

# Overview of Factors Affecting Lifetime of TBCs in Land-Based GTs

- Ian Wright, Allen Haynes, Mike Lance,
- Karren More, Bruce Pint, Ying Zhang
  
- Oak Ridge National Laboratory

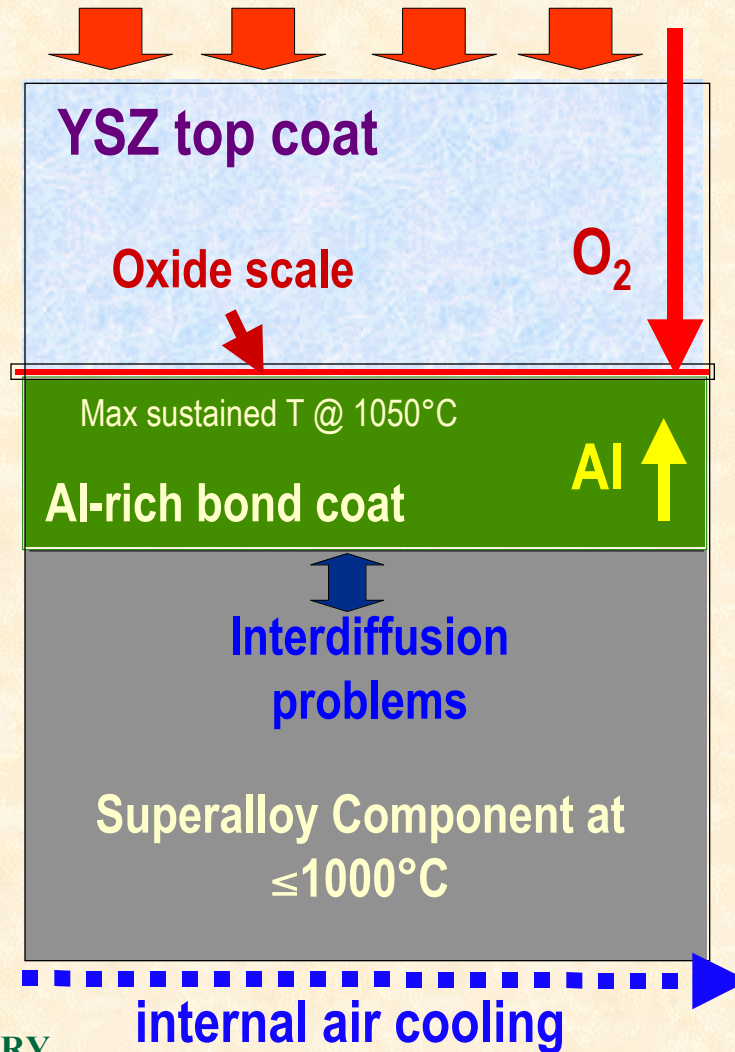
EPRI Conference, Orlando, Florida, March 11-13, 2002

# Outline

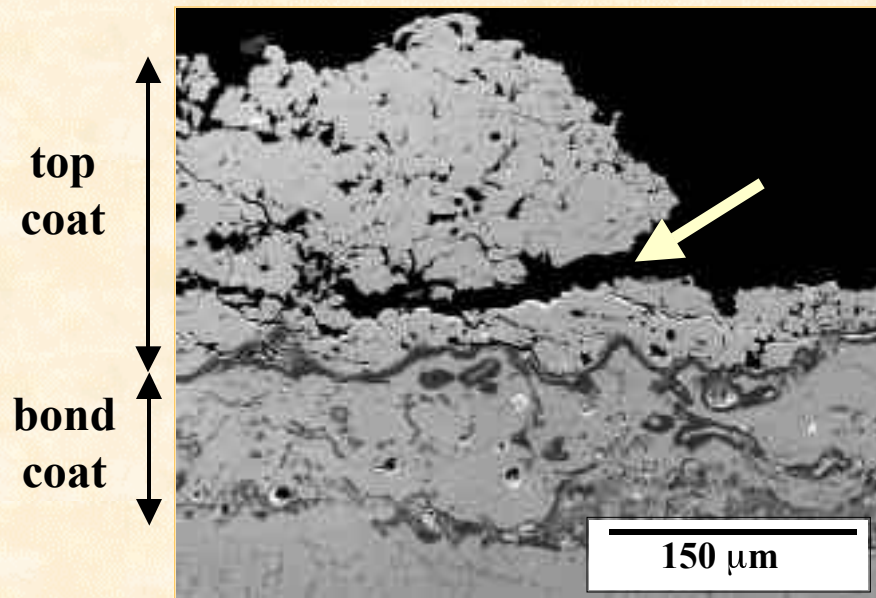
- **Overview of the modes of degradation**
- **Discuss the major life-determining issues**
  - experimental results
  - guidelines
- **Condition monitoring**
- **Summary**

# TBCs are complex systems

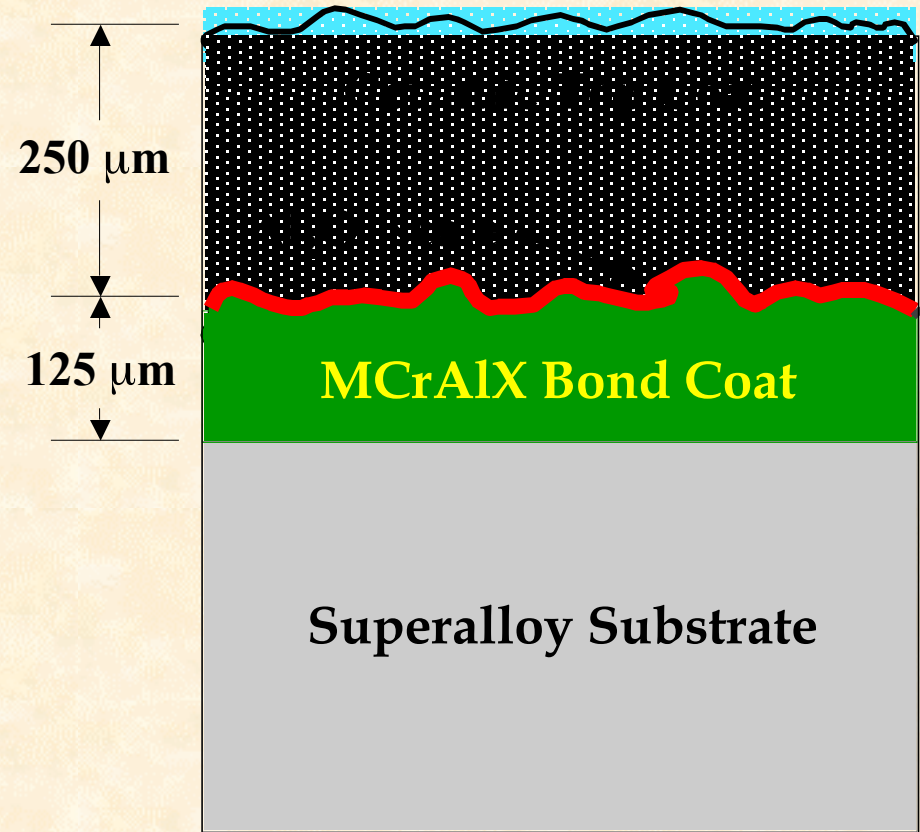
Combustion gases at @1500°C



# Plasma-Sprayed Thermal Barrier Coatings



Haynes, et al., 2000



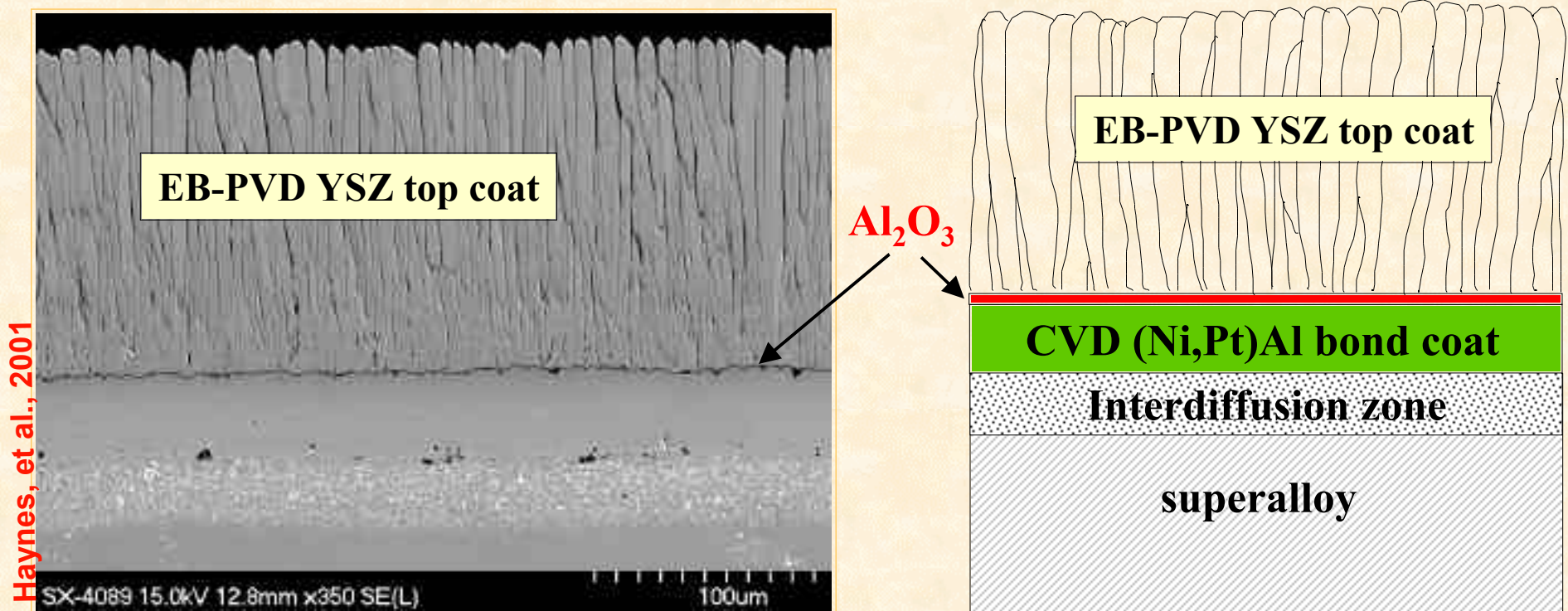
- $Y_2O_3-ZrO_2$  (YSZ) top coat
  - provides thermal insulation
- Metallic bond coat
  - provides oxidation resistance
  - facilitates YSZ adherence
- Interfacial  $Al_2O_3$  scale

\* $M = Ni$  and/or  $Co$ ,  $X = Y, Hf$ , or  $Si$

APS = air plasma-spray

VPS = vacuum plasma-spray

# EB-PVD Thermal Barrier Coatings

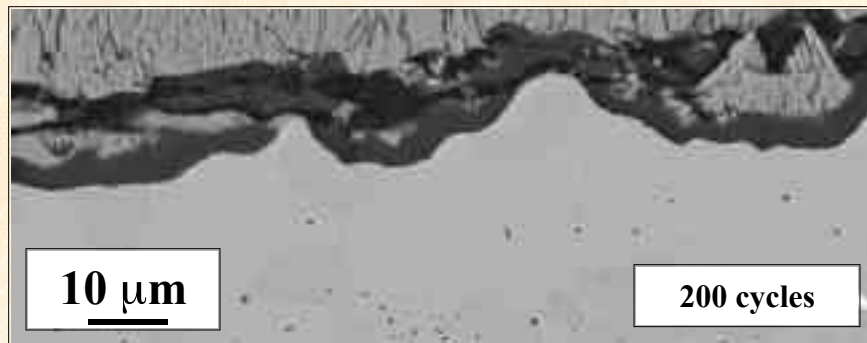
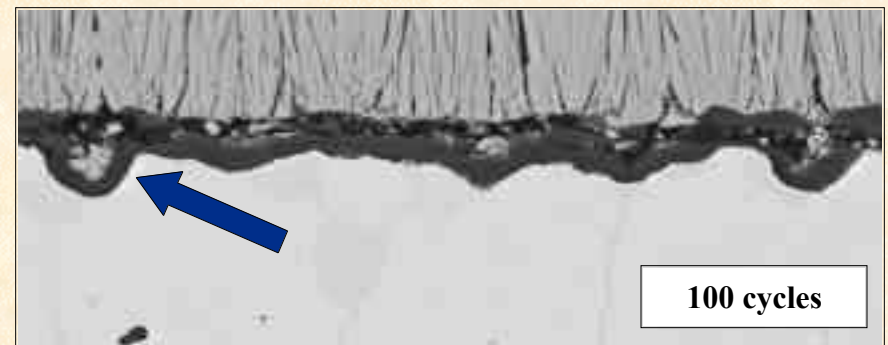
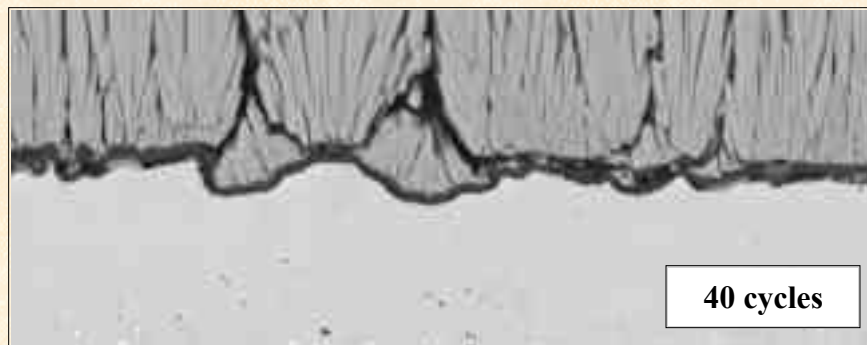
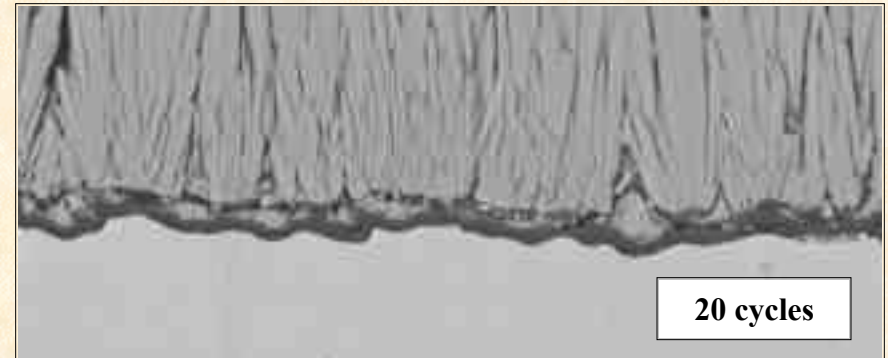
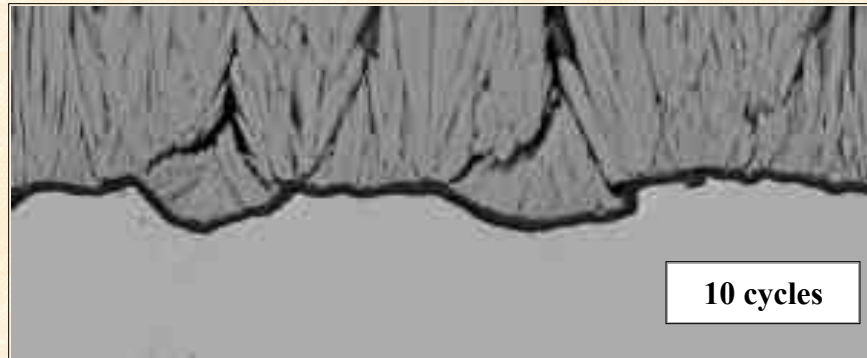


