# Tailoring the Next Generation $Si_3N_4$ Ceramics to Enhance Performance

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Research supported by the U. S. DOE, Office of Basic Energy Science,
Division of Materials Sciences and Engineering

2003 Environmental Barrier Coating Workshop
Nashville, TN

# Supported by The Important Contributions by the Following

**Sample fabrication:**

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D.-S. Park, Korean Institute of Machinery and Materials
K. Hirao & M. Brito, Synergy Ceramics Center, AIST, Japan

**Characterization:**

*HREM, STEM*

S. J. Pennycook and N. Shibata (JSPS Research Fellow),
Oak Ridge National Laboratory

Y. Ikuhara, University of Tokyo,

*Raman spectroscopy*

M. J. Lance, Oak Ridge National Laboratory

**Theoretical studies:**

G. S. Painter and W. A. Shelton, Jr., Oak Ridge National Laboratory

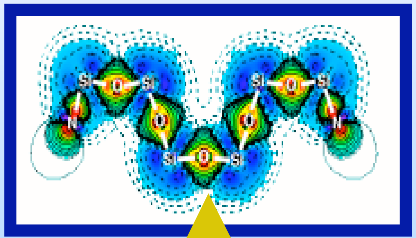
# Different Length-Scale Approaches to Enhance the Mechanical Performance of Ceramics (e.g., $Si_3N_4$)

Enhanced toughness: Self-reinforced $Si_3N_4$-based ceramics

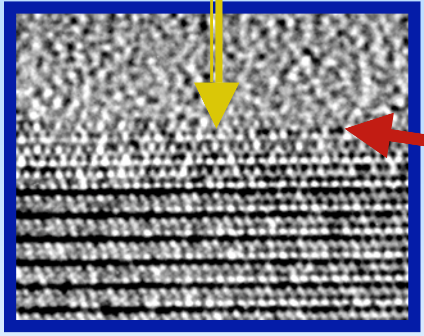
- Micro-scale composite: large elongated grains-- well documented
  - Seeding concept (Hirao *et al.*)
  - □□SiAlONs: I-Wei Chen *et al.*
- Atomic-scale: Microstructure & interface characteristics
  - Adsorption versus preferential segregation of additives
  - Interfacial debonding & role of Intergranular films (IGF)
    - □□SiAlON: Influence of Al:Y ratios in additives
    - □□$Si_3N_4$: Influence of rare earths

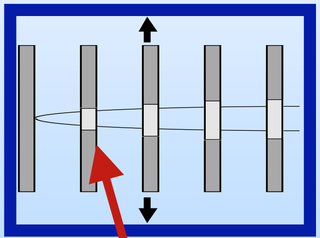
**USE PROCESSING TO DEVELOP AND CONTROL THE FORMATION OF A TOUGH/STRONG MICROCOMPOSITE MICROSTRUCTURE**

# A COMBINATION OF MECHANISMS AT ALL LENGTH SCALES INVOLVED IN TOUGHENING CERAMICS

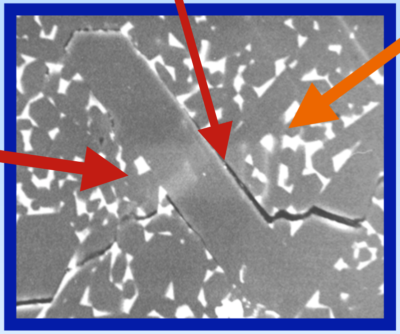


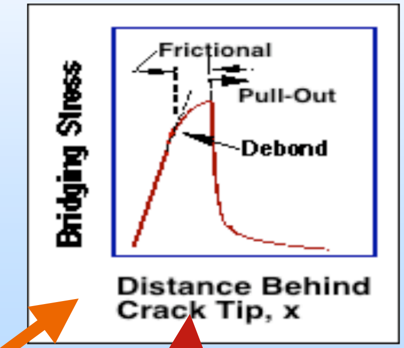
**Atomic - scale**



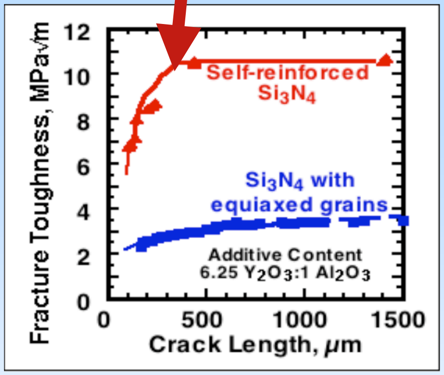


**Micro - scale**





**Macro - scale**



Atom structure of the interface influences

Interfacial debonding &, thus, bridging of the crack (and crack deflection that affects

Closure stresses acting on crack&, thus, toughness

# Elongated Grains Act as Reinforcements, Which Toughen the Ceramics When They Debond and Bridge the Crack

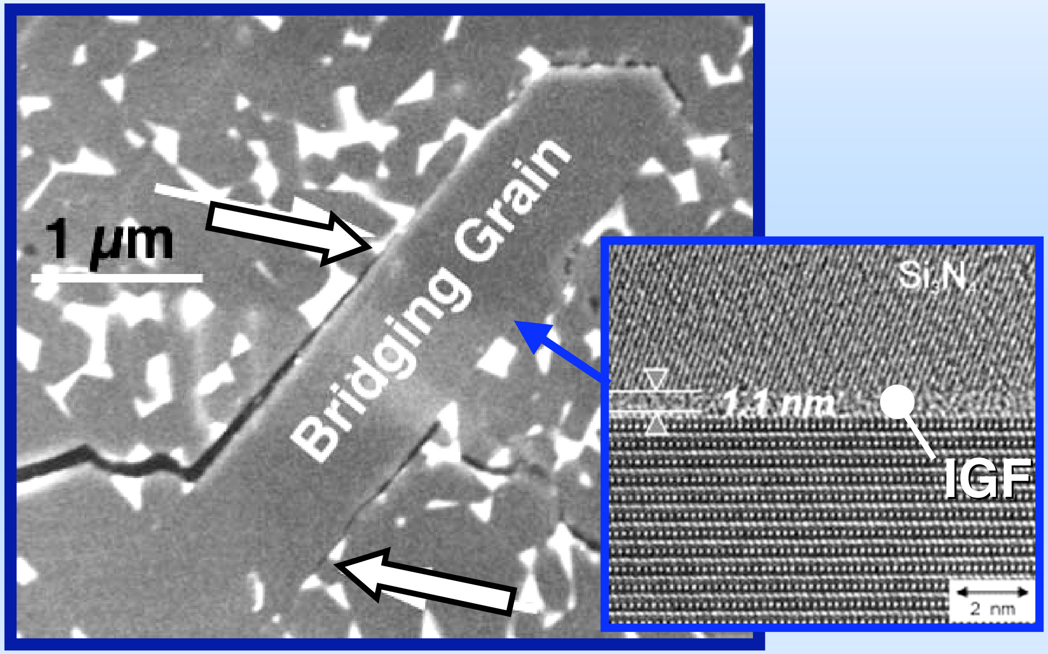
**Toughness Increased By Formation Of:**

