

# Factors Affecting the Performance of Bond Coatings

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- Oak Ridge National Laboratory

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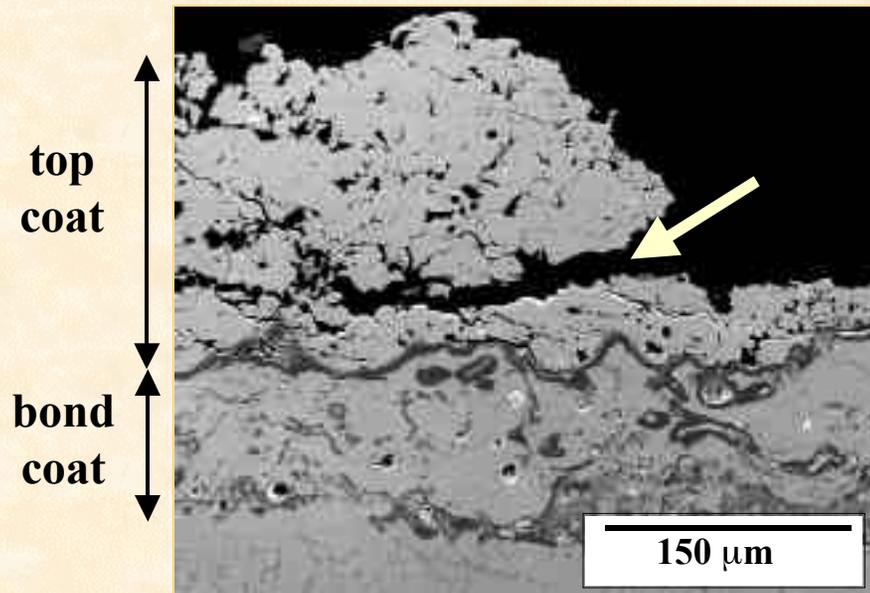
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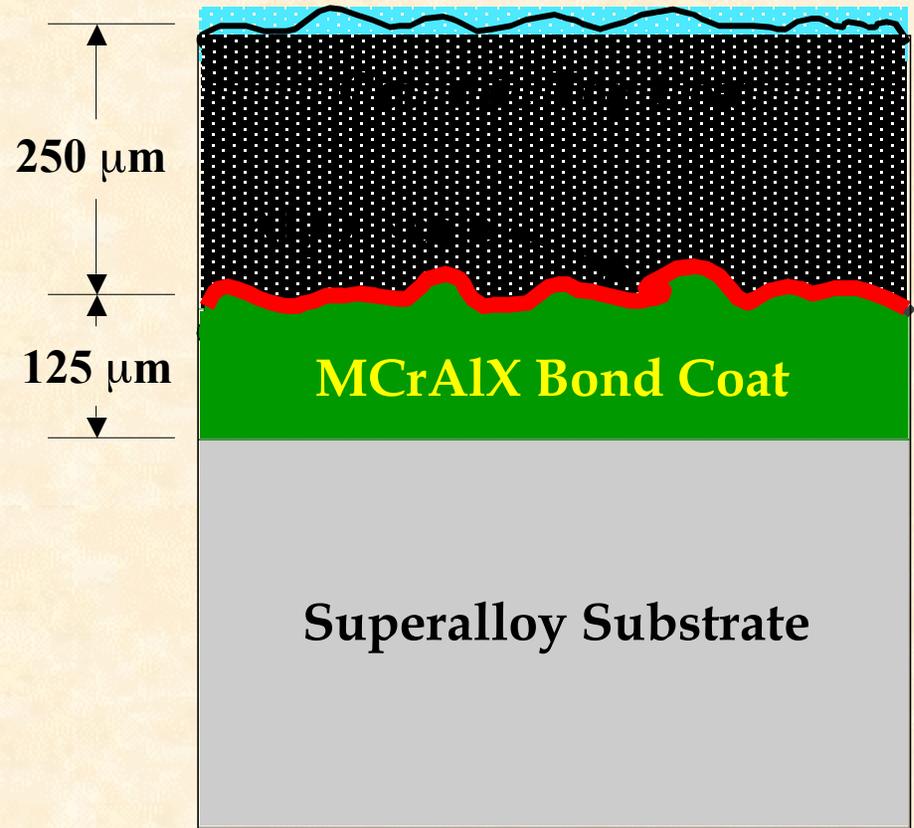
# Outline

