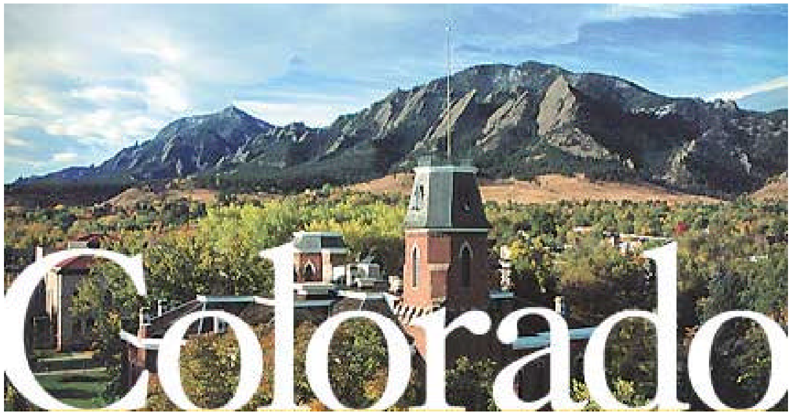
- Materials System Approach
- The Criteria
- Basic Research Issues



Polymer Derived Graded EBCs

Rishi.Raj@Colorado.edu (Boulder)

In Alliance with
Honeywell ES&S (Phoenix AZ)

ORNL-EBC (Nashville)
Nov. 6-7, 2002

THE PROBLEM

Silicon Nitride Vanes

1066^{o}C-1260^{o}C; 8.9 atm, $p_{H_2O} = 0.101$

162m/s to 573 m/sec

- 27% of cross section lost in 1818 h
- recession and mechanical degradation
- Si_3N_4 grains are oxidizing and then volatilizing

“Evaluation of Mechanical Reliability of Silicon Nitride Vanes after Field Tests in an Industrial Gas Turbine” Liu, Ferber, Westphal and Macri(ORNL report - I assume)

A Tenet

silica passivation mechanism for oxidation protection is not viable for the exposed surfaces of Si_3N_4 vanes and blades in humid combustion environment

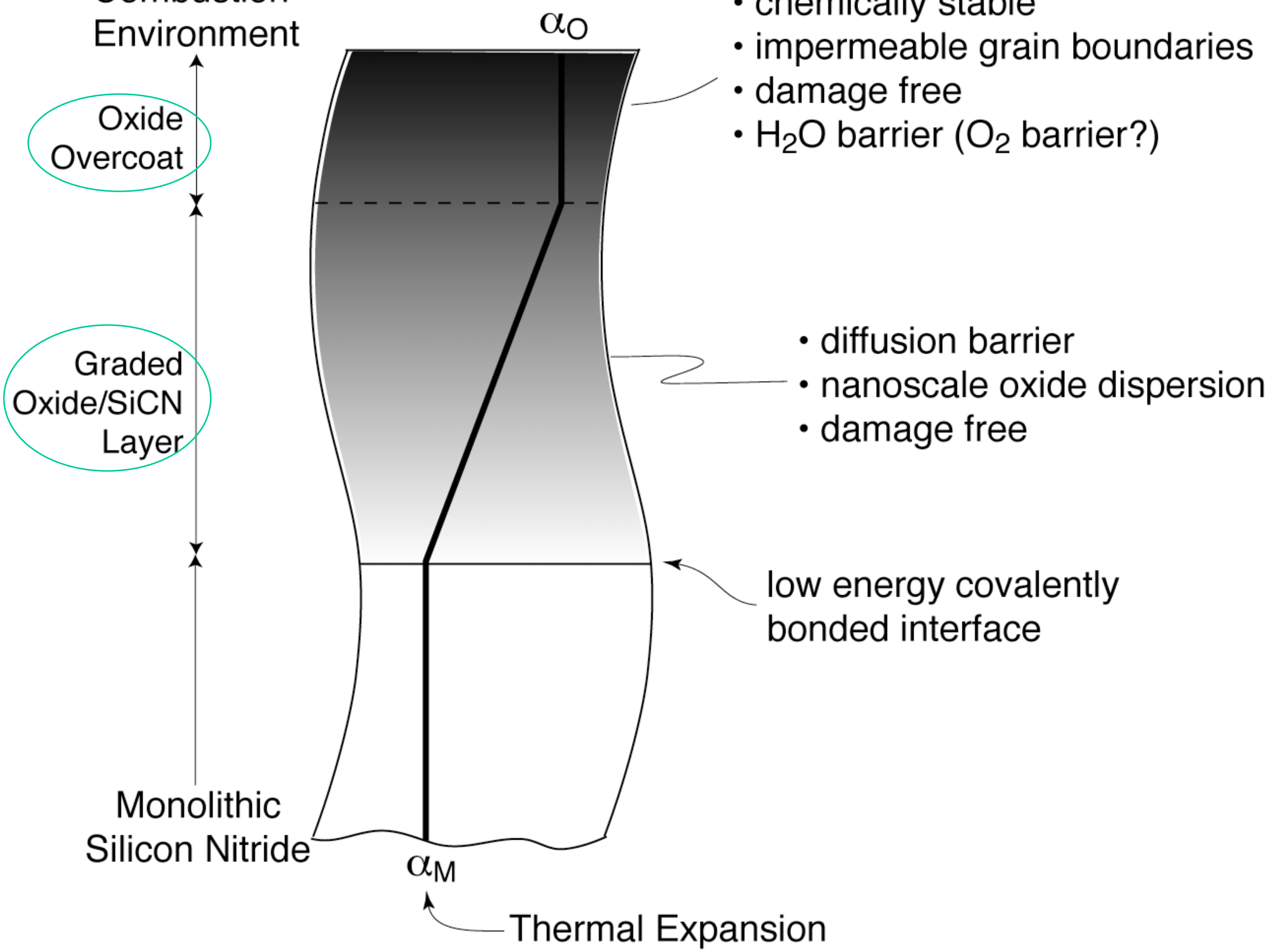
Opila et al. (JACerS)

The Design of a Graded Interface

Objective: prevent silicon nitride (SiO_2) volatilization

- oxide overlayer for chemical stability, isolation from humid environment
- graded interface prevents thermal shock, provides diffusion barrier for oxygen
- interfaces mechanically robust, nucleation barriers to silica formation

The EBC System



Combustion Environment

Oxide Overcoat

Graded Oxide/SiCN Layer

Monolithic Silicon Nitride

α_O

α_M

Thermal Expansion

- chemically stable
- impermeable grain boundaries
- damage free
- H_2O barrier (O_2 barrier?)

- diffusion barrier
- nanoscale oxide dispersion
- damage free

low energy covalently bonded interface

graded interface for thermal shock resistance - ANALYSIS

Elastic Energy Density is given by:

Monolithic Coating

$$U_V^o = f(\text{Elastic constants}) \, . \, \Delta\alpha_o^2 \quad / \text{vol}$$