**Strong Elastic Bridges**

- Thin Single Crystals Can Exhibit Very High Strengths

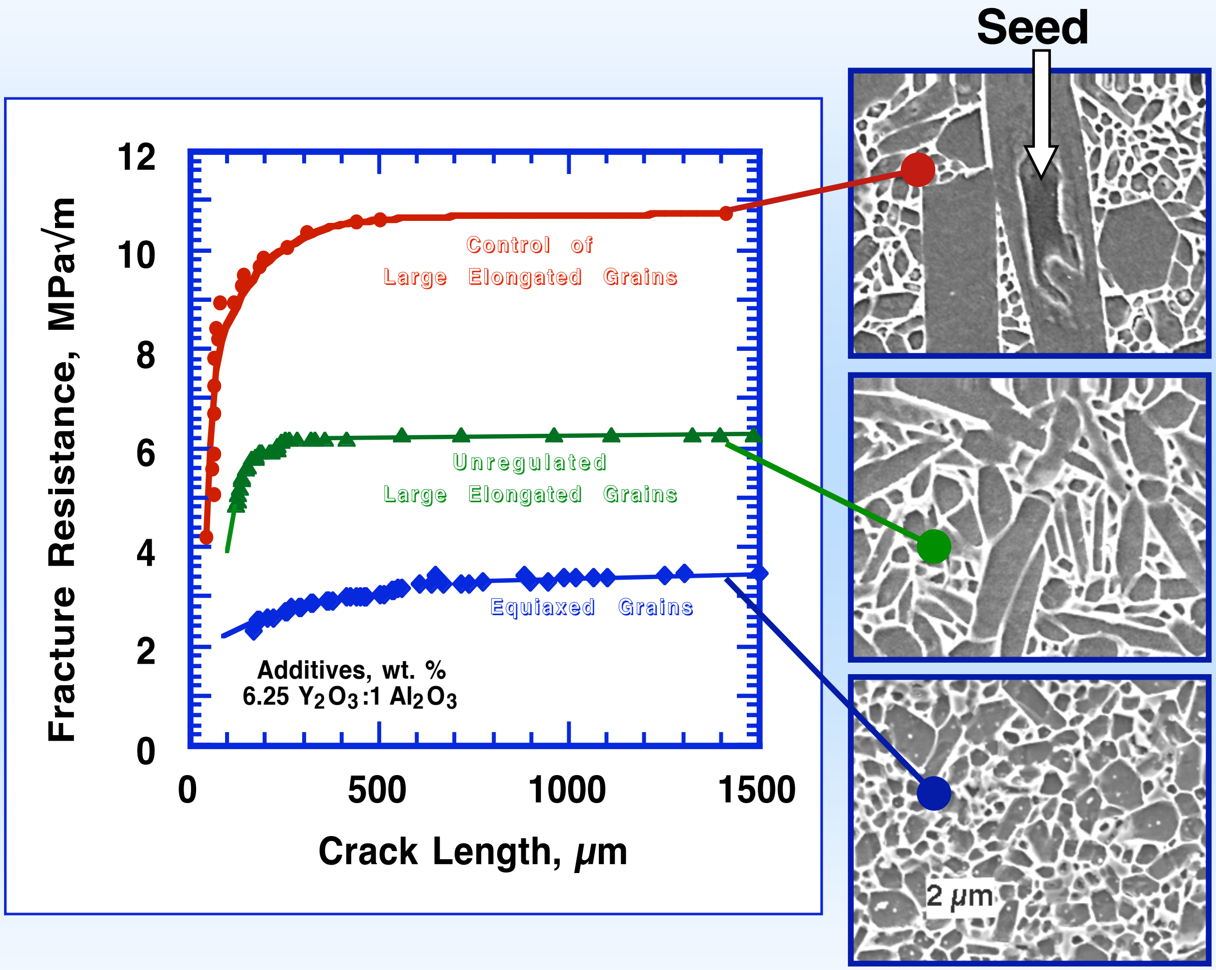
**Frictional Bridges and Pull-Out**

- Friction Effectively Dissipates Applied Strain Energy



Grains are surrounded by a continuous amorphous intergranular film (IGF) as a result of liquid phase sintering

# Large Elongated Grains in Fine Grained Silicon Nitride Matrix: Strong R-Curve, $K_{IC} > 10$ MPa√m, $\sigma_f > 1$ GPa & m > 30



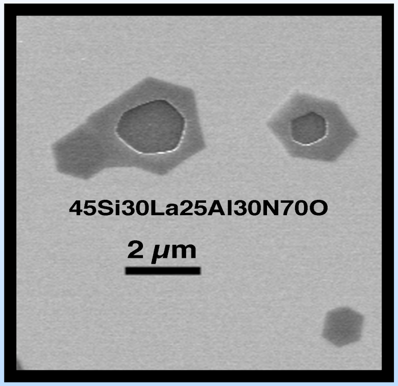
$\sigma_f$ = 1400 MPa
**Controlled microstructure**

$\sigma_f$ = 850 MPa
**Uncontrolled microstructure**

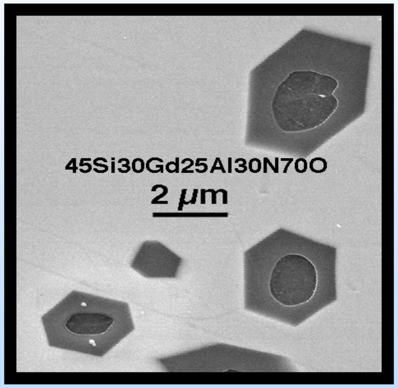
$\sigma_f$ = 660 MPa
**Equiaxed Grains**