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

# Plasma-Sprayed Thermal Barrier Coatings



Haynes, et al., 2000



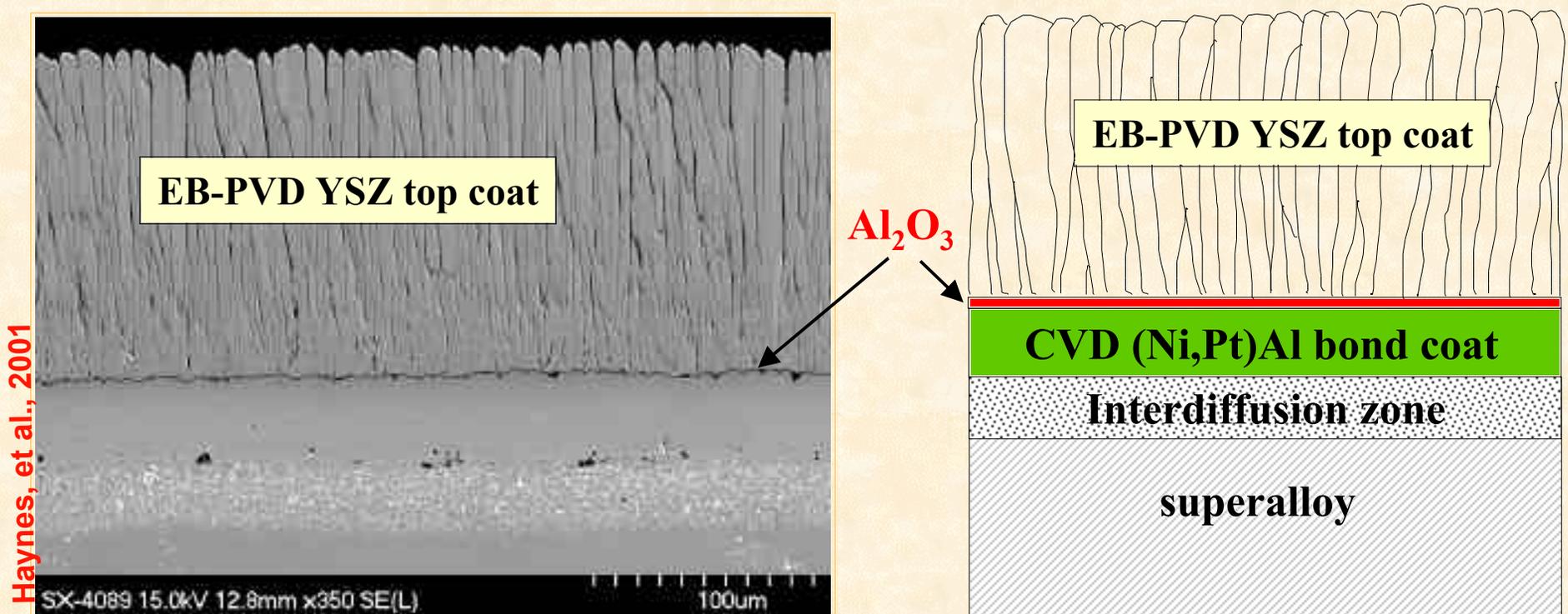
- $\text{Y}_2\text{O}_3\text{-ZrO}_2$  (YSZ) top coat
  - provides thermal insulation
- Metallic bond coat
  - provides oxidation resistance
  - facilitates YSZ adherence
- Interfacial  $\text{Al}_2\text{O}_3$  scale