- Strain-tolerant ceramic top coating deposited by electron beam-physical vapor deposition (EB-PVD)
- Metallic bond coating of single-phase (Ni,Pt)Al produced by Pt electroplating + pack, or chemical vapor deposition (CVD) aluminizing

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# Lab. thermal cycling at 1135°C: interfacial roughness increased with time



Haynes et al., 2001

# Major TBC Life-Determining Issues

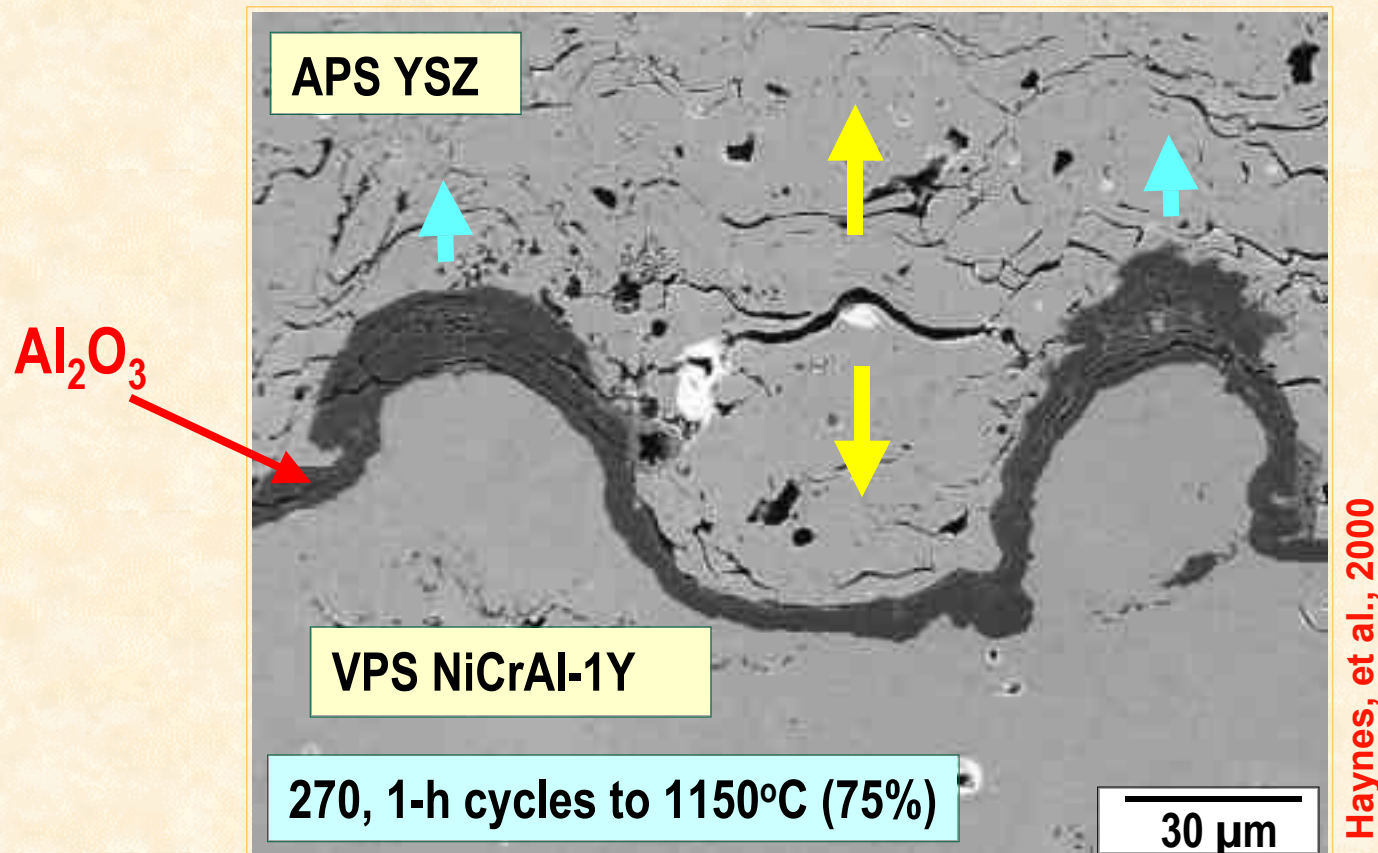
- **TBC application:** ability to apply the specified coating
- **Operating temperature:** assurance of providing the design T at design conditions
- **Cyclic operation:** effects on durability
- **Loss of ceramic:** especially erosion/FOD
- **Other duty cycle issues:** off-specification fuel
- **Lifetime modeling/monitoring:** assurance; early warning

# Coating Application Issues

- **PS vs EB-PVD**
  - cost
  - size limitations
  - control of ceramic microstructure
- **Function of the bond coating**
  - MCrAlY or aluminide
  - effect of surface finish
  - BC 'conditioning' - aim to quickly establish an  $\text{-Al}_2\text{O}_3$  layer
- **Microstructure and thickness**
  - complexity of shape  $\pm$  determines processing route
- **Cost**
  - low infant mortality



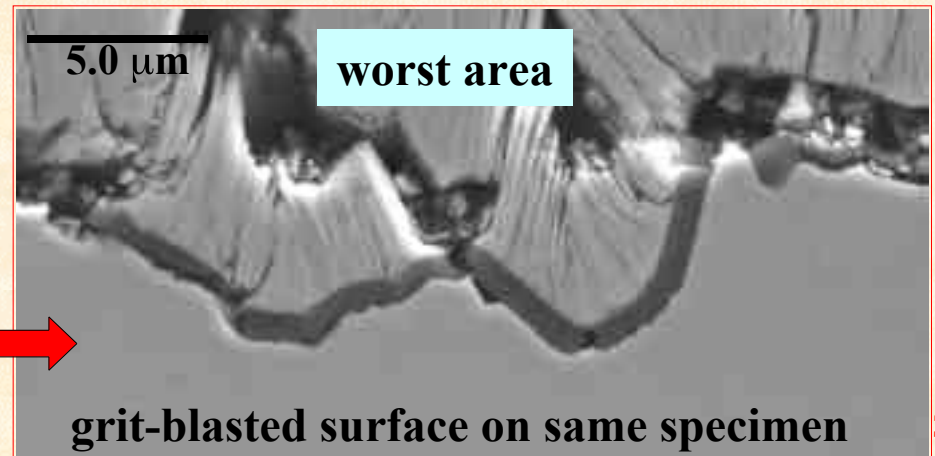
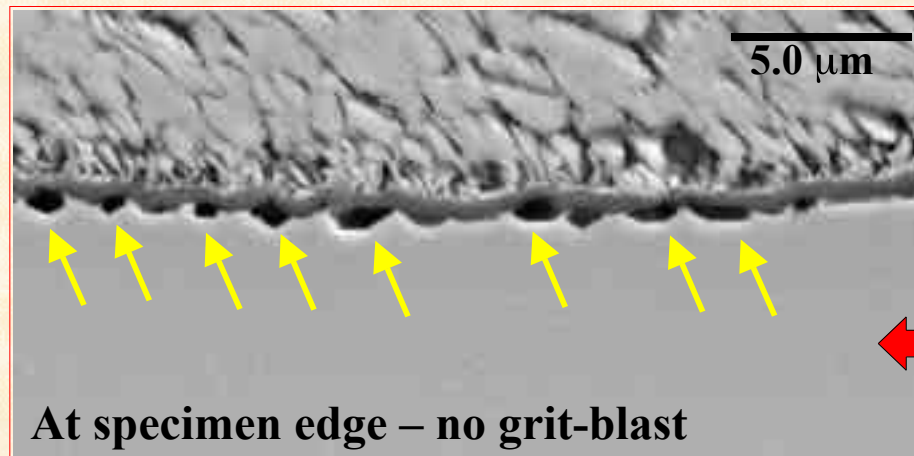
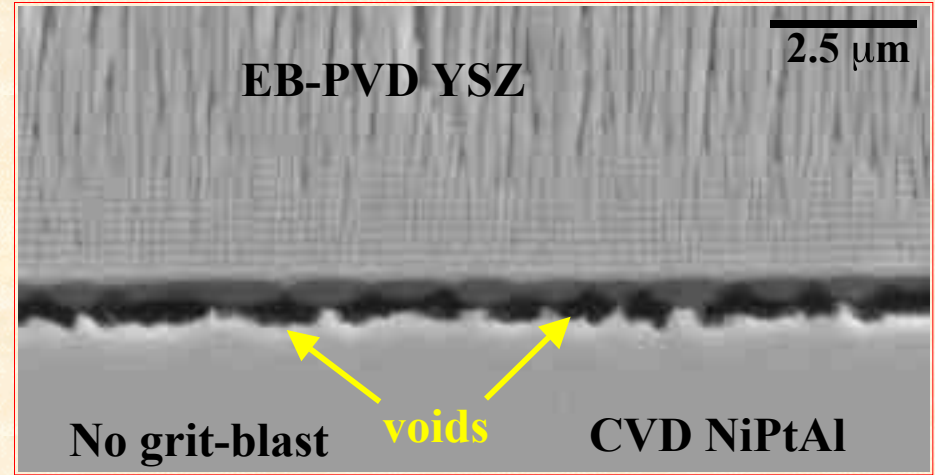
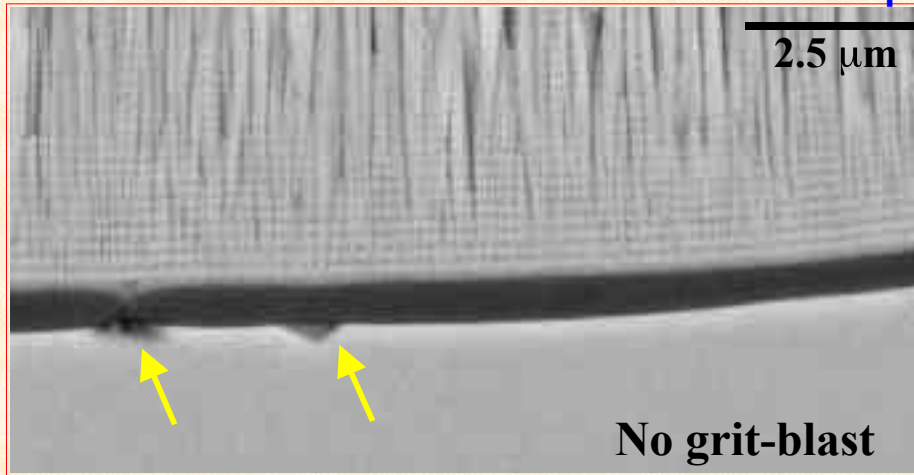
# Rough BC surface is an intrinsic feature & problem of PS TBCs



- Evidence of localized oxidation-induced YSZ damage
- Localized Al<sub>2</sub>O<sub>3</sub> scale damage very variable—not clear whether it was a factor in determining relative TBC lifetimes on the various MCrAlX bond coatings

# Grit-blasting of CVD (Ni,Pt)Al has unexpected benefit for BC oxidation

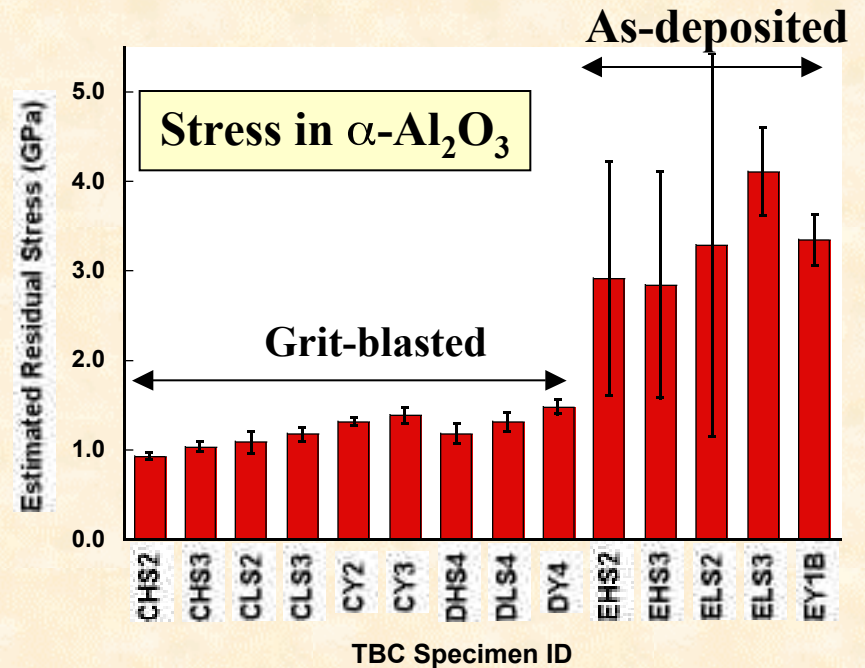
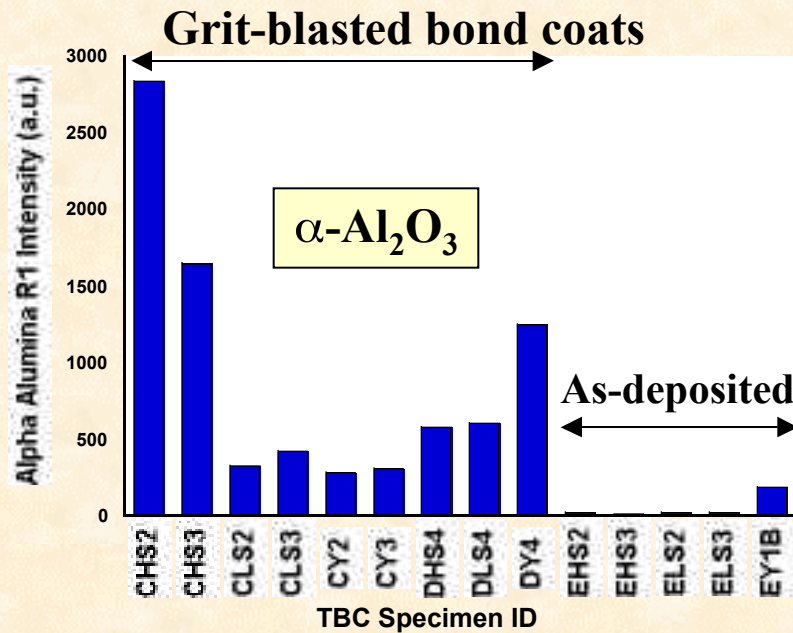
As-deposited TBCs



Haynes, et al., 2001

- All surfaces not grit-blasted contained voids at the metal-oxide interface
- Void density & scale thickness varied from grain to grain
- Grit-blasted surfaces contained no obvious voids at the metal-oxide interface

# Bond coating surface finish influences first-formed oxide

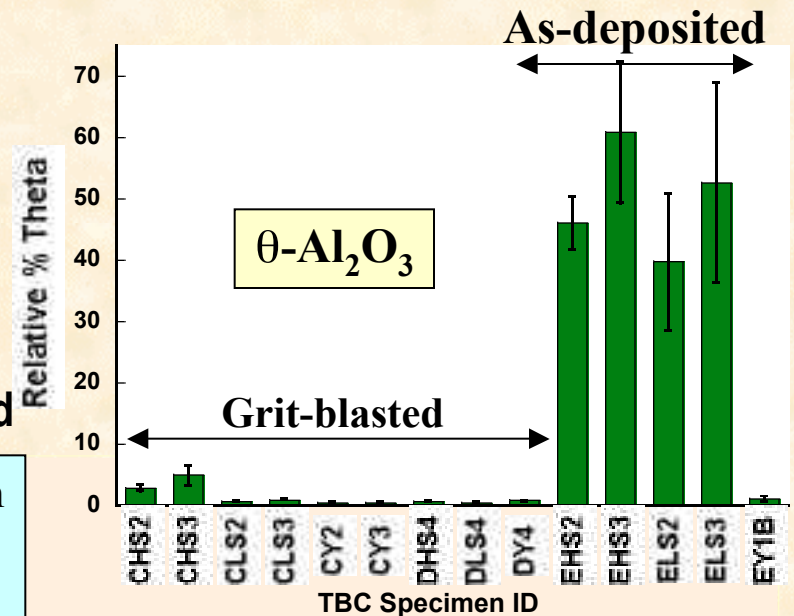


## Laser fluorescence of as-deposited EB-PVD TBCs

- Laser fluorescence detectable through the YSZ.
- Grit-blasted surfaces formed more  $\alpha\text{-Al}_2\text{O}_3$ .
- Average stress was lower on grit-blasted surfaces.
- All specimens contained detectable  $\theta\text{-Al}_2\text{O}_3$ .
- Greater amounts of  $\theta\text{-Al}_2\text{O}_3$  formed on most as-deposited (Ni,Pt)Al surfaces.