Graded Coating

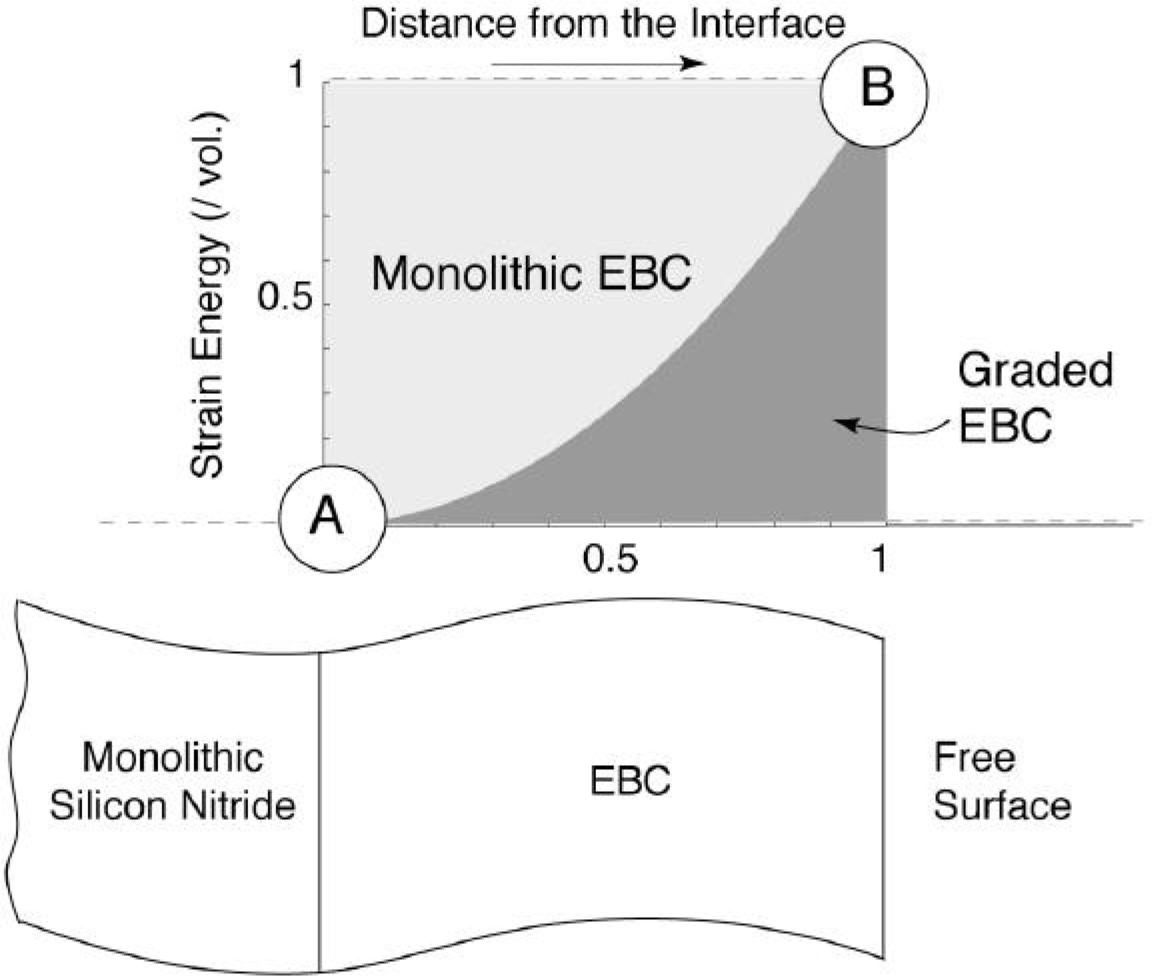
$$\Delta\alpha = \Delta\alpha_o \, . \, \frac{z}{h}$$

$$U_V(z) = f. \, (\Delta\alpha_o \, . \, \frac{z}{h})^2$$

	Energy Density /vol	Total Energy /area
Monolithic	$f. \, \Delta\alpha_0^2$	$f. \, \Delta\alpha_0^2 . h$
Graded	$f. \, (\Delta\alpha_o \, . \, \frac{z}{h})^2$	$\frac{1}{3} f. \, \Delta\alpha_0^2 . h$

h= total EBC thickness

	Strain Energy	Strain Energy Gradient
A: cracks cannot nucleate	[✓ LOW]	POS.
B: cracks cannot grow	HIGH	[✓ NEG.]



Materials Selection (Oxide Overlayer)

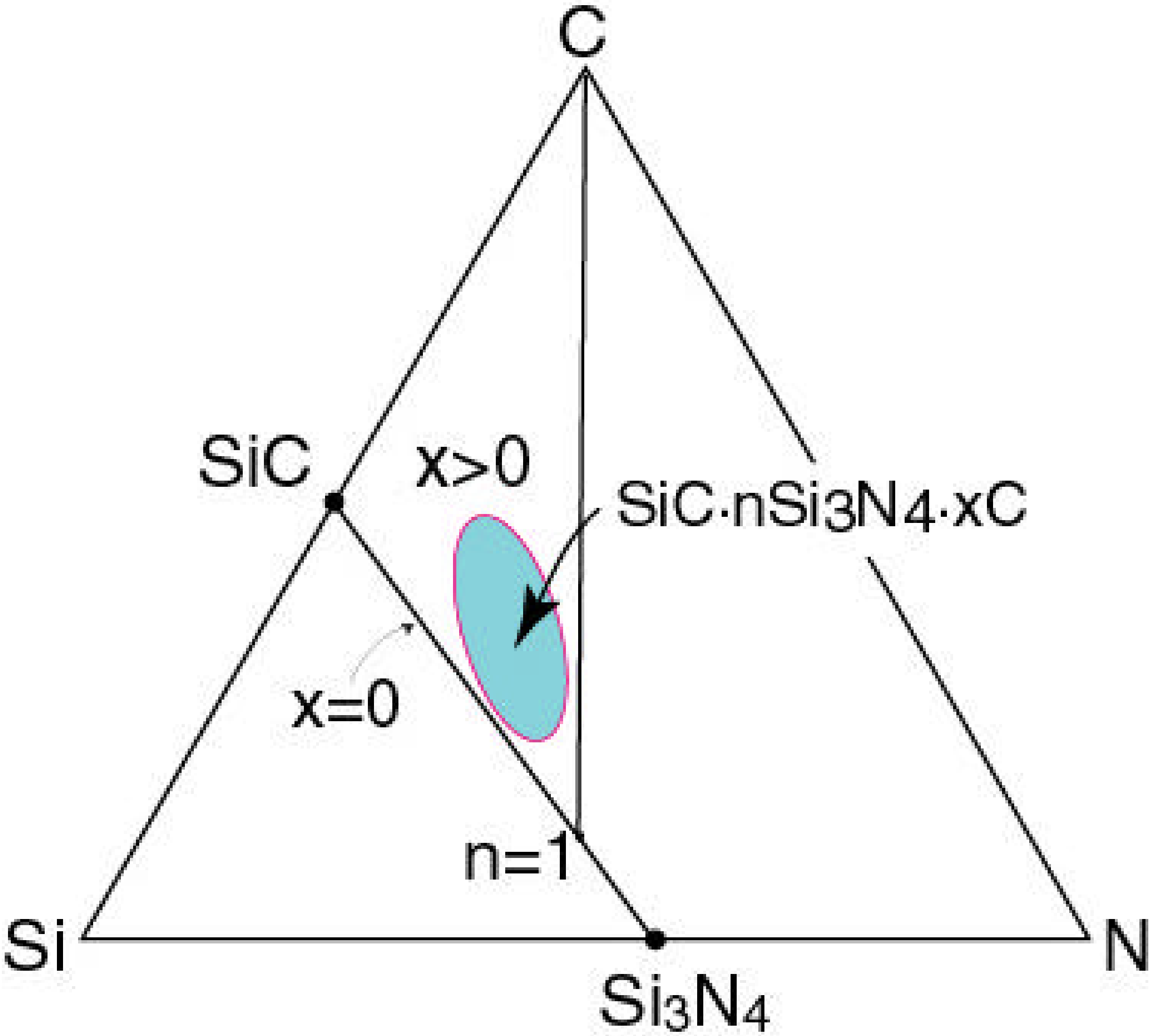
- Transition Metal Oxides (ZrO_2, HfO_2, Ta_2O_5, TiO_2)
- Base Metal Oxides (Al_2O_3, MgO etc.)
- Complex Oxides (YAG, Perovskites, etc.)
- Silicates (Mullite, etc.)

simple oxides are process friendly -
more likely to be implemented

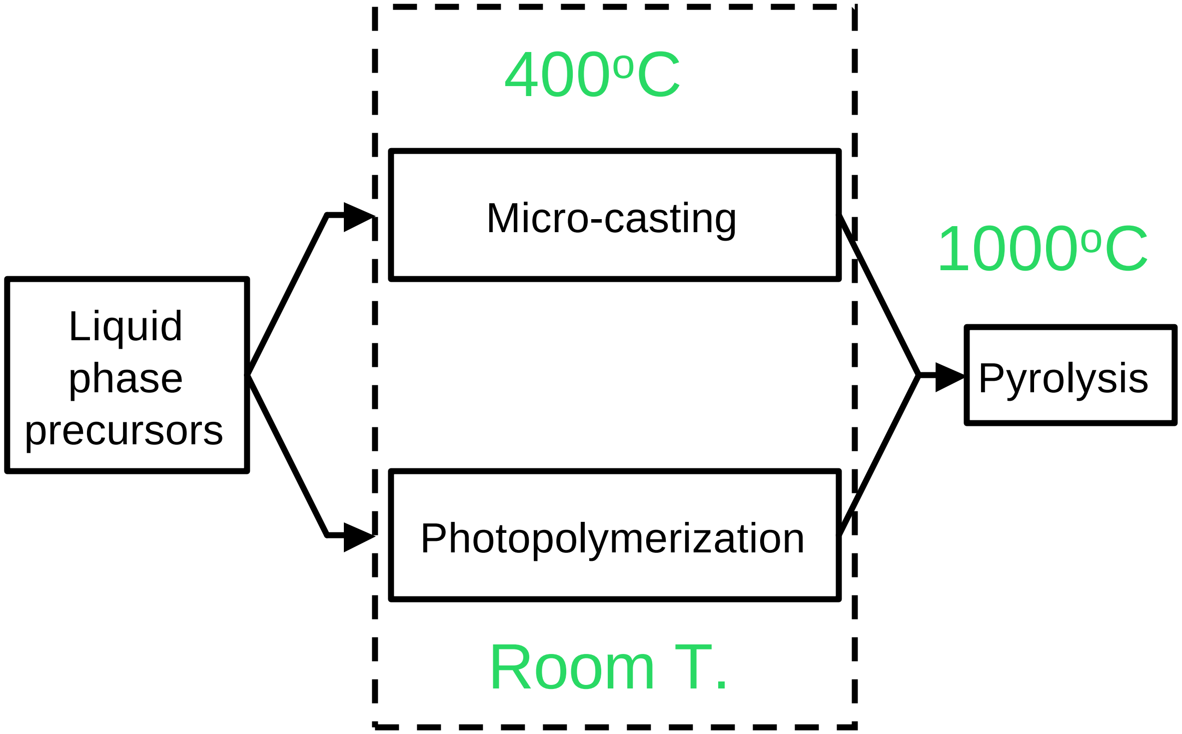
Why PDCs for the Gradient Layer?

