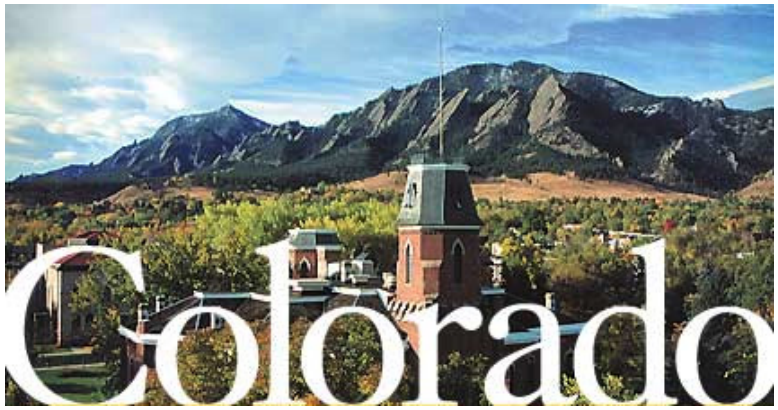


Rishi.Raj@Colorado.EDU (Boulder)

Polymer Derived EBCs for Protecting Si_3N_4 in Gas Turbine Environments

ORNL-EBC Meeting (Nashville)
Nov. 18-19, 2003

Sponsors: Honeywell and Oak Ridge National Laboratory

THE PROBLEM

Silicon Nitride Vanes

1066°C-1260°C; 8.9 atm, p_{H2O} = 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

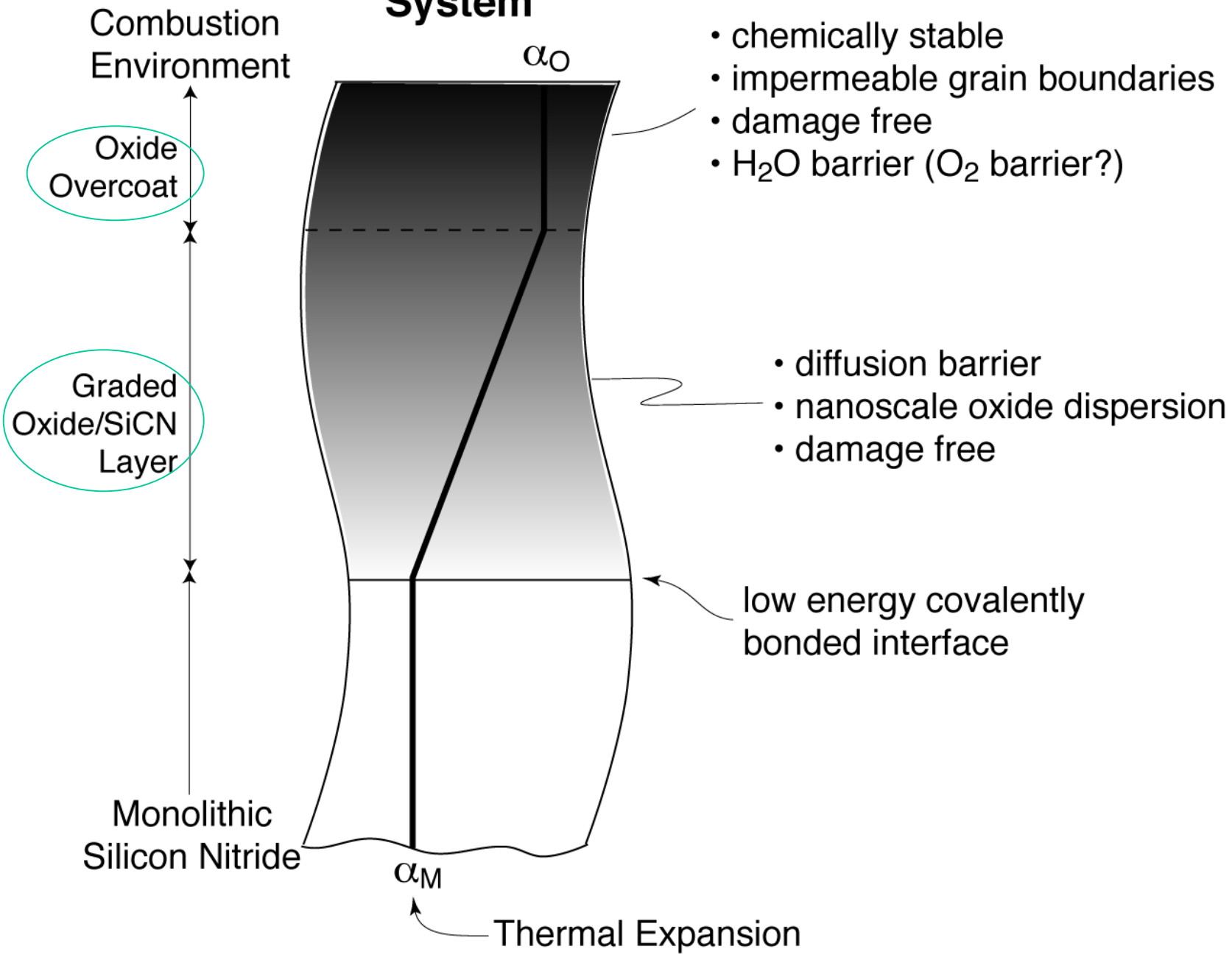
silica passivation mechanism for oxidation protection is not viable for the exposed surfaces of Si_3N_4 vanes and blades in humid combustion environment

Opila et al. (JACerS)

Design Elements of EBCs

- *oxide overlayer*: for chemically stable
- *graded interface:* prevent thermal shock
- *diffusion barrier:* for oxygen
- *interfaces*: as nucleation barriers to silica

The EBC System



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

Materials Selection (Bond Layer)

Why PDCs (silicon carbonitride-SiCN)?

- apparently compatible with oxides
- apparently ultra-slow diffusion at ultrahigh temperatures
- reasonable processing experience at Colorado

PDCs (silicon carbonitride-SiCN)?

Missing Science

- apparently compatible with oxides

the nature of oxide-SiCN interface not known

- apparently ultra-slow diffusion at ultrahigh temperatures

information is phenomenological not mechanistic

- reasonable processing experience at Colorado

structure of SiCN (and how it relates to process) not known

Where we are and where we are going?

Current Knowledge:

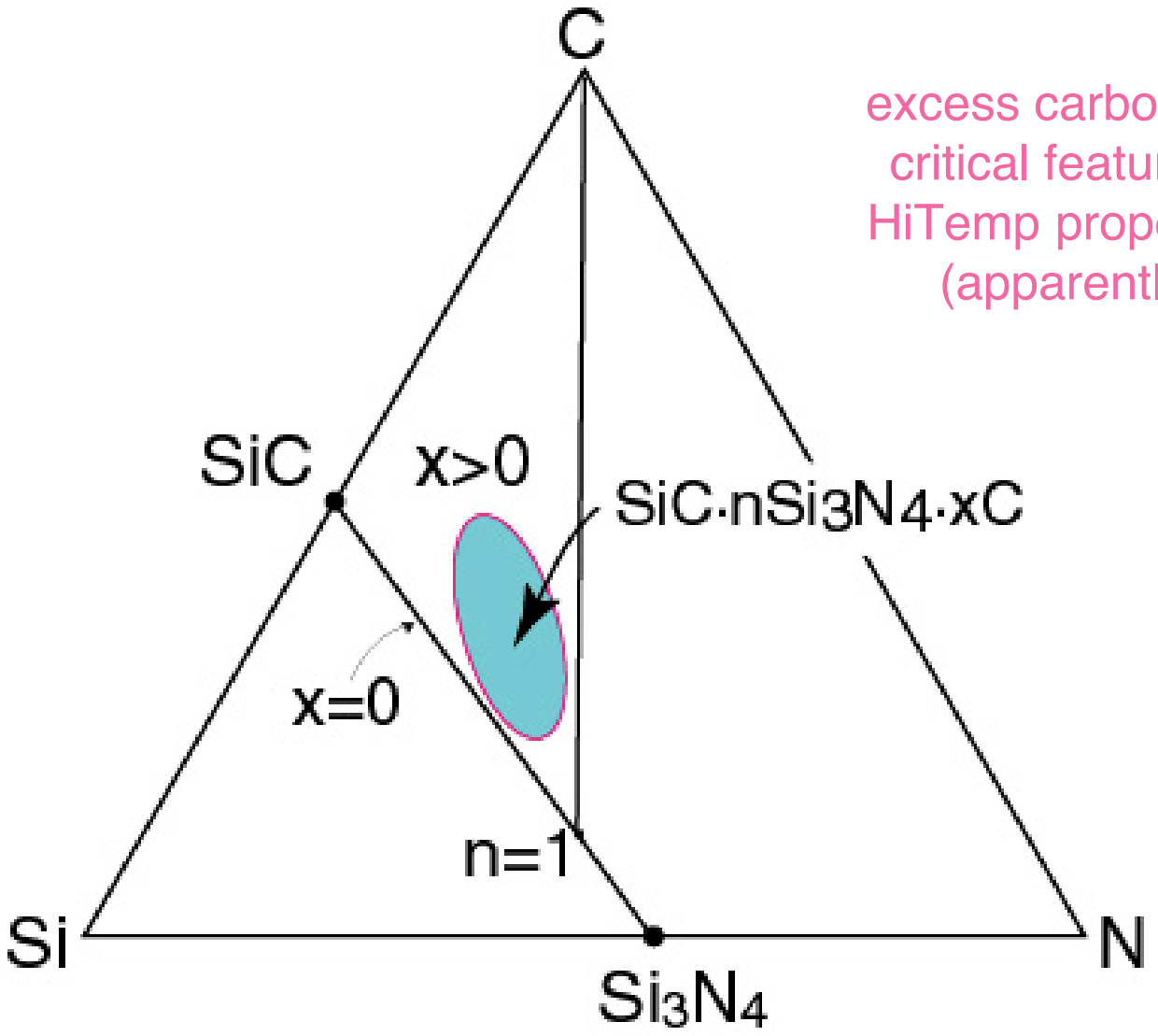
- ultralow diffusivity suggested by resistance to creep and crystallization
- emerging evidence of compatibility with oxides
- emerging knowledge of the fundamental unit of SiCN-SiCO structure

Research Plan:

- ABC* composites to evaluate interfacial reactions after exposure to Keiser Rig - comprehensive evaluation *and* modeling
- evaluate thermal shock in ABC composites

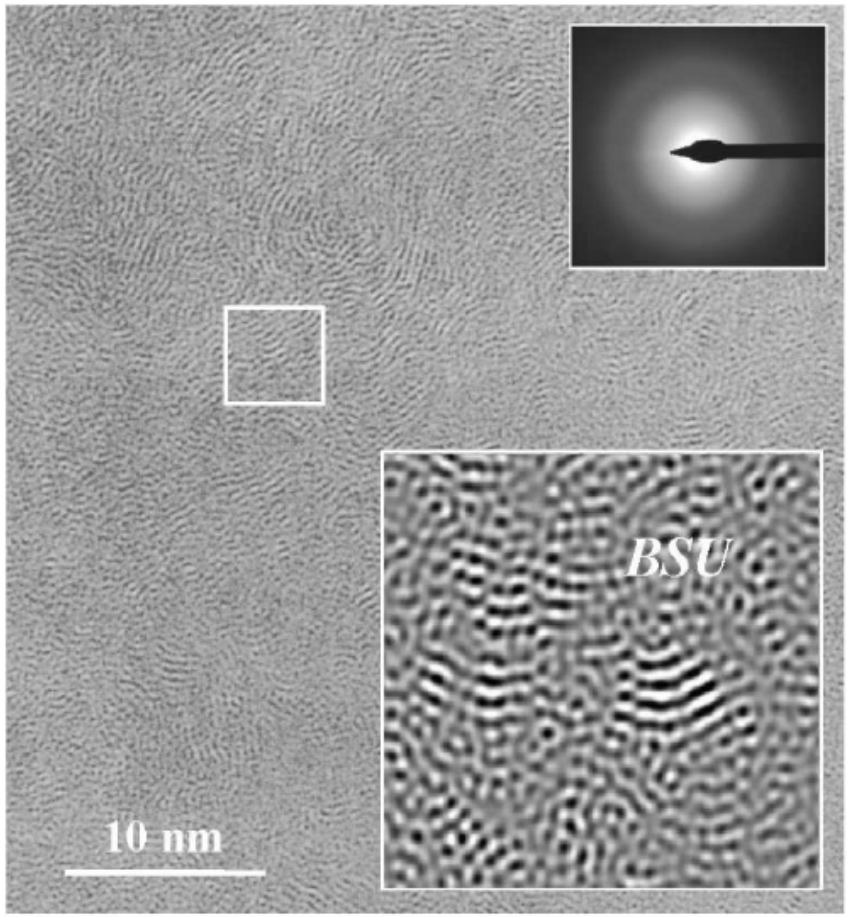
*SiCN-Oxide-Si_3N_4 composites

Composition Diagram for SiCN



excess carbon is a critical feature of HiTemp properties (apparently)

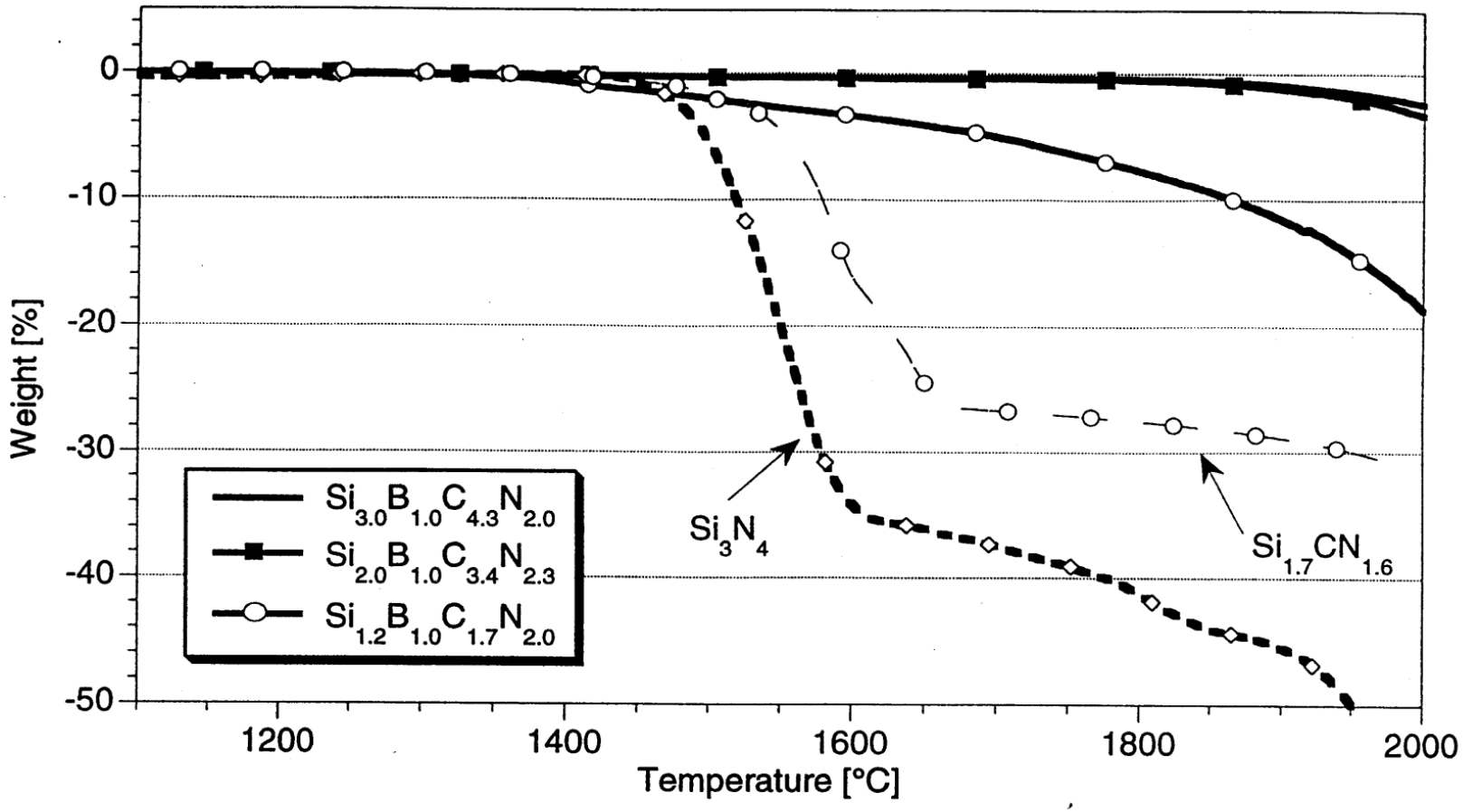
Silicon Carbonitride (SiCN)



Structure?

H.-J. Kleebe (CSM)

Wt. Loss at Hi Temperatures

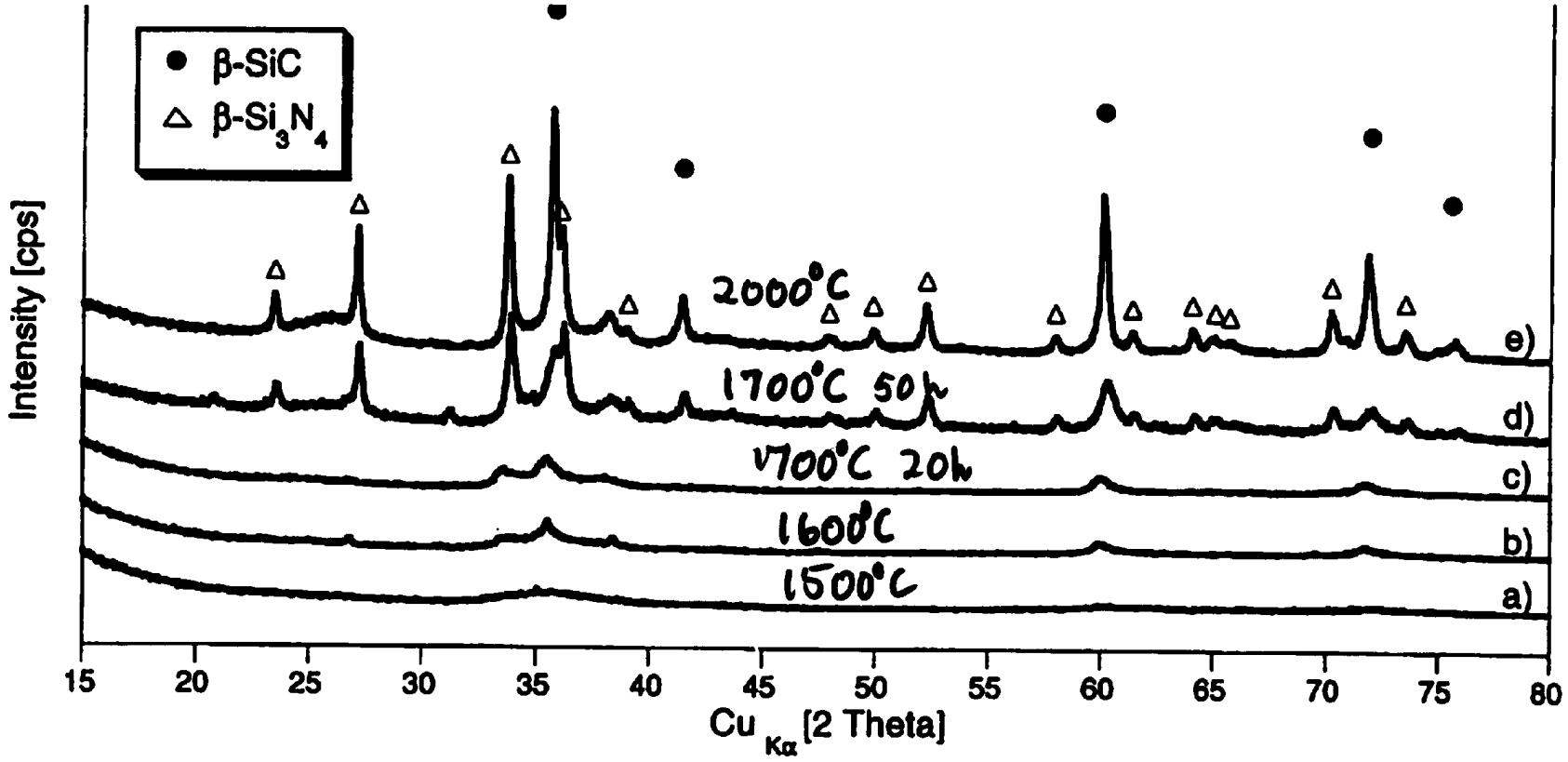


Courtesy: Riedel

Resistance to Crystallization

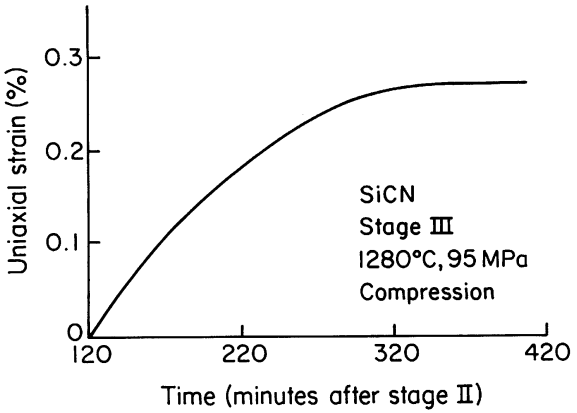
X-ray powder diffraction of $Si_{3.0}B_{1.0}C_{4.3}N_{2.0}$ after annealing

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)

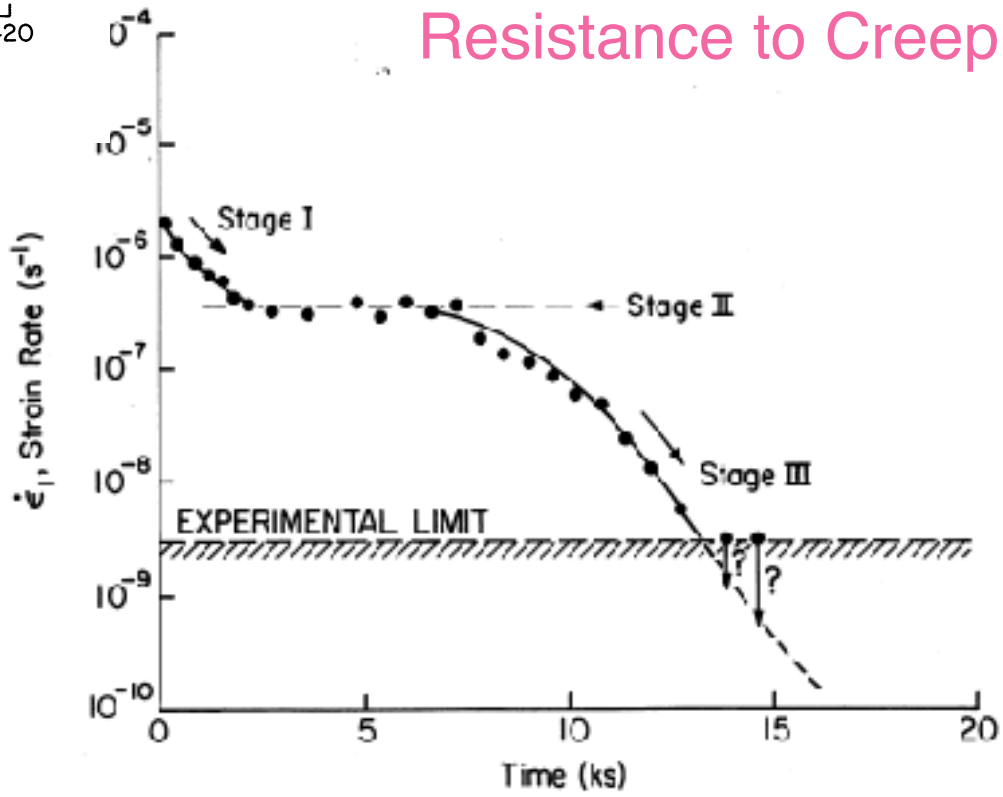


Creep Rate Declines with Time

SiCN, 1350°C, 100 MPa



Resistance to Creep



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

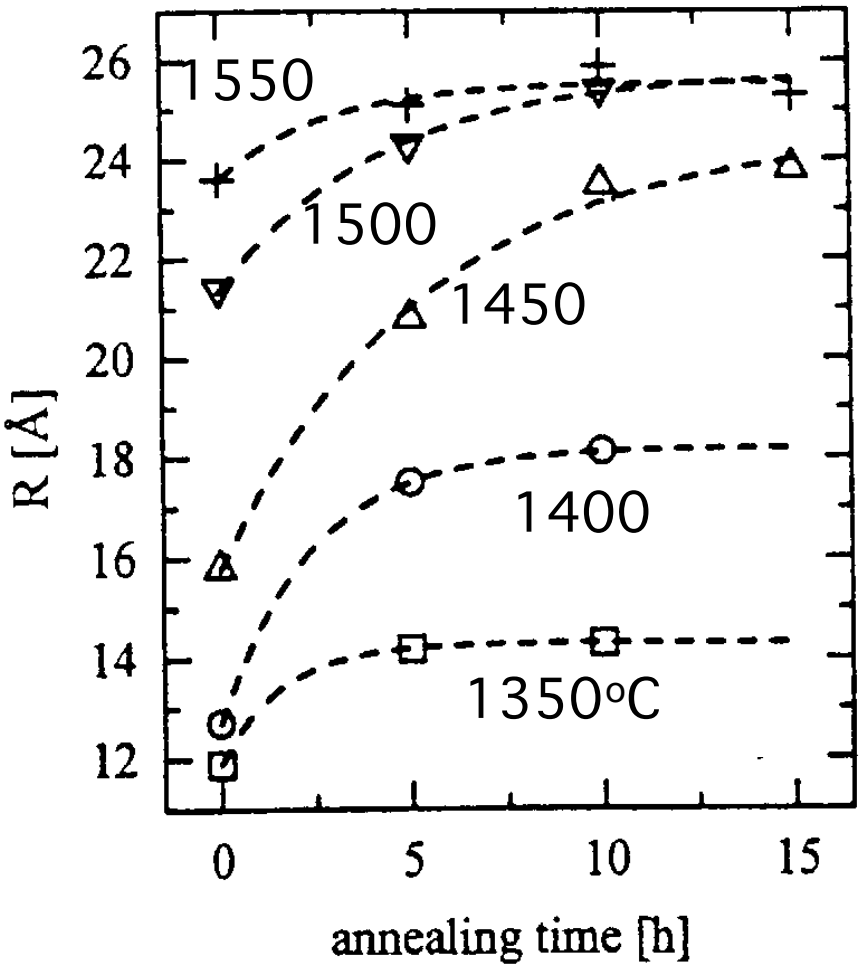
crystallization and creep studies show that self diffusivity in SiCN is extremely slow

what is the structural origin? - cannot be explained by diffusion in “glass”

SiCN apparently has a NanoDomain structure which remains intact up to ultrahigh temperatures

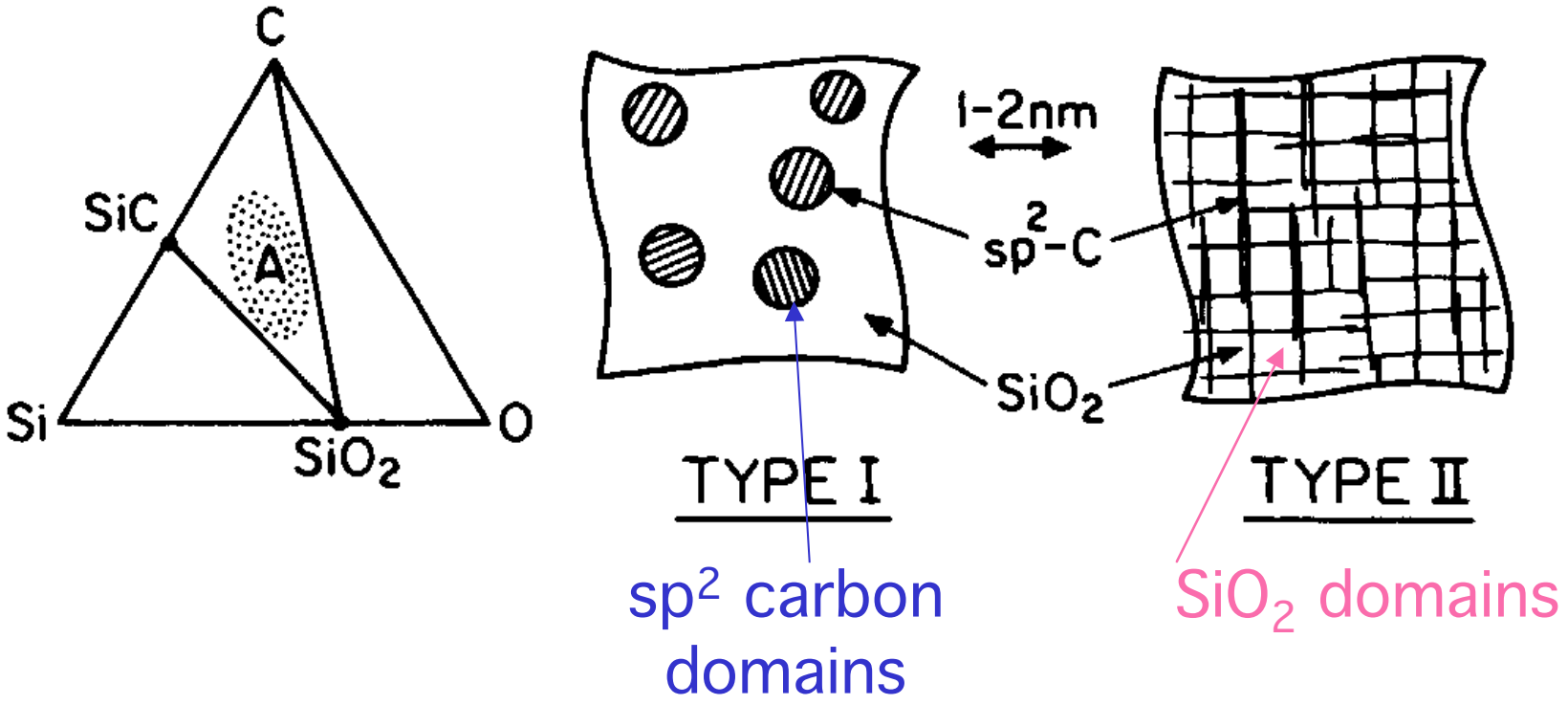
Schempp, Duerr, Lamparter, Bill and Aldinger (1998):

The Size of NanoDomains from SAXS+SANS



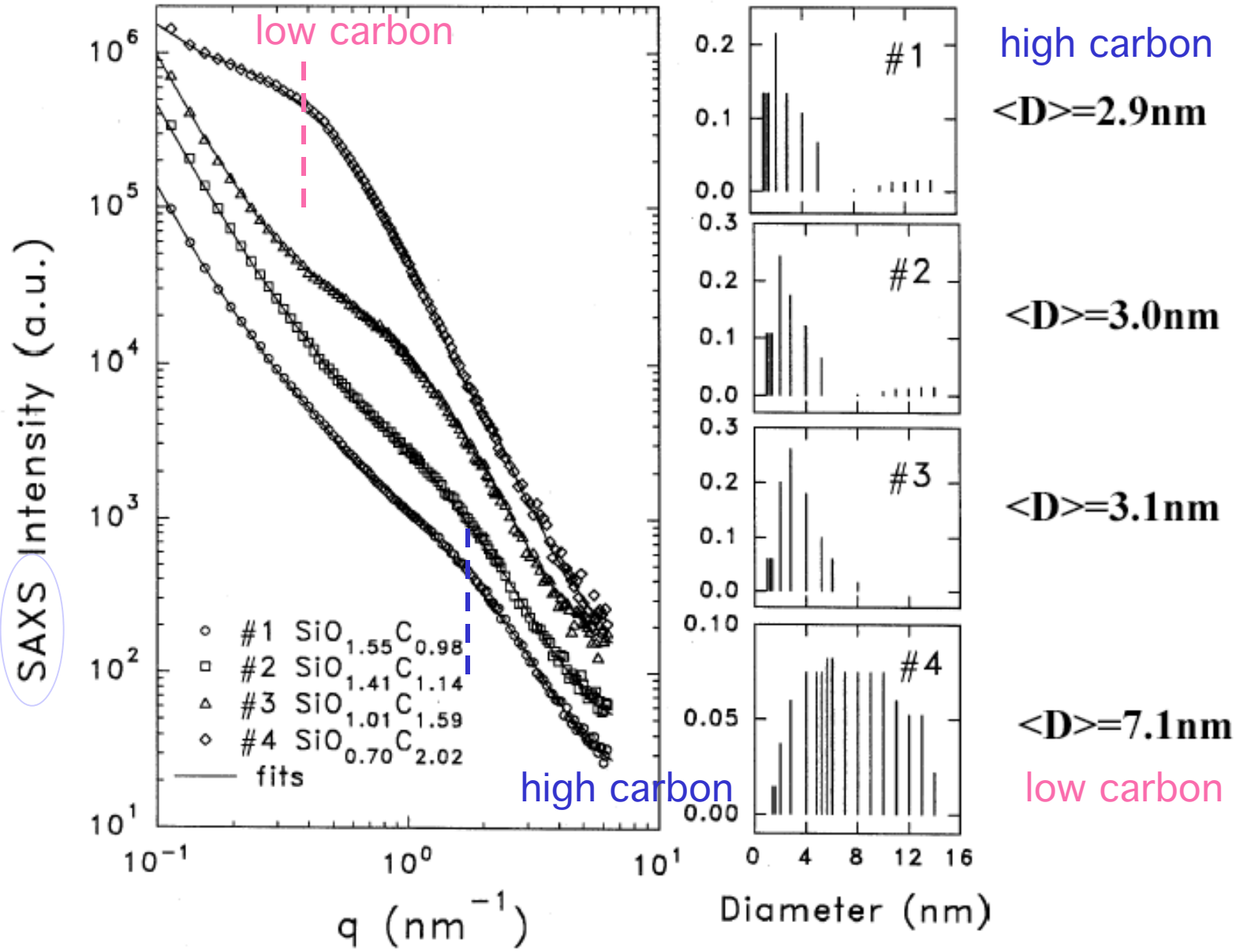
Structure of the NanoDomains?

Two Types of Structures May be Conceptualized

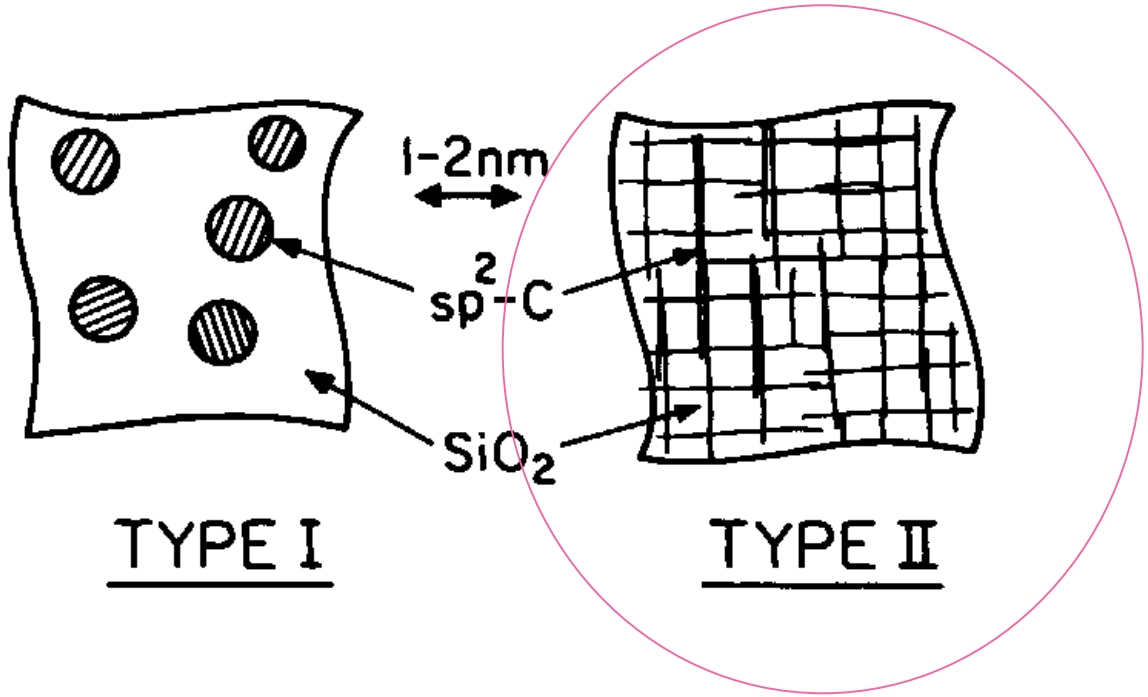


"domain size is controlled by the number of Si-O-C bonds"

Higher Carbon Decreases the Domain Size: Type II



Since the domain size increases with lower carbon (or higher oxygen) the Type II structure is accepted

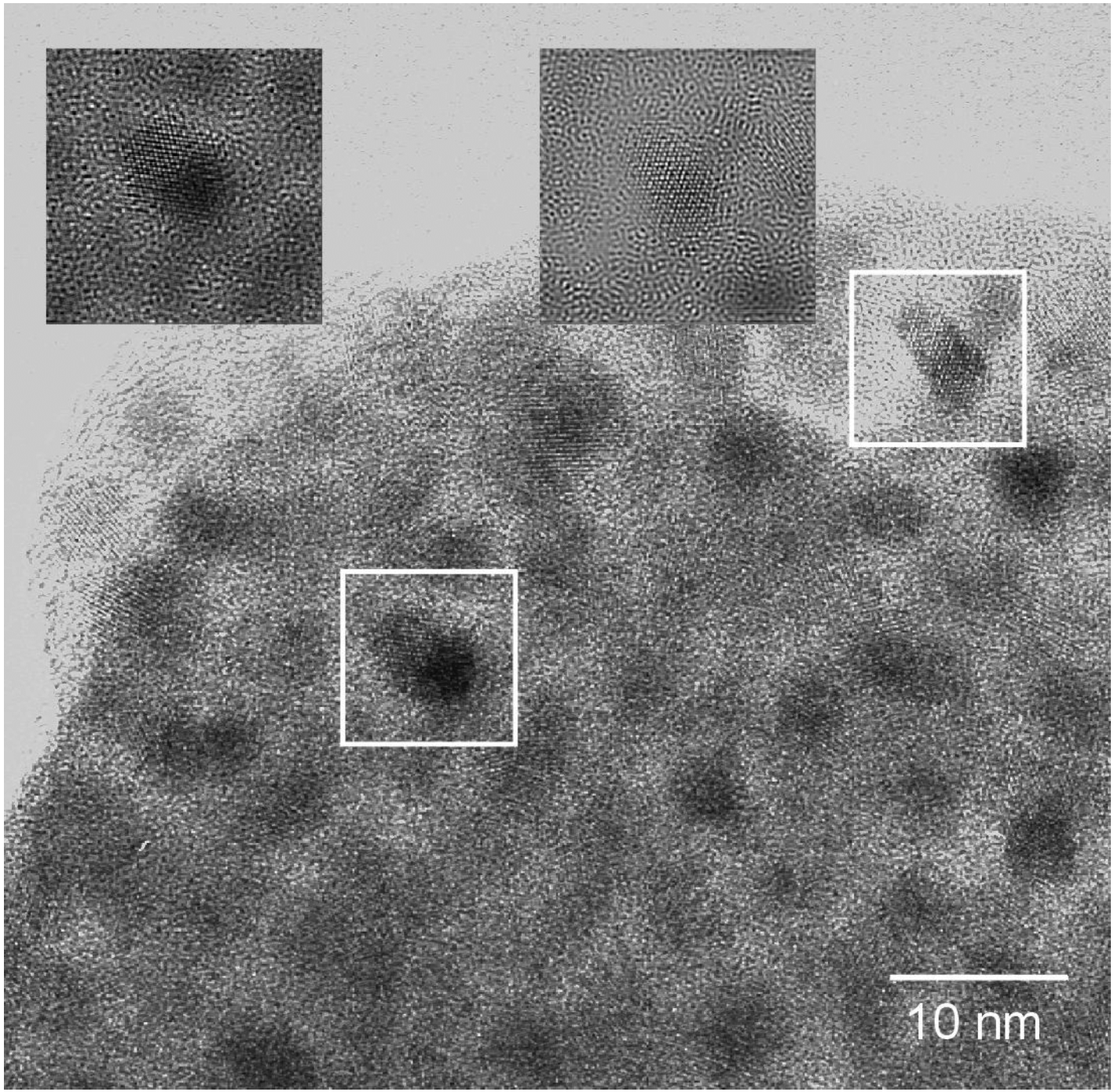


inference: carbon walls prevent diffusion

Emerging Picture of the Structural Unit in SiCN

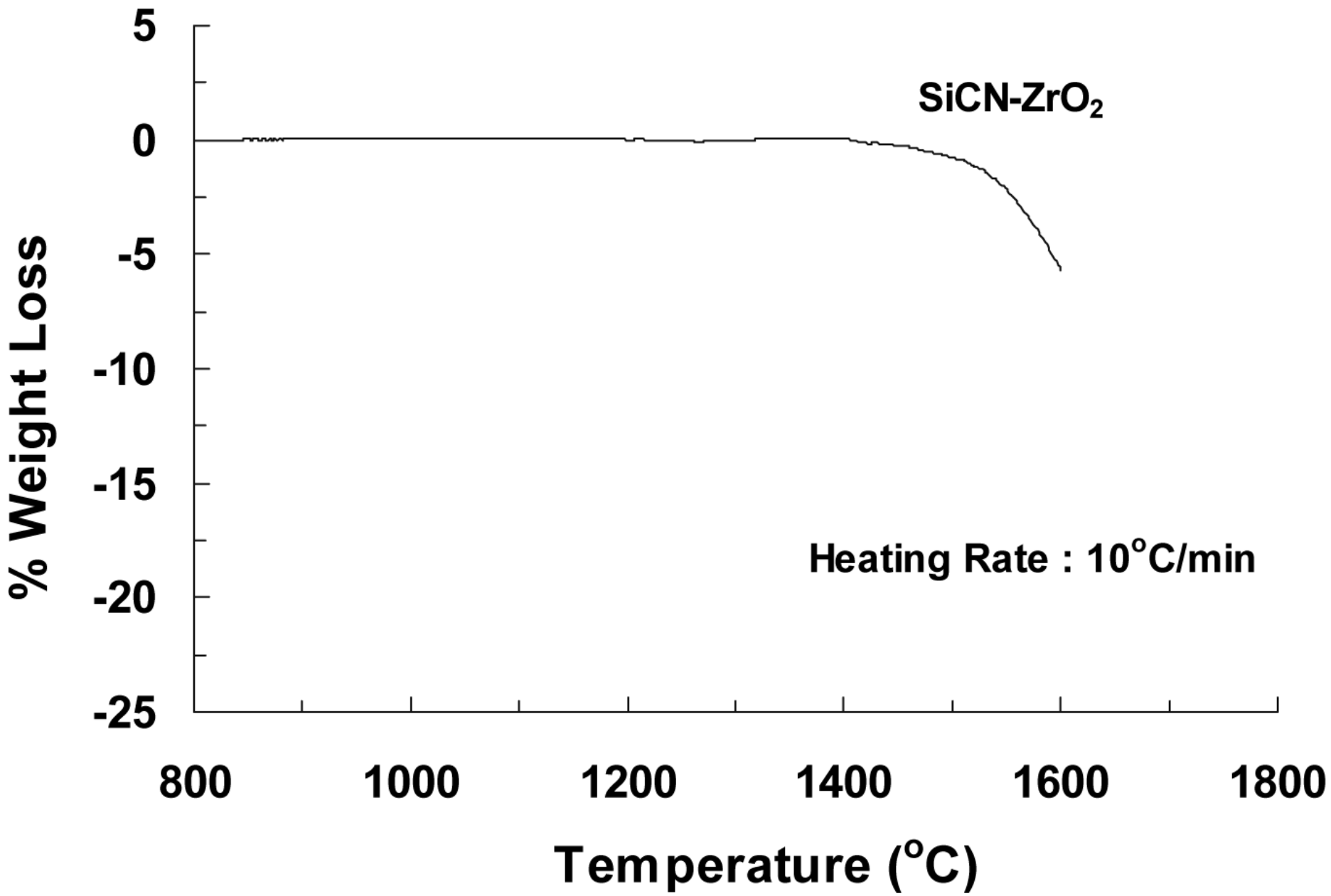
a carbon cage structure with sequestered nanodomains of silica or silicon nitride which are unable to coarsen by diffusion, and are too small to nucleate crystals

SiCN - Zirconia NanoComposites



SiCN-Zirconia:

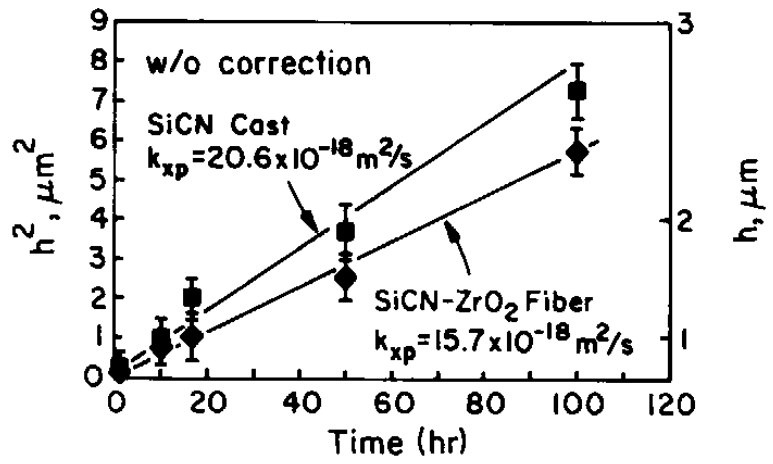
Courtesy
Kleebe

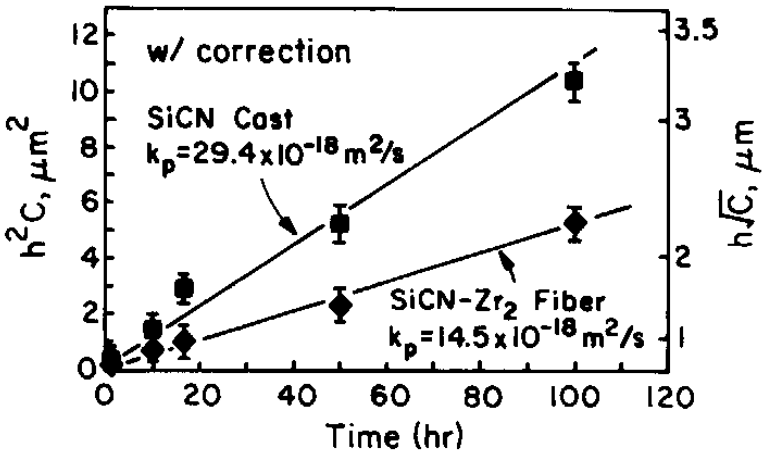

5
0
-5
-10
-15
-20
-25
% Weight Loss
SiCN-ZrO2
Heating Rate : 10°C/min
800
1000
1200
1400
1600
1800
Temperature (°C)

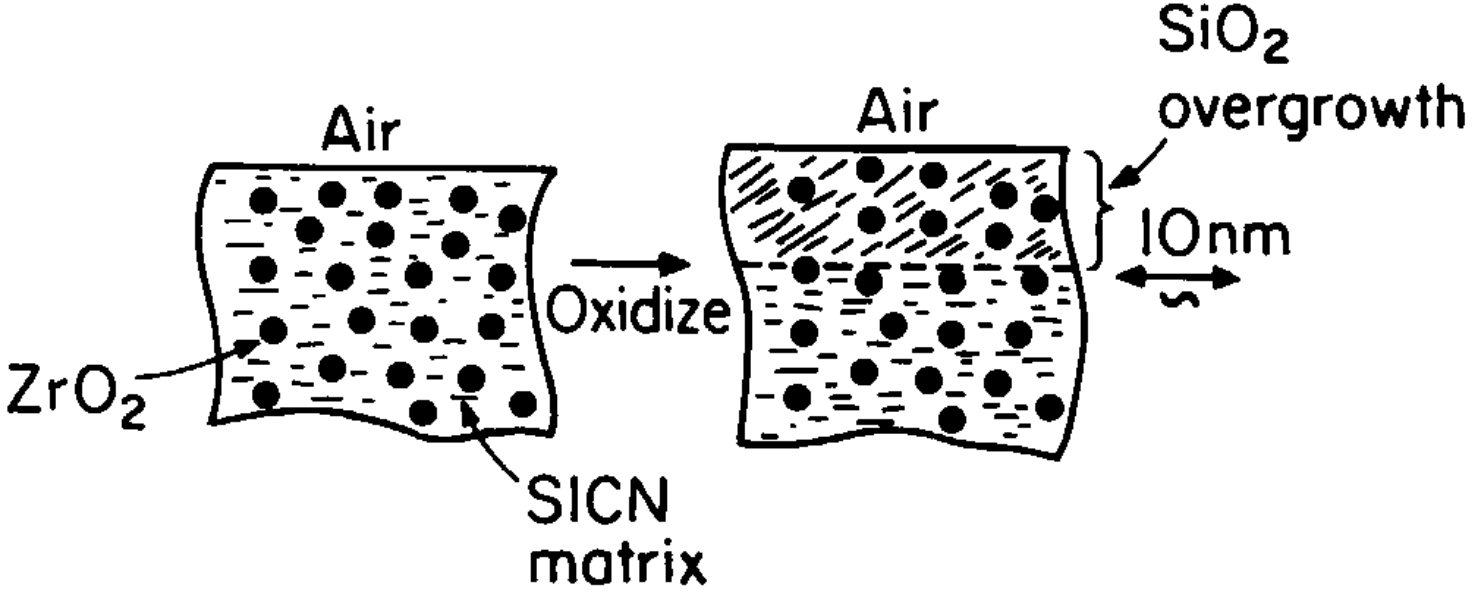
Oxidation Study of SiCN-ZrO_2

theme: modeling!

Parabolic Oxidation Kinetics at 1350°C






Air
Air
SiO_2
overgrowth
10nm
Oxidize
ZrO_2
SICN
matrix

Phenomenology: $h^2 = k_{xp} t$ $\quad k_p = C.k_{xp}$

Reaction is Composition Dependent:

$$SiC_xN_yO_z + (1 + \frac{x}{2} - \frac{z}{2}).O_2 = SiO_2 + xCO + \frac{y}{2}N_2 \qquad \alpha = (1 + \frac{x}{2} - \frac{z}{2})$$

Mass Balance and Geometry:

$$V_{OX} = V_{SiO_2} + n_{Zr}.V_{ZrO_2} \qquad \frac{dh}{dt} = J_{O_2}.\frac{V_{SiO_2} + n_{Zr}.V_{ZrO_2}}{\alpha}$$

Flux Equation: $J_{O_2} = \frac{D_{O_2}}{V_{SiO_2} RT}.\frac{\Delta\mu_{O_2}}{h}$

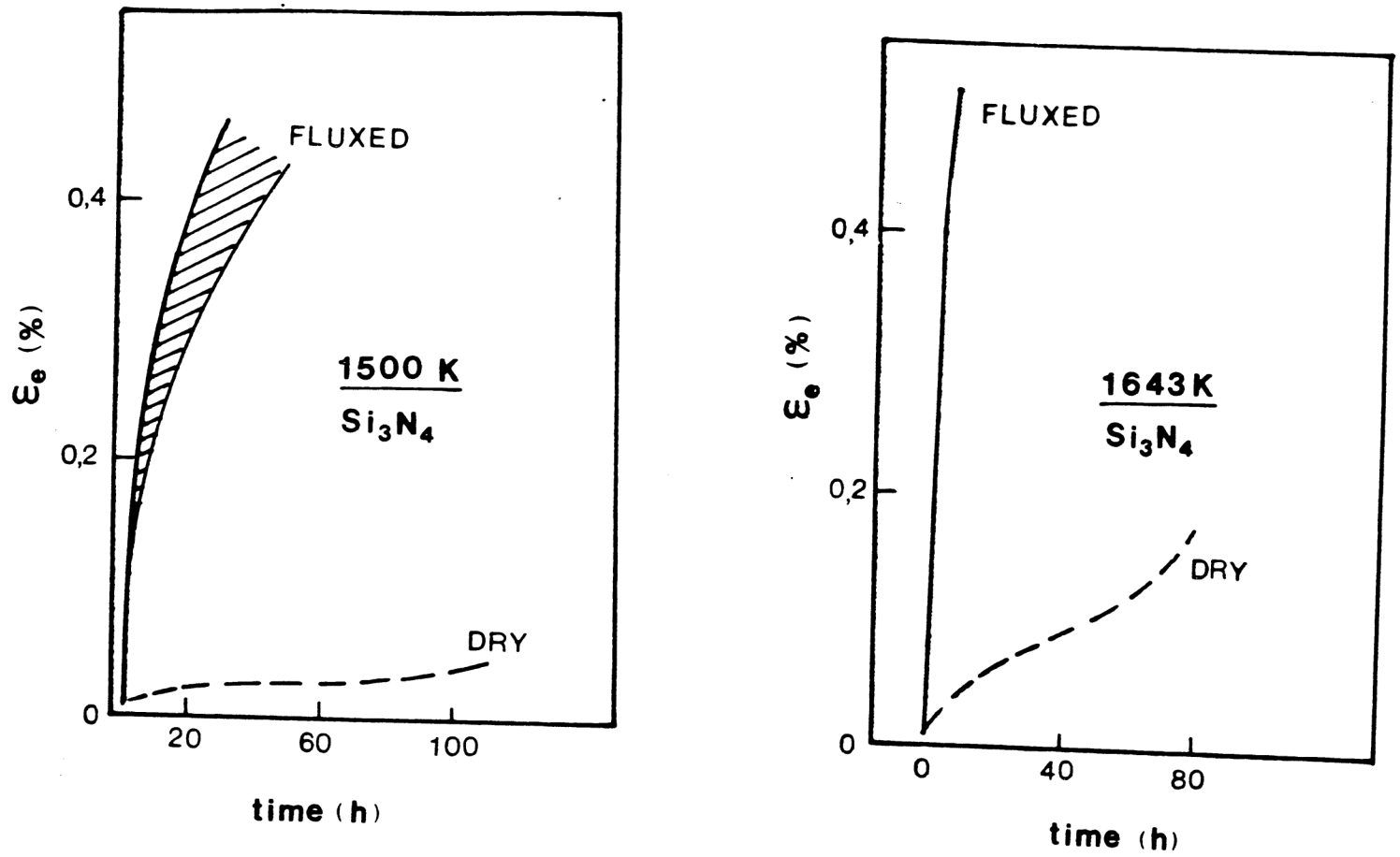
Final Result: $h^2 = \frac{D_{O_2}.\Delta\mu_{O_2}}{RT}.\frac{1}{\alpha}.(1 + n_{Zr}\frac{V_{ZrO_2}}{V_{SiO_2}}).t$

$$k_{xp} = k_p.\frac{1}{\alpha}.(1 + n_{Zr}\frac{V_{ZrO_2}}{V_{SiO_2}})$$

$$k_p = \frac{D_{O_2}.\Delta\mu_{O_2}}{RT}$$

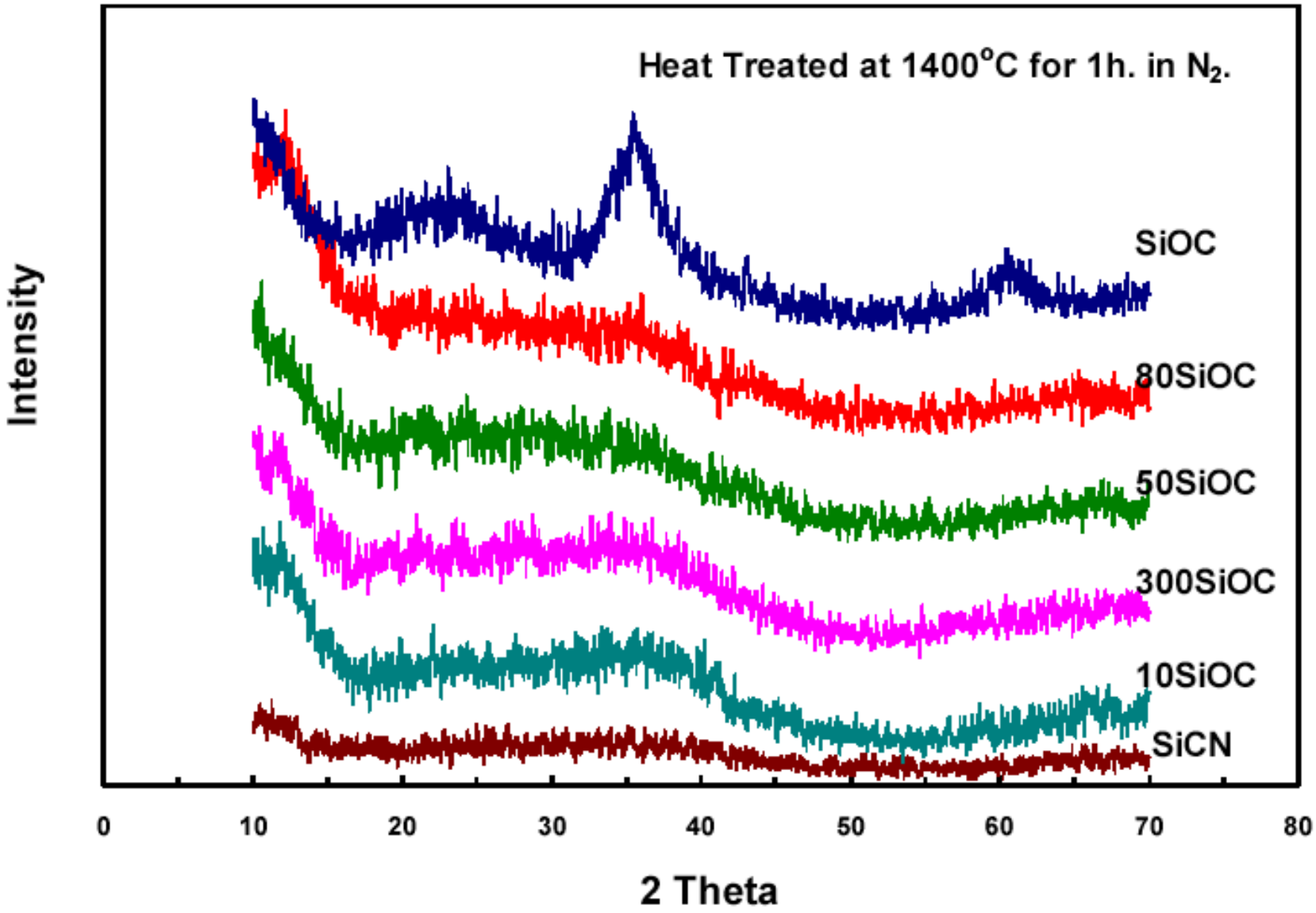
More on the compatibility of Oxides and Non-Oxides in PDC structures.

Influence of 1-5% Silica Flux on Creep Behavior of Polycrystalline Silicon Nitride



OSBORNE, PROC. BRITISH CERAMIC SOC. #25, 1975.

SiCN can tolerate high oxygen content without degradation of HT properties.



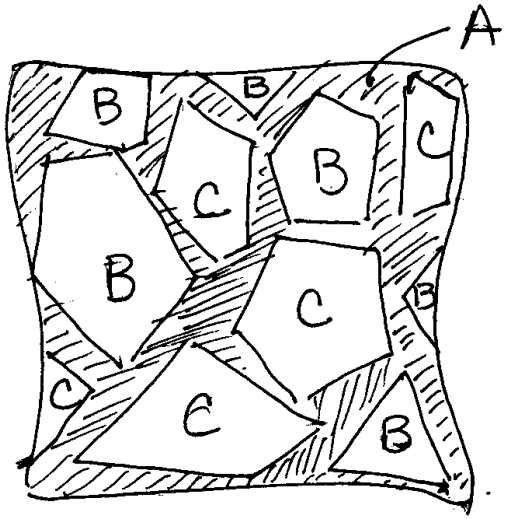
The Approach

Phase I

The detailed study of ABC composites will provide scientific knowledge of the interface reactions, rate of propagation of the oxidation front (in the Keiser Rig), and the thermal shock behavior.

ABC Composites

Case I: SiCN Phase is Interconnected.

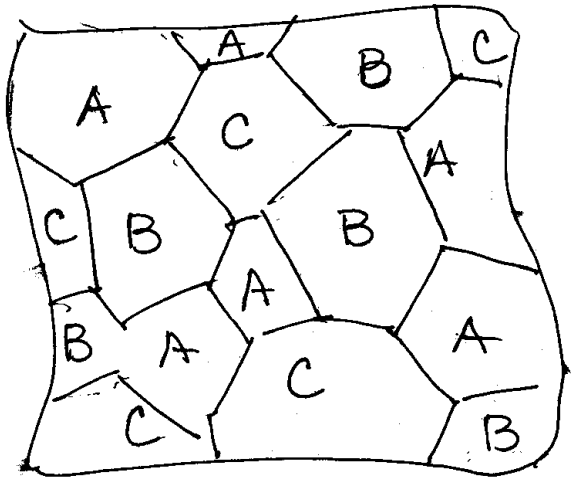


A: SiCN

B: Oxide

C: Si_3N_4

Case II: W/o interconnected phase



Basic research issues which will be addressed by the ABC composites.

- Diffusivity - study progression of the oxidation overgrowth.
- Thermal Shock - study damage as a function of particle size and the three kinds of interfaces (AB, BC and AC).
- Subsurface Nucleation of Silica - study nucleation a oxide/SiCN and SiCN/Si_3N_4 interfaces.

Merits of PDC based EBCs

- Low Diffusivity
- Compatibility of SiCN with Oxides

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)