Haynes et al., 2002

Dilor XY 800 Raman  
5145 Å, 500 mw  
10-12 μm spot size

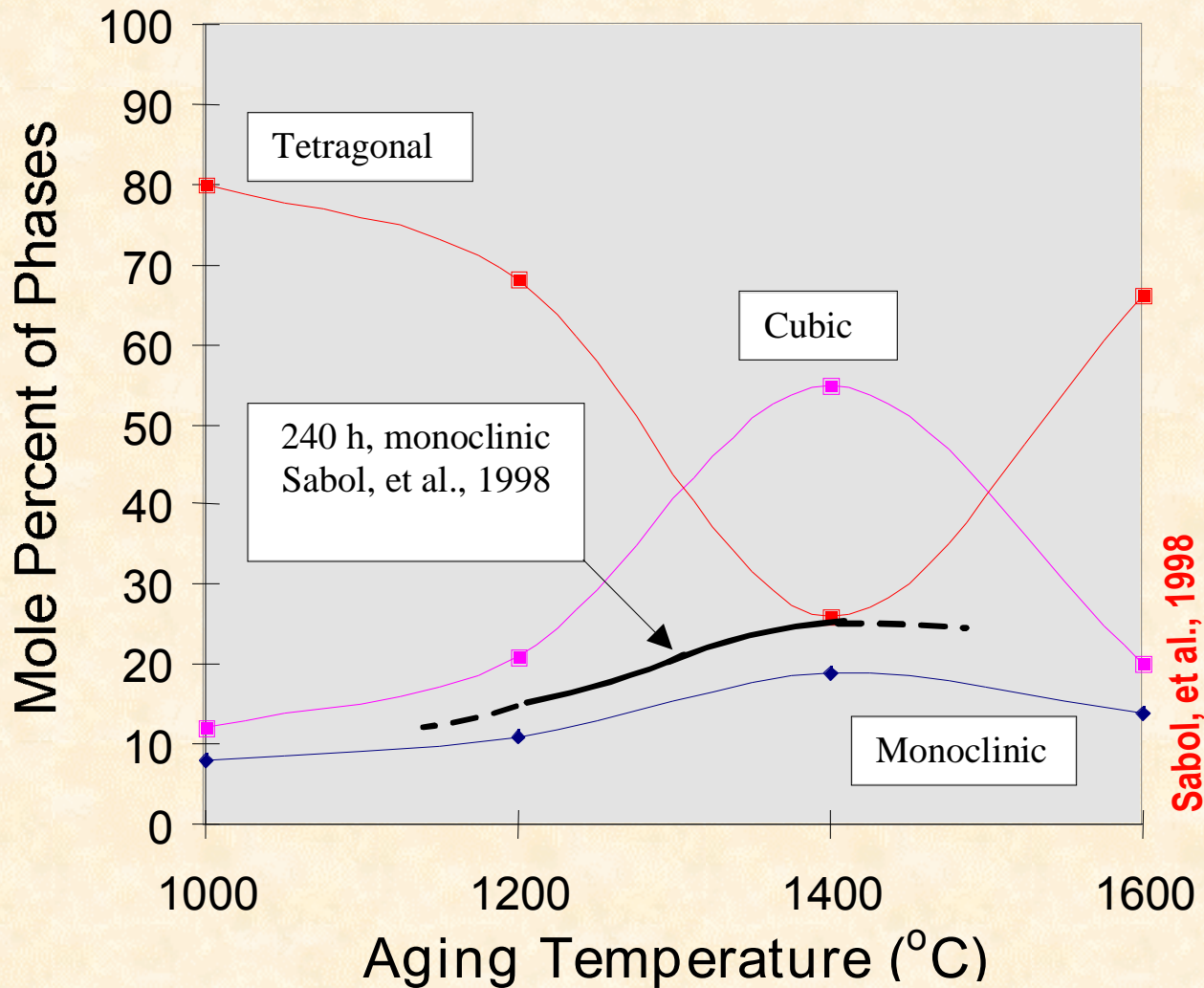


# Operating Temperature Issues

Concerned with the effects of time at temperature:

- Effects on the ceramic layer
  - phase change of YSZ
  - sintering of ceramic surface
    - modification of microstructure
    - change in mode of failure
- BC oxide growth
  - some lifing models based on rate of oxide thickening
  - exhaustion of Al reservoir--formation of voluminous base metal oxides
- BC-superalloy interdiffusion
  - depletion of Al
  - BC phase change/effect on CTE
  - ingress of unwanted elements from superalloy

# Effect of 100 hr Aging on Phase Stability of YSZ (after Miller, et al., NASA, 1981)

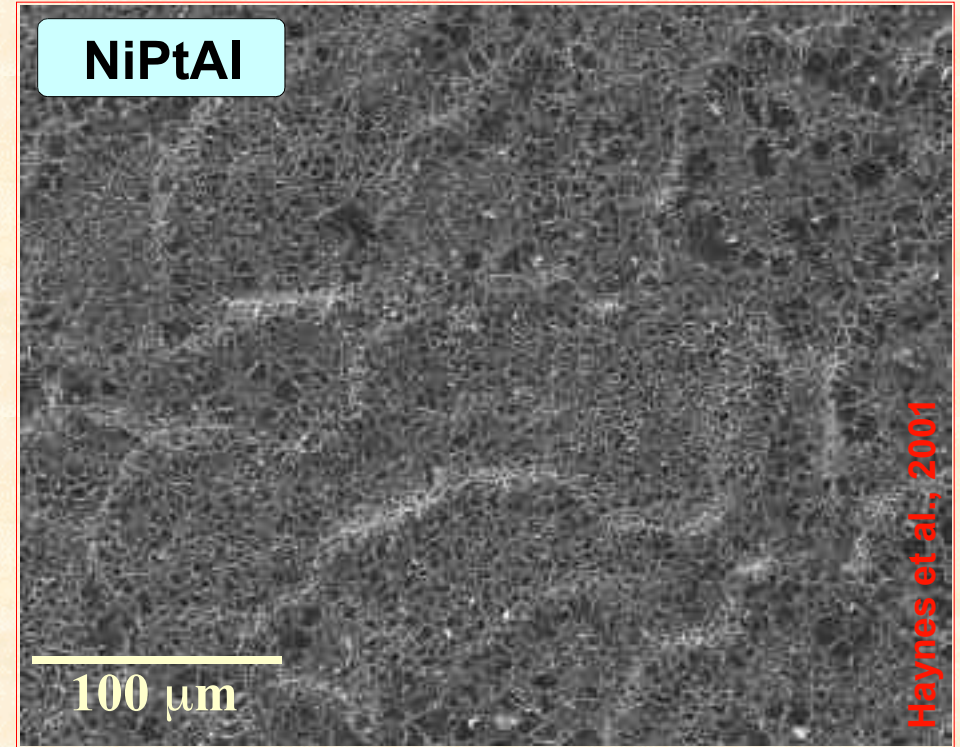
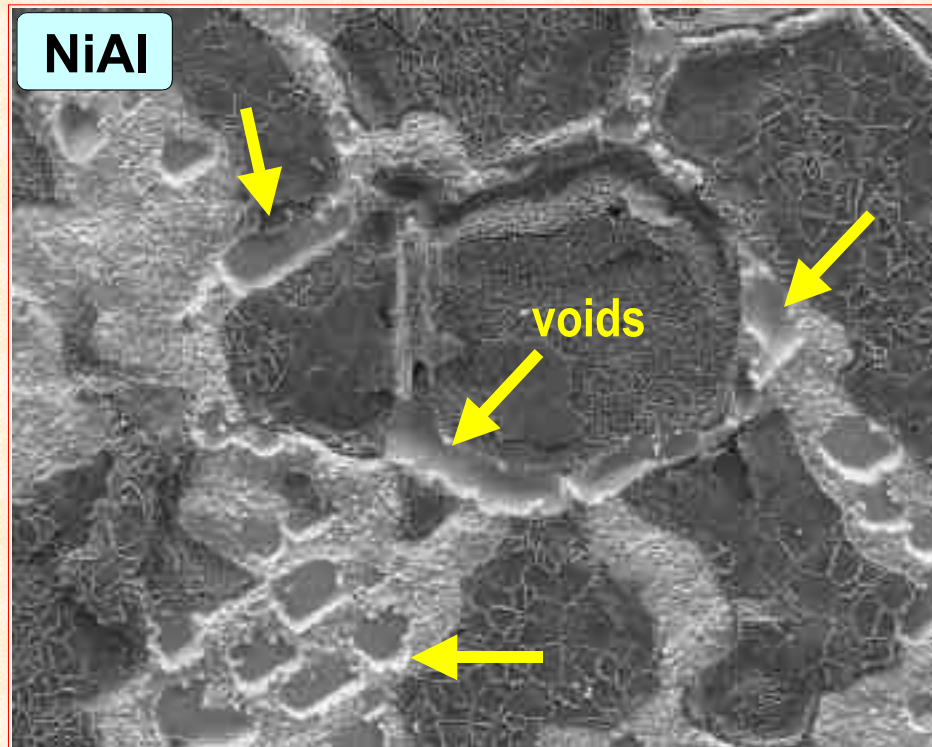


# BC oxide thickness increases with t at T

- Increasing oxide thickness equates to:
  - *increased stress generation*
    - increased tendency for scale spallation
  - *increased consumption of Al reservoir*
    - loss of  $\gamma$ -phase in BC (lower-Al phases do not form the desired oxide)
    - approach to non-protective oxidation (voluminous scales)
    - with Pt addition, min. Al content for protective oxidation is reduced from 43 to 38 at%Al
- Oxide growth rate can be minimized by:
  - *forming  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as soon as possible (Pt effects)*
  - *controlled addition of a reactive element (Y, Hf, ...)*
    - MCrAlYs
    - aluminides
- Resistance to scale spallation can be improved by:
  - *Pt additions*
  - *removal of alloy/BC tramp S to  $\ll 1$  ppm*
  - *RE additions*

'High' superalloy S—increased interfacial void growth and scale spallation on CVD-NiAl; but no voids formed on CVD-NiPtAl

200-h isothermal @ 1150°C (substrate: Hi-S N5A, S = 3.6 ppmw)

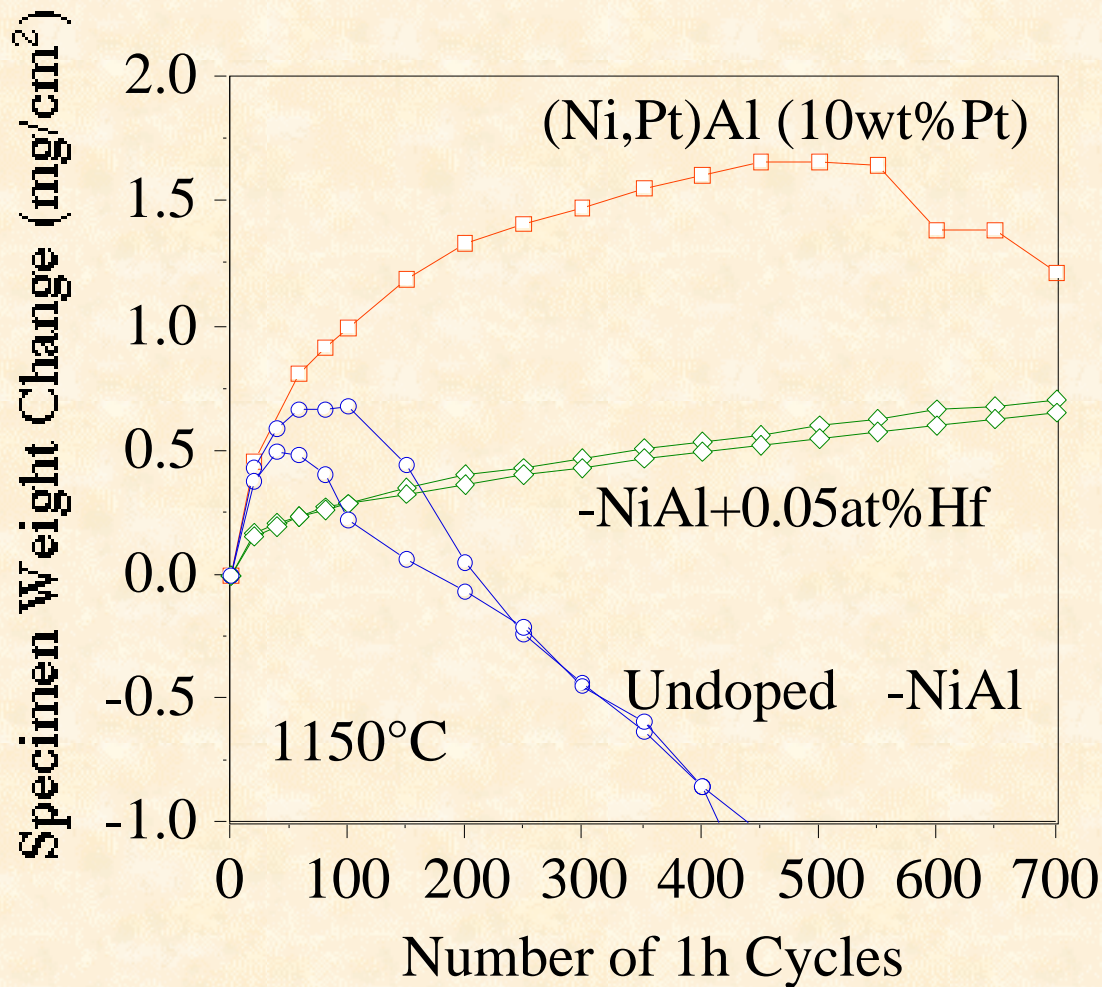


**NiAl on High-S Rene N5**

**NiPtAl on High-S Rene N5**

- Increased substrate S resulted in massive void formation & scale spallation on grain boundaries & grain surfaces of NiAl.
- Neither voids nor scale spallation were observed on NiPtAl despite the increased S impurities (and high C) of the Hi-S N5 substrate.