- compatible with oxides
- liquid precursors: CVD, dip coating, for step-coverage
- low energy interfaces with oxides, Si_3N_4
- ultra-slow diffusion at ultrahigh temperatures

Composition Diagram for SiCN



The PDC Process



400^{o}C

Liquid phase precursors

Micro-casting

Photopolymerization

Room T.

1000^{o}C

Pyrolysis

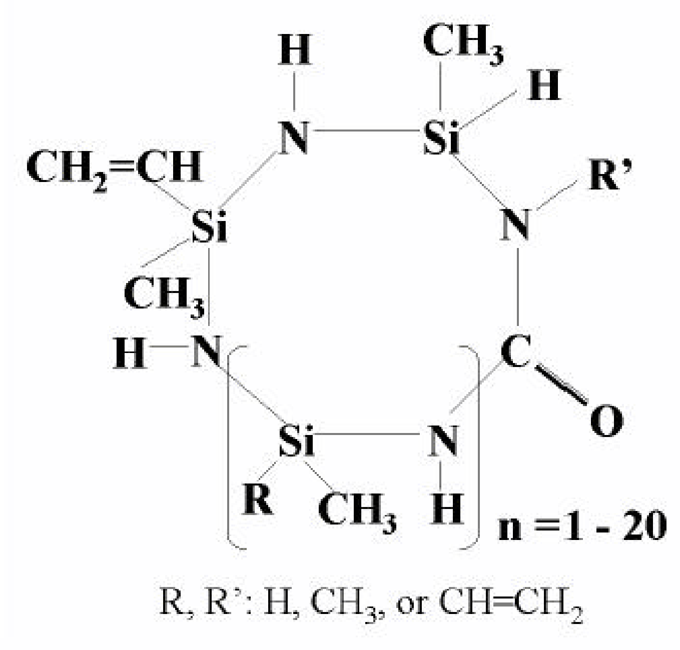
Liquid Precursor

Plastic Net-Shape

Ultrahigh T. Ceramic

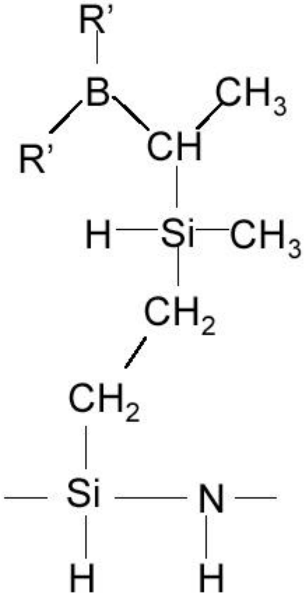
Organic Precursors for SiCN

<u>CERASET</u>

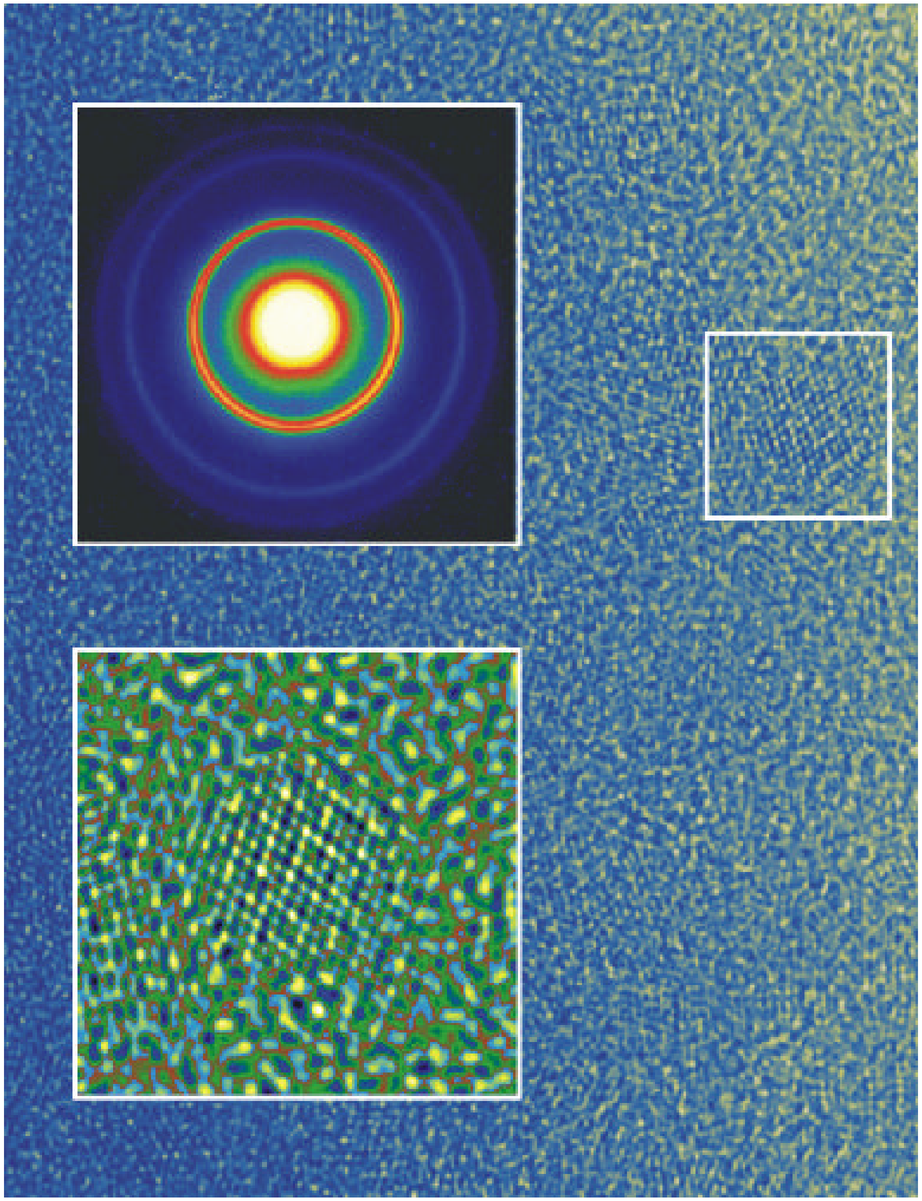


SiCN

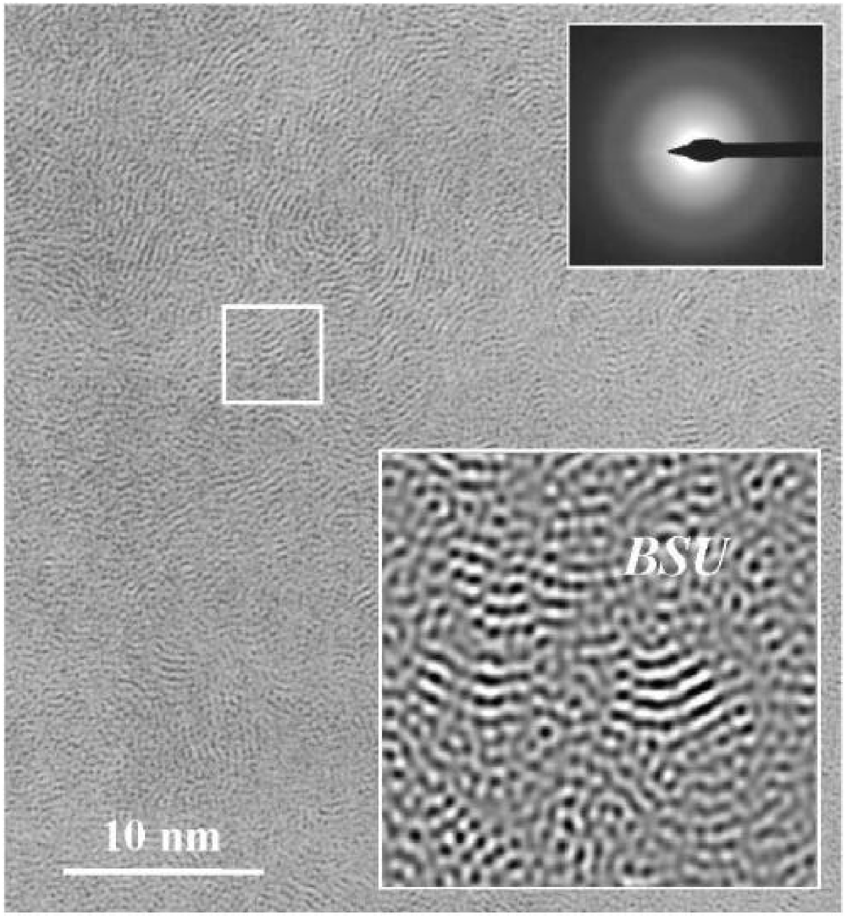
<u>PBMS</u>



SiCN Doped with B



Special Issue JACerS, Oct. 2001
Ultrahigh Temperature PDCs



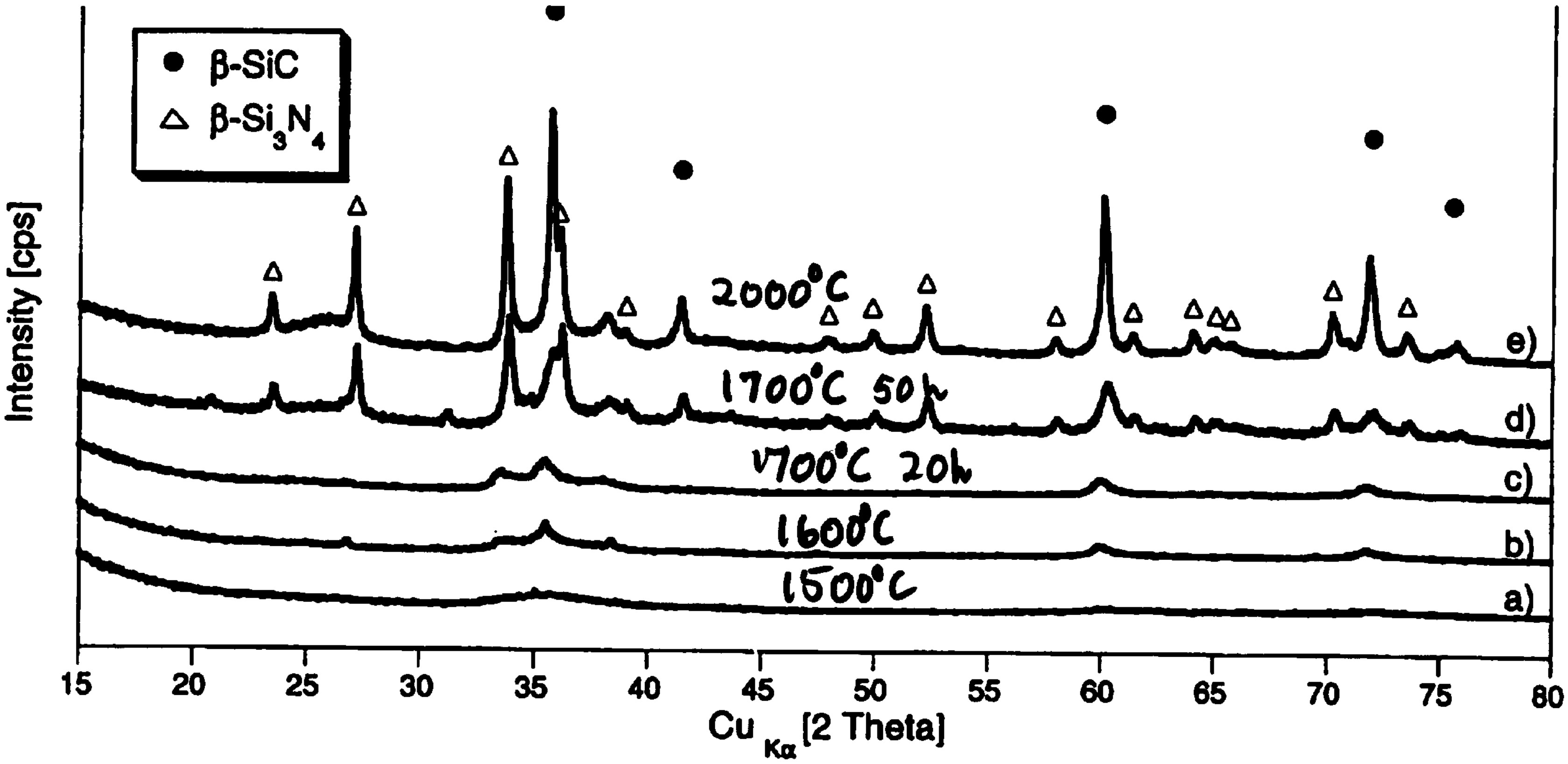
H.-J. Kleebe (CSM)