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

APS = air plasma-spray

VPS = vacuum plasma-spray

# EB-PVD Thermal Barrier Coatings

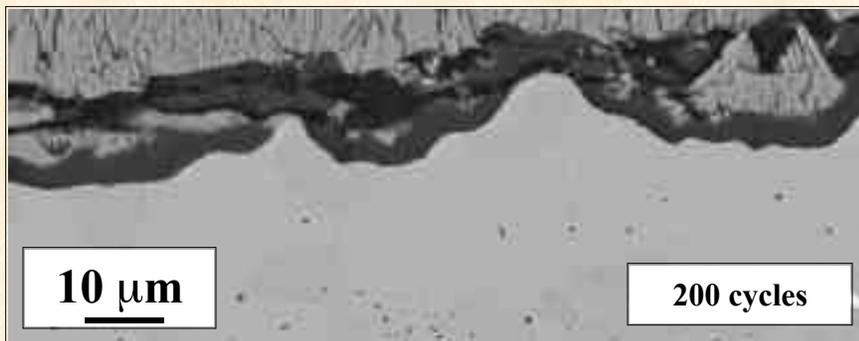
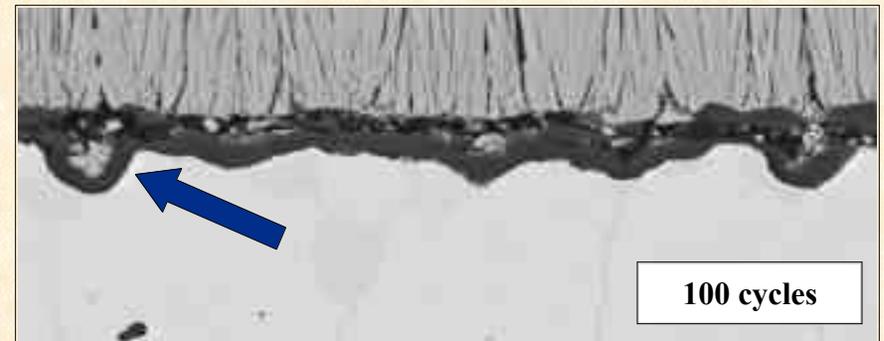
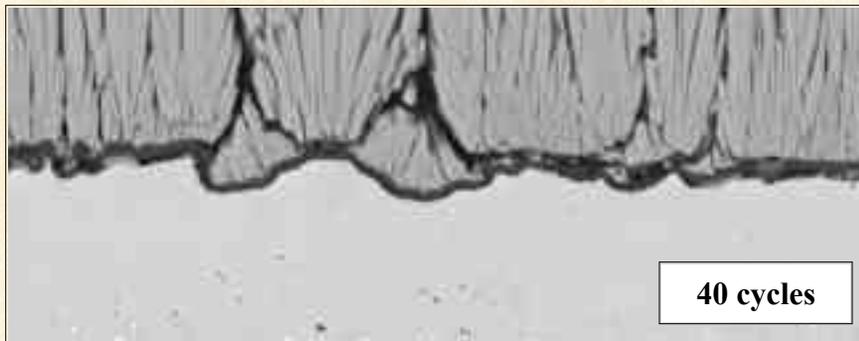
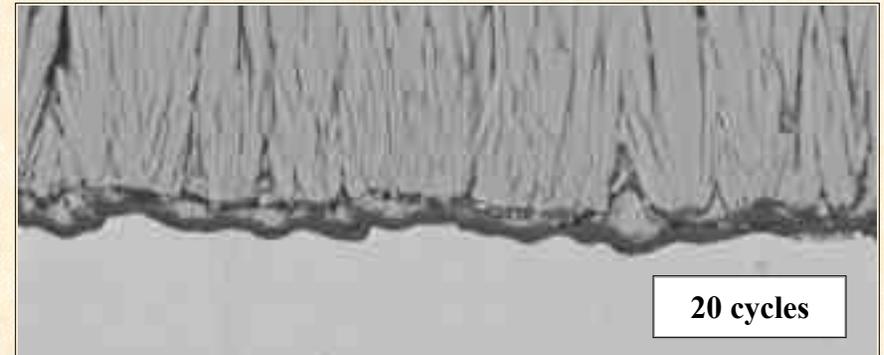
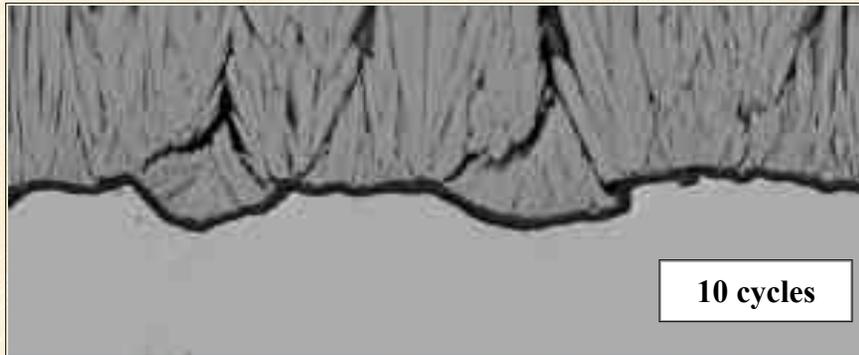


- Strain-tolerant ceramic top coating deposited by electron beam-physical vapor deposition (EB-PVD)
- Metallic bond coating of single-phase (Ni,Pt)Al produced by Pt electroplating + pack, or chemical vapor deposition (CVD) aluminizing