# RE & Pt additions improve scale spallation lifetimes; RE additions are more potent



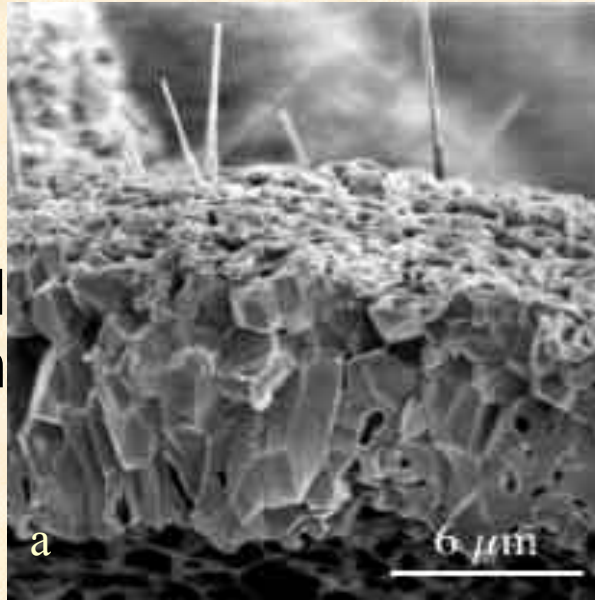
- *Undoped:*—rapid scale spallation
- *Pt:* improved resistance to spallation...for a time
- *RE-doping:*—lower scale growth rate + greatly improved spallation resistance

(Pint, et al., 1998)

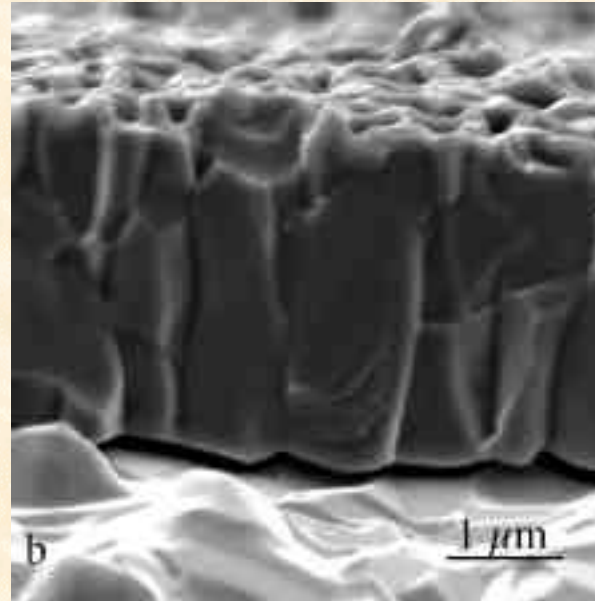


# RE additions modify scale morphology and reduce growth rate; Pt does not (1200°C)

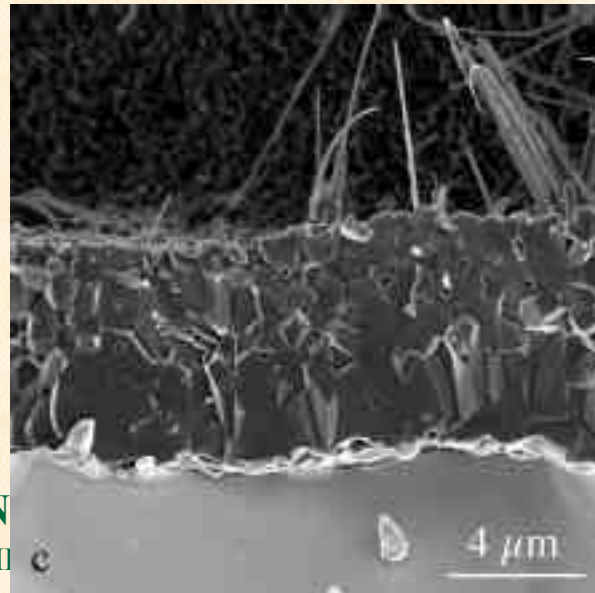
Undoped NiAl, 200h



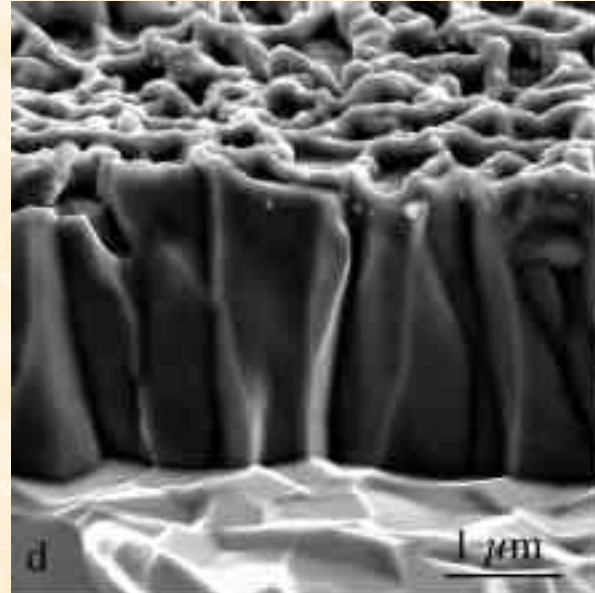
NiAl+Hf, 100h



PtAl, 100h



NiPtAl+Hf, 100h



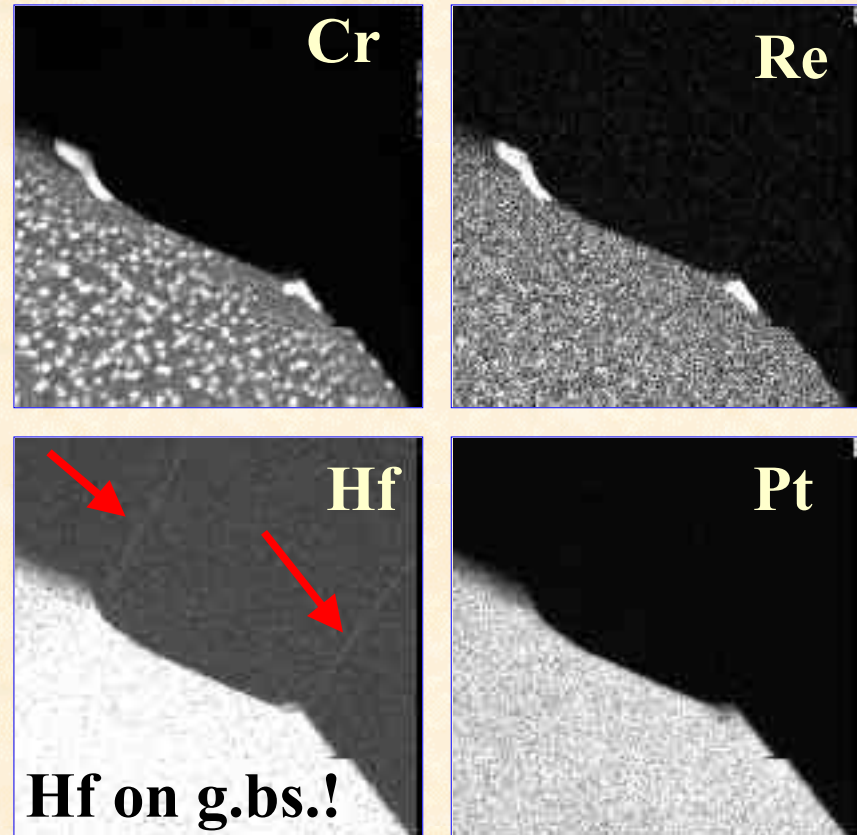
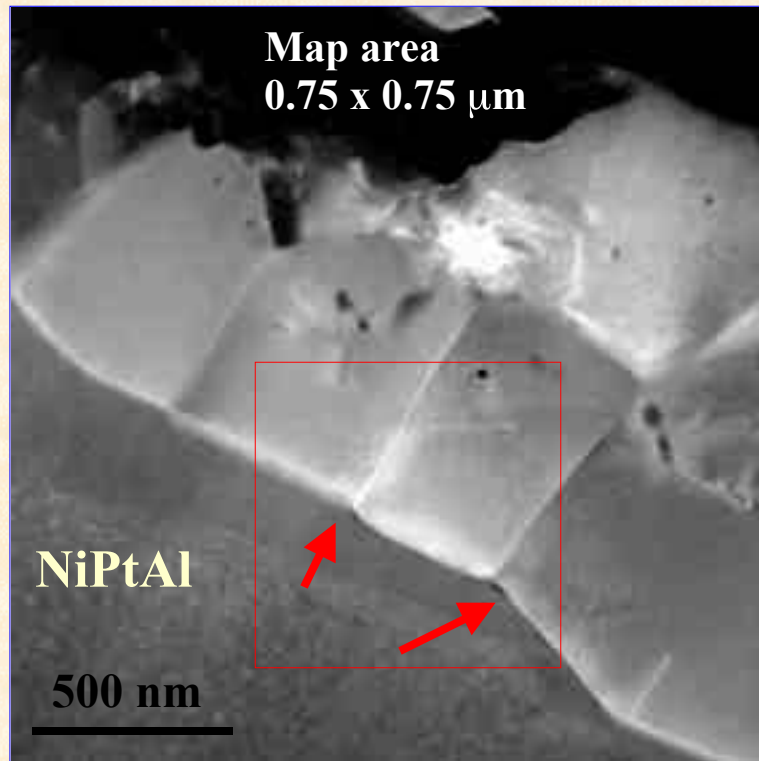
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Pint et al., 1998



# STEM/EDS Mapping of Alumina Scales on NiPtAl

100-h isothermal @ 1150°C (substrate S ~ 0.8 ppmw, C ~ 1000 ppmw)



More, et al., 2001

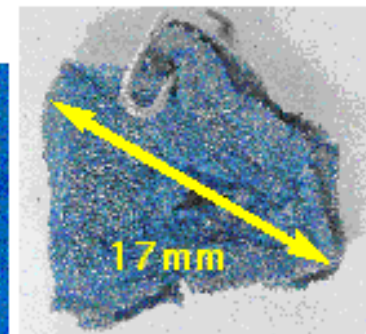
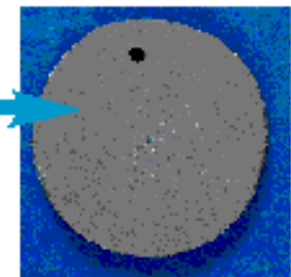
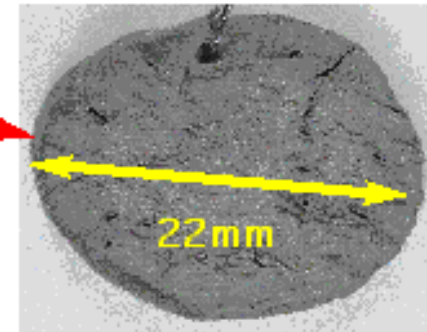
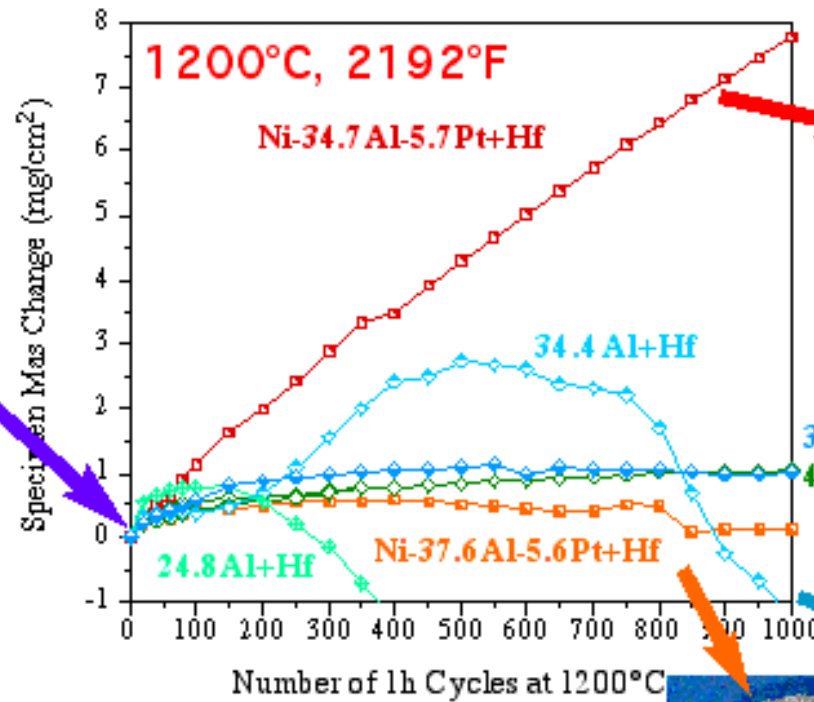
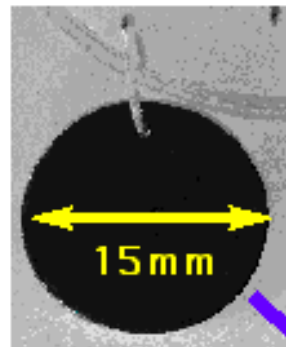
- Hf from the Rene N5 substrate was detected on the columnar oxide grain boundaries of NiPtAl, but not in the equiaxed outer grains.
- No Hf was detected on oxide grain boundaries on NiAl.
- Apparently, Hf diffused more rapidly through NiPtAl than NiAl.

# BC-Superalloy Interdiffusion

- **Concern over loss of Al reservoir**
  - minimum Al level for maintaining  $\gamma$ - $\text{Al}_2\text{O}_3$
  - Pt beneficial
- **Ingress of other elements** is typically detrimental to the protective nature of the oxide scale
  - Ti, Cr, Re...
  - Hf: from good to bad
- **NiAl BC phase change**
  - critical range appears to be 35-37.5 at% Al
  - at RT:  $\gamma$  +  $\beta$ ; at 1100°C: one phase (  $\beta$  ? )
  - effect on CTE

# NiAl+Hf: Critical Effect of Al Content

cast alloys, oxidized 1000x1h cycles at 1200°C in O<sub>2</sub>

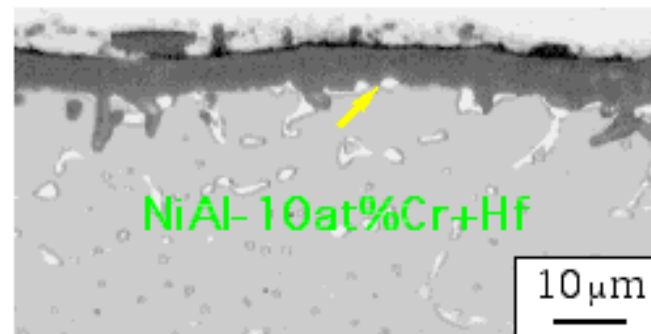
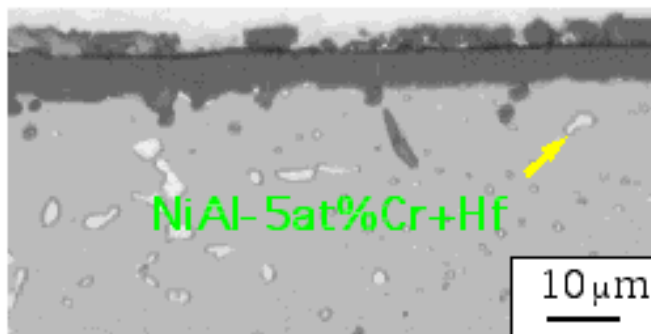
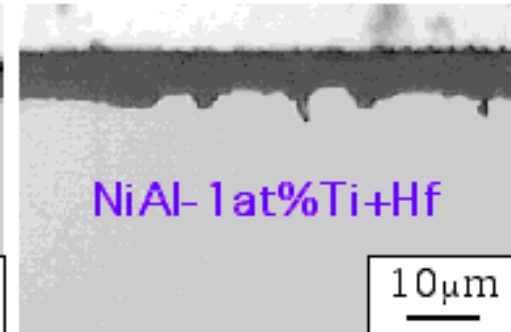
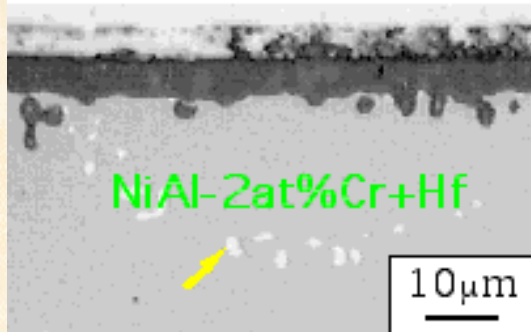
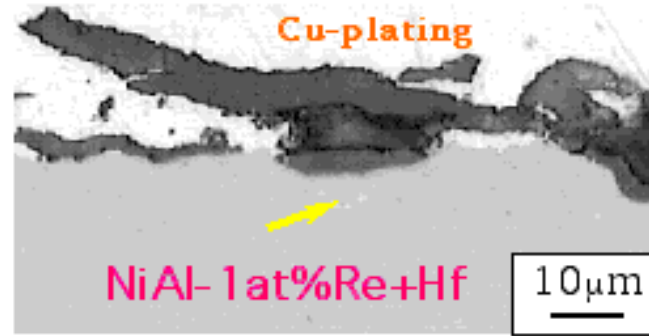
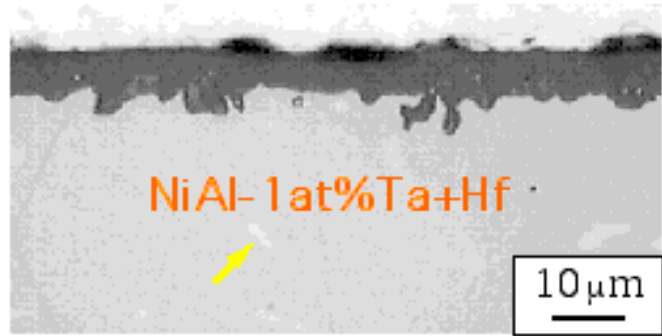


Critical range: 35-37.5%  
two phase vs. one phase?