Nanostructure Stable to
UltraHigh Temperatures

(Extremely Low Mobility)

X-ray powder diffraction of $Si_{3.0}B_{1.0}C_{4.3}N_{2.0}$ after annealing

in nitrogen at (a)1500°C, (b) 1600°C,(c) 1700°C for 20 hours,
and in argon (d) 1700°C for 50 hours and (e) 2000°C for 2 hours.
(Courtesy Riedel)



Properties of SiCN as compared to other materials

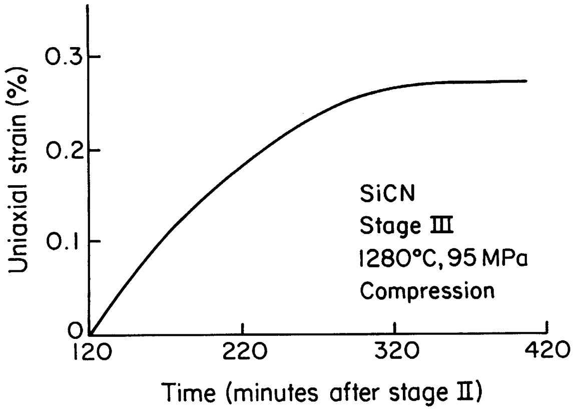
Property	SiCN	SiC	Si_3N_4
Density (g/cm^3)	2.35	3.17	3.19
E Modulus (GPa)	140-170	405	314
Poisson's Ratio	0.17	0.14	0.24
CTE (x10-6/K)	~ 3	3.8	2.5
Hardness (GPa)	25	30	28
Fracture Strength (MPa)	500-1200	418	700
Fracture Toughness (MPa.m1/2)	3.5	4 -6	5 - 8
Thermal Shock FOM*	1100-5000	270	890

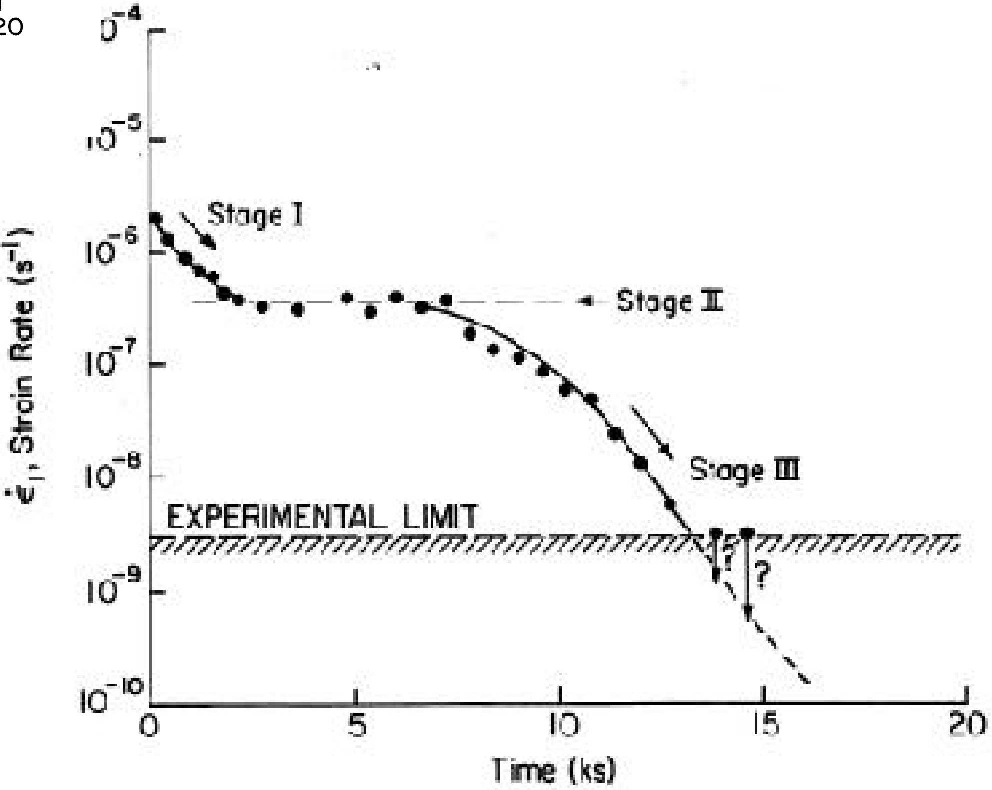
*FOM=strength/(E-Modulus x CTE)