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



Haynes et al., 2001

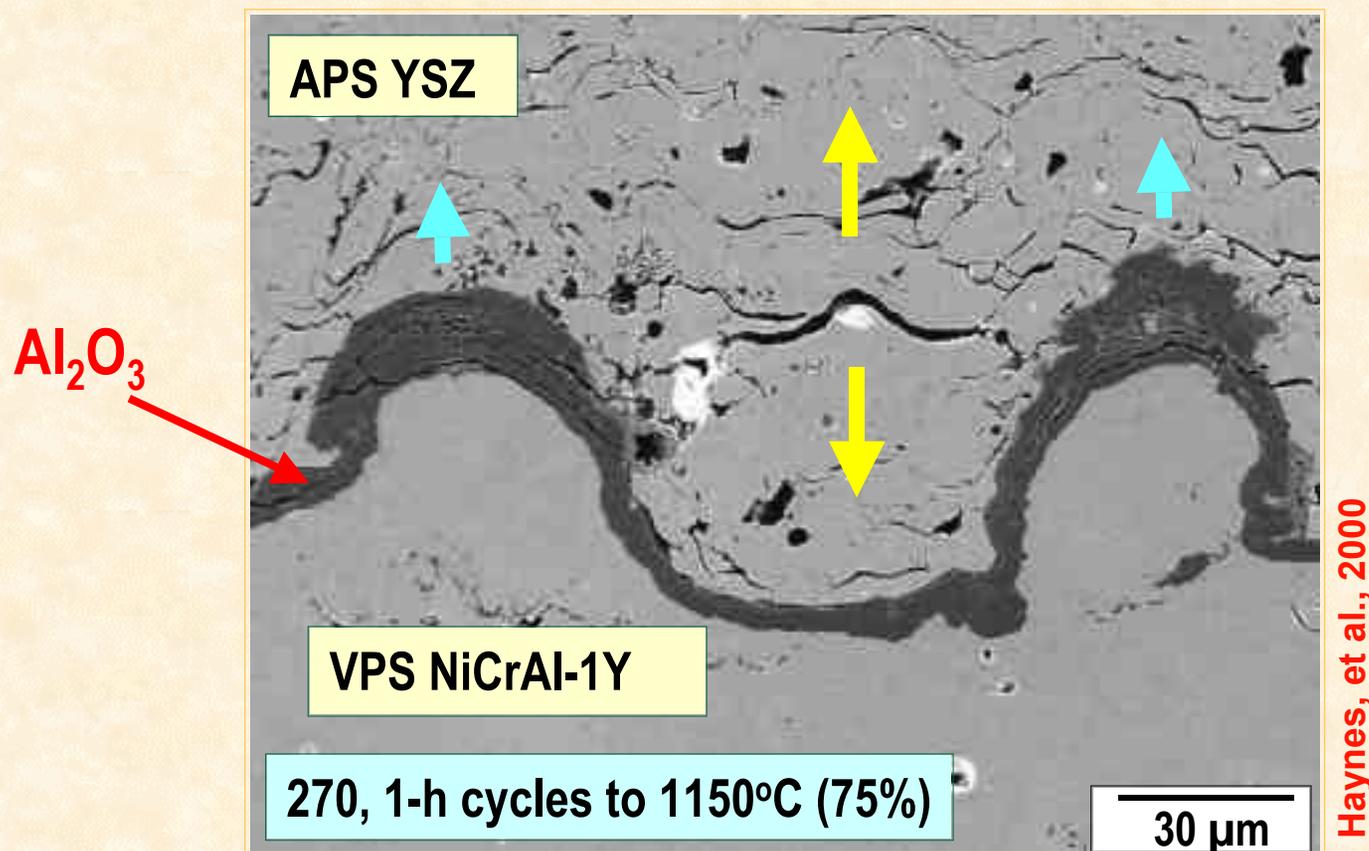
# Major TBC Life-Determining Issues

- **TBC application:** ability to apply the specified coating (composition, thickness, structure)
- **Operating temperature:** TBC must provide the design T at design conditions
- **Cyclic operation:** effects on oxidation behavior/coating durability
- **Loss of ceramic:** especially erosion/FOD: local T increase
- **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
  - effect of  $t$  at  $T$
- **Microstructure and thickness**
  - complexity of shape  $\pm$  determines processing route
- **Cost**
  - low infant mortality

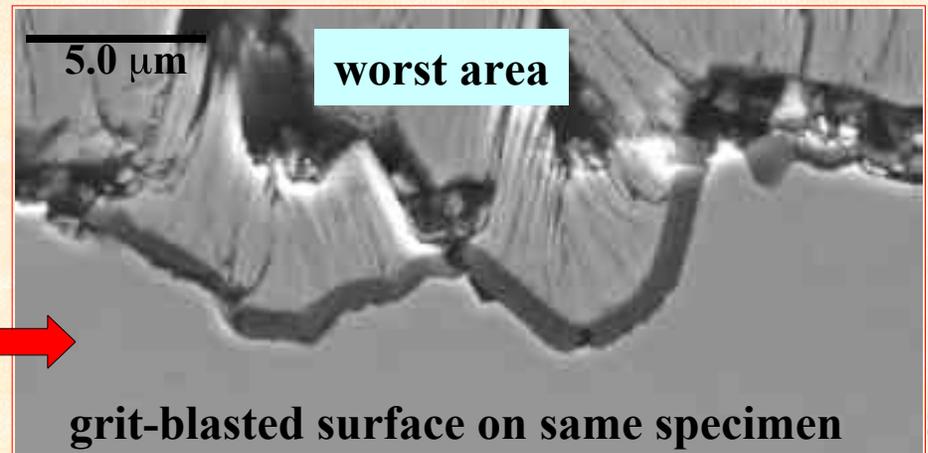
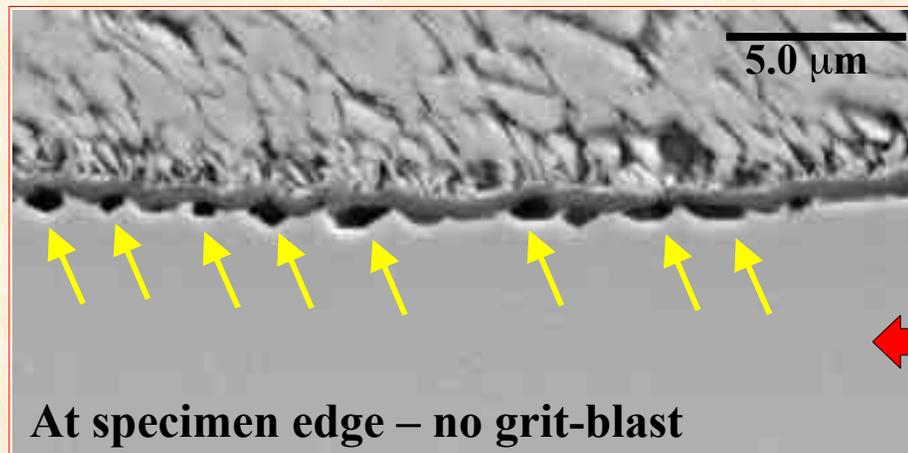
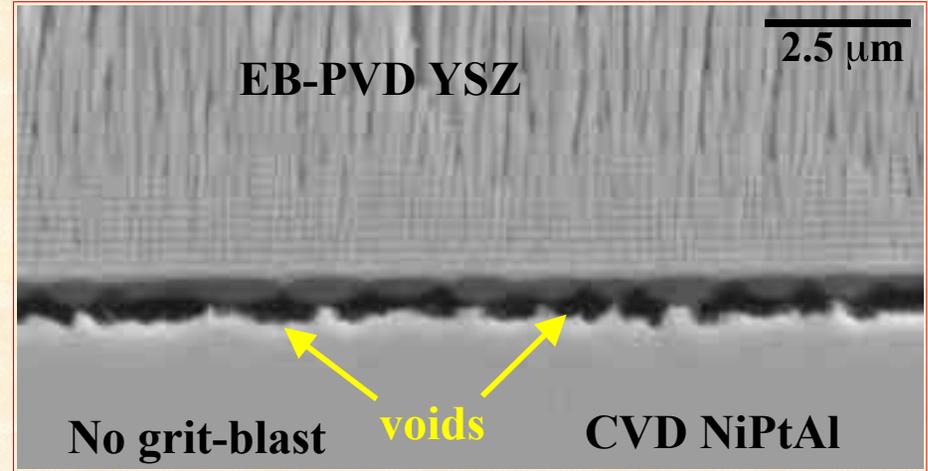
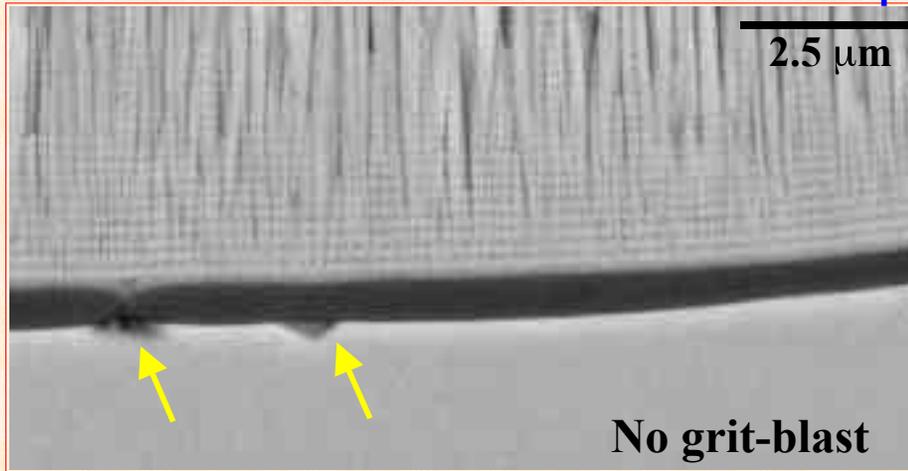
# Rough BC surface is an intrinsic feature & problem of PS TBCs