- Al contents < 37.5 at% have significant oxidation problems
- Macroscopic deformation occurs for low-Al two-phase alloys
- Addition of Pt does not stop deformation, or spallation (but no blue oxide)

# Tramp elements are detrimental to NiAl+Hf

polished cross-sections after 1000x1h at 1150°C in O<sub>2</sub>



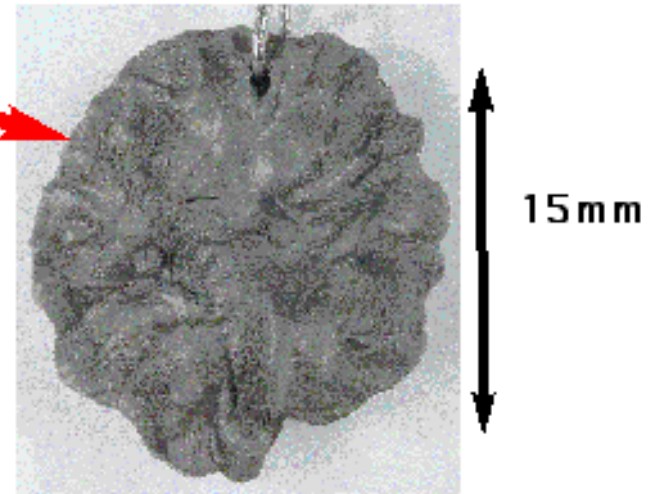
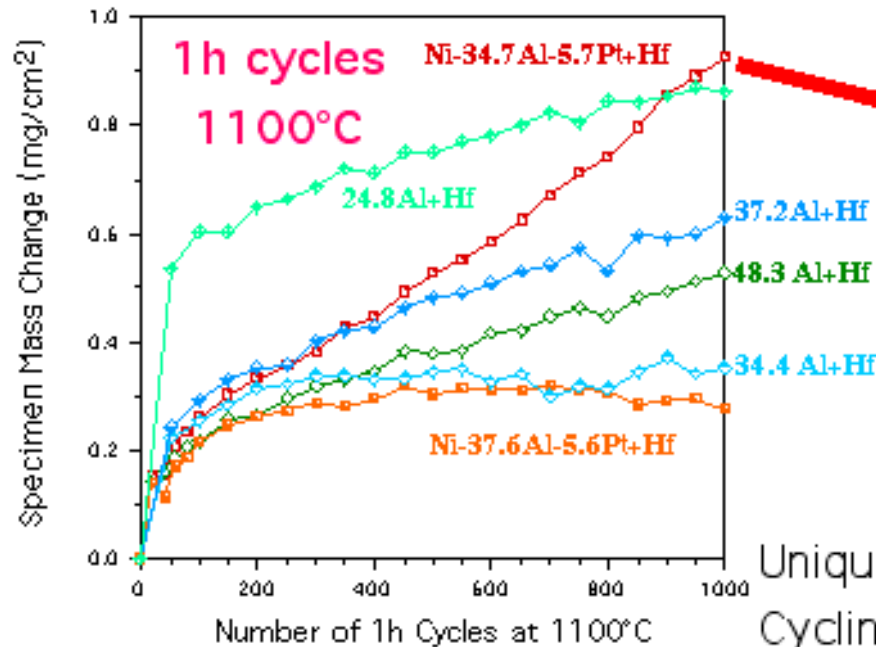
All additions accelerate scale growth rate compared to NiAl+Hf

Problems with scale adhesion with Cr and Re -> precipitates

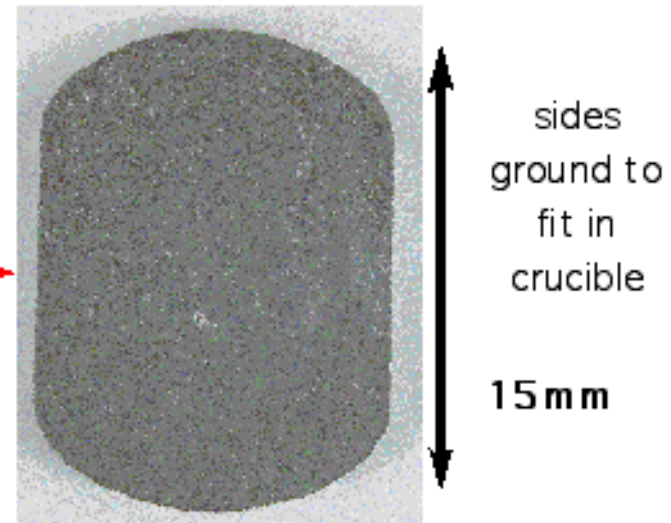
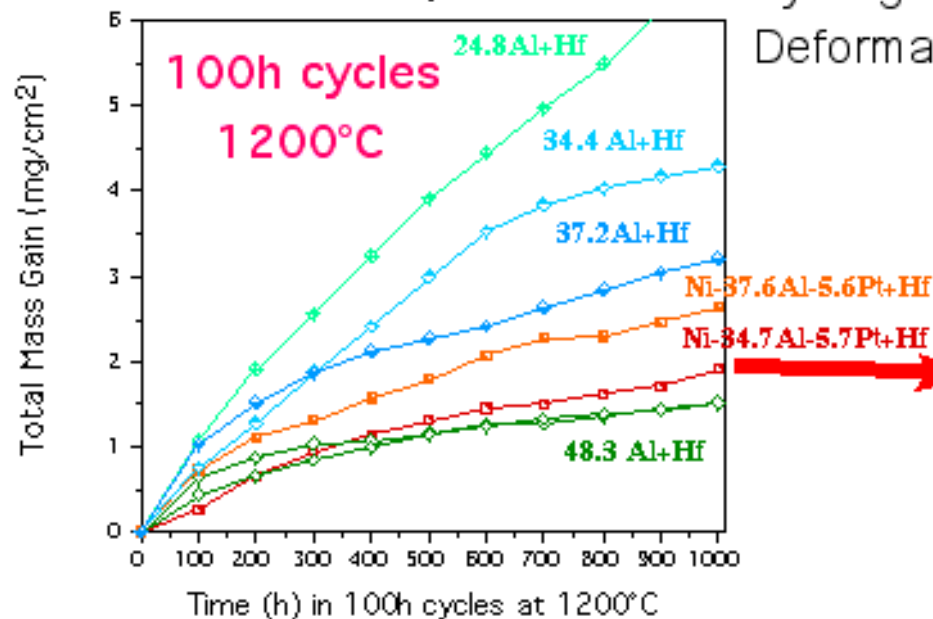
# Cyclic Operation Issues

- Increased stress generation due to:
  - CTE mismatch YSZ - oxide scale - BC
  - BC - superalloy CTE mismatch
  - oxide growth
- Need to consider matching superalloy and BC CTEs
- Can't do much to modify the YSZ - oxide scale CTE mismatch
- Need to maximize adherence of oxide scale to BC
  - Pt,S,RE effects
- Are long or short cycles worse?
  - long cycles: more oxide growth between cycles, but increased opportunity for stress relief-localized rather than massive damage?
  - short cycles: more cycles/unit time

# Deformation of BC: depends on T & cycle frequency

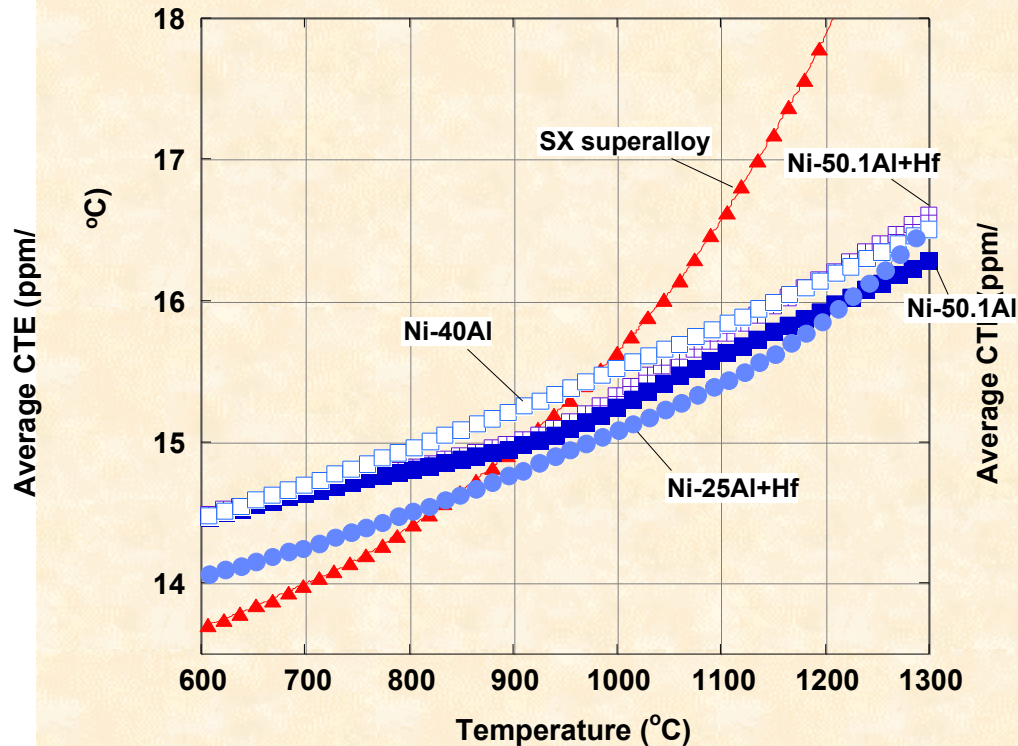


Unique behavior of Ni-34.7Al-5.7Pt+Hf  
Cycling causes repeated phase change  
Deformation similar to aluminide coatings!

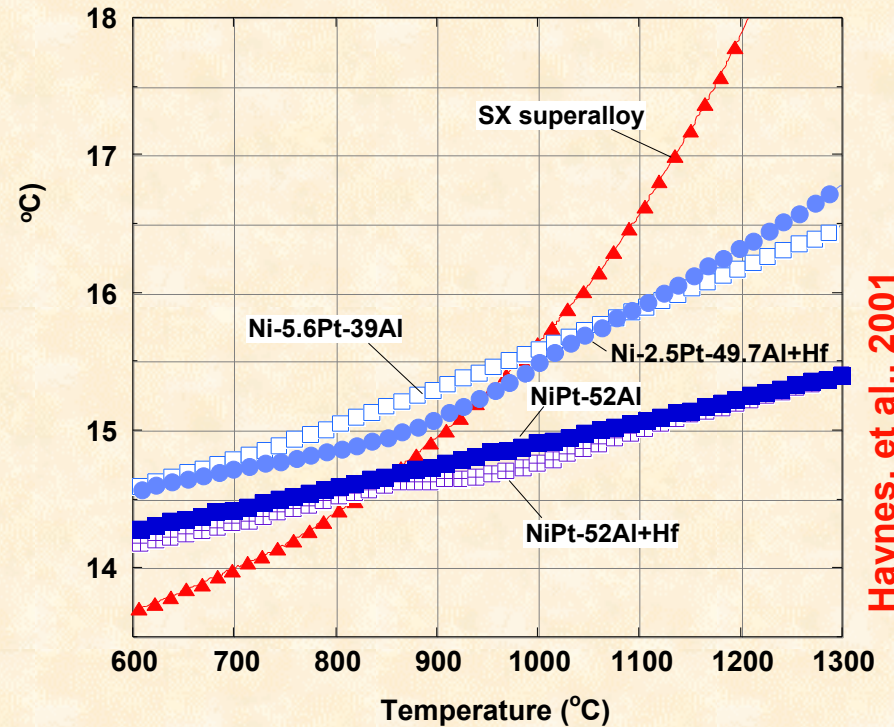


# Effect of Pt on CTE of Aluminide Bond Coating Alloys

NiAl<sub>s</sub>: 25 to 50.1 at%Al



(Ni,Pt)Al<sub>s</sub>: 39 to 52 at% Al

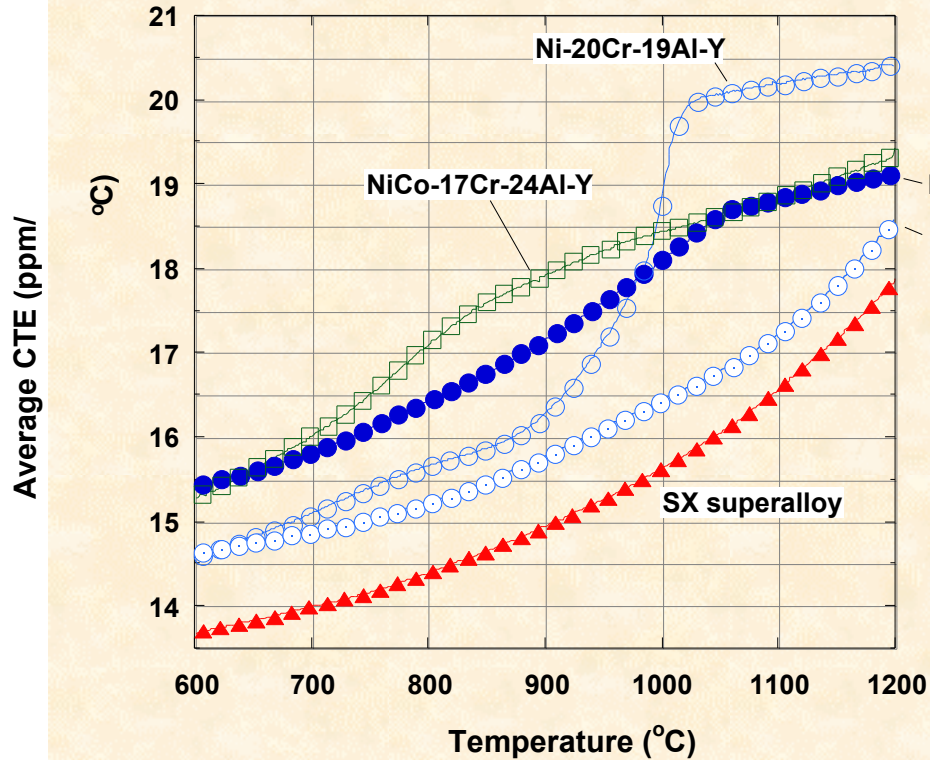


Haynes, et al., 2001

- The CTE difference generates stress in the BC at temperature, which could cause deformation