**$\beta$–particles are nuclei for the formation of large reinforcing grains.**
**Rice-like $\beta$–seeds used to control microstructure.**

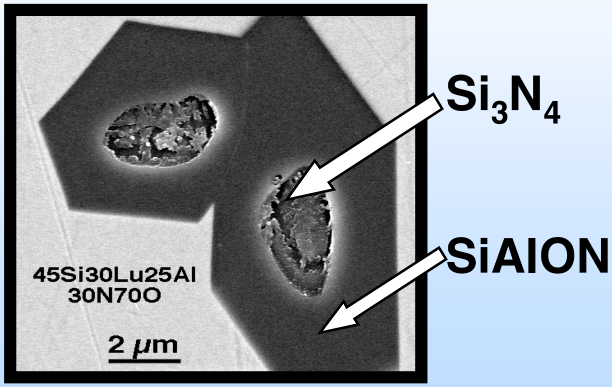
# Size and Shape of Reinforcing Grains Altered by Sintering Additives



**Lu**

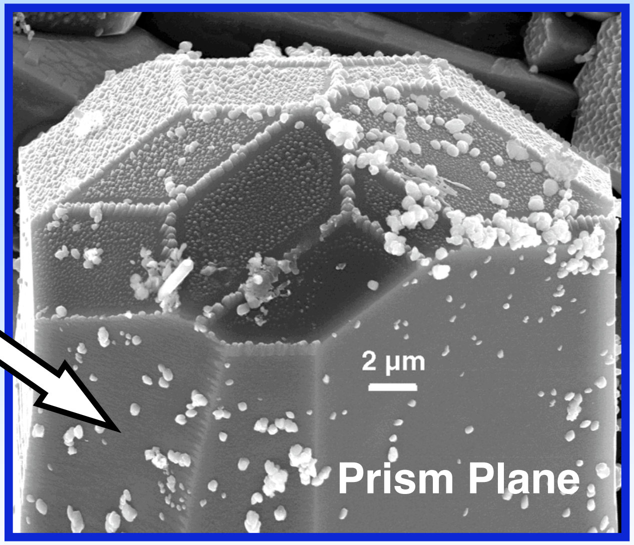


**Gd**

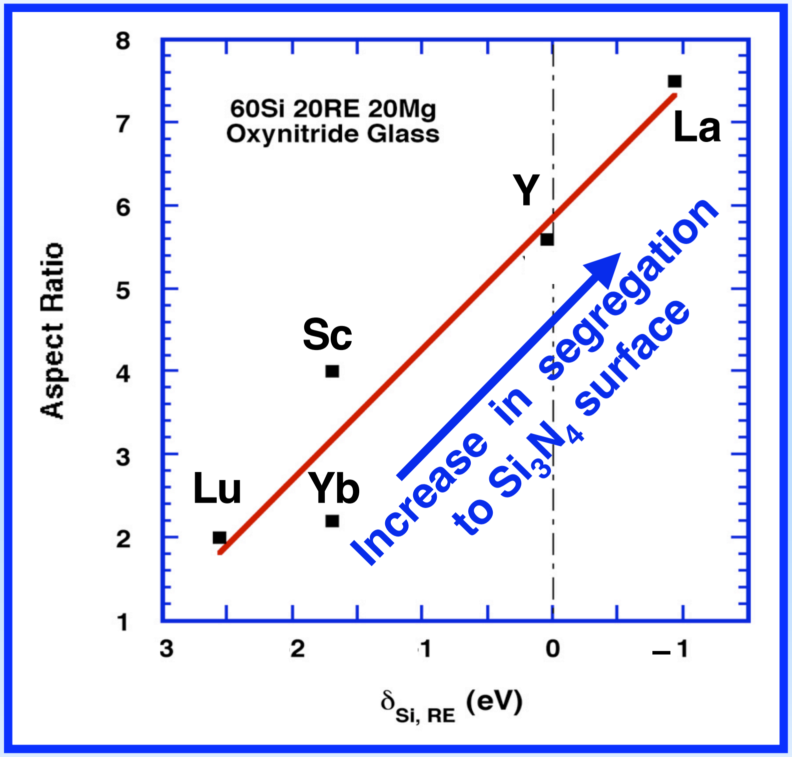


**La**

- c-axis growth is fast diffusion controlled
- diametrical growth is slow interface reaction controlled on smooth prism planes
- Same behavior: RE + Me oxide additives where Me = Al or Mg
- So what’s behind the effects of RE elements?



# RE Segregation to $Si_3N_4$ Prism Surface Is a Critical Factor in the Anisotropy of Grain Growth
## -- Formation of Elongated Reinforcements



Now can predict effects rather than trial and error.

Painter, Becher and Shelton, 2003

**Why?**

- Diametrical growth is controlled by reaction rate at prism surface.

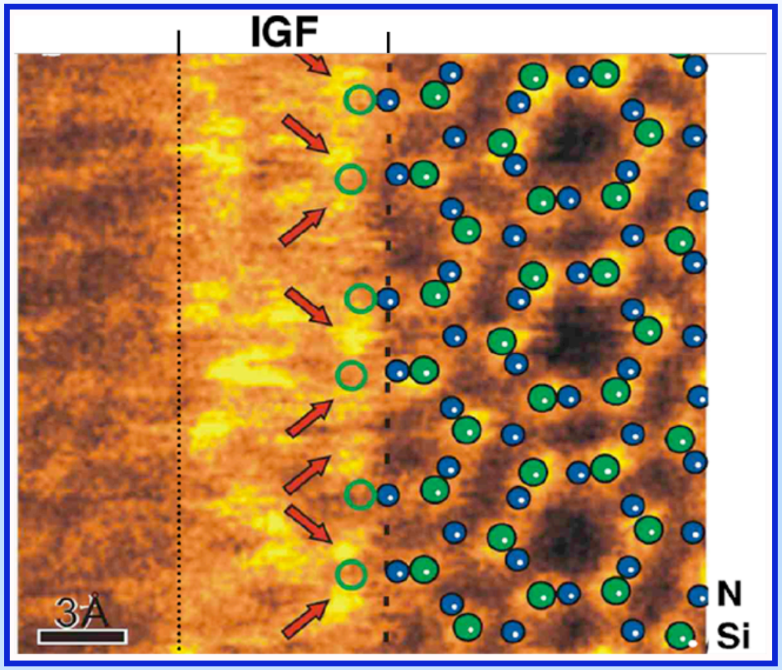
Theoretical calculations show:

- RE form strong bonds with N on terminal surfaces & most do.
- RE with strongest attraction vs. Si for prism surface limit diametrical growth most effectively.

