Additive Effects on Si_3N_4 Oxidation/Volatilization in Combustion Environments

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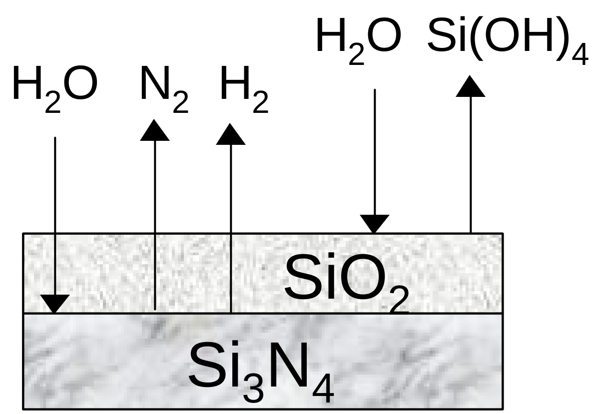
Paralinear oxidation/volatilization of Si_3N_4 in water vapor

- Parabolic oxidation reaction to form silica scale

  $Si_3N_4 + 6H_2O(g) = 3SiO_2 + 2N_2(g) + 6H_2(g)$

- Linear volatilization reaction to remove silica scale

  $SiO_2 + 2H_2O(g) = Si(OH)_4(g)$

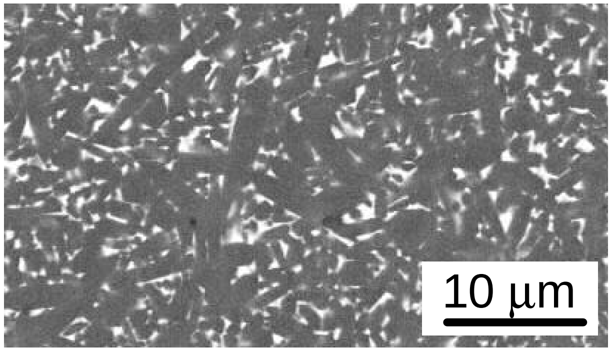


Additives in Si_3N_4

- Rare earth oxides added as sintering aids
- Additives present in grain boundary phase

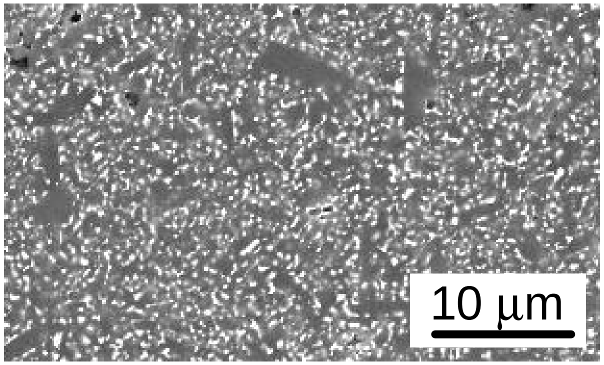
AS800, AlliedSignal

- La_2O_3, Y_2O_3, SrO additives
- $7RE_2O_3 \cdot 9SiO_2$ grain boundary phase

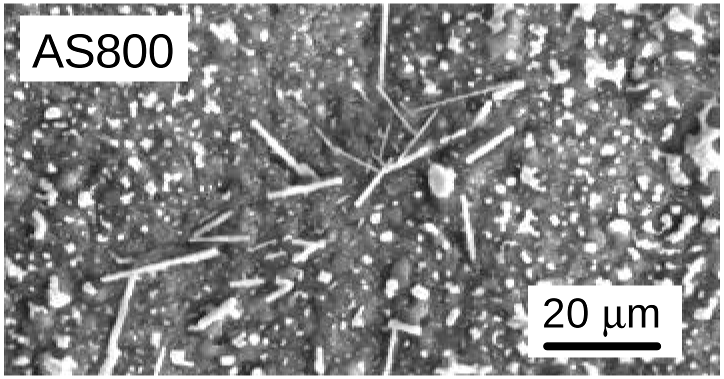


SN282, Kyocera

- Lu_2O_3 additive
- $Lu_2Si_2O_7$ and Lu_2SiO_5 grain boundary phase



Oxidation of Si_3N_4 with additives



In dry oxygen:

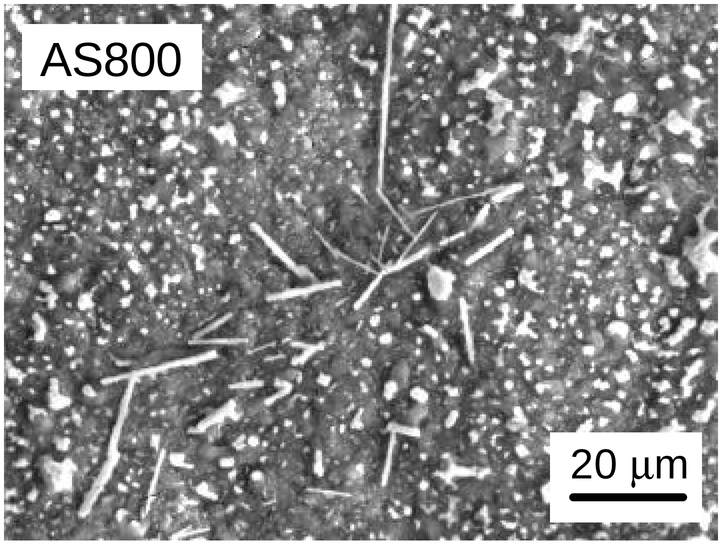
- Silica scale forms
- High aspect ratio $RE_2Si_2O_7$ grains form on surface of scale
- Outward diffusion of RE cations control oxidation rate

Cubicciotti and Lau, JECS, 126 [10] 1723 (1979).

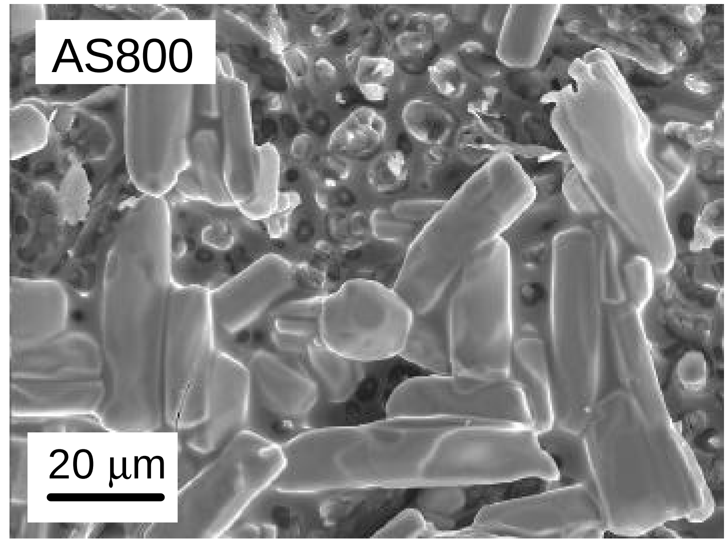
How does surface $RE_2Si_2O_7$ formation affect volatility and recession in water vapor ?

Effects of surface $RE_2Si_2O_7$ formation on volatility

- Preferential volatilization of silica
- Surface enrichment of $RE_2Si_2O_7$



1300°C, 1 atm O_2, 100h, 0.4 cm/s



1300°C, 6 atm, 0.6 atm H_2O, 50h, 20 m/s

Do sintering additives offer an in situ opportunity for oxide surface modification that may lower volatility rate?

Experimental

- Si_3N_4 exposures, 1066-1400°C
  - TGA, 1 atm dry oxygen, 0.4 cm/s,
  - TGA, 1 atm, 0.5 atm H_2O, 4 cm/s,
  - HPBR, 6 atm, 0.6 atm H_2O, 20 m/s,
  - Turbine, 8.7 atm, 0.9 atm H_2O, 160-572 m/s

    Exxon, Mobile, AL - Rolls Royce - DOE Advanced Turbine Systems Program

↓ Increasing SiO_2 volatility

- Weight change/recession, XRD, SEM, EDS

Si_3N_4 exposed in TGA

1300°C, 1 atm, dry oxygen, 0.4 cm/s, 100h

Oxidation, no volatilization

AS800

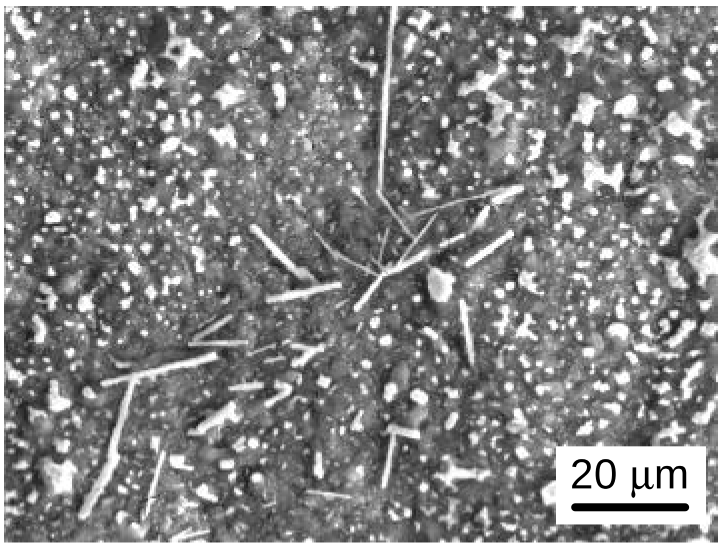
k_p= 3 x 10^{-4} mg^2/cm^4 h

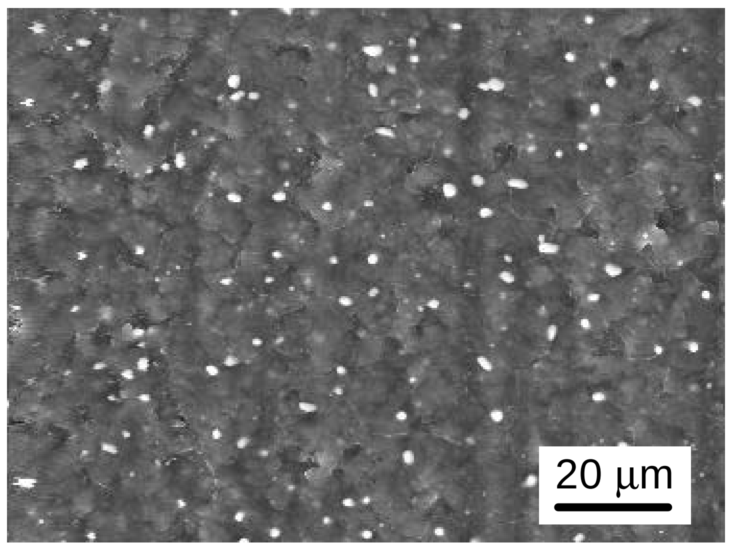
cristobalite, $La_2Si_2O_7$

SN282

k_p= 6 x 10^{-5} mg^2/cm^4 h

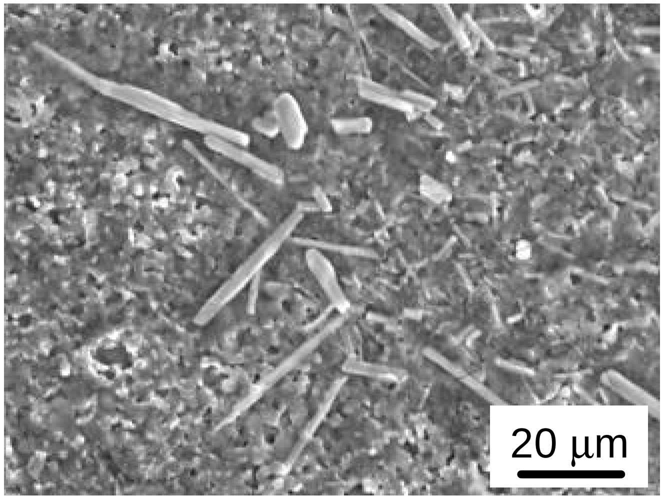
cristobalite, $Lu_2Si_2O_7$, Lu_2SiO_5

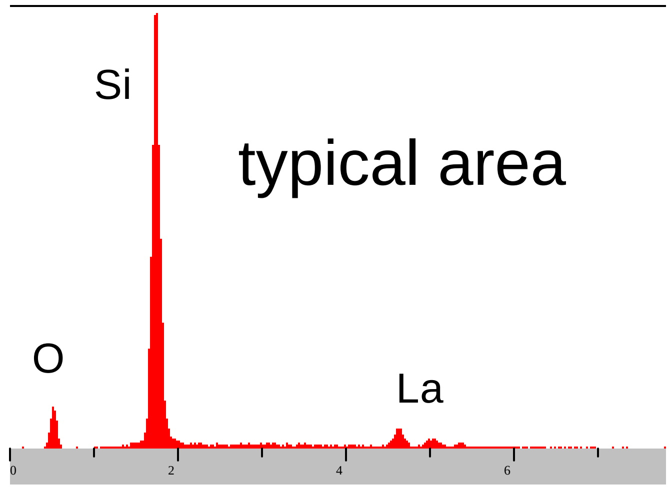


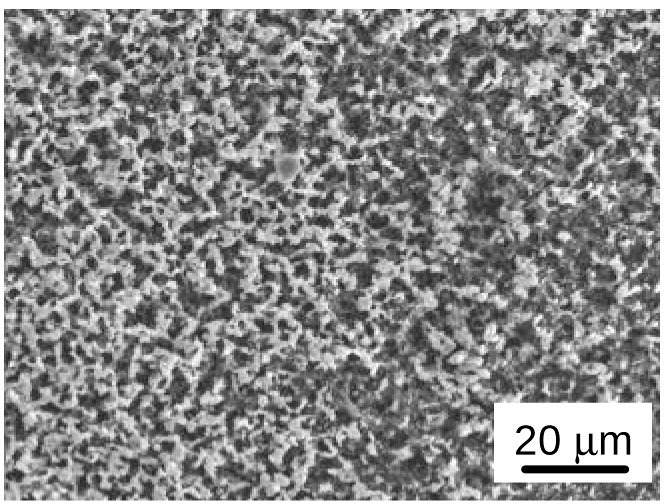


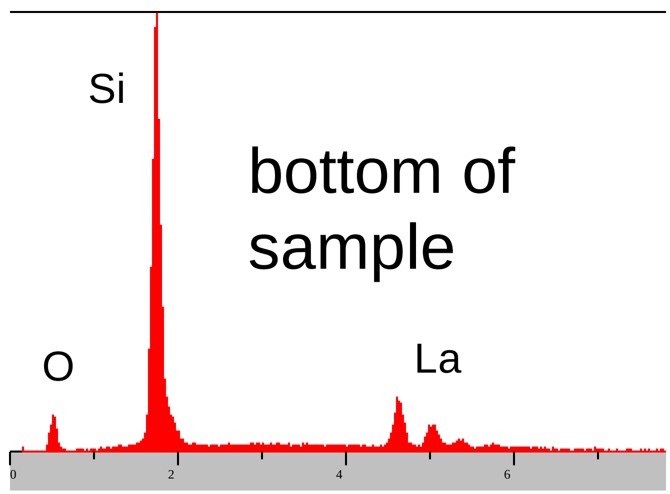
AS800 exposed in TGA

1300°C,1 atm, 0.5 atm H_2O, 4.4 cm/s, 100h









Si_3N_4 exposed in TGA

1300°C,1 atm, 0.5 atm H_2O, 4.4 cm/s, 100h

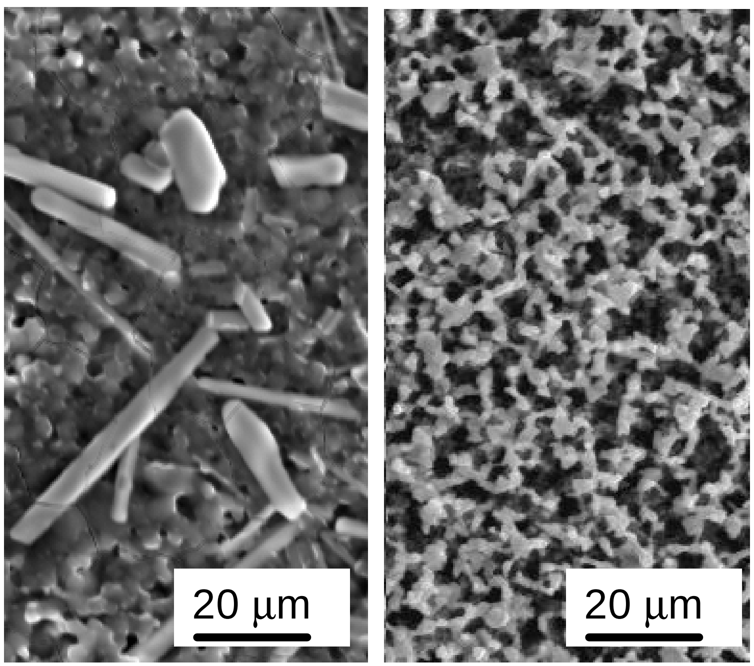
Paralinear oxidation/volatilization

AS800

k_p= 9 x 10^{-4} mg^2/cm^4 h

k_l= 4 x 10^{-3} mg/cm^2 h

cristobalite, $La_2Si_2O_7$

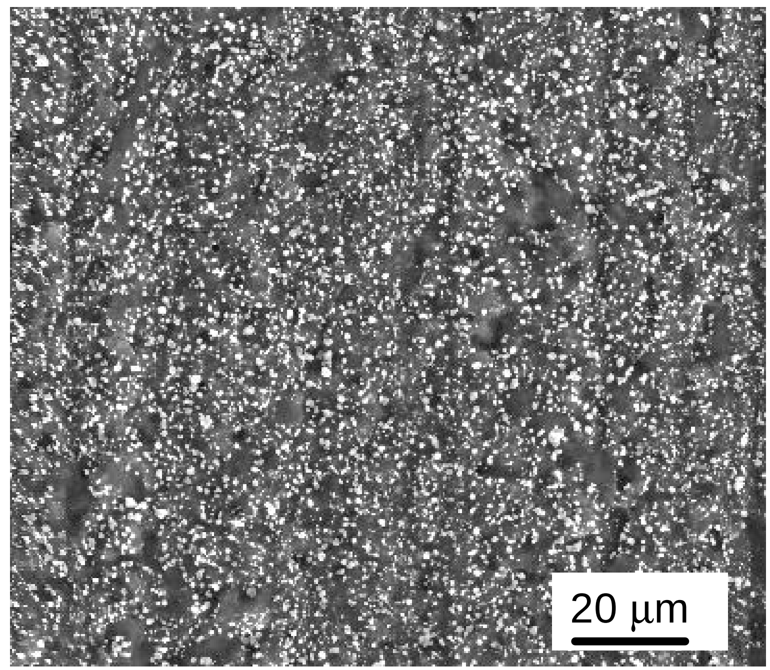


SN282

k_p= 4 x 10^{-4} mg^2/cm^4 h

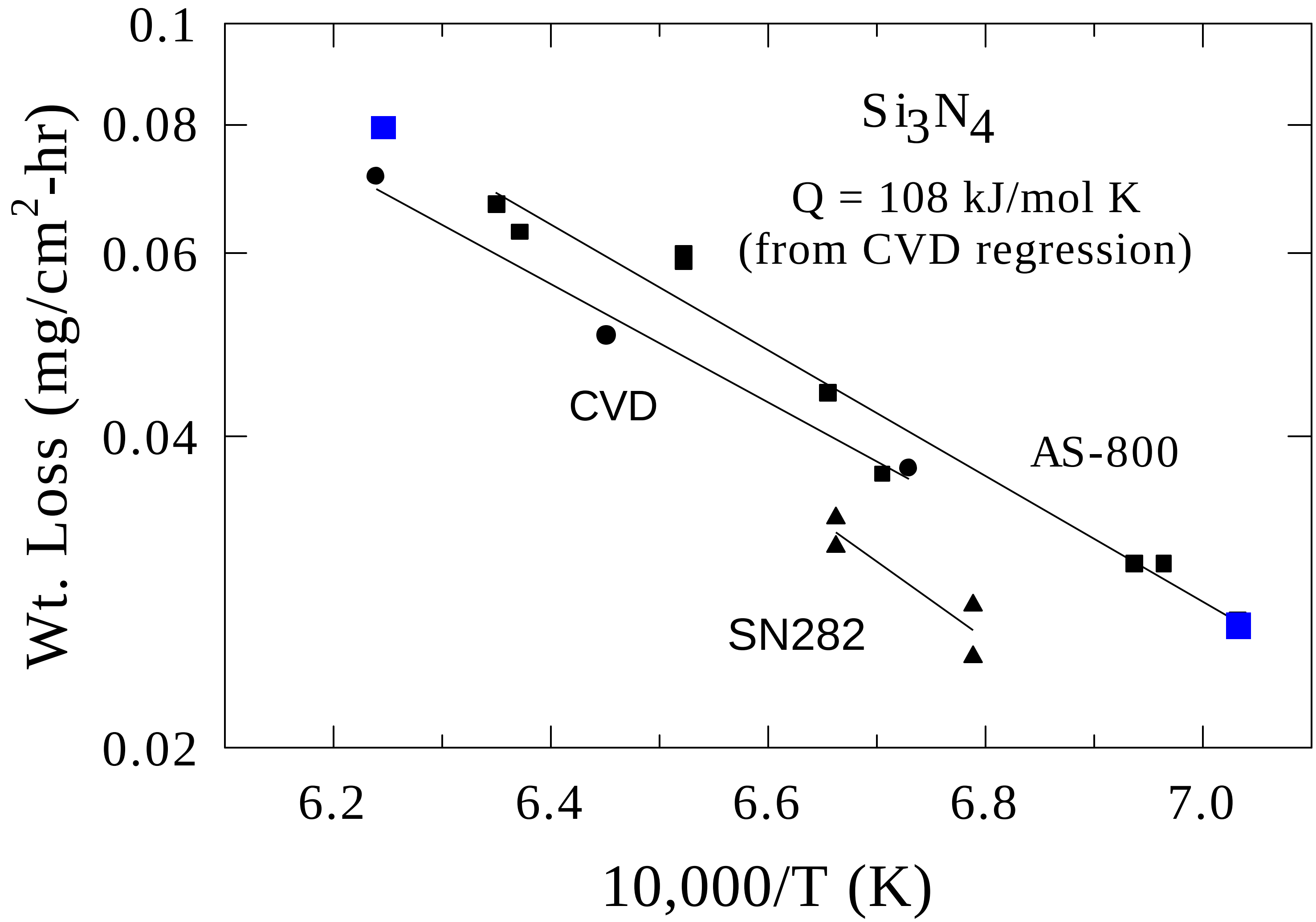
k_l= 2 x 10^{-3} mg/cm^2 h

cristobalite, $Lu_2Si_2O_7$



Si_3N_4 exposed in HPBR

6 atm, 0.6 atm H_2O, 20 m/s



AS800 exposed in HPBR

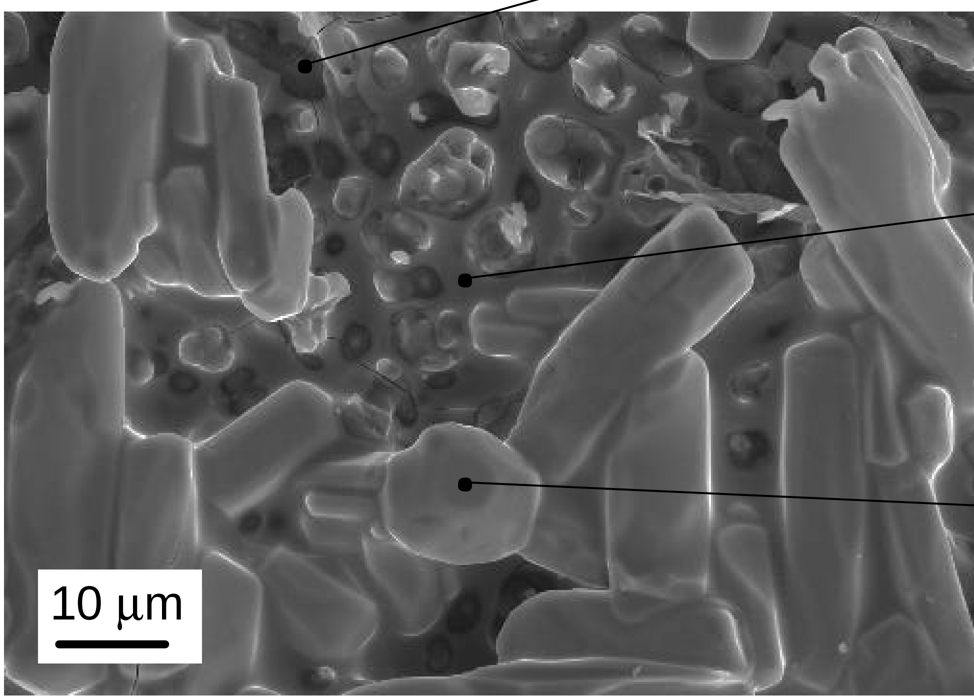
1300°C, 6 atm, 0.6 atm H_2O, 20 m/s, 50h

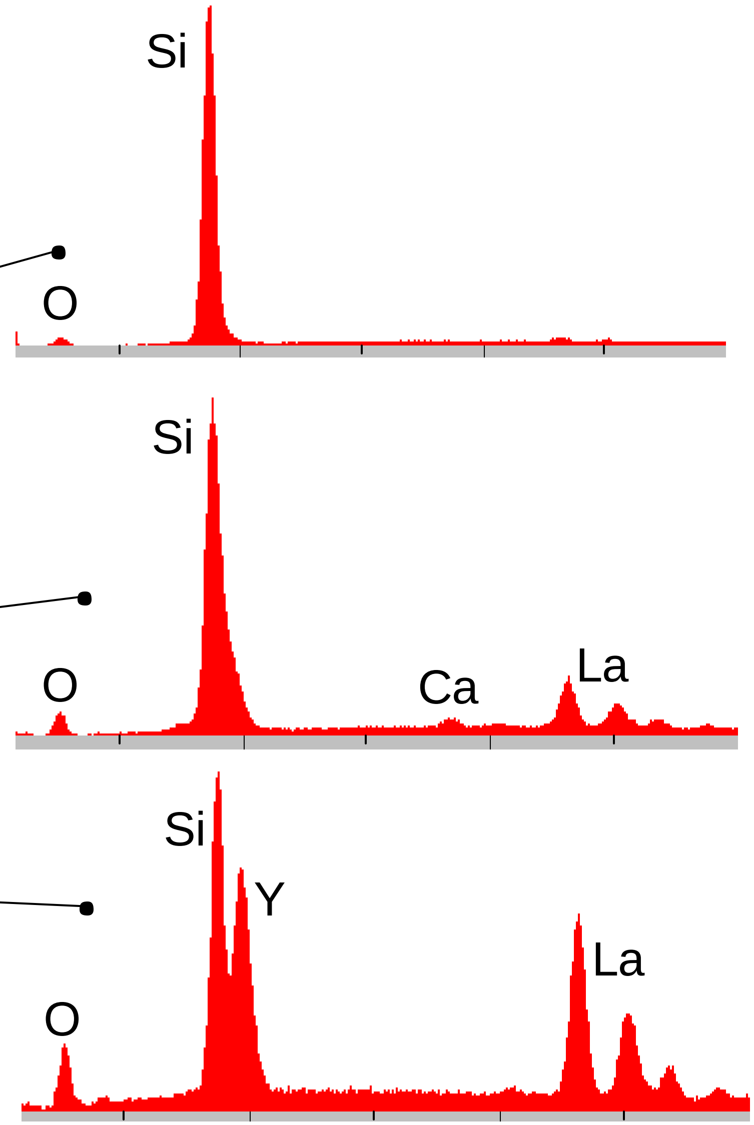
Oxidation/volatilization

$k_p = 5 \times 10^{-2}\ mg^2/cm^4\ h$

$k_l = 6 \times 10^{-2}\ mg/cm^2\ h$

cristobalite, $La_2Si_2O_7$, Y_2O_3?





SN282 exposed in HPBR

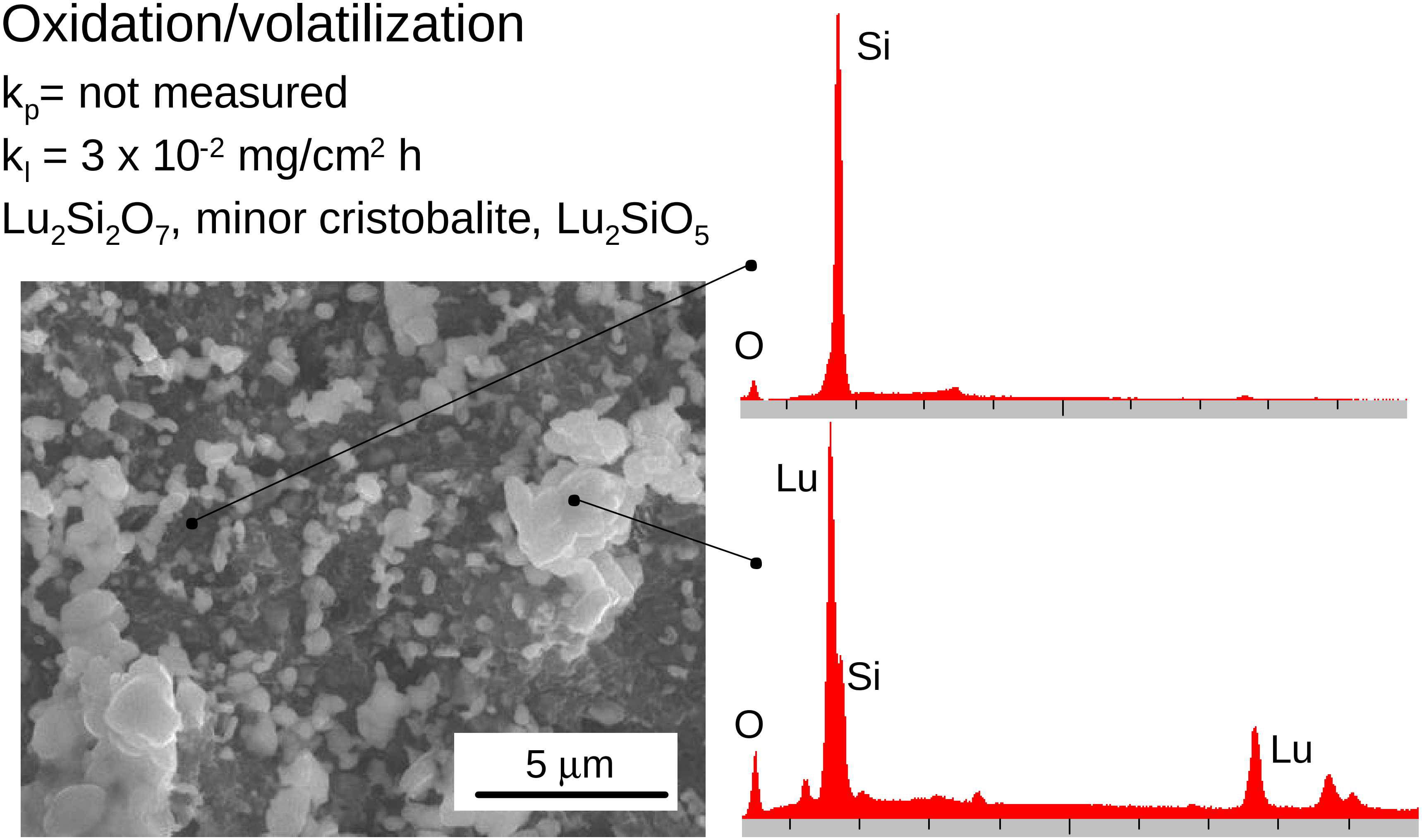
1225°C, 6 atm, 0.6 atm H_2O, 20 m/s, 102h

Oxidation/volatilization

k_p= not measured

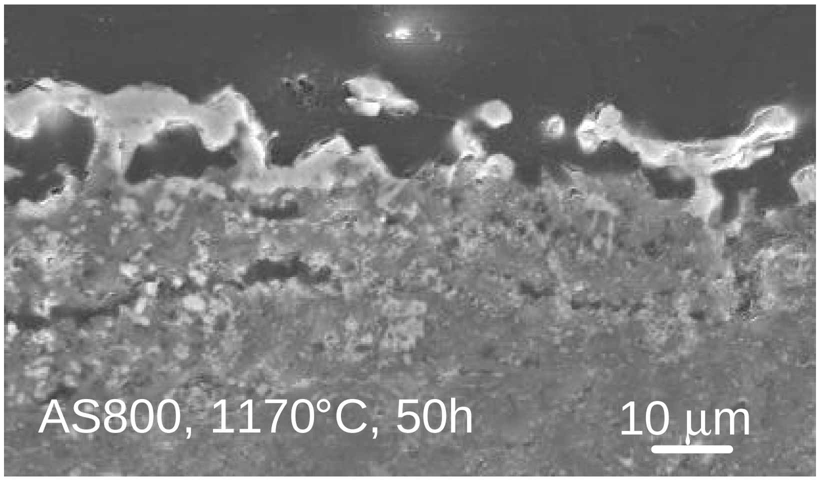
k_l = 3 x 10^{-2} mg/cm^2 h

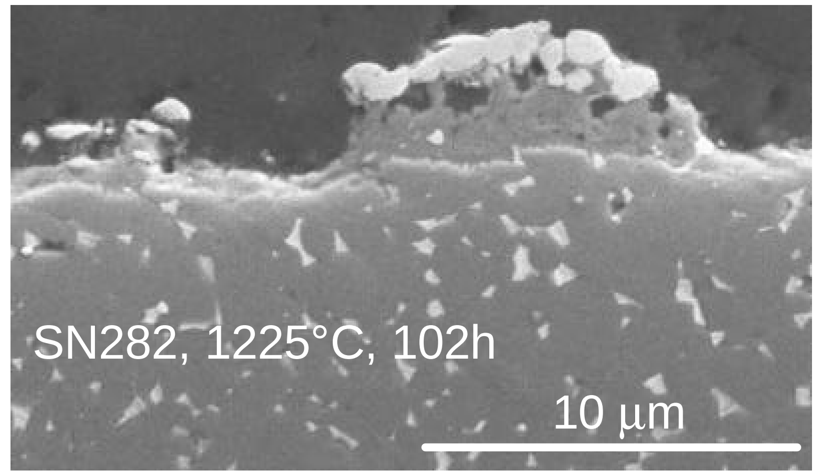
$Lu_2Si_2O_7$, minor cristobalite, Lu_2SiO_5

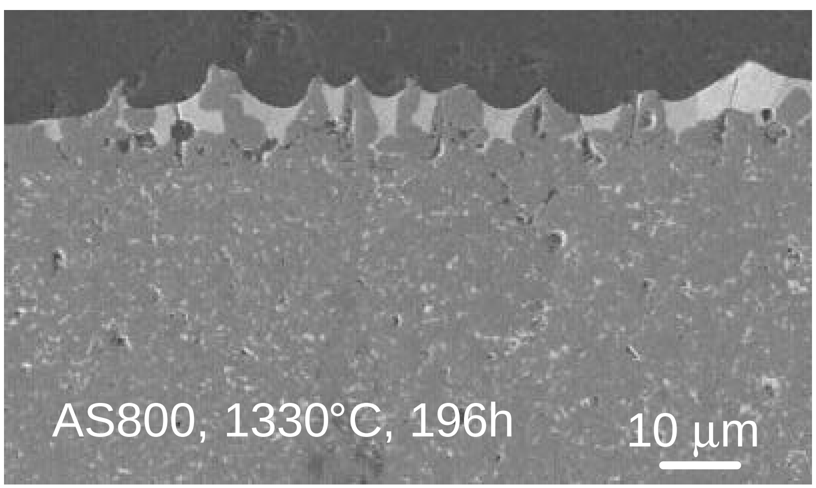


Comparison of AS800 and SN282 exposed in HPBR

6 atm, 0.6 atm H_2O, 20 m/s

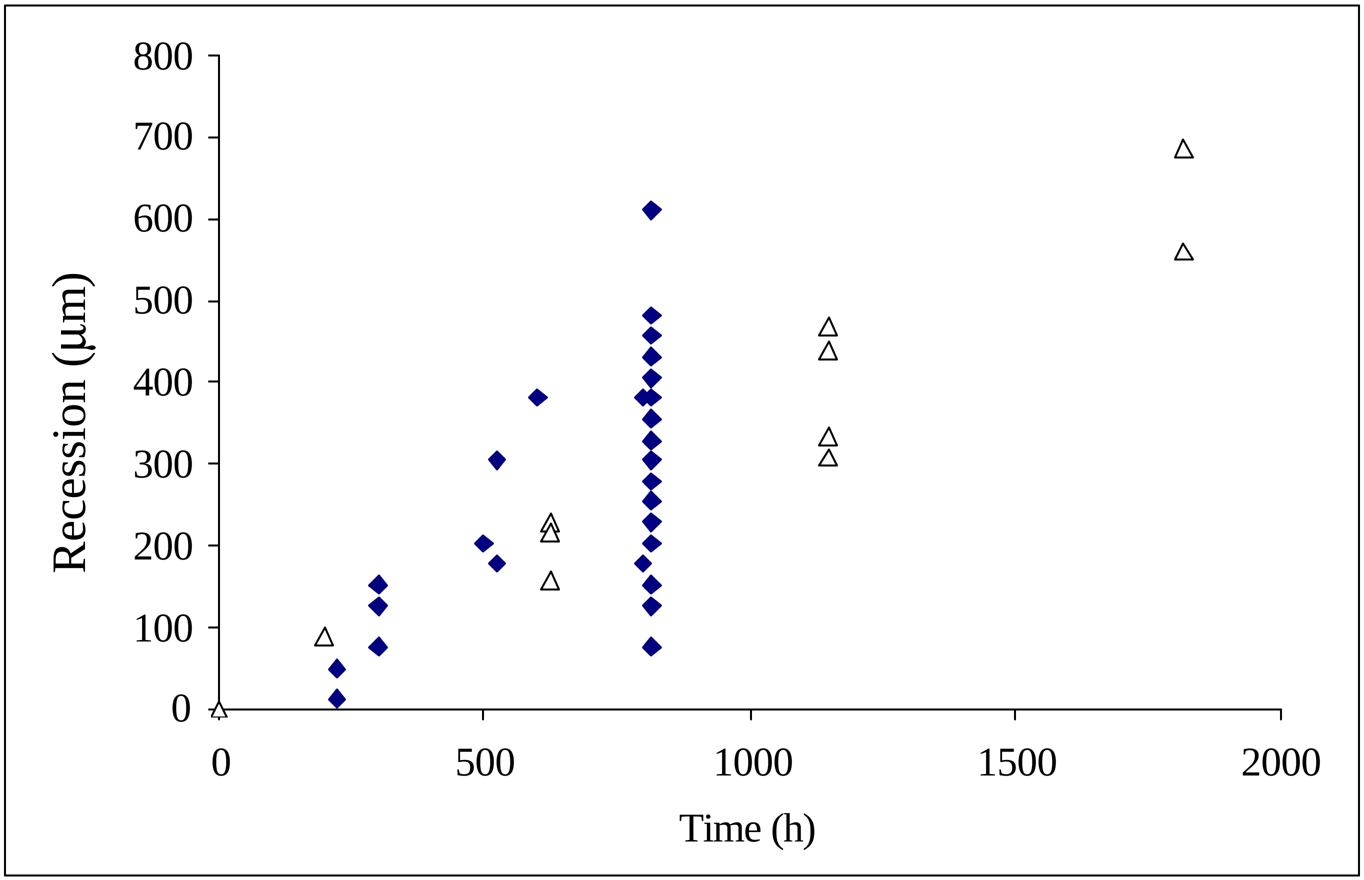






- AS800
  - 1170°C: spalling of $La_2Si_2O_7$, sub-surface damage
  - 1330°C: low melting phase, does not protect SiO_2
- SN282
  - 1225°C: "stalks" of SiO_2 with $Lu_2Si_2O_7$ on top

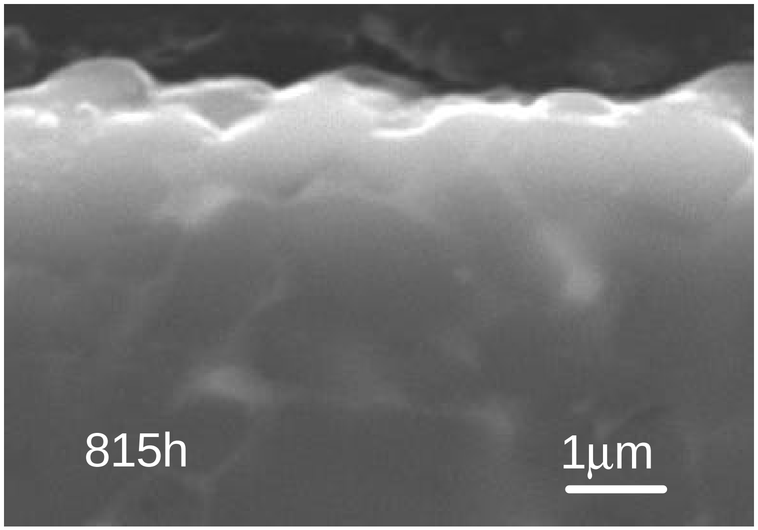
Si_3N_4 turbine vanes,
1066-1260°C, 8.7 atm, 0.9 atm H_2O, 160-570 m/s

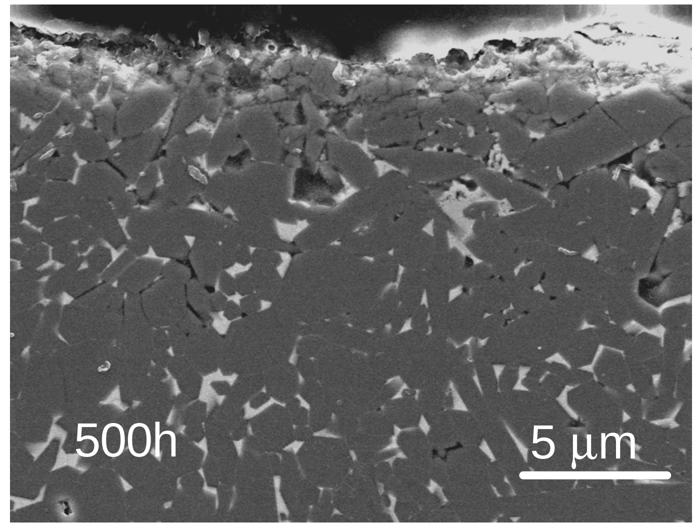


Comparison of trailing edge thickness values for uncoated AS800 ◆ and uncoated SN282 △. Courtesy Matt Ferber, ORNL - Rolls Royce ceramic vane program – DOE ATS Program.

AS800 turbine vane

1066-1260°C, 8.7 atm, 0.9 atm H_2O, 160-570 m/s





No oxide found on surface by SEM. XRD indicates La_2O_3 + Si_3N_4. No $La_2Si_2O_7$ found.

This vane was in a position where less oxidation and lower velocities were expected than elsewhere in turbine.

$La_2Si_2O_7$ or accumulated intergranular phase found on surface. Subsurface damage.

Photo courtesy of Matt Ferber, ORNL

SN282 turbine vane

1066-1260°C, 8.7 atm, 0.9 atm H_2O, 160-570 m/s, 1148h

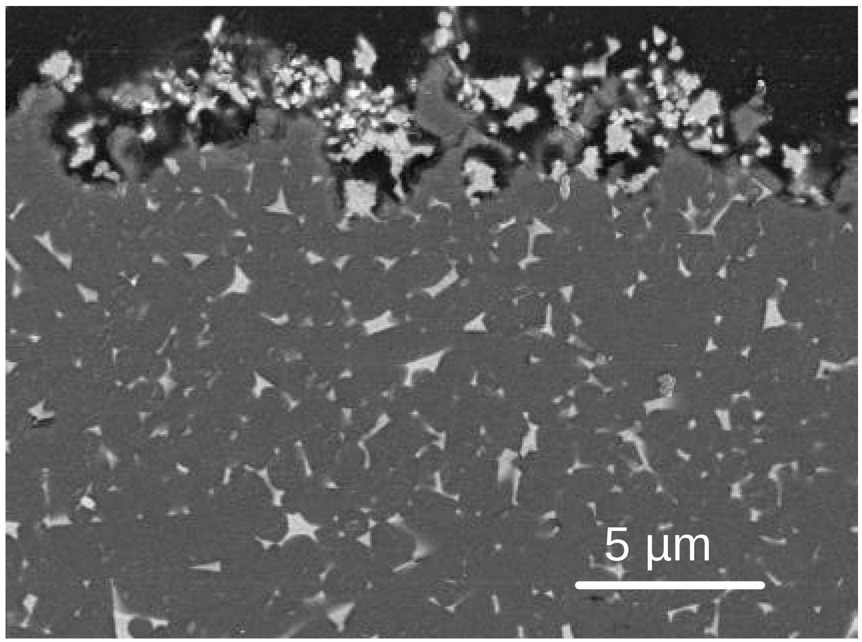


Photo courtesy
Matt Ferber, ORNL

Accumulation of $Lu_2Si_2O_7$ at vane surface

Summary

- AS800
  - Weight loss and recession rates same as pure Si_3N_4
  - T< 1300°C: poorly adherent surface acicular grains of $(La,Y)_2Si_2O_7$ formed
  - T>1300°C: low melting phase also formed
  - High velocity: surface oxide generally missing, La_2O_3 detected
  - Subsurface grain boundary damage occurred
- SN282
  - Weight loss and recession rates about half that of pure Si_3N_4 and AS800
  - Small, spherical $Lu_2Si_2O_7$ particles found on surface
  - $Lu_2Si_2O_7$ particles may be more adherent than $(La,Y)_2Si_2O_7$ grains on AS800
  - Subsurface grain boundary damage not observed

Factors which affect in situ surface modification of Si_3N_4 by RE additions

- Cation mobility effects
- CTE match between RE silicate, silica and Si_3N_4
- Phase stability of $RE_2Si_2O_7$
- Silica activity of $RE_2Si_2O_7$

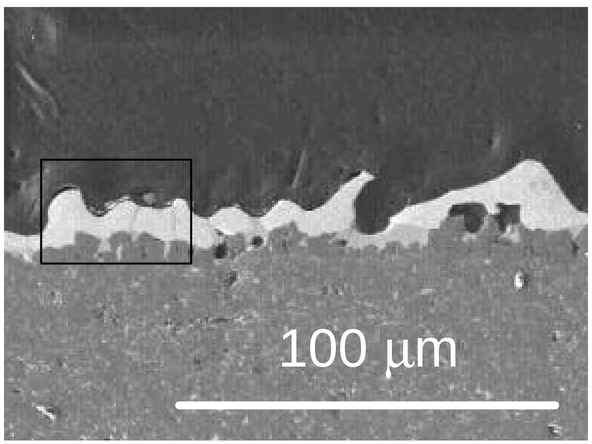
Cation mobility effects on in situ surface modification of Si_3N_4 by RE additions

- Cation diffusivity increases relative to silica growth rate as temperature increases.
  - Larger $RE_2Si_2O_7$ grains on oxide surface as temperature increases. Demonstrated for Yb in SN362, Kyocera (Lee and Readey, J Am Cer Soc. 85 [6] 1435-1440, 2002)
- Cation mobility for Lu < La. Due to different grain boundary phases in AS800 and SN282?
  - Si_3N_4 oxidation rates lower for Lu_2O_3 additions than for La_2O_3 additions
  - Less $RE_2Si_2O_7$ found on surface in SN282 than on AS800
  - Depletion of RE from grain boundary phase leads to subsurface damage, cracking in AS800 but not in SN282 (Ferber)

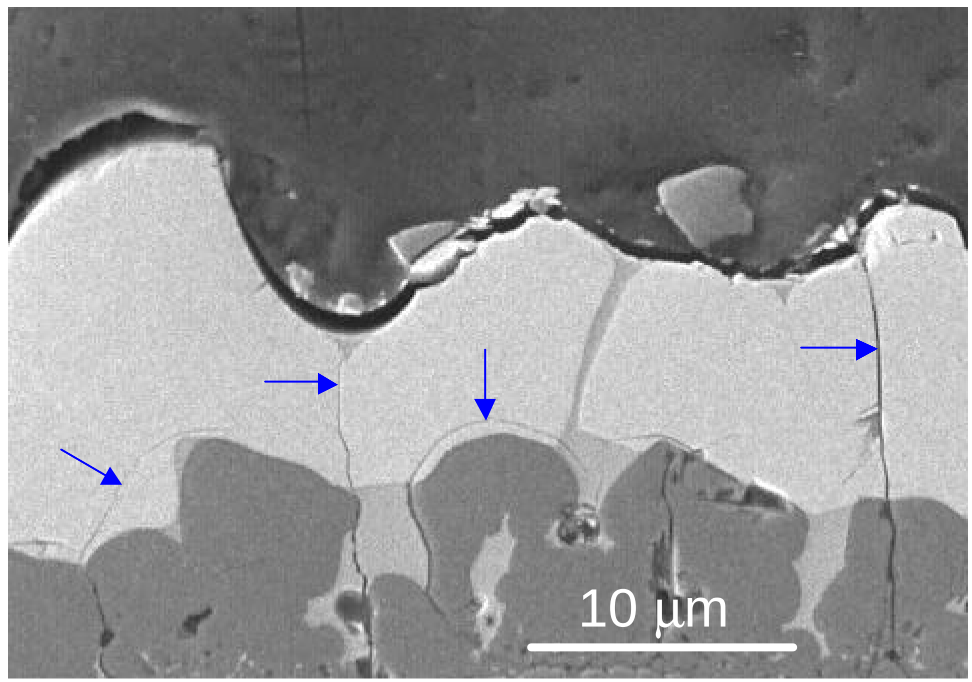
Balance desired formation of surface $RE_2Si_2O_7$ with undesirable subsurface grain boundary depletion.

CTE effects on in situ surface modification of Si_3N_4 by RE additions

- Possible CTE mismatch between $La_2Si_2O_7$, SiO_2, and Si_3N_4
- No cracks observed for $Lu_2Si_2O_7$
- Unable to find CTE values for $RE_2Si_2O_7$ in open literature



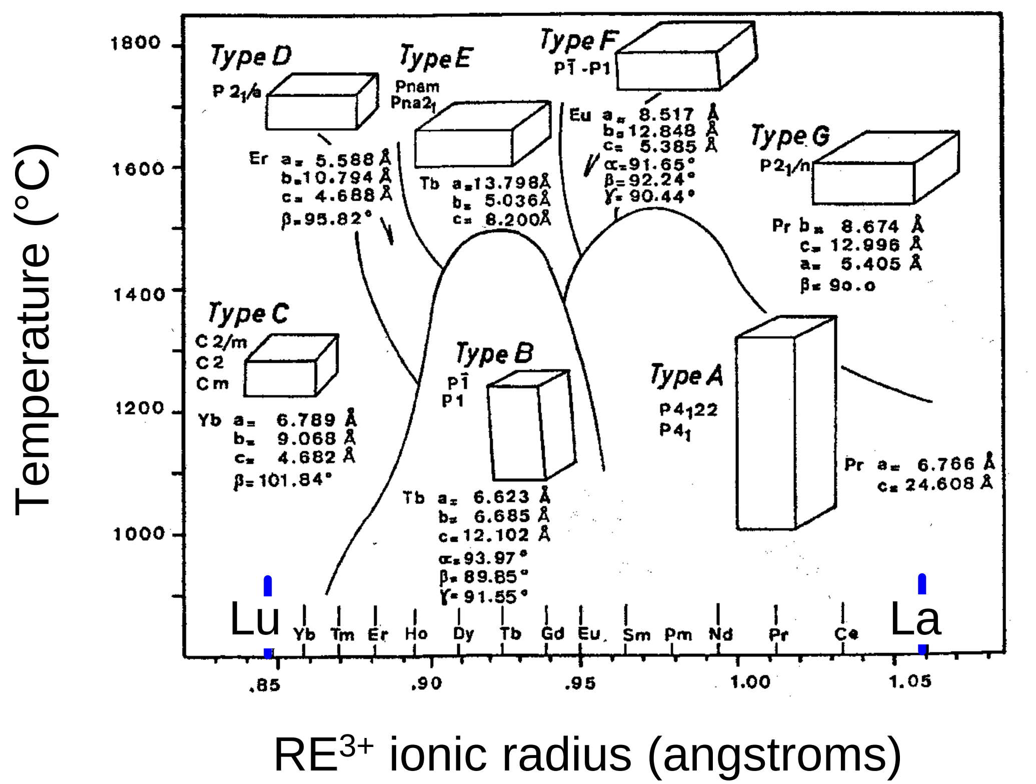
AS800, HPBR, 1330°C, 196h



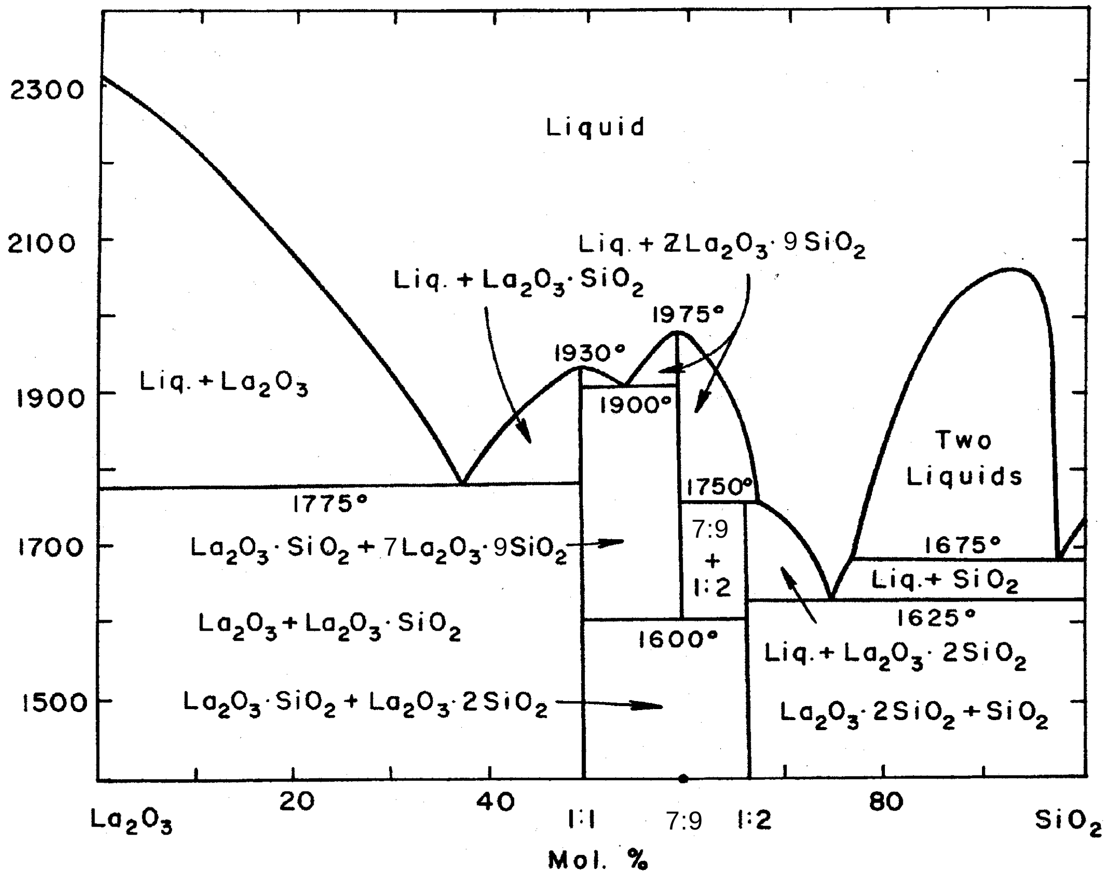
Phase stability effects on in situ surface modification of Si_3N_4 by RE additions

- Reconstructive phase transformations of $RE_2Si_2O_7$ occur between 1200-1500°C

  (J. Felsche, Structure and Bonding 13, Rare Earths, 1973.)



Silica activity effects on in situ surface modification of Si_3N_4 by RE additions



I.A. Bondar,
Cer.Int. 8 [3] 83 (1982)

Silica activity in this system nearly ideal. A factor of two reduction in silica volatility expected for $RE_2Si_2O_7$.

Summary

- AS800 in combustion environments
  - Weight loss/recession at least as great as CVD Si_3N_4
  - $T<1300^{\circ}C$
    - $La_2Si_2O_7$ spalls off
    - Subsurface damage
  - $T>1300^{\circ}C$
    - Low melting phase forms
    - Melt phase does not protect SiO_2
  - High velocity
    - $La_2Si_2O_7$ decomposes to La_2O_3
    - Bare Si_3N_4 observed

Summary

- SN282 in combustion environments
  - Volatility/recession reduced by a factor of two relative to CVD Si_3N_4 and AS800
  - Partial surface coverage by $Lu_2Si_2O_7$
  - $Lu_2Si_2O_7$ may offer slight protection from volatility to underlying silica at moderate to high velocities

Conclusions

- In combustion environments preferential volatilization of silica and surface enrichment of $RE_2Si_2O_7$ has been observed for Si_3N_4 containing RE additives.

- Factor of two reduction in weight loss and recession rates observed for SN282 in combustion environments may be due to reduction in silica volatility by enrichment of $Lu_2Si_2O_7$ surface phase.

Conclusions

- Factors which affect in situ formation of an adherent $RE_2Si_2O_7$ phase have been identified.
  - RE mobility: balance $RE_2Si_2O_7$ surface coverage with grain boundary depletion. Dependent on temperature, RE cation, and grain boundary phase.
  - CTE match of $RE_2Si_2O_7$ with SiO_2 and Si_3N_4
  - $RE_2Si_2O_7$ phase stability: Yb-, Lu-disilicates most stable
  - Ideal silica activity limits protective capability of in situ formed $RE_2Si_2O_7$ surfaces.
- EBC's needed for long-term application of additive-containing Si_3N_4 in combustion environments.

Acknowledgments

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