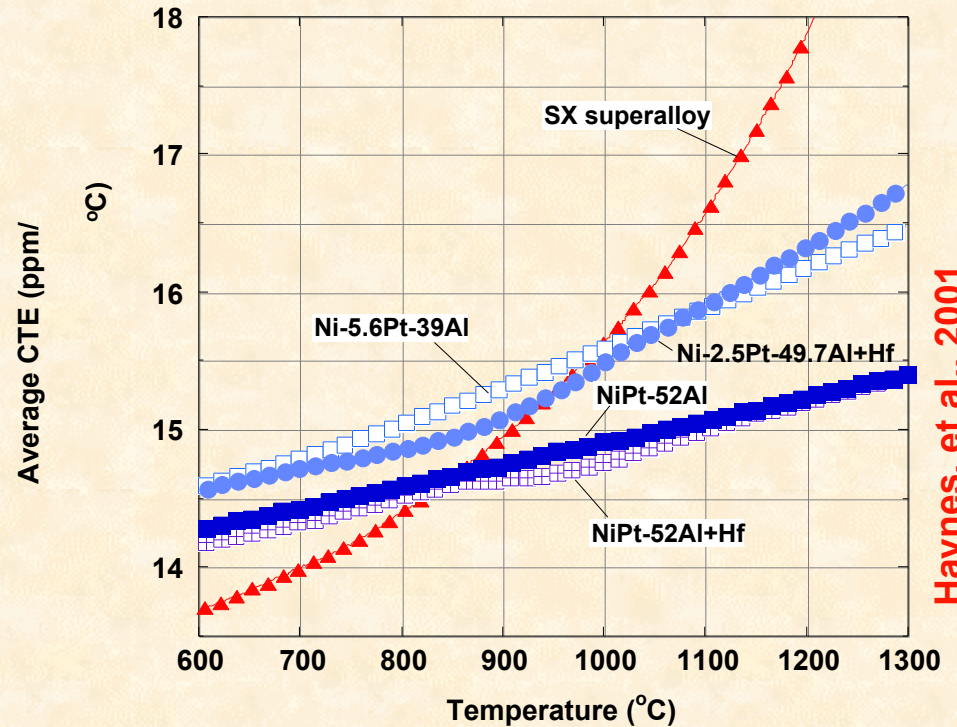


# Comparison of CTE of Bond Coating Alloys



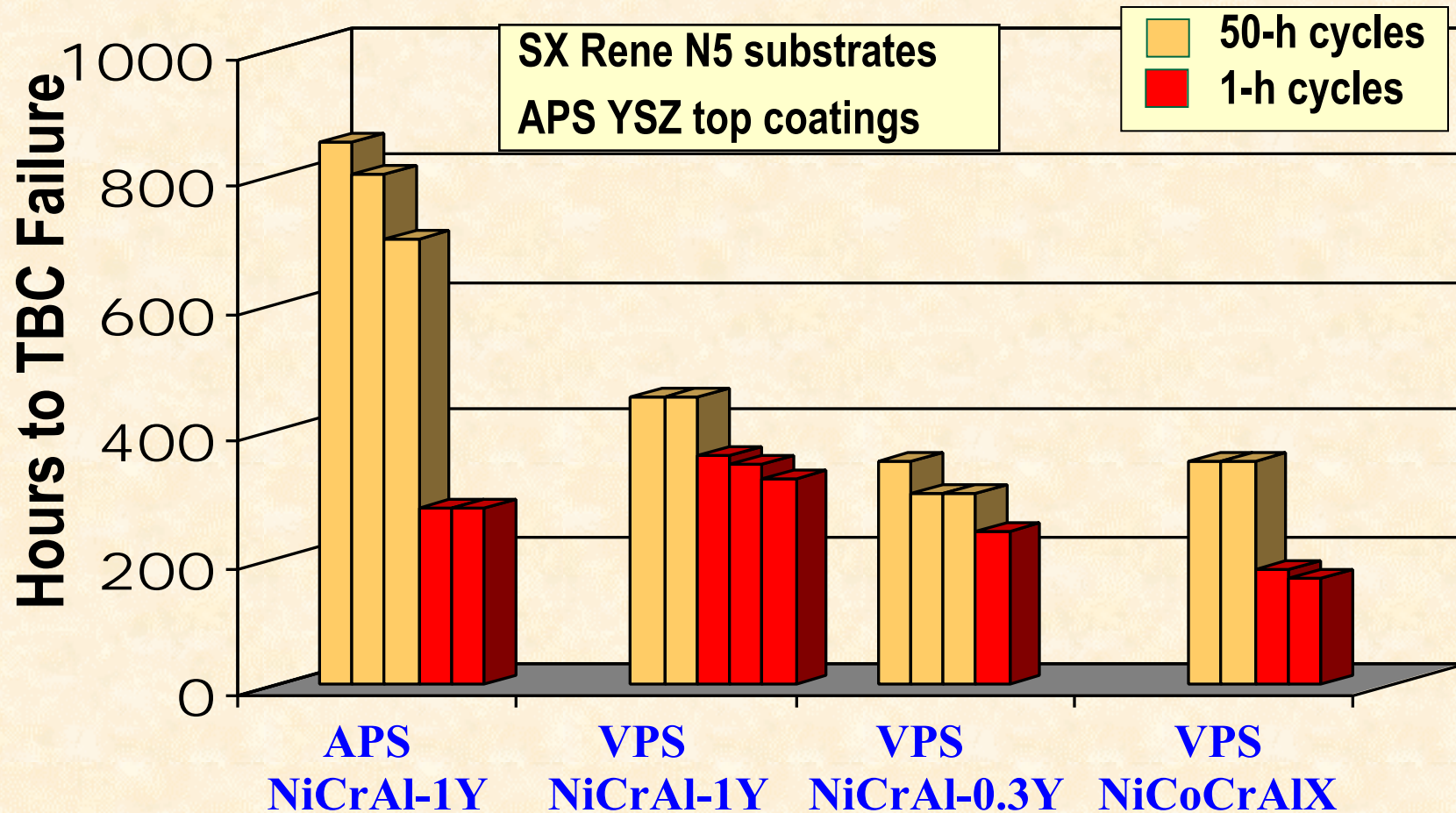
MCrAlYs: CTE > SC Superalloy

(Ni,Pt)Als: CTE < SC superalloy at 850/1000°C



Haynes, et al., 2001

# TBC Lifetimes: 1-h & 50-h cycles (1150°C)

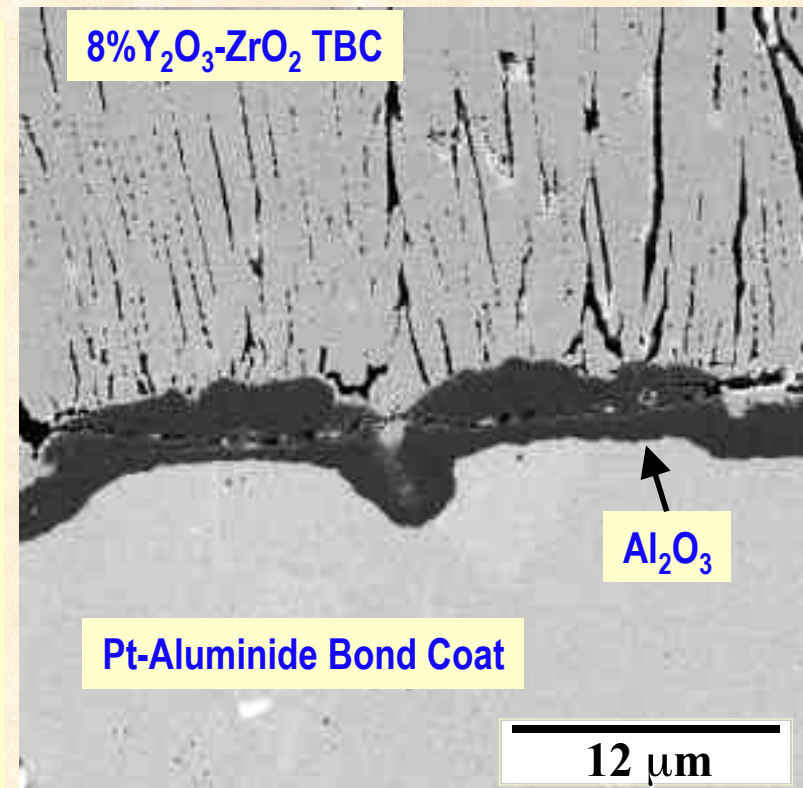
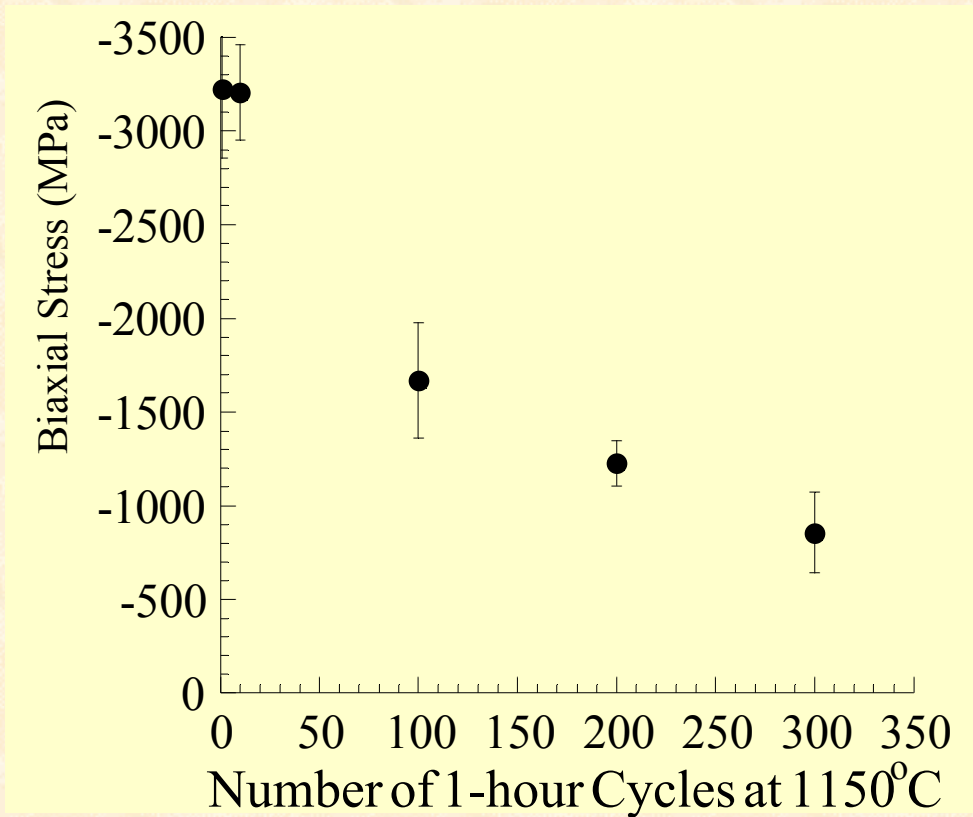


- For PS TBCs: lifetimes longer for longer cycles
- Suggests MCrAlX CTE more dominant than oxidation-related factors?

# For EB-PVD/aluminide BC, stress in oxide decreases with thermal cycling

Thermal Cycling at 1150°C

100 1-hr Cycles at 1150°C



Lance, et al., 2000

- The Al<sub>2</sub>O<sub>3</sub> compressive stress gradually decreases during thermal cycling due to interface roughening and scale cracking

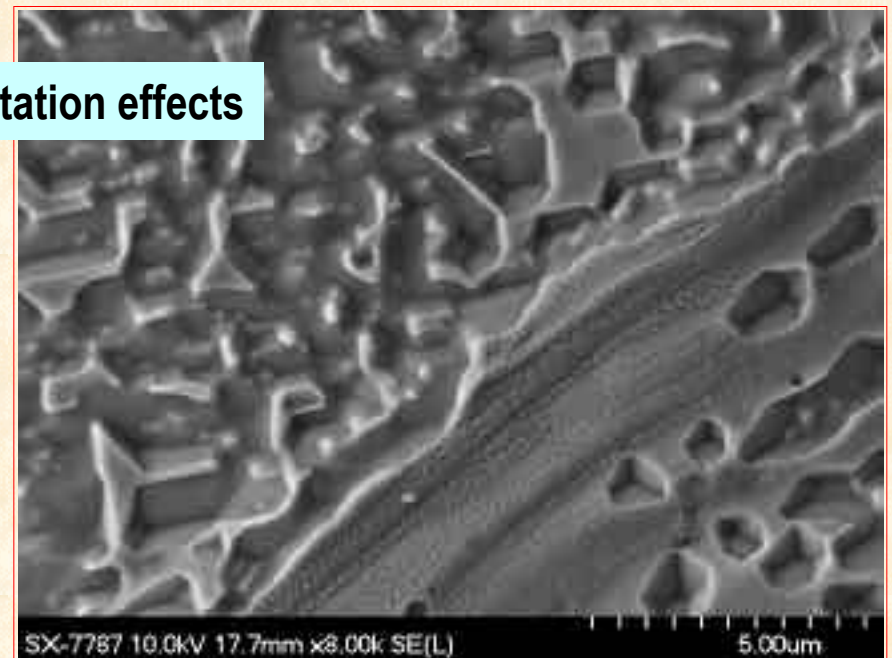
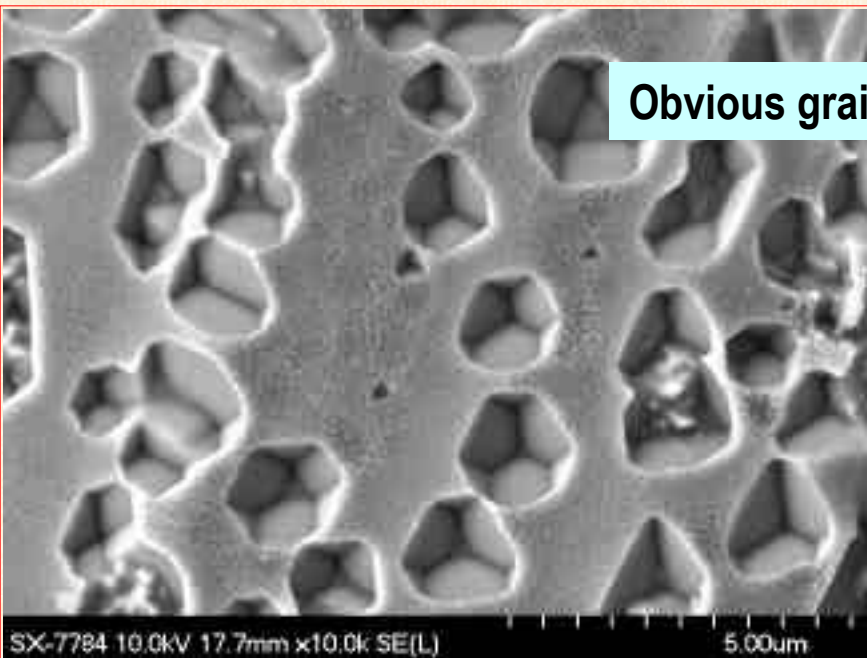
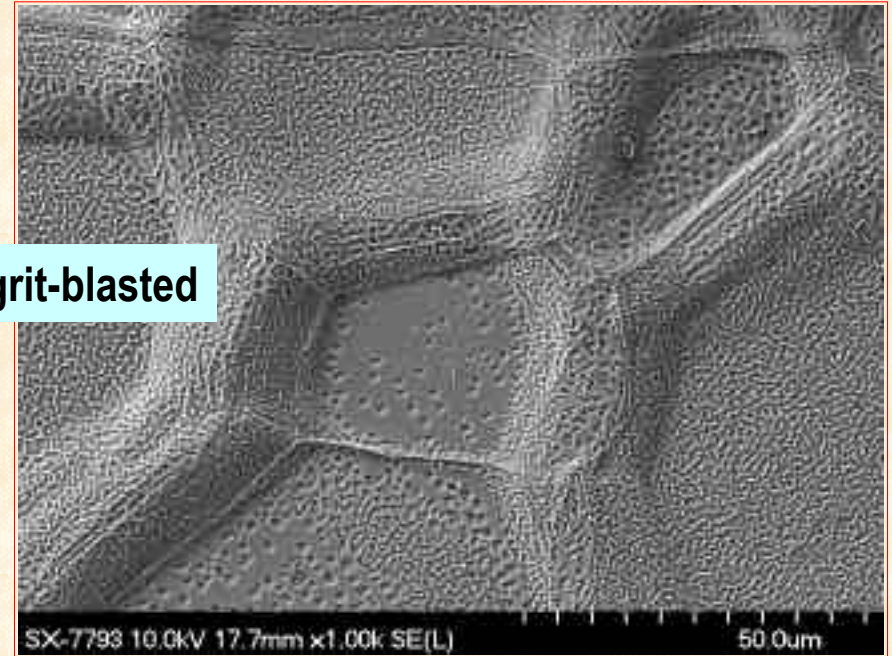
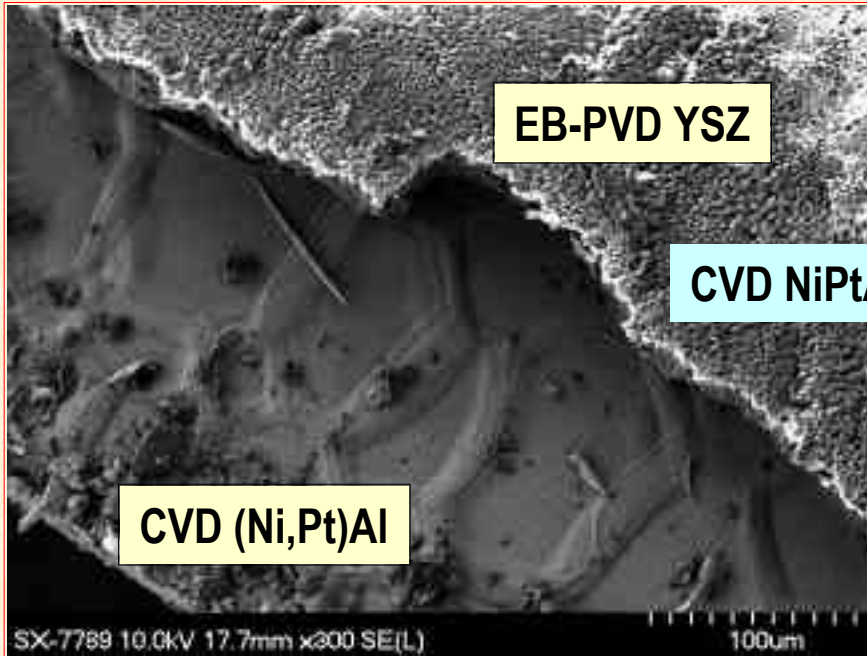
# Condition Monitoring