- Evidence of localized oxidation-induced YSZ damage
- Localized Al<sub>2</sub>O<sub>3</sub> scale damage very variable—not clear whether it is 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

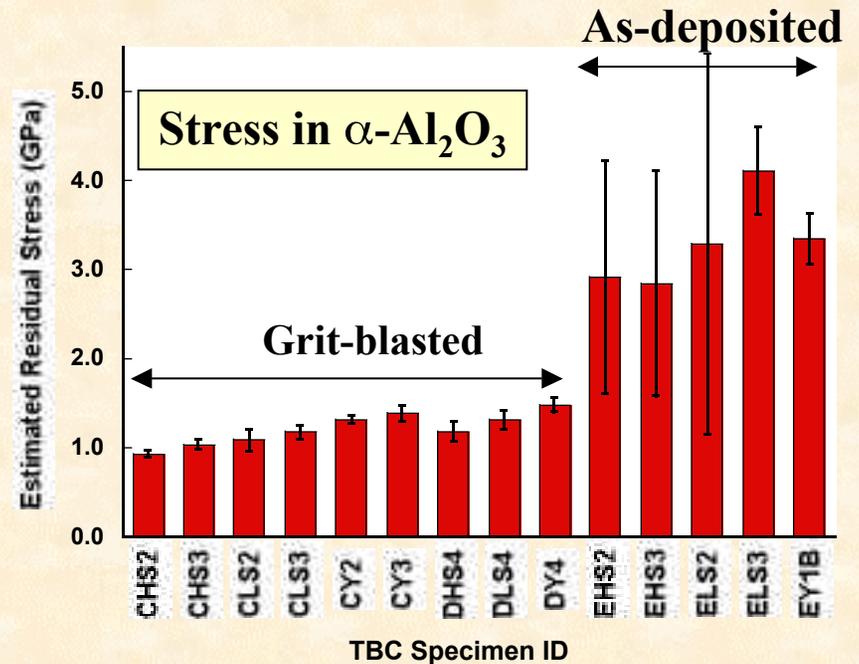
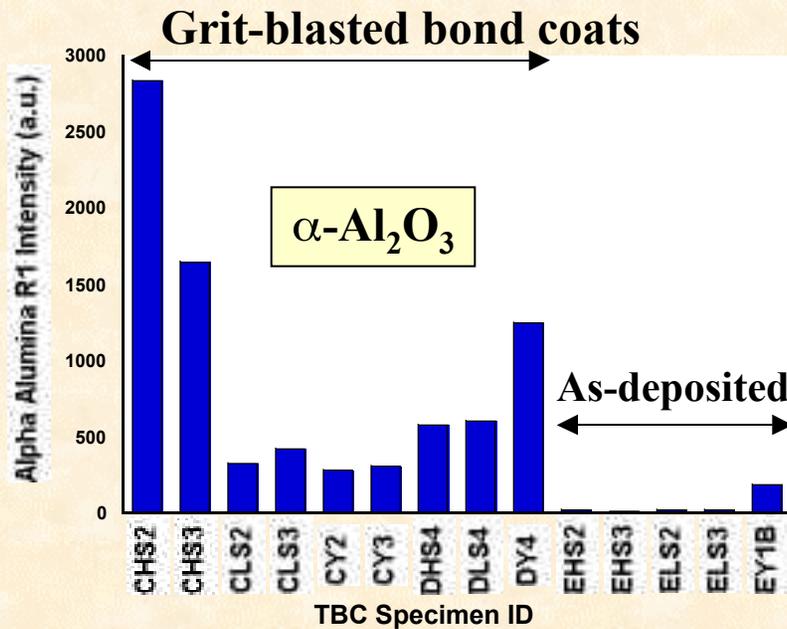
As-deposited TBCs