Creep Studies in Uniaxial Compression

Creep Rate Declines with Time

SiCN, 1350^{o}C, 100 MPa





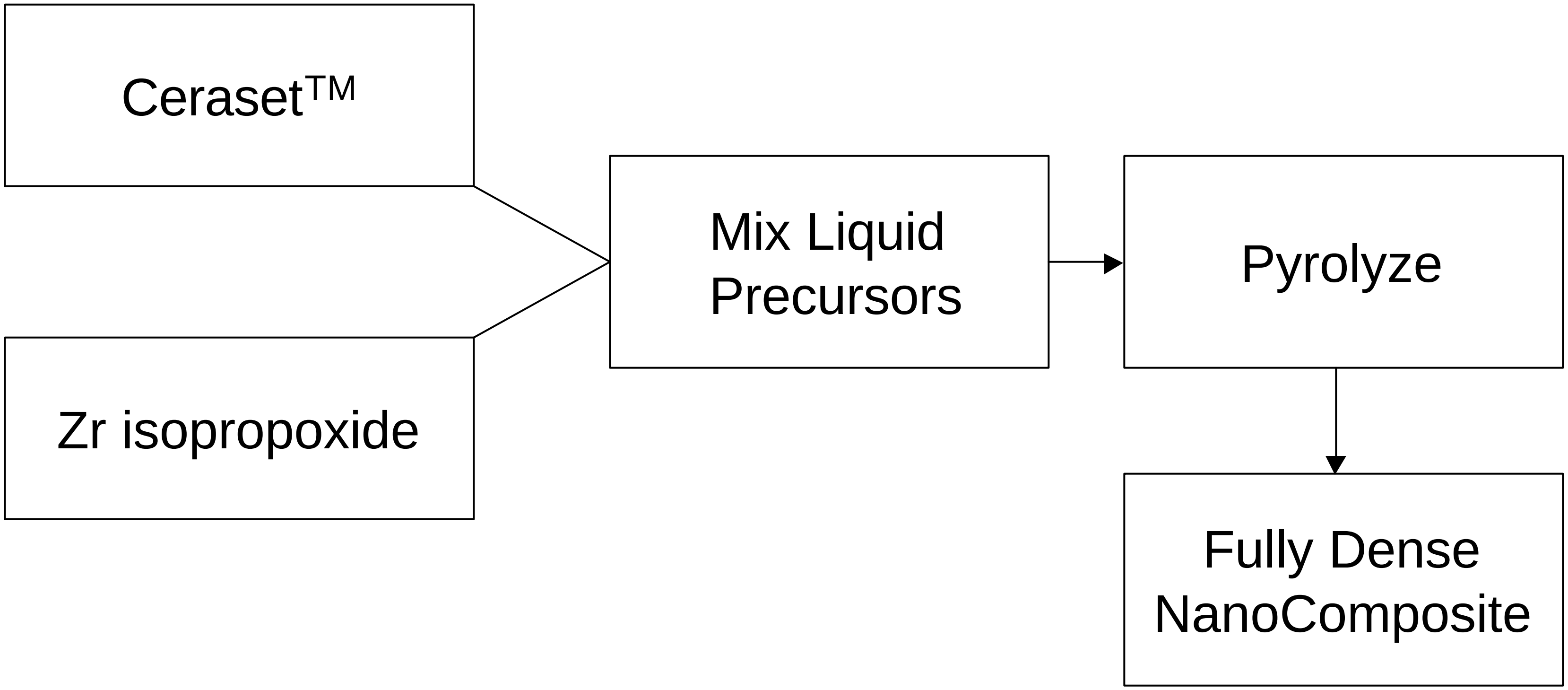
Summary of Creep Results

- mobile molecules are LARGE (~ 1-2 nm)
- long range diffusion extremely slow

Concepts of Creep in (silicate) Glasses and in Polycrystalline Materials are NOT Applicable