- IR imaging (Siemens Westinghouse; ORNL)
  - hot spots/debonding
- Laser flash (ANL)
  - oxide-BC interface roughness
  - thermal properties
- PSLS (UCSB; UConn; Howmet; ORNL; NPL and Imperial College, UK; Universita' di Trieste, Italy)
  - stress levels in BC oxide layer
  - phase content of oxide
- Eddy current techniques (Jentek; EPRI; Structural Analysis Assoc.)
  - BC Al content change with time
- EIS (U. Central Florida)
  - debonding

# Summary

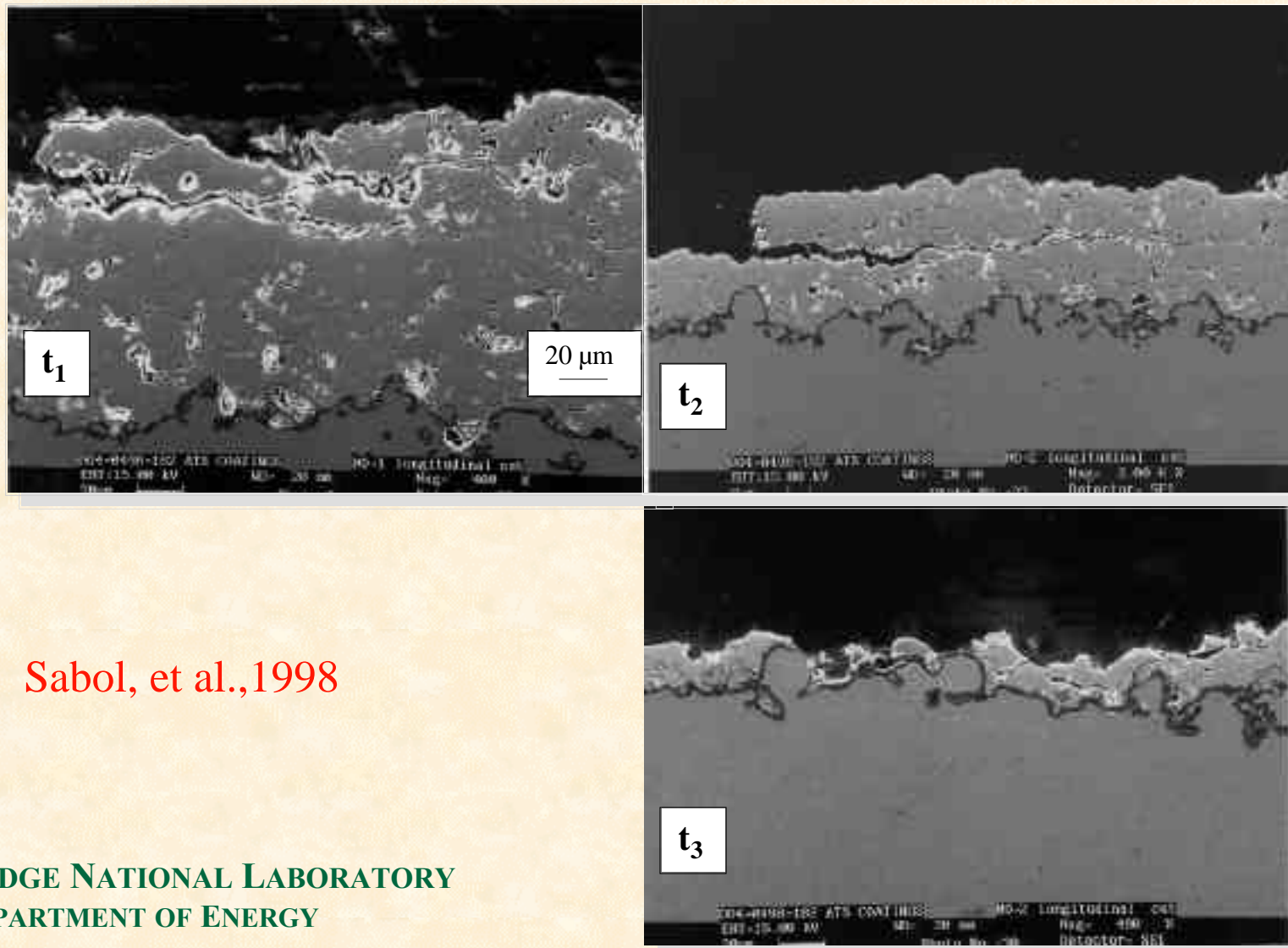
- **Many variables contribute to the performance of TBCs**
  - application route for ceramic: APS vs EB-PVD
  - bond coating composition; structure; mode of application, surface finish
  - superalloy substrate composition and structure
  - vendor-to-vendor differences (processing parameters, e.g. surface preparation)
- **The factors to be addressed to optimize TBC performance depend on the mode of degradation, *i.e.*, are *system-specific***
- **Need to understand the processes involved in TBC degradation in order to identify the factors that have the largest contributions**

# Voids in As-Deposited (Ni,Pt)Al Surfaces After EB-PVD Processing



Haynes, et al., 2001

# Progressive failure of an APS TBC in a high thermal gradient cycling test



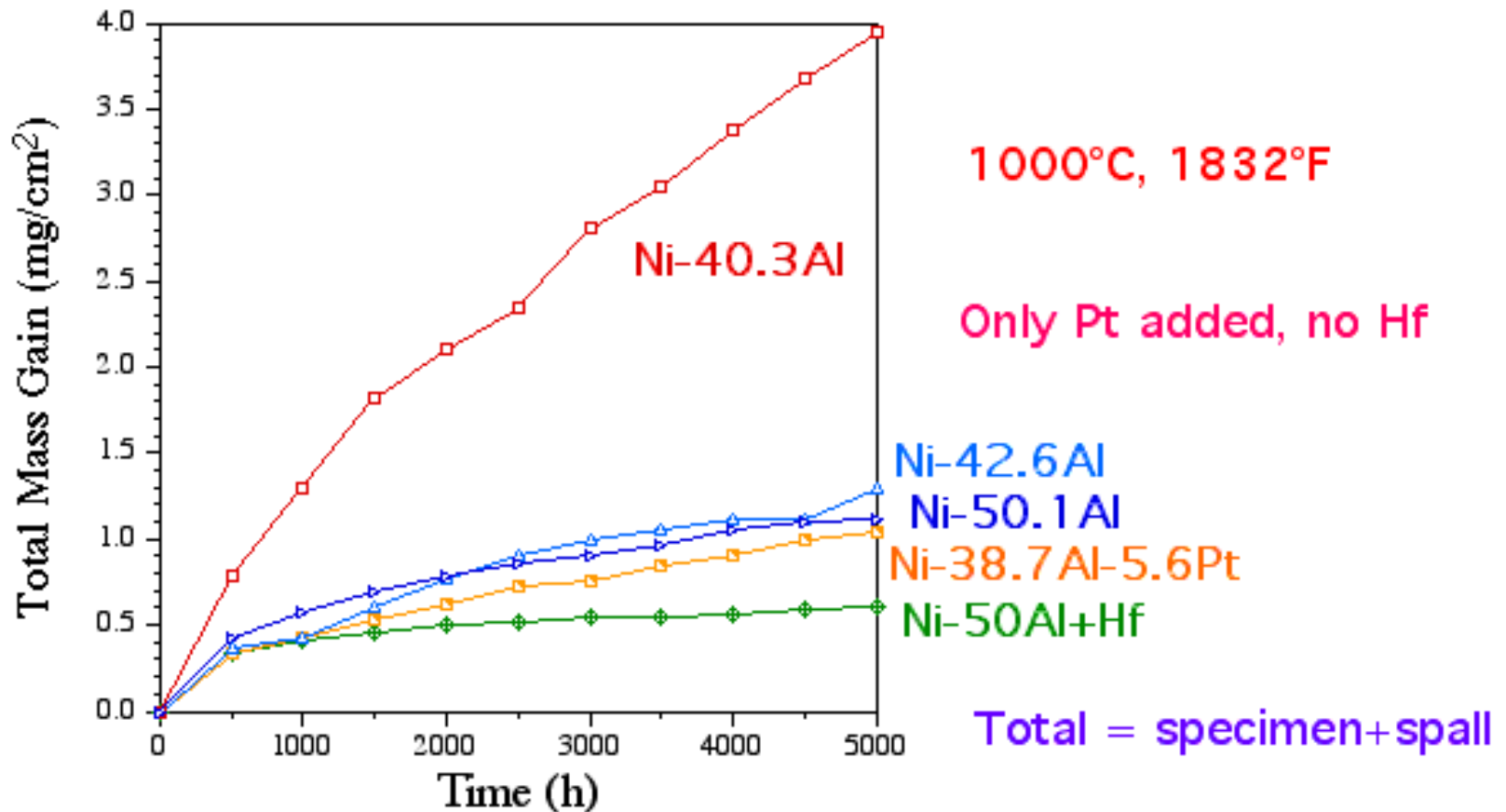
Sabol, et al., 1998

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TELLE

# Improved selective oxidation with Pt

Total Mass Gain during 500h cycles at 1000°C



NiAl+Hf - lower because of better adhesion and slower growth rate

Ni-42.6Al & Ni-50.1Al - undoped alumina growth + some spallation

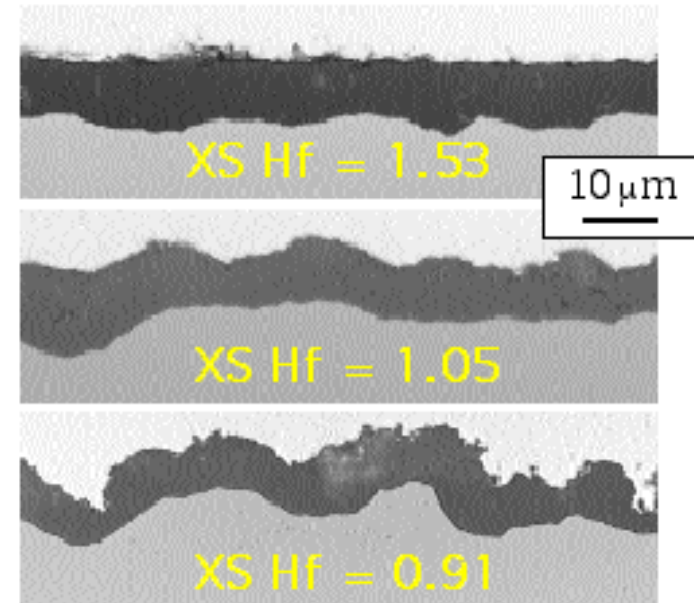
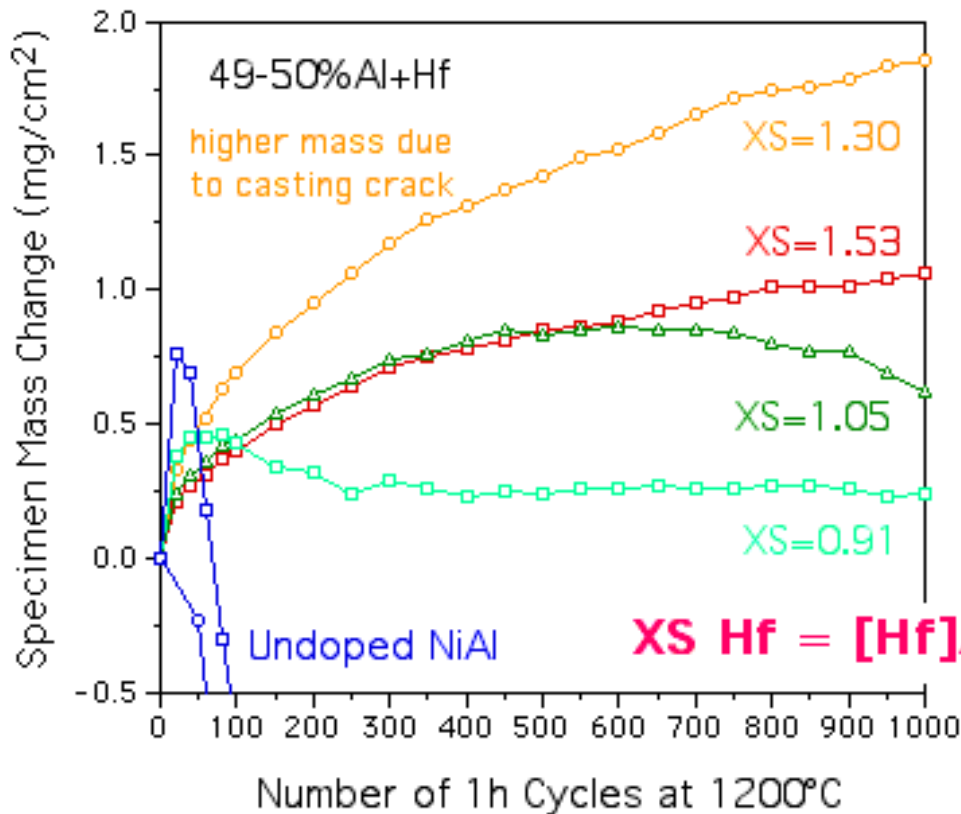
Ni-40.3Al - spinel formation increased total mass + some spallation