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

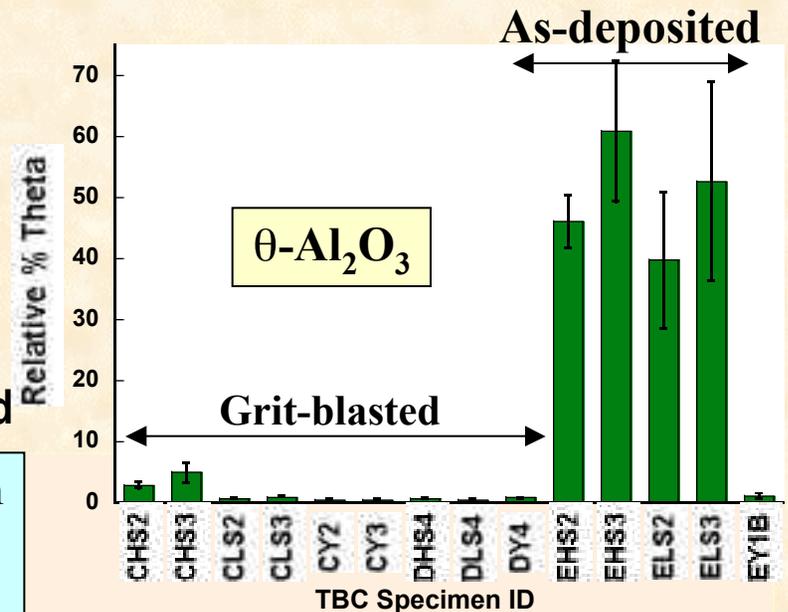


## Laser fluorescence of as-deposited EB-PVD TBCs

- 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

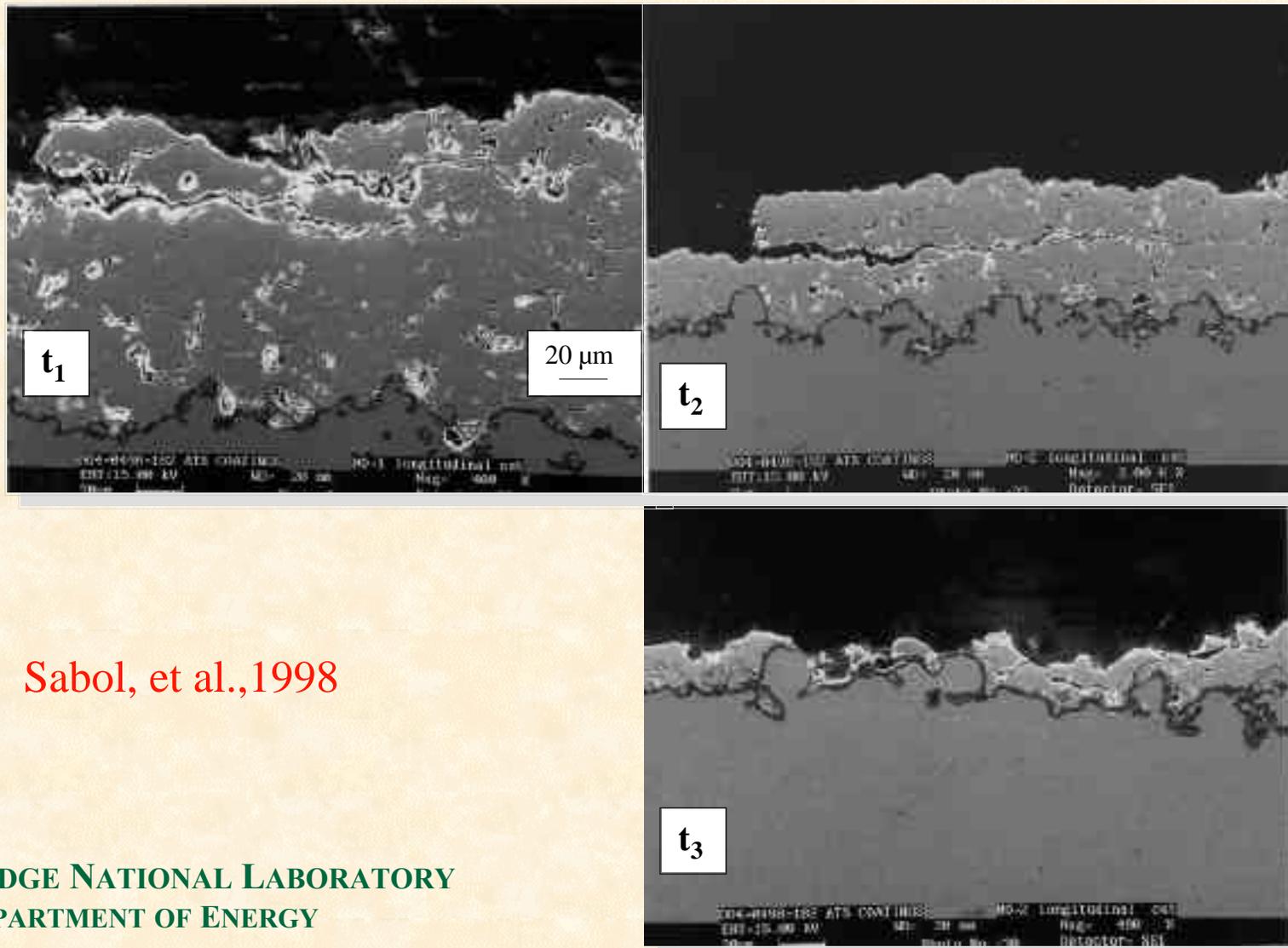


# Operating Temperature Issues

Concerned with the effects of time at temperature:

- Effects on the ceramic layer
  - phase change of YSZ
  - sintering of ceramic surface
    - can it occur?
