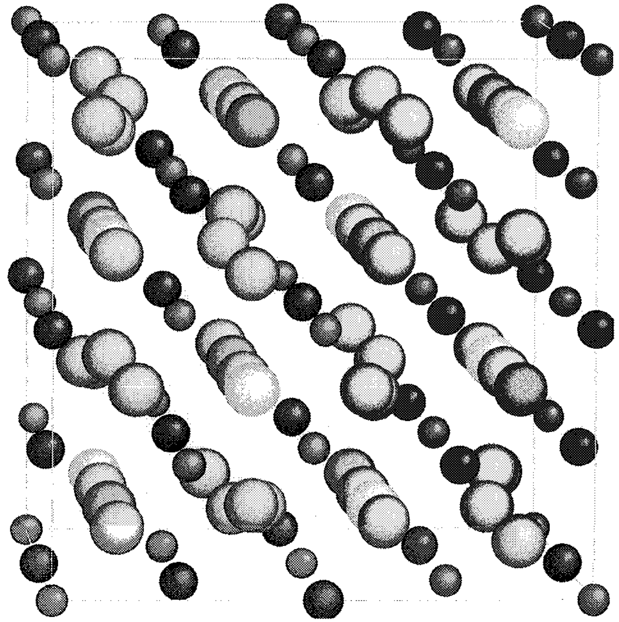
Fluorite and Pyrochlore Structures



Fluorite: MX_2

- Cation
- Anion



Pyrochlore: $A_2B_2O_7$

- A - cation
- B - cation
- O- 48f
- O′
- Vacant O site

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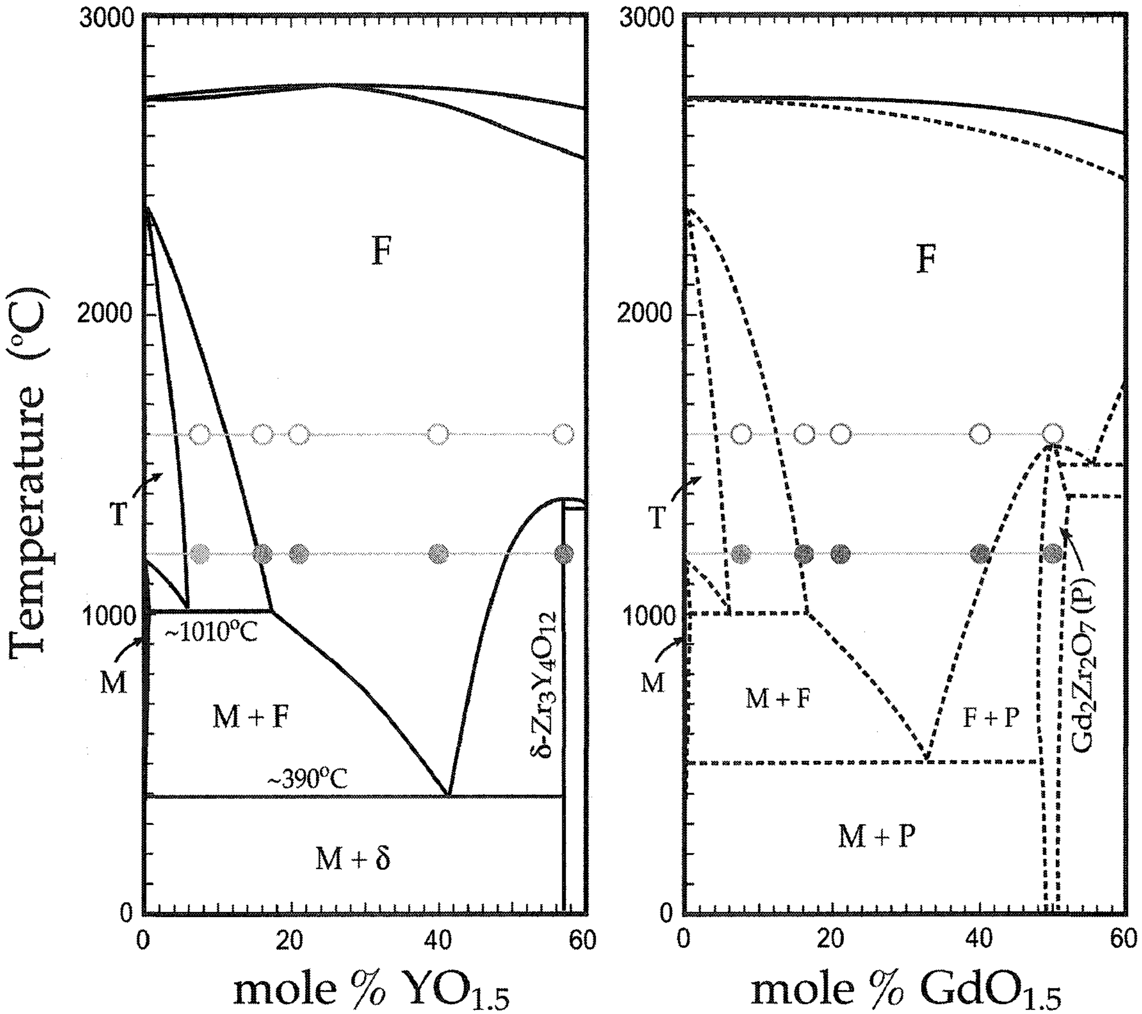
ZrO_2-(Y/Gd)$O_{1.5}$ Phase Diagrams



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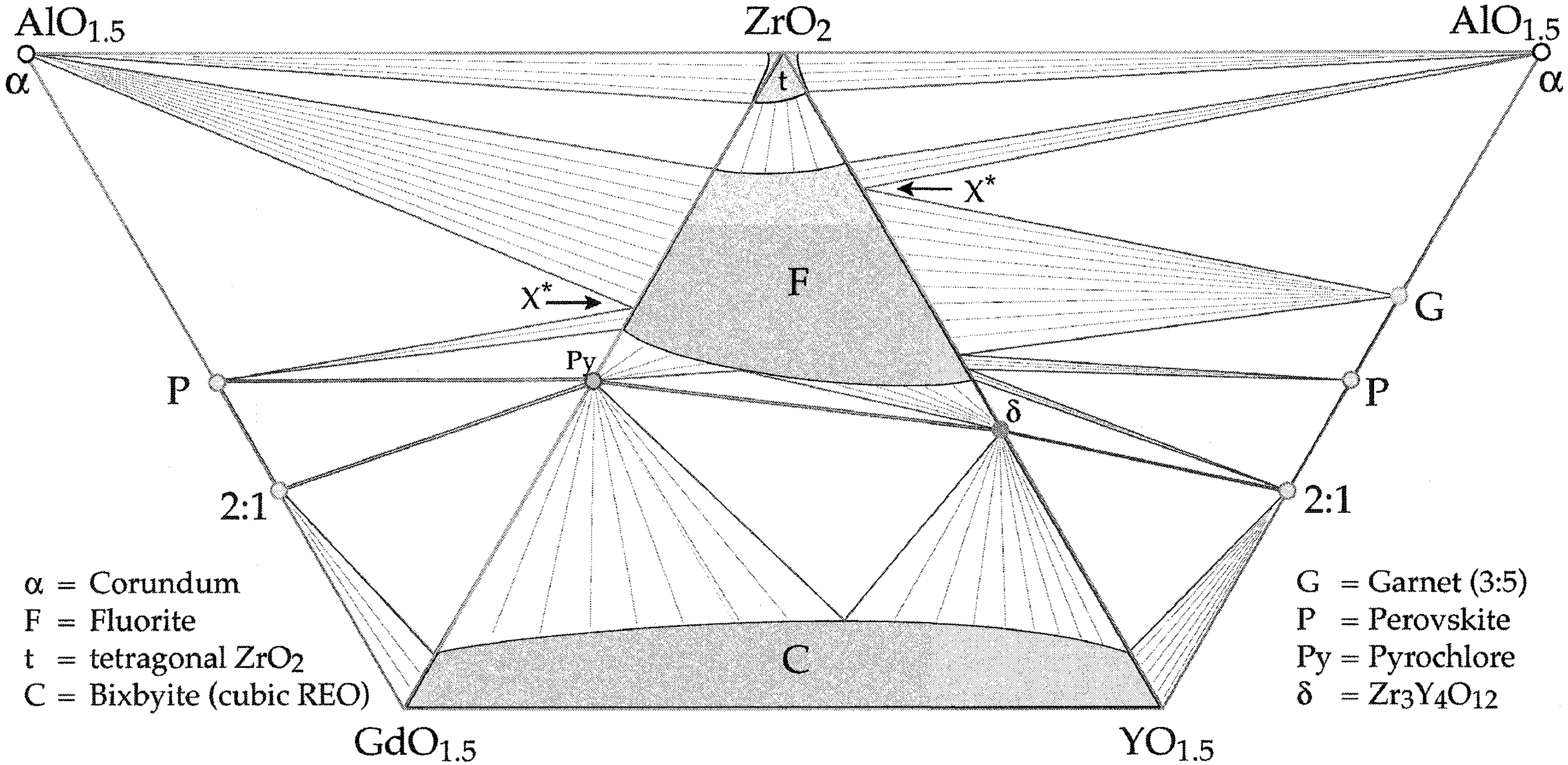
Schematic Ternary Sections at 1200 °C ZrO_2-$YO_{1.5}$-$GdO_{1.5}$-$AlO_{1.5}$ Systems