Ni-38.7Al-5.6Pt(20wt%) - better selective oxidation, i.e. no spallation



# Effects of C-Hf interactions on NiAl+Hf

testing in 1 h cycles at 1200°C



after 100h at 1200°C

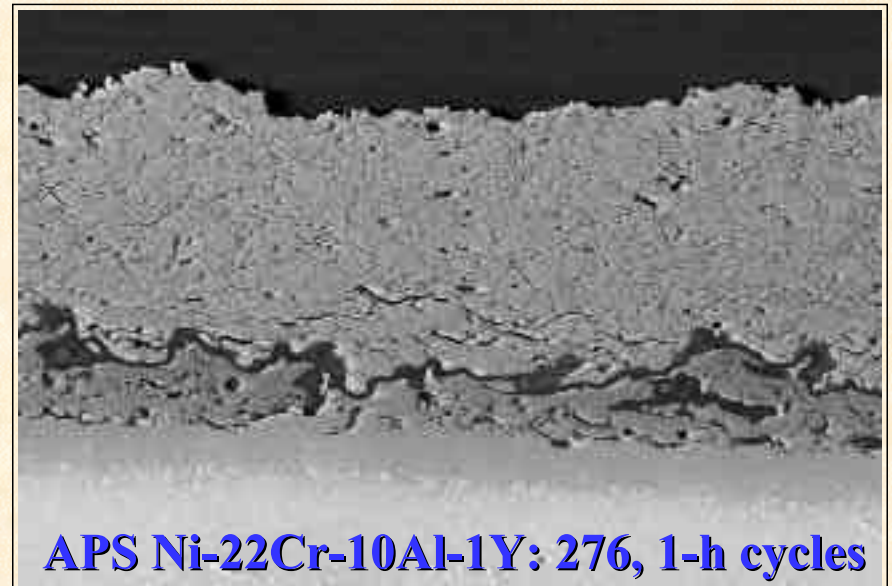
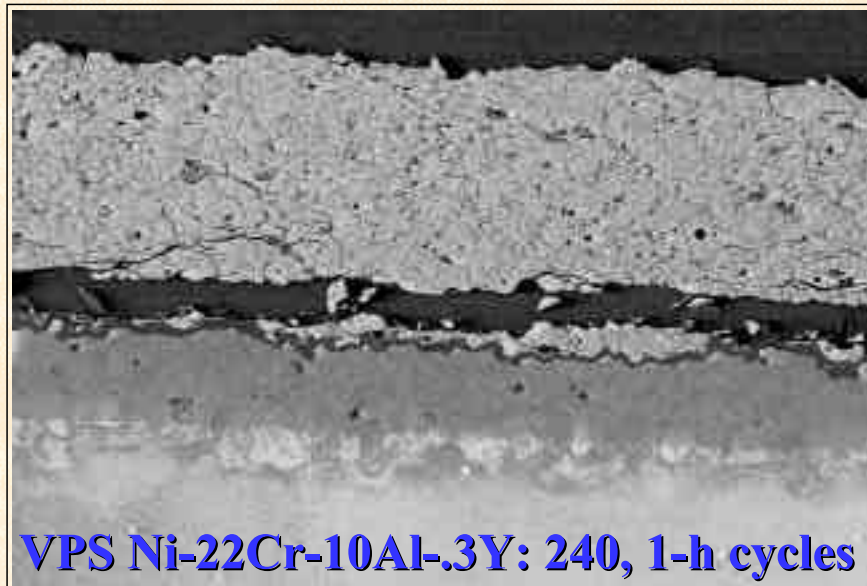
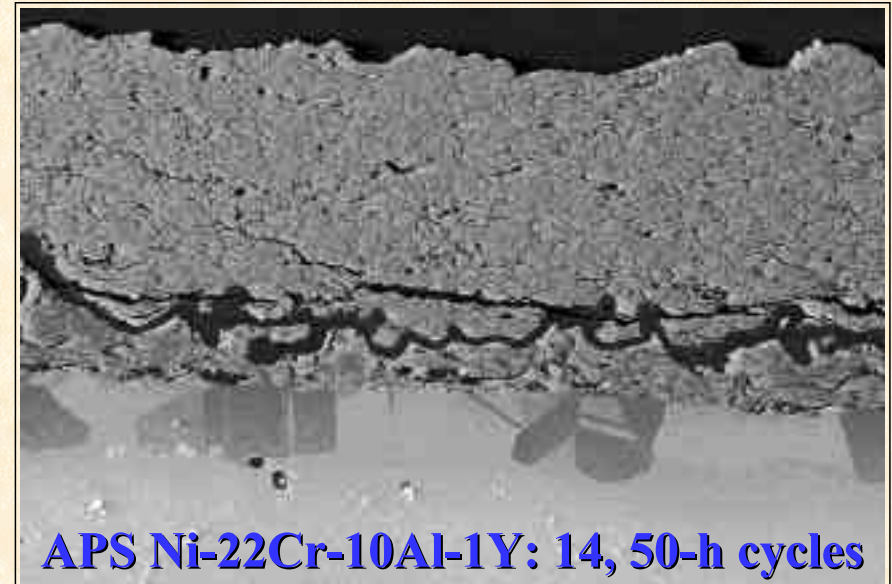
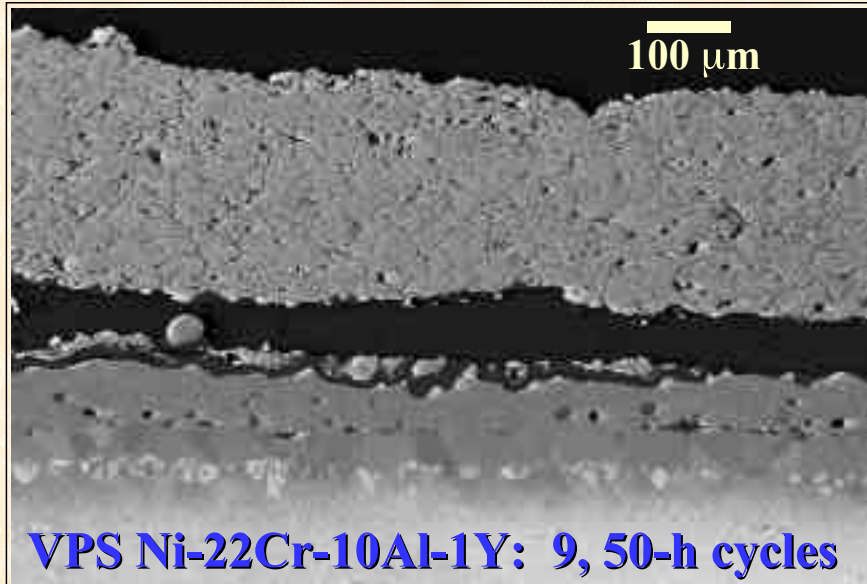
$$XS \text{ Hf} = \frac{[Hf]}{([C] + 0.5[O] + [N])}$$

Typically, [Hf] = 450-550ppma (plasma analysis)  
 [N] = <4ppma (LECO) [S] = <2ppma (by GDMS)  
 [O] = 20-30ppma (LECO)

XS varied by changing [C] -> making graphite additions to the casting

**Is XS Hf > 1 a critical parameter?**

# PS-TBC Microstructures at Failure

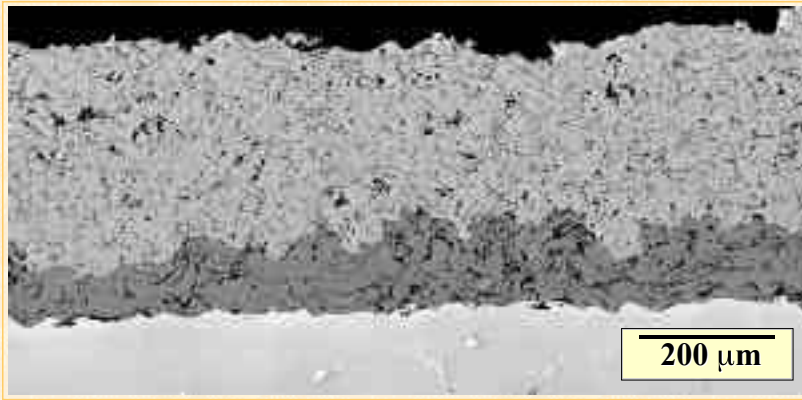


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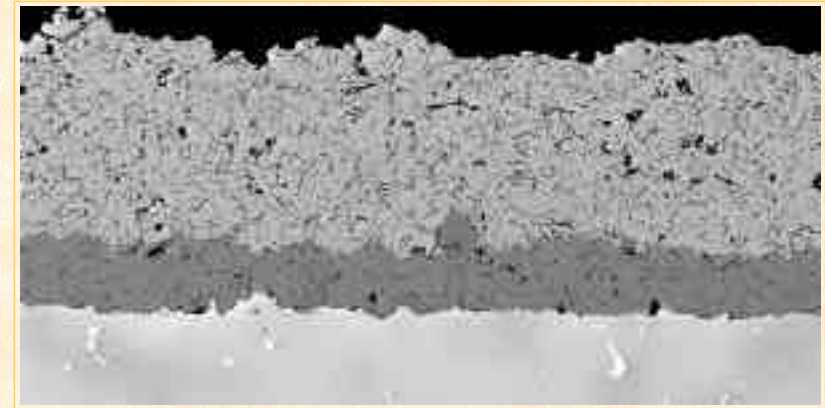


Haynes, et al., 2000

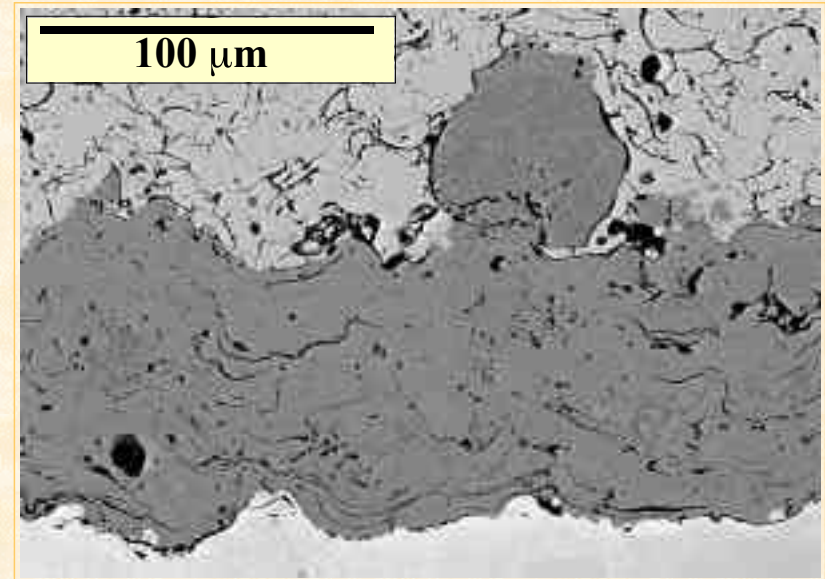
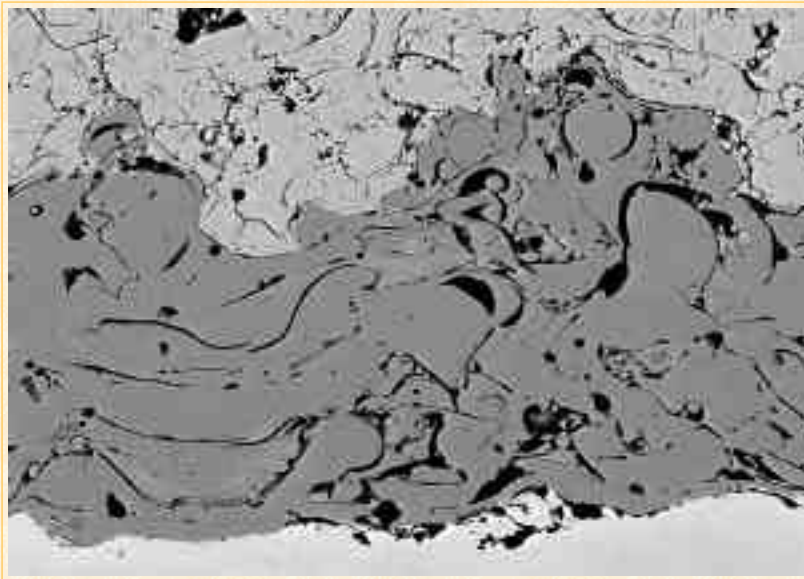
# As-Deposited TBC & BC Microstructures



**APS NiCrAlY on René N5**



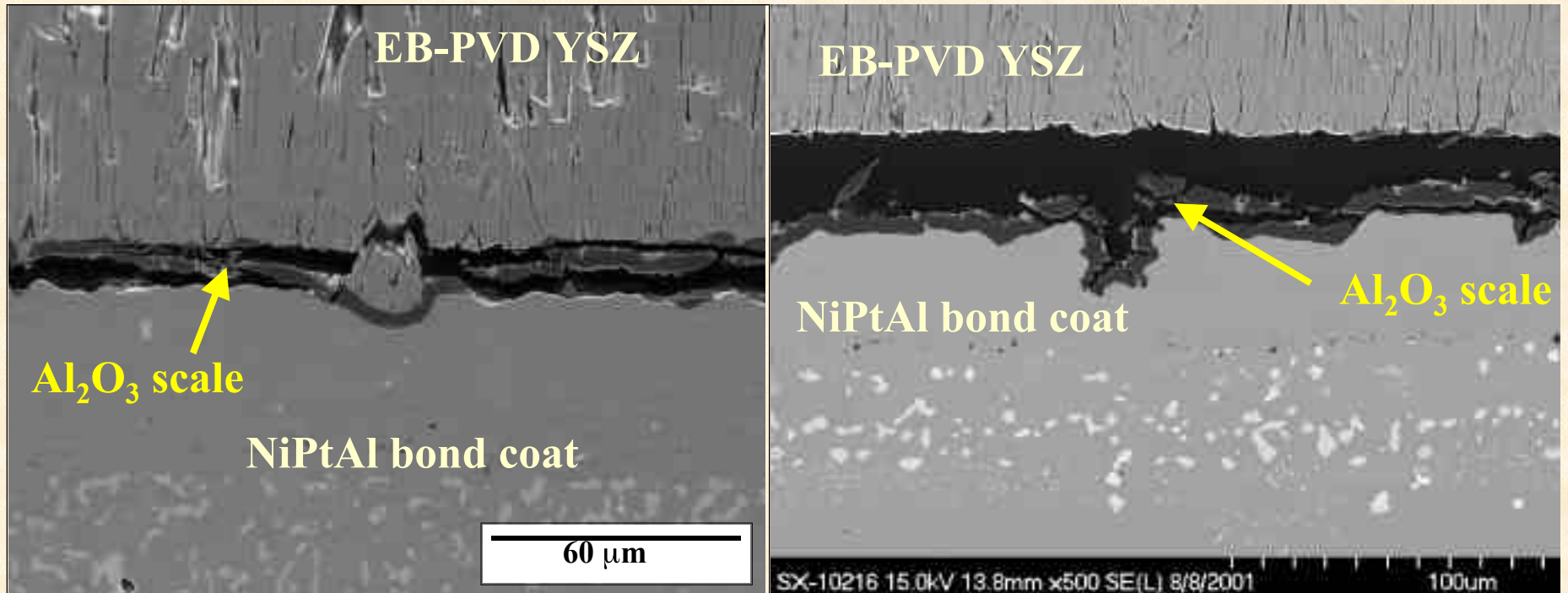
**VPS NiCoCrAlYHfSi on René N5**



Haynes, et al., 2000

**Conventional wisdom: VPS bond coats provide superior TBC lifetimes**

# EB-PVD Microstructures at Failure



Haynes, et al., 2001

- TBC failure mode = delamination and spallation of the Al<sub>2</sub>O<sub>3</sub> scale and/or the overlying YSZ top coating at or near the metal-ceramic interface.
- Interfacial degradation is associated with bond coat oxidation and, in some cases, surface deformation