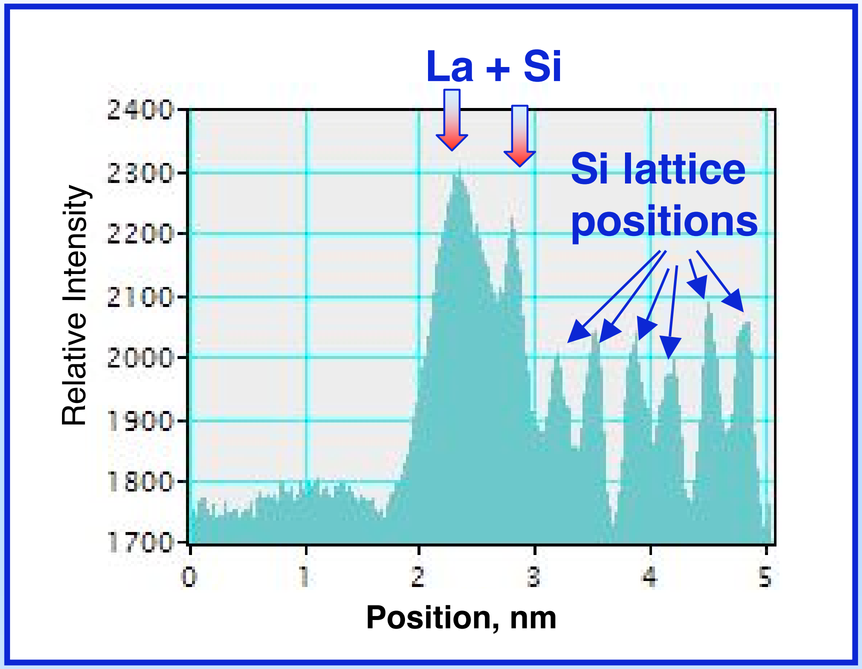
Thus, Lu predicted to avoid prism surfaces and have little effect on grain growth.

La should prefer $Si_3N_4$ surface and limit diametrical growth.

# La Not Only Present Within IGF But Prefers $Si_3N_4$ Terminal Surface As Predicted by Theory



HAADF STEM Image



$Si_3N_4$ (7.0 wt%$La_2O_3$ + 2.0 wt%MgO)

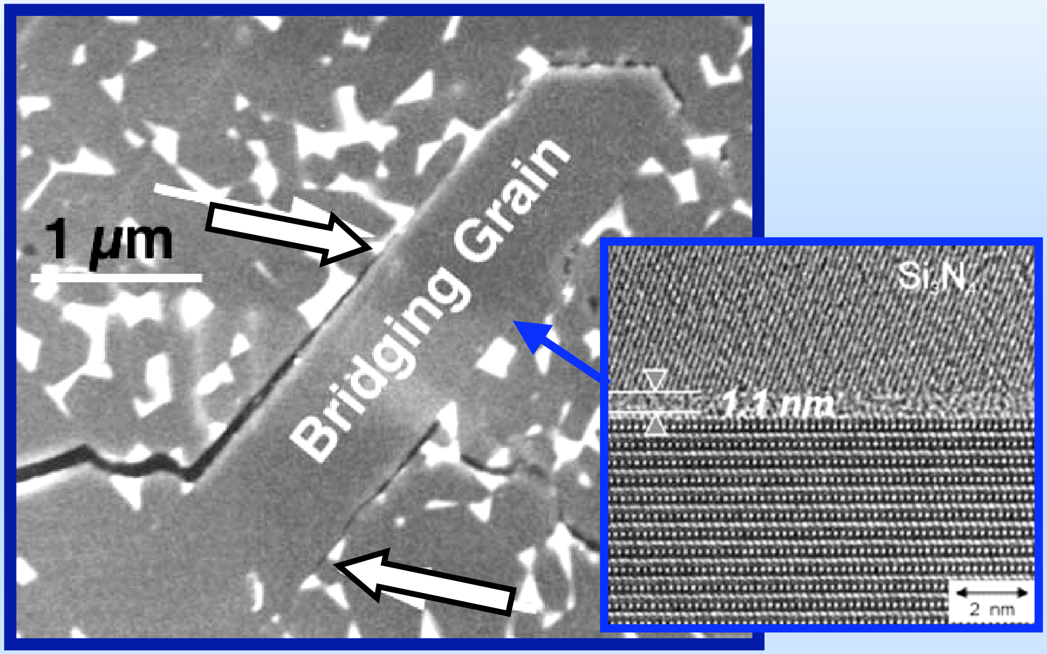
**La (arrows note La locations) prefer $Si_3N_4$ terminal surface. Representative line scan across IGF illustrating maximum La content at each interface and minimum within IGF.**