α = Corundum
F = Fluorite
t = tetragonal ZrO_2
C = Bixbyite (cubic REO)

G = Garnet (3:5)
P = Perovskite
Py = Pyrochlore
δ = $Zr_3Y_4O_{12}$

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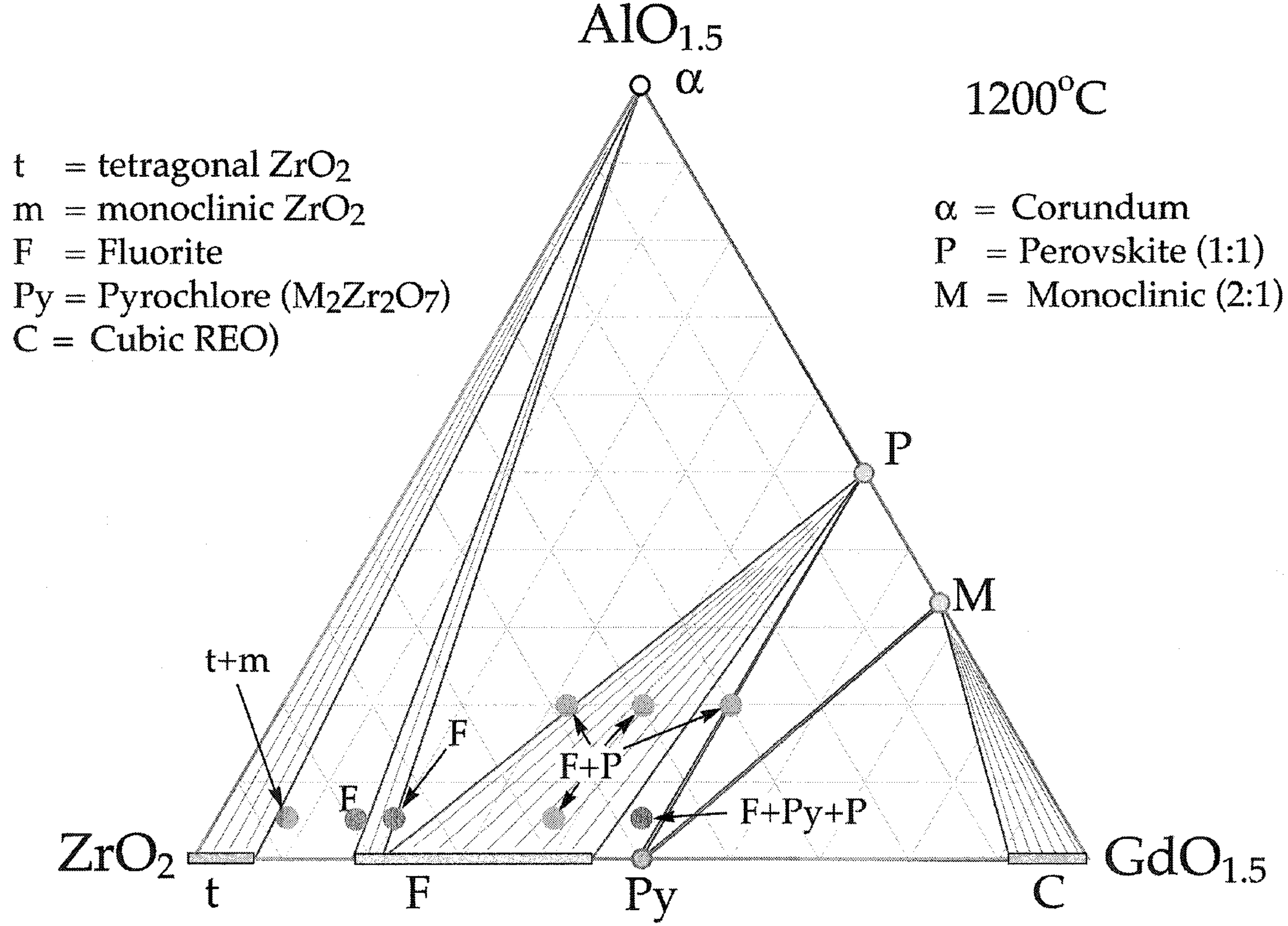
Thermochemical Compatibility of ZrO_2-$GdO_{1.5}$ with Alumina



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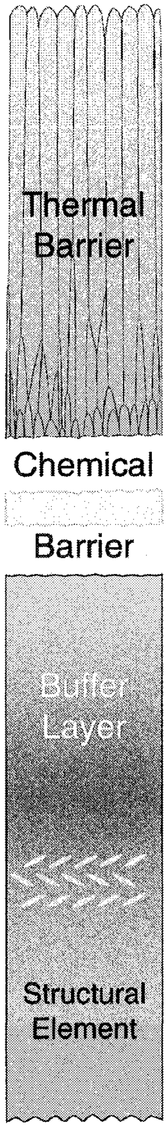
Increasing Temperature Capability →



Thermal Barrier	7%Yttria Partially Stabilized Zirconia (7YSZ)	Rare Earth Zirconate + Compatible layer	?	?
Chemical Barrier	Alumina	Alumina	Silica	BSAS + Mullite + Silica
Buffer Layer	**(Ni,Pt) Al MCrAlY**	**(Ni,Pt) Al MCrAlY**	**Refractory Silicide**	**Silicon Alloy**
Structural Element	**Ni-Base Superalloy**	**Ni-Base Superalloy**	**Refractory Metal Alloy**	**Si-based Ceramic**

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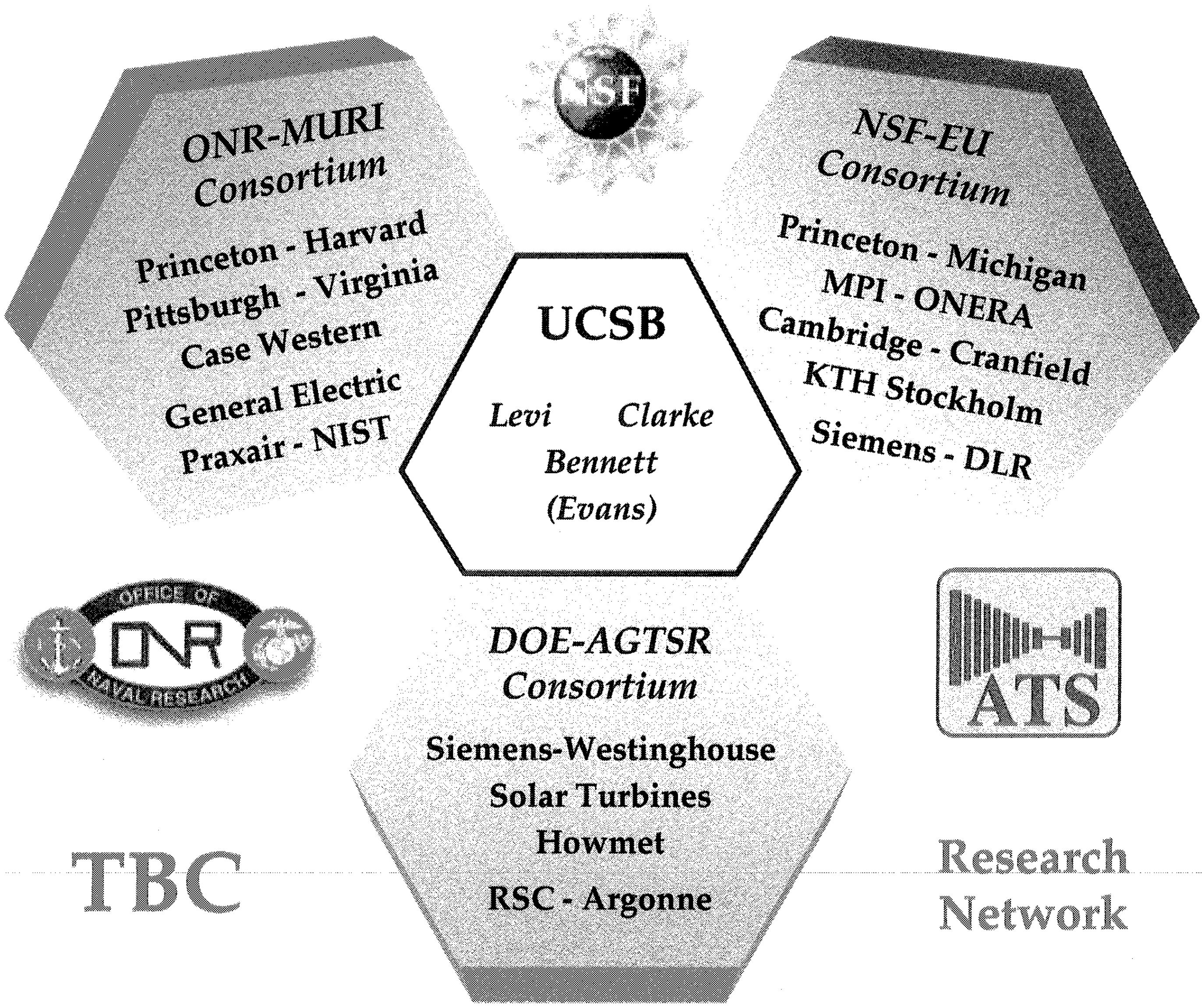
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Princeton - Harvard
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Case Western
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