    - 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

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



Sabol, et al., 1998

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# Operating Temperature Issues

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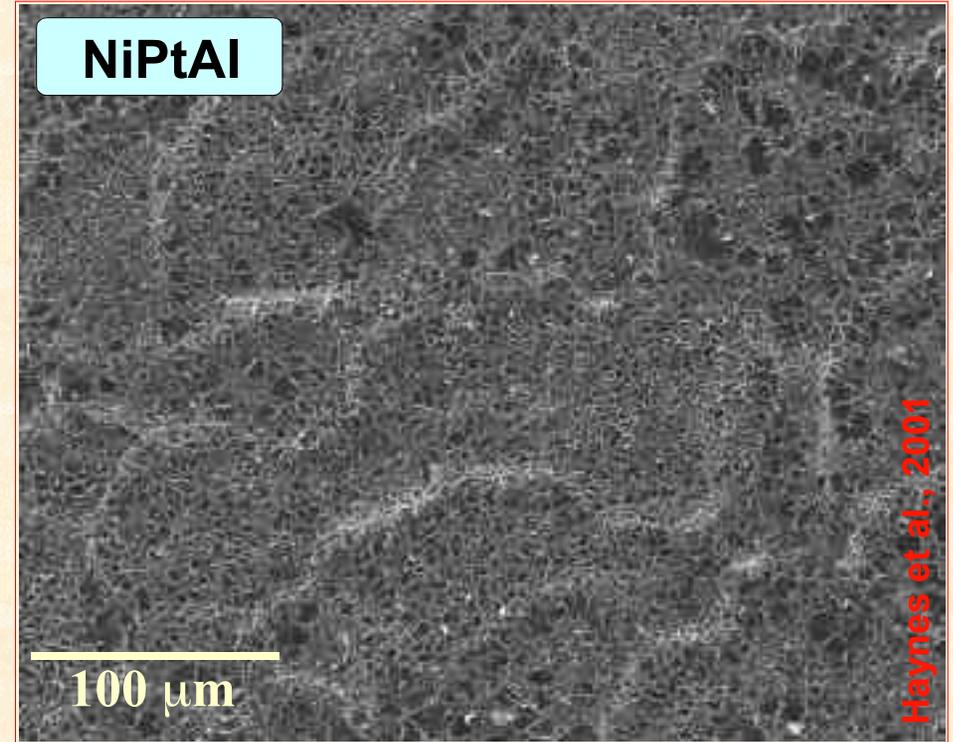
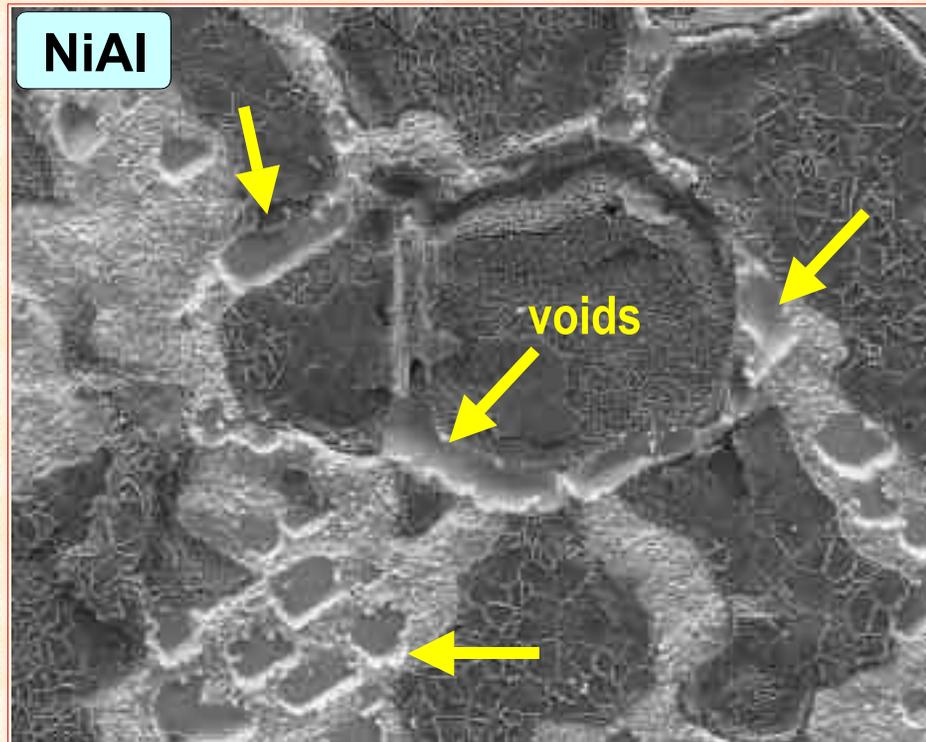
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# Factors Affecting BC Oxide Thickness

- 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 (control of initial oxidation stages; Pt effects)*
  - *controlled addition of a reactive element (Y, Hf, ...)*
    - MCrAlYs
    - aluminides
- Resistance to scale spallation can be improved by:
  - *removal of alloy/BC tramp S to  $\ll 1$  ppm*
  - *Pt additions*
  - *RE additions*
  - *reducing the CTE mismatch*

'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**

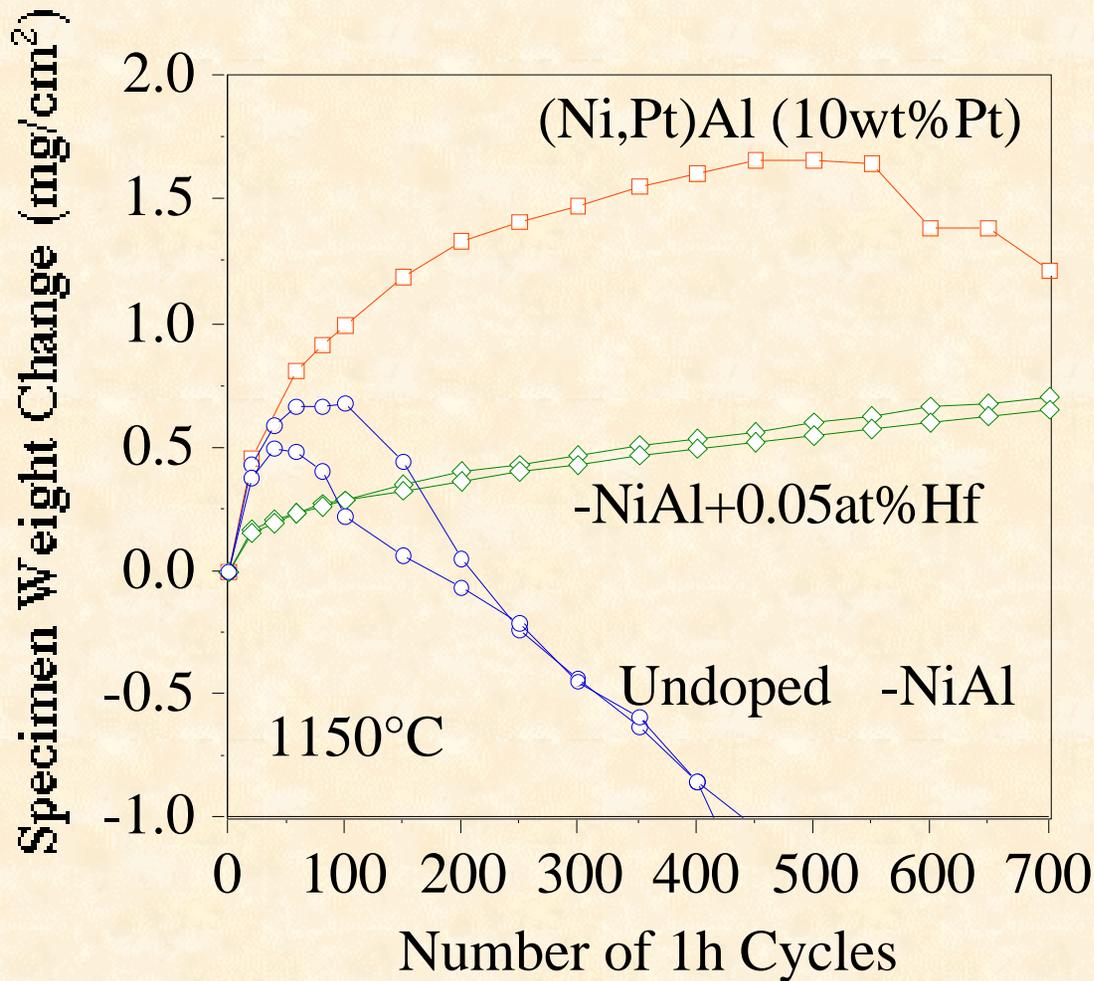
**NiPtAl on High-S Rene N5**

- 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.

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