Shibata & Pennycook, 2003

# More Than a Reinforced Microstructure Is Required - The Reinforcing Grains Must Also Debond from the Matrix

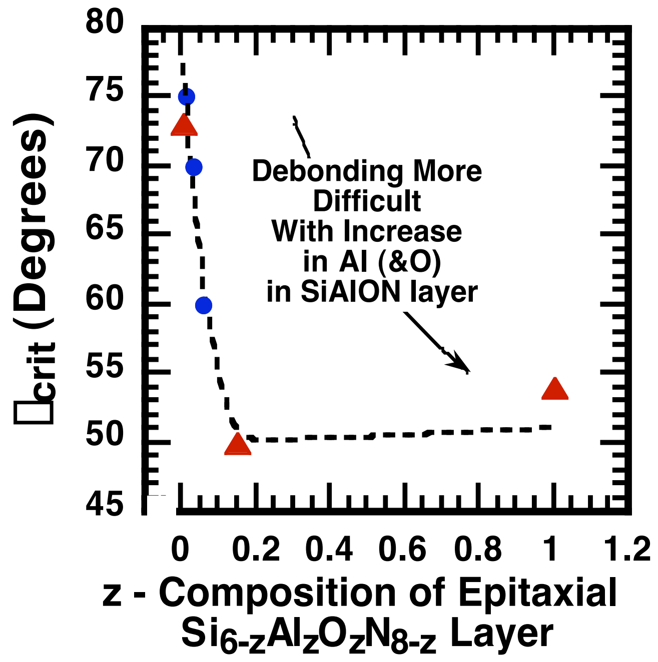
**1 to 2 nanometer thick intergranular film (IGF) surrounds $Si_3N_4$ grains.**

**IGF plays a critical role in the debonding of the interfaces and in grain growth.**

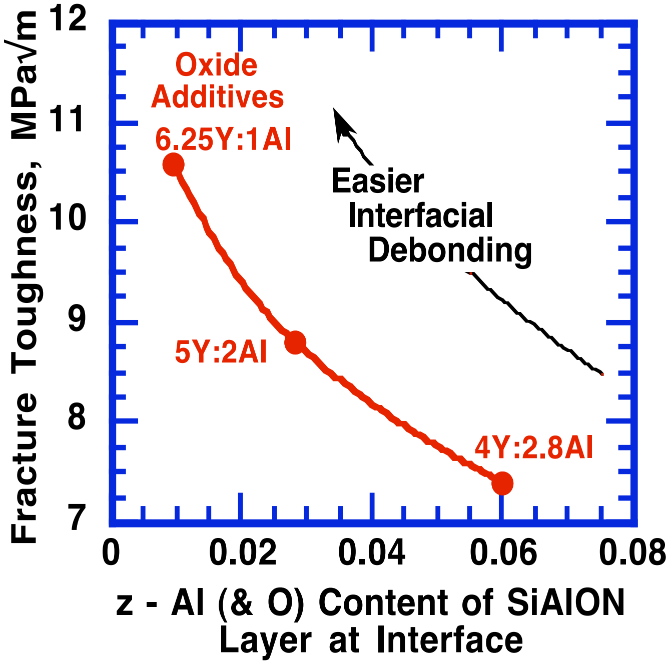


**Arrows highlight the end of debonded interfaces of a bridging grain in the crack-tip wake.**

# IGF Composition Dominates Interface Debonding & Toughness (e.g., $Y_2O_3$ + $Al_2O_3$ Additive System)



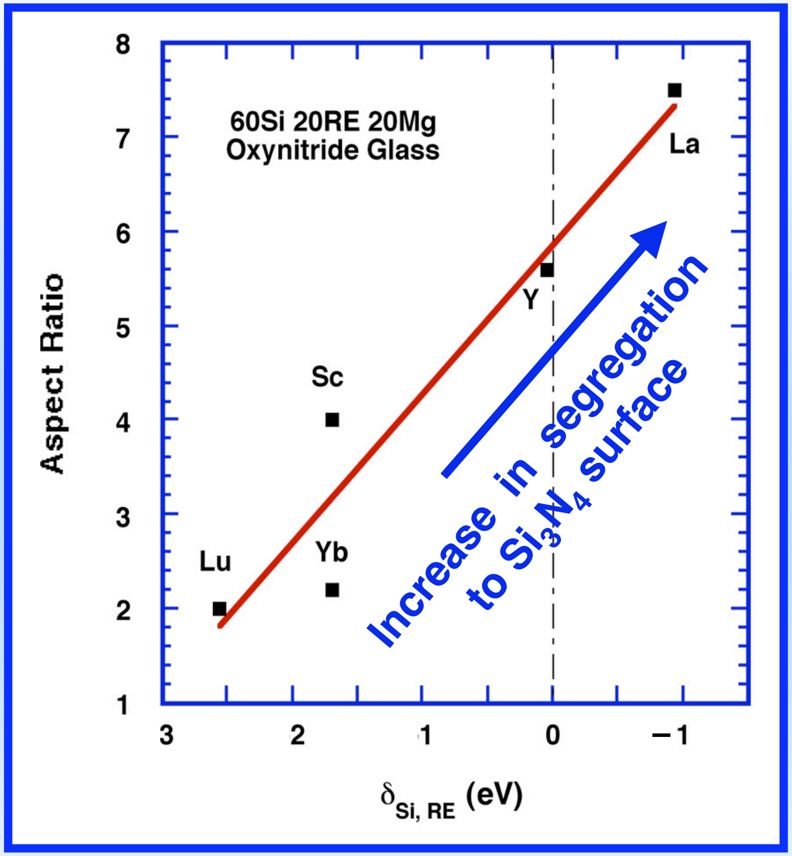
Example: $Si_3N_4$ with combined additives of $Al_2O_3$ + $Y_2O_3$

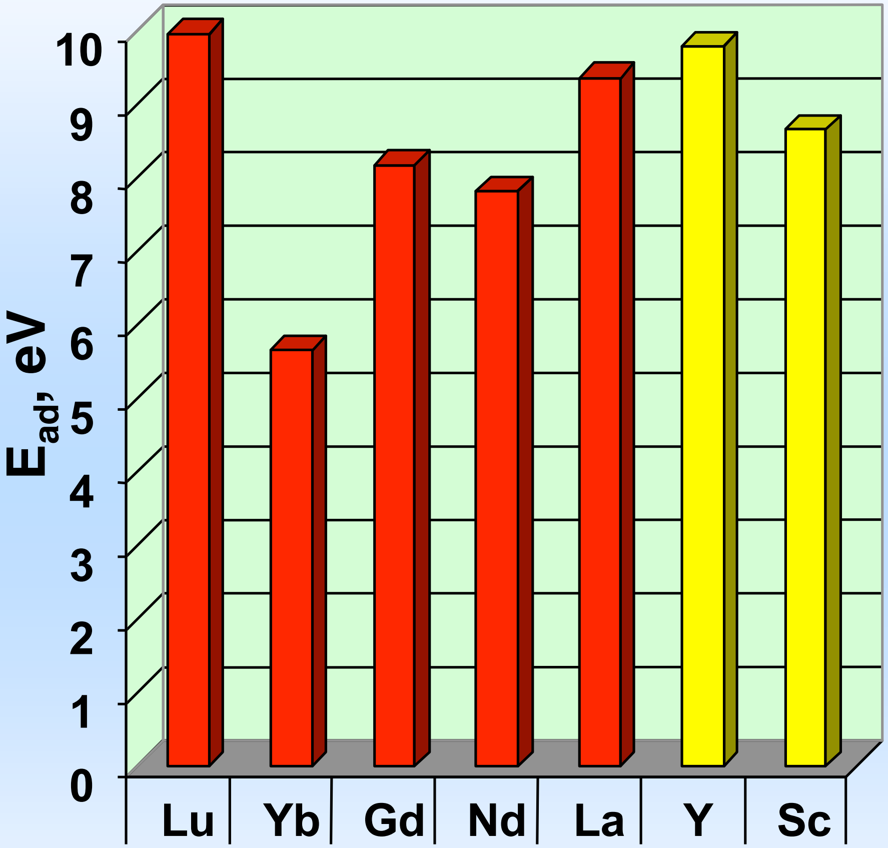


Interface Strength Decreases as Reduce Al & O content of epitaxial SiAlON growth layer.

Fracture Toughness Increases as raise $Y_2O_3$ : $Al_2O_3$ ratio of additives in self-reinforced $Si_3N_4$.

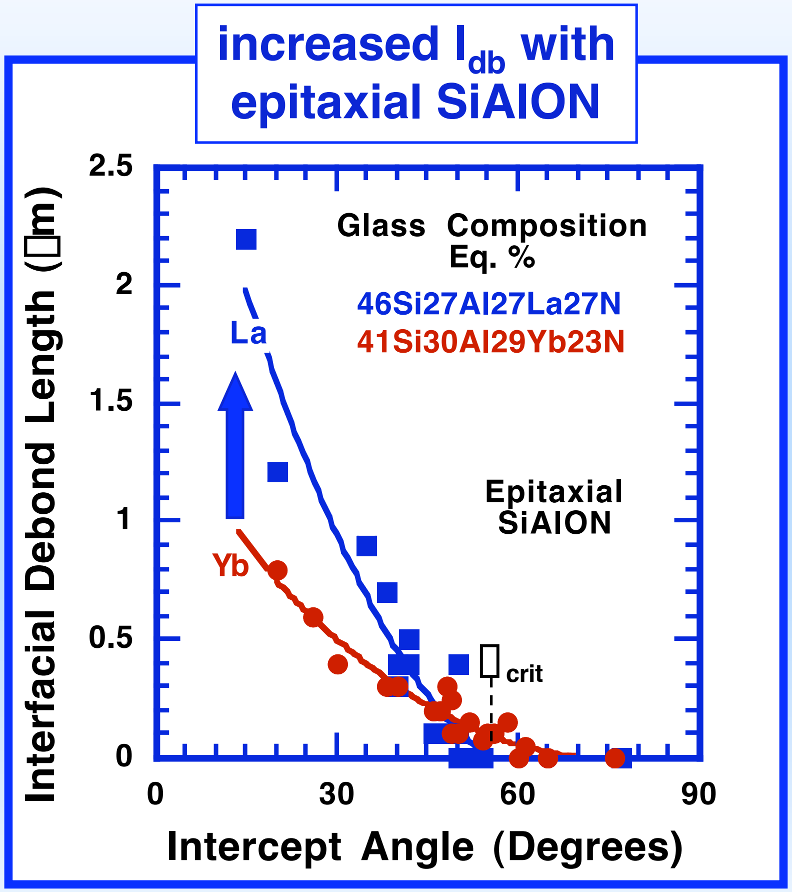
# Many RE Have High Binding Energies at $Si_3N_4$ Prism Plane; Stronger Tendency to Segregate ➡ Weaker Interface



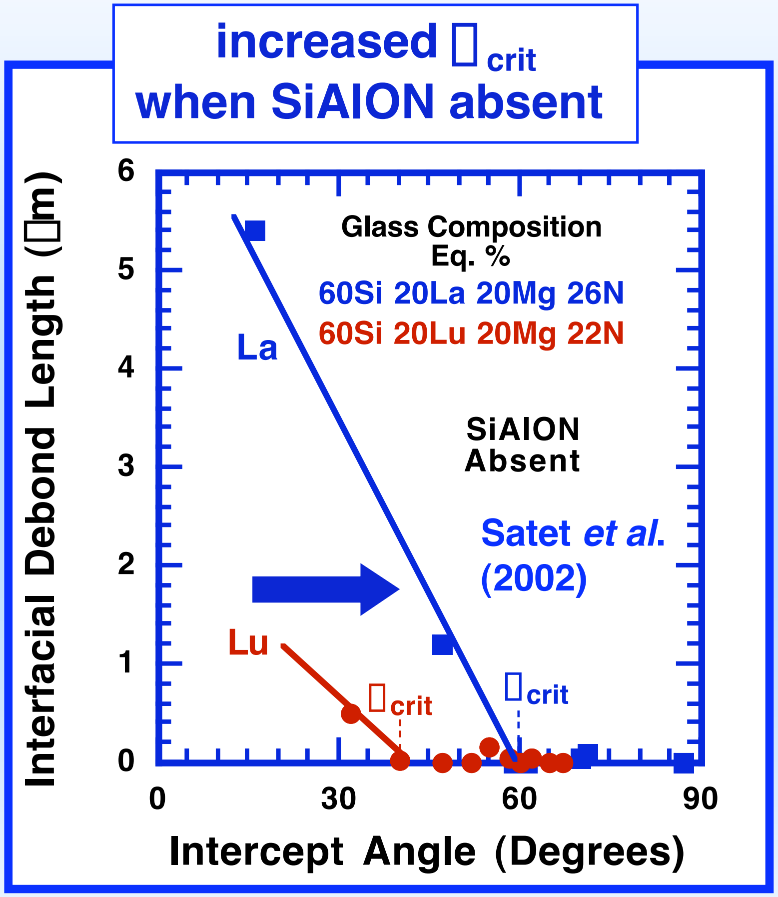


**Increasing Weakness of Interface: Lu ➜ Sc ➜ Y ➜ La**

# Rare Earths Predicted to Alter Interfacial Debonding Behavior



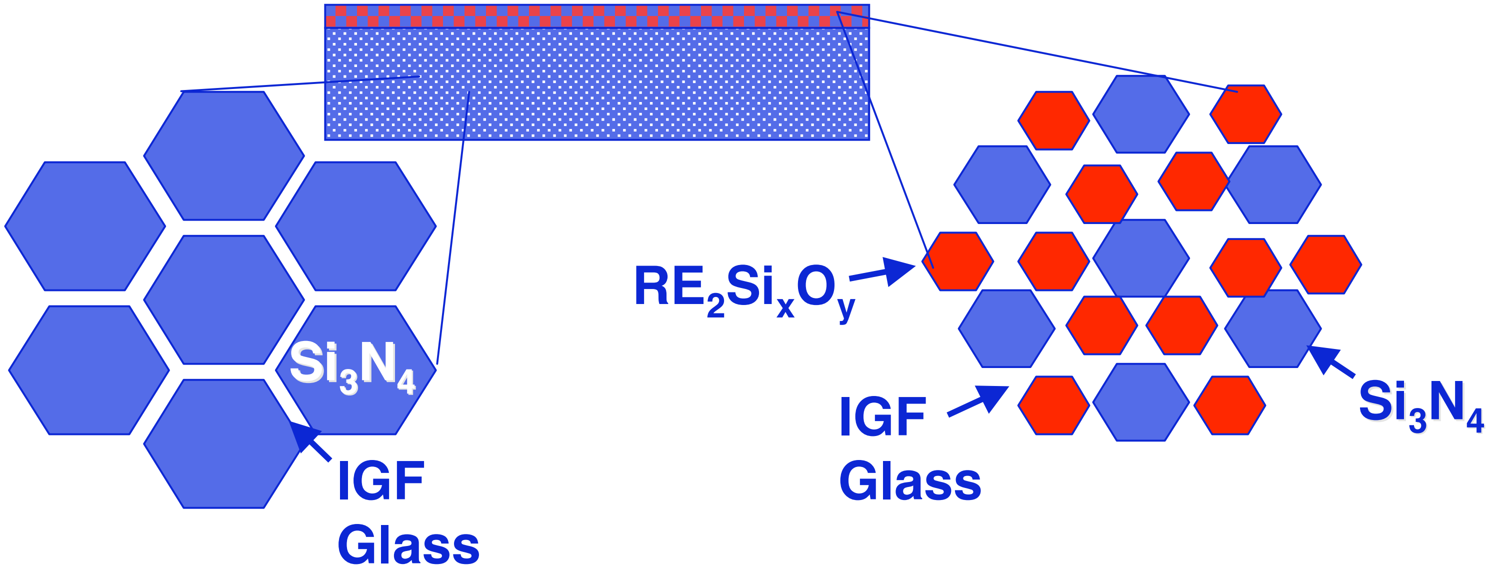
increased $l_{db}$ with epitaxial SiAlON



increased $\theta_{crit}$ when SiAlON absent

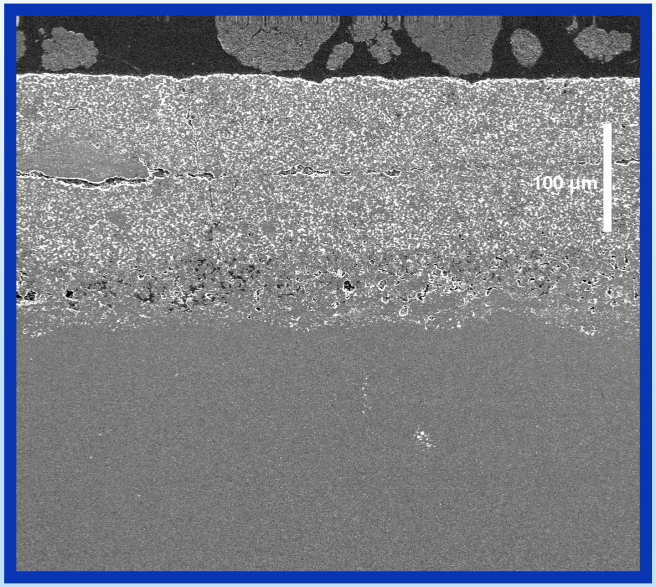
**RE to N bonding at $Si_3N_4$ surface weakens interface, especially effective with increasing RE segregation to the interface.**

# Tailored $Si_3N_4$ Surfaces to Improved EBC Performance

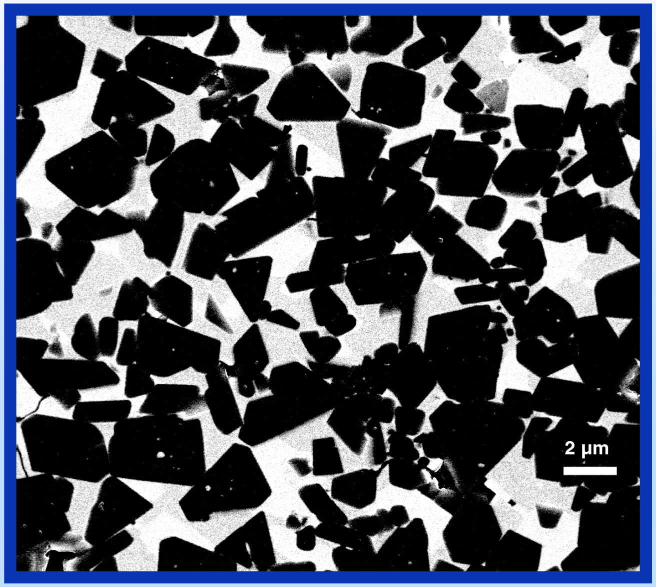


| | $\alpha$, ppm/°C | E, GPa | $T_g$, °C |
|---|---|---|---|
| $Si_3N_4$ | 2.9 - 3.1 | 350 | |
| $RE_2Si_2O_7$ | 3.8 - 9.5 | 130 - 155 | |
| SiREMe Oxynitride IGF Glass | 3.5 - $7^+$ | 120 - 165 | 850 - 1050 |

# Surface Region of Si3N4 Ceramic with High RE Silicate Content Has Greater Thermal Expansion Coefficient



As-sinter-forged Si$_3$N$_4$ with 8 wt.% Lu$_2$O$_3$ + 2 wt.% SiO$_2$with ~ 200 *μ*m surface layer.



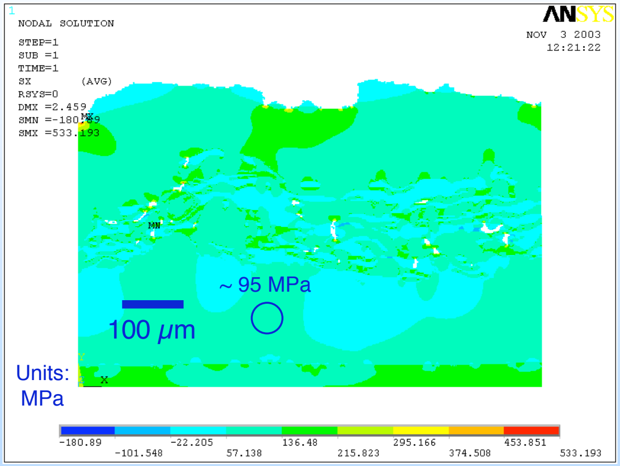
□-Si$_3$N$_4$ grains (dark) in a matrix consisting of possibly two phases. Two shades of gray indicate two Lu levels (e.g., Lu$_2$SiO$_5$ vs. Lu$_2$Si$_2$O$_7$?) as confirmed by EDS.

**Linear Thermal Expansion Coefficient, ppm/°C**

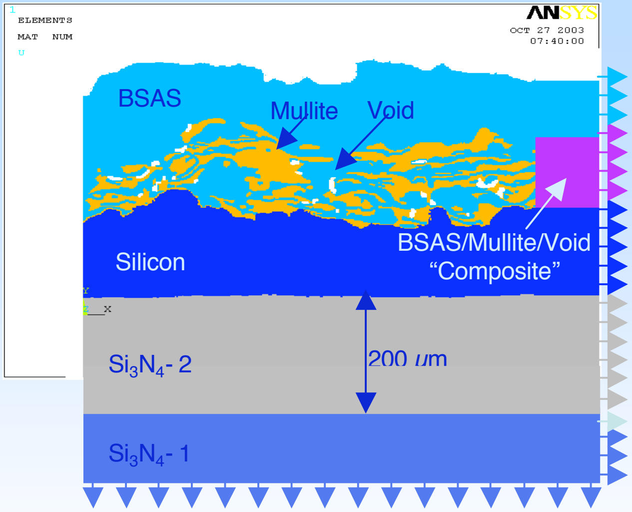
**Si$_3$N$_4$ 2.9 - 3.1 RE Silicates 3.8 - 7+ Surface region ~ 4**

# Reducing Residual Stress Fields in EBC-$Si_3N_4$ System by Surface Modification

$CTE_{Si}$ = 4.0 ppm/C, $CTE_{Si3N4}$ = 3.8 ppm/C

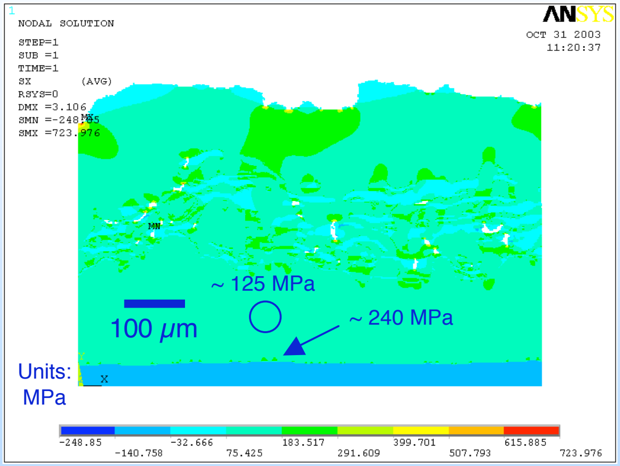


## With tailored surface region

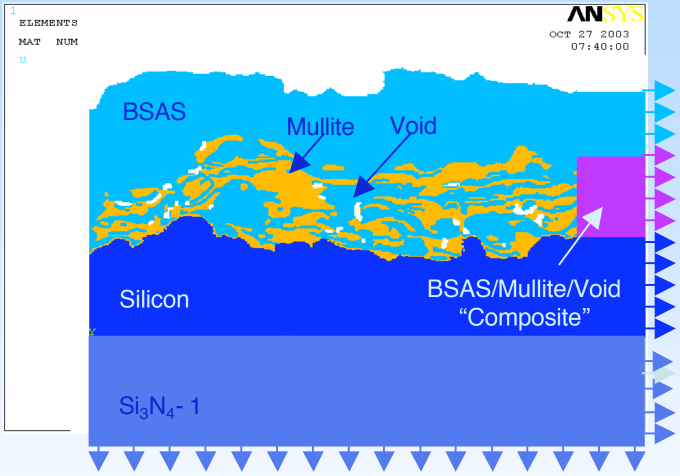


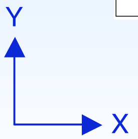
□x

$CTE_{Si}$ = 4.9 ppm/C, $CTE_{Si3N4}$ = 2.9 ppm/C



## Without tailored surface region





μ-FEA Reconstructed Model

**Wereszczak & Ferber - 03Nov03**

# Summary

- Can tailor the microstructure and mechanical properties of silicon nitride ceramics by selection of additives.
- Seeding used to control self-reinforced microstructure
- Additives influence grain growth and fracture properties
  - $Si_{6-Z}Al_zO_zN_{8-Z}$ formation with $Al_2O_3$ additions increase interface strength and reduce toughness as z increases.
  - Increasing RE segregation to $Si_3N_4$ surface sites: Lu ➡ La

    - Limits diametrical grain growth, which combined with
    - High $E_{ad}$ leads to *decrease* in interface strength &
    - Increased toughness.
- Tailoring the composition of surface region of $Si_3N_4$ component may offer approach to improving EBC performance.