SiCN - Zirconia NanoComposites

The Process



CerasetTM

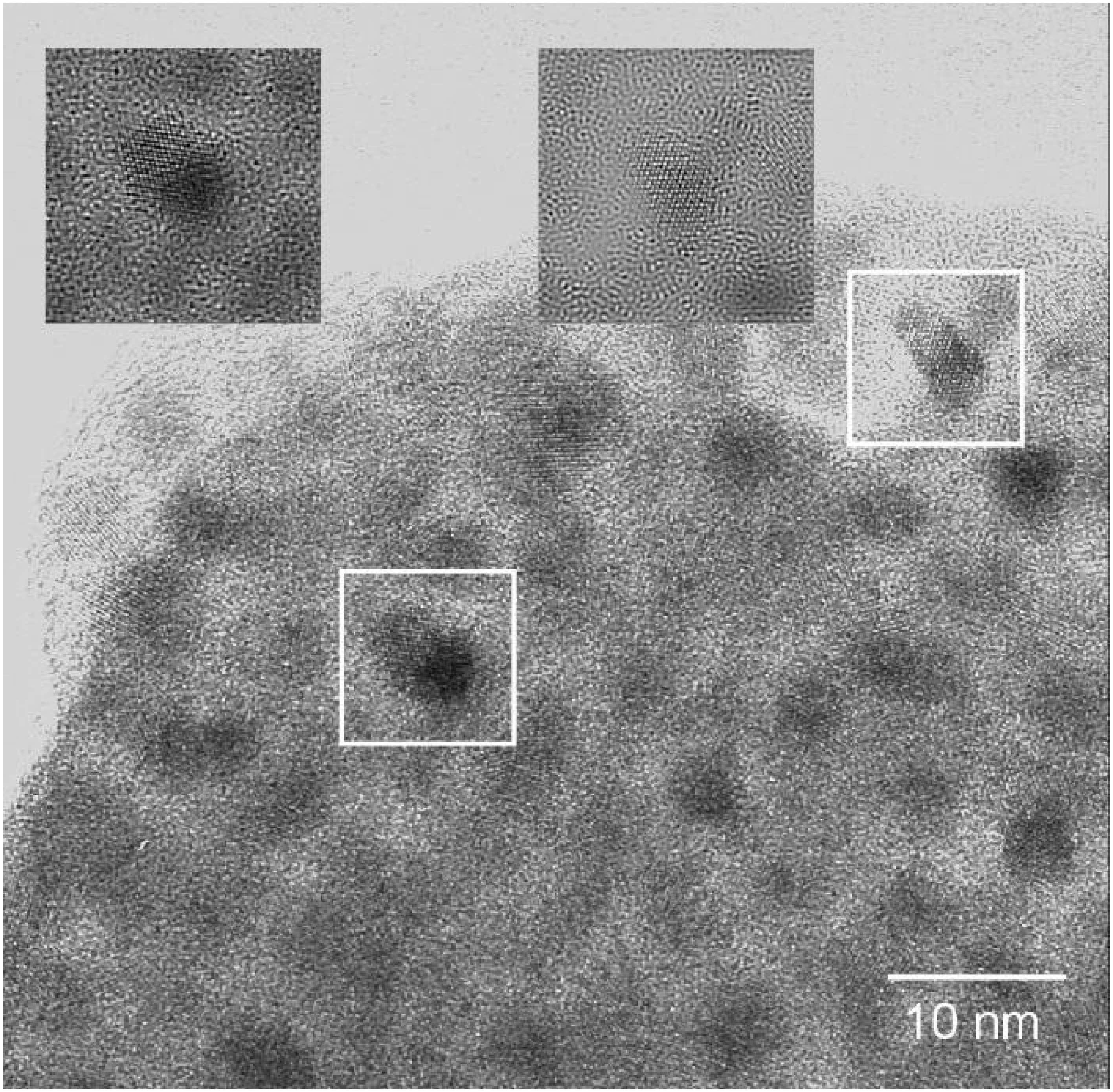
Zr isopropoxide

Mix Liquid Precursors

Pyrolyze

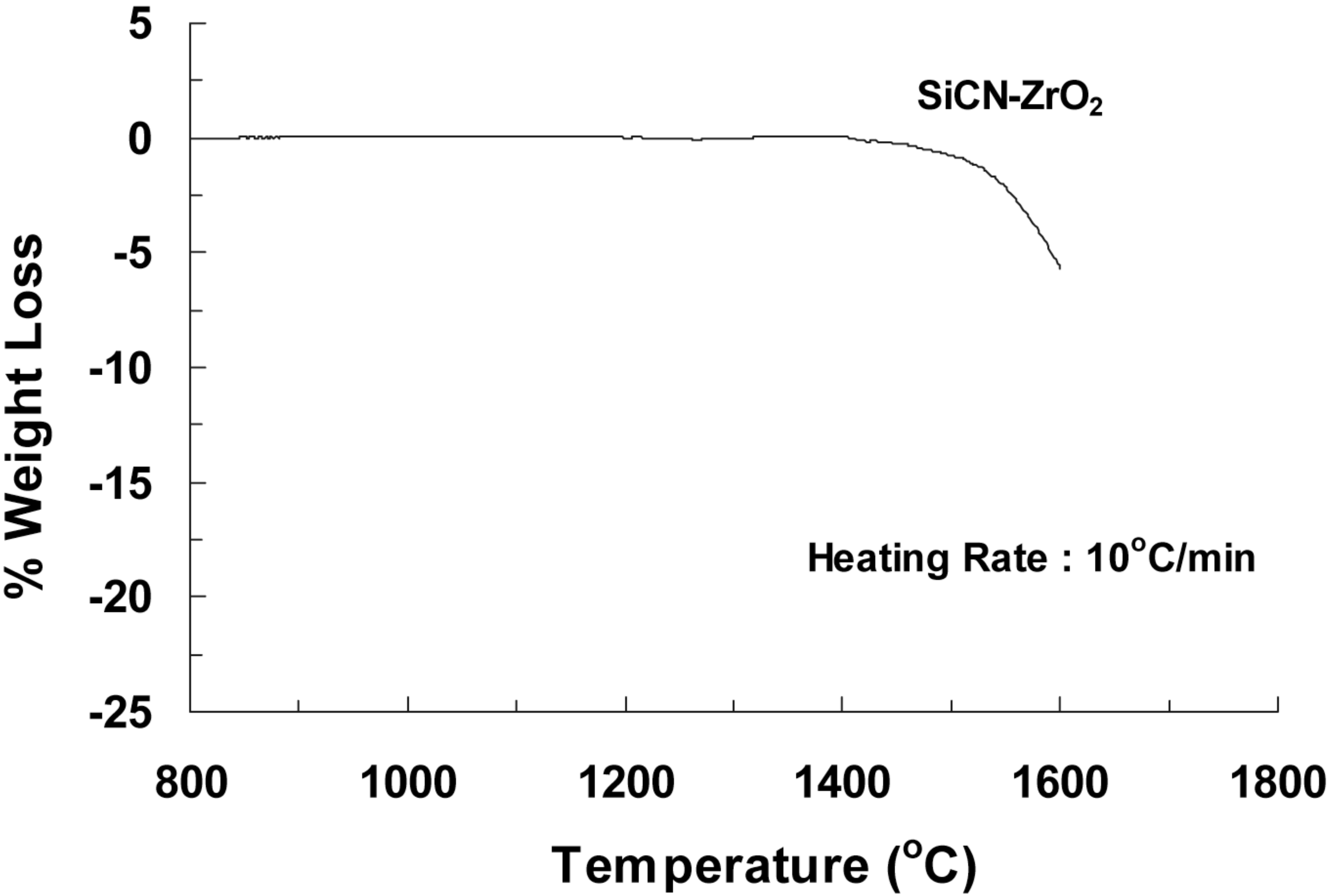
Fully Dense NanoComposite

$\mathbf{SiZr_{0.13}C_{0.461}N_{0.785}O_{0.69}}$



SiCN-Zirconia:

Courtesy
Kleebe


SiCN-ZrO_2
Heating Rate : 10°C/min
% Weight Loss
5
0
-5
-10
-15
-20
-25
800
1000
1200
1400
1600
1800
Temperature (°C)

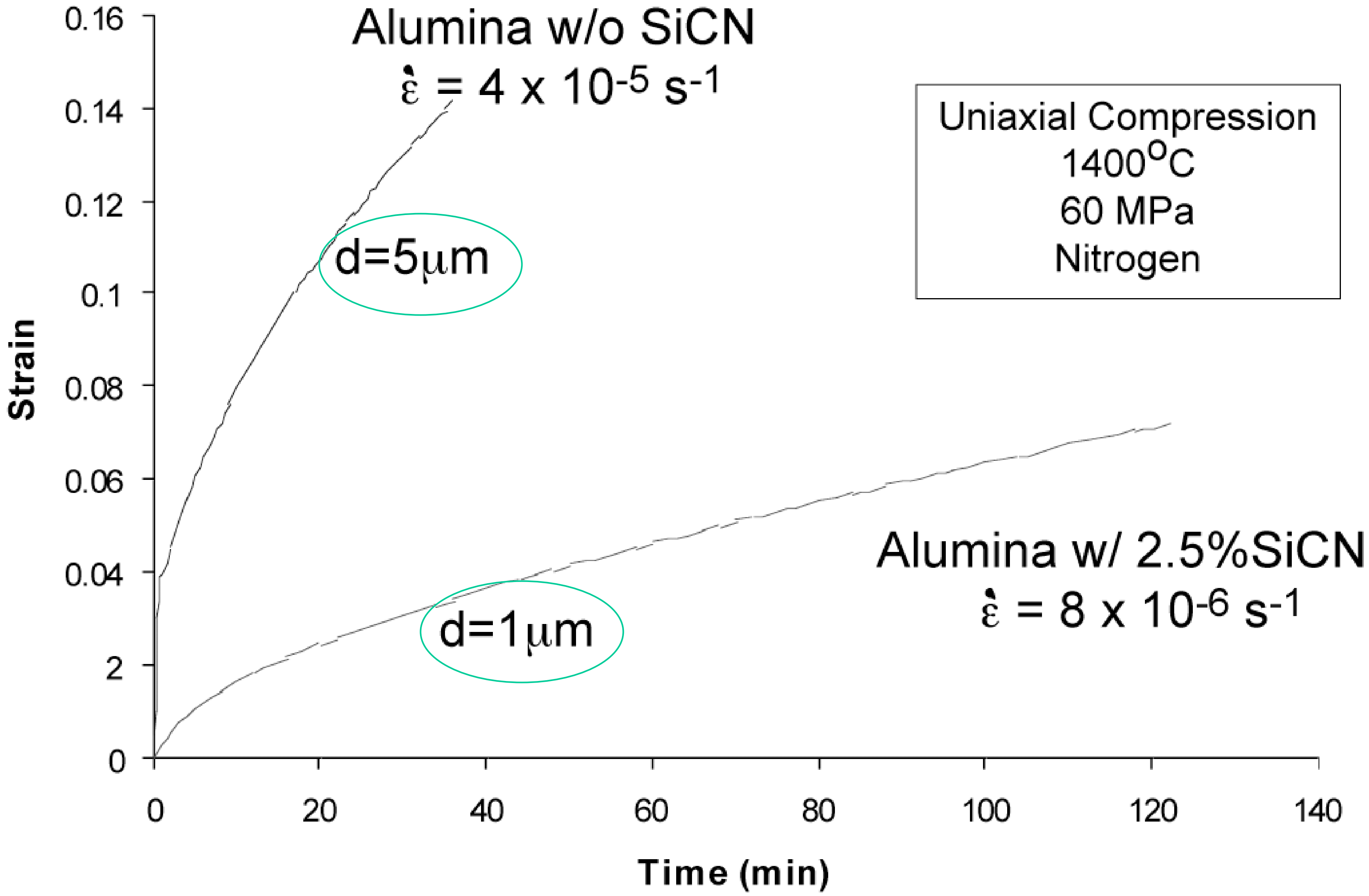
Summary of SiCN-ZrO_2 Results

- nanoscale oxide phase (will not thermal shock)
- high strength (2-3 GPa)
- thermally stable

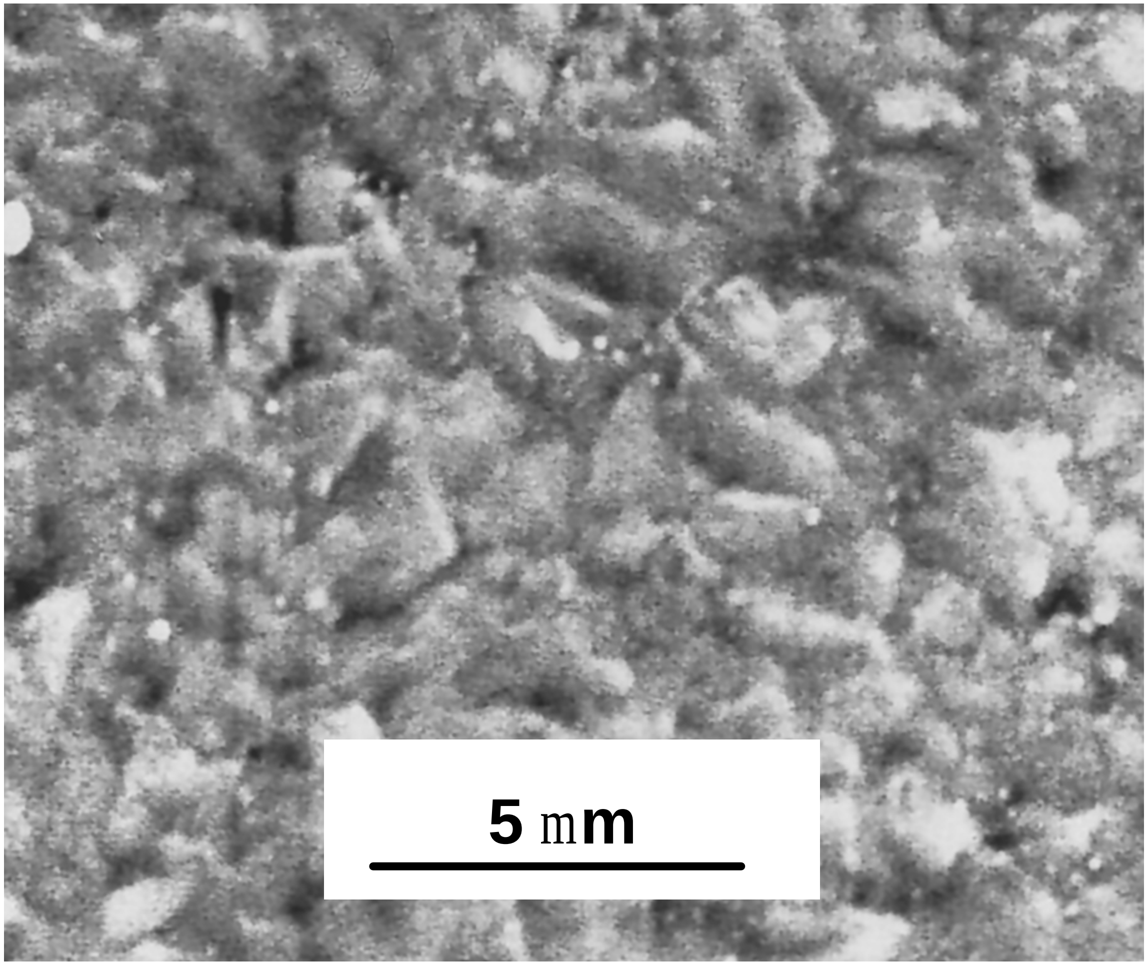
Al_2O_3 - SiCN Composites

- Al_2O_3 powder and SiCN liquid precursor-hot press
- compare grain growth w/ and w/o SiCN
- compare creep w/ and w/o SiCN

SiCN at Alumina-Grain Boundaries Reduces "d"-Normalized Creep Rate by 1/100 to 1/1000



Alumina w/ 2.5% SiCN



appearance unlike polycrystalline alumina

Preliminary Results from Al_2O_3 - SiCN Composites

- grain boundary kinetic phenomena (creep and grain growth) retarded by SiCN interfacial phase
- Al_2O_3 and SiCN form low-energy interfaces

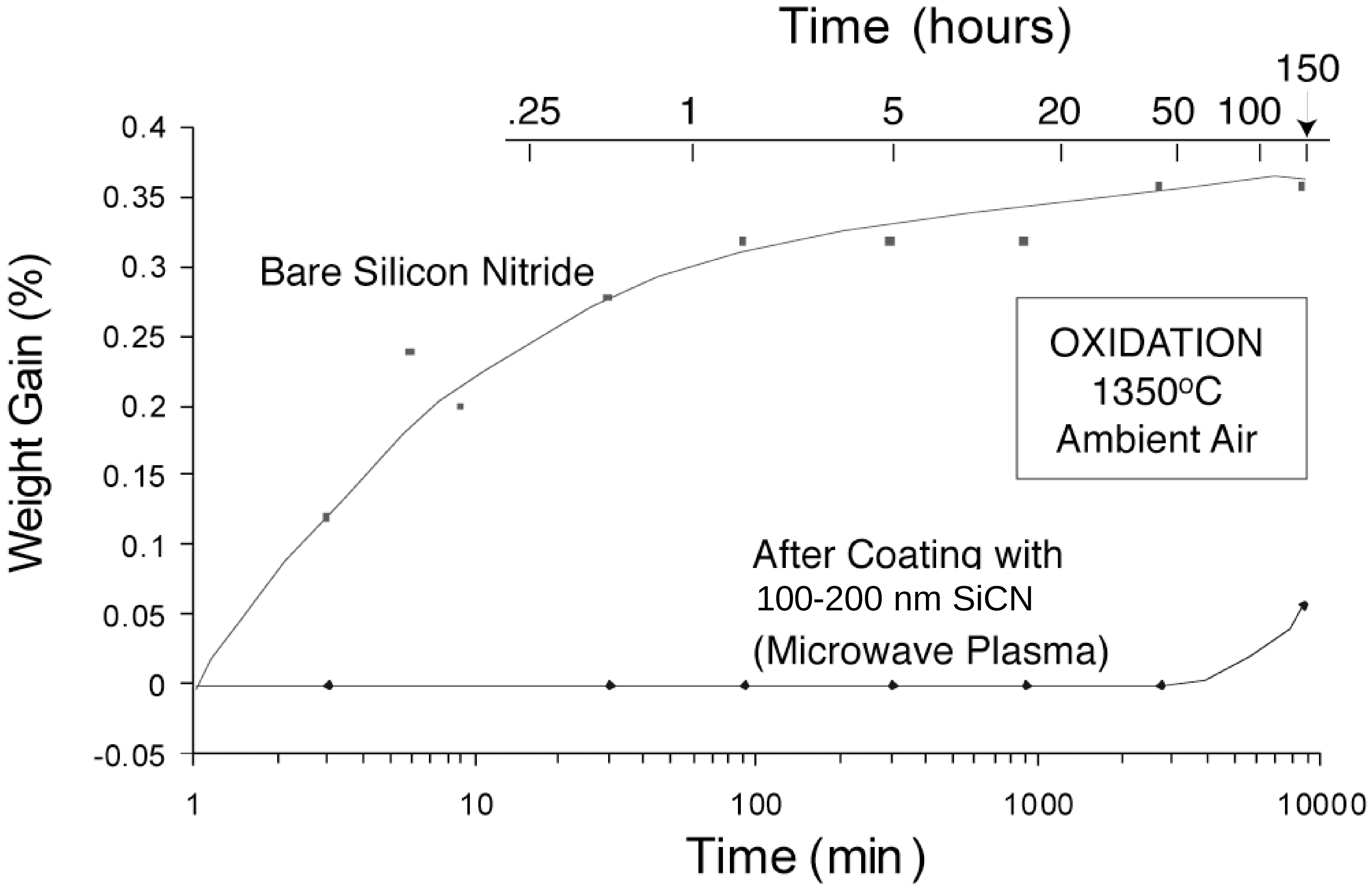
Oxides and SiCN good candidates for graded interfaces

The SiCN - Si_3N_4 Interface

Thin Film SiCN on Si_3N_4

- processed by liquid injection/microwave plasma CVD
- 0.1-0.2 μm thick film of SiCN on Si_3N_4
- compare oxidation of bare and coated Si_3N_4

Oxidation Protection from SiCN Thin-Films on Silicon-Nitride



Summary of Results:

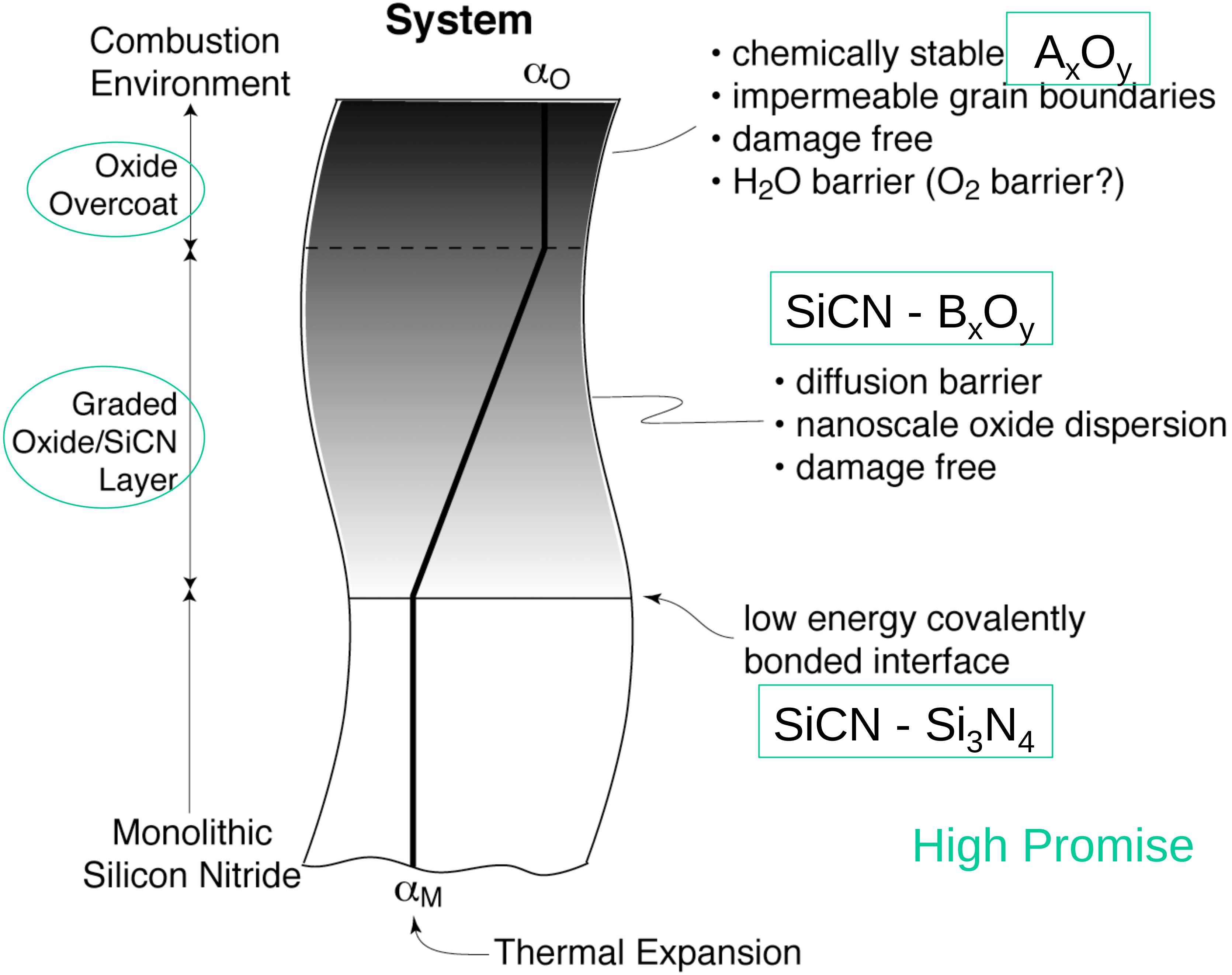
- good bonding of film to substrate

(SiO_2 cannot nucleate at the SiCN/Si_3N_4 interface)

or

- SiCN effective as oxygen diffusion barrier

The EBC System



Combustion Environment

Oxide Overcoat

Graded Oxide/SiCN Layer

Monolithic Silicon Nitride

α_O

α_M

Thermal Expansion

- chemically stable
- impermeable grain boundaries
- damage free
- H_2O barrier (O_2 barrier?)

A_xO_y

SiCN - B_xO_y

- diffusion barrier
- nanoscale oxide dispersion
- damage free

low energy covalently bonded interface

SiCN - Si_3N_4

High Promise

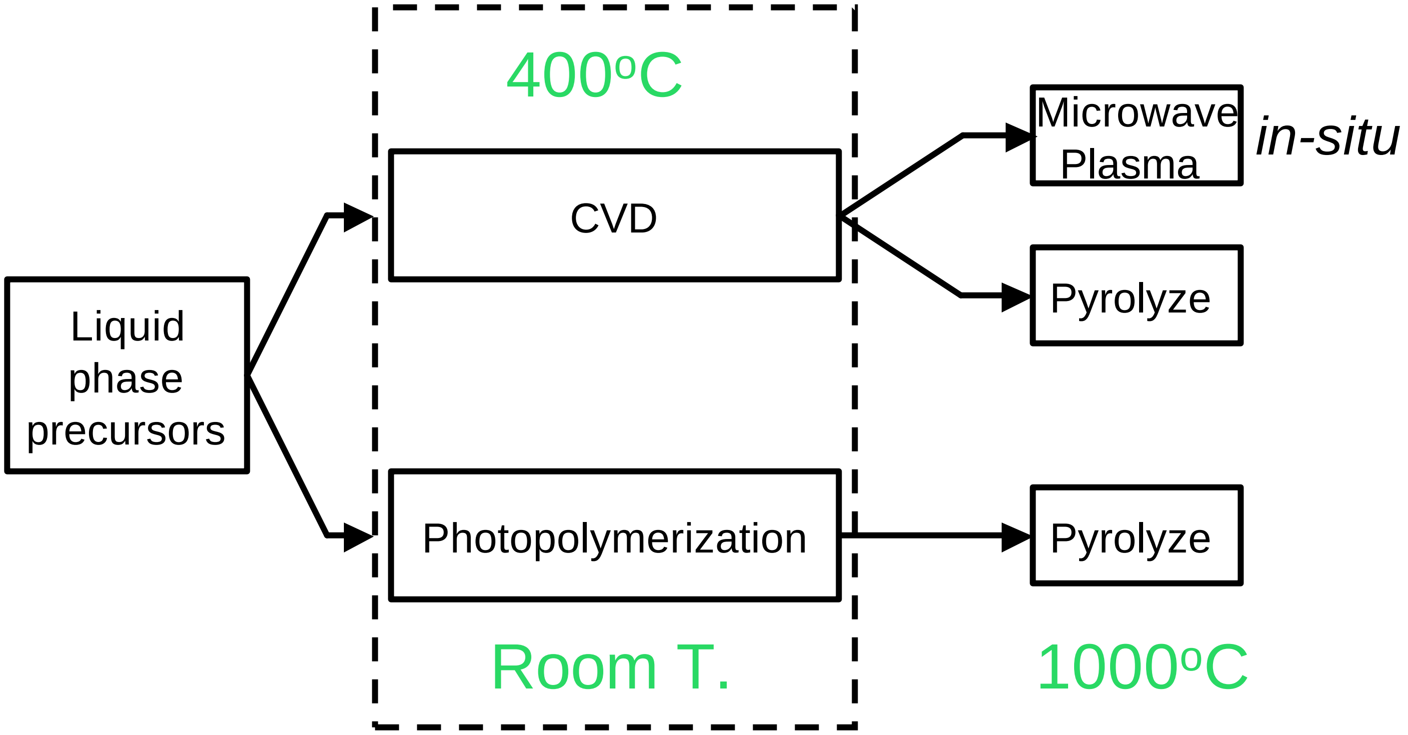
What are the basic research issues?

Objective: Suppress Volatilization (prevent silica growth)

- The surface oxide-overlayer - damage free? -chemically stable? - diffusion barrier?
- The oxide/SiCN *interface* - prevents nucleation of silica?
- The graded PDC/oxide interlayer - damage free? -immune to thermal shock? - effective diffusion barrier? - PDC & oxide phase equilibria?
- The SiCN/Si_3N_4 *interface* - prevents nucleation of silica? - not attacked by the sintering additives?

- Processing - graded construction? - step coverage? - low cost?

the graded PDC coating process



Liquid phase precursors

400°C

CVD

Photopolymerization

Room T.

Microwave Plasma *in-situ*

Pyrolyze

Pyrolyze

1000°C

Liquid Precursor

Polymer Films

Ultrahigh T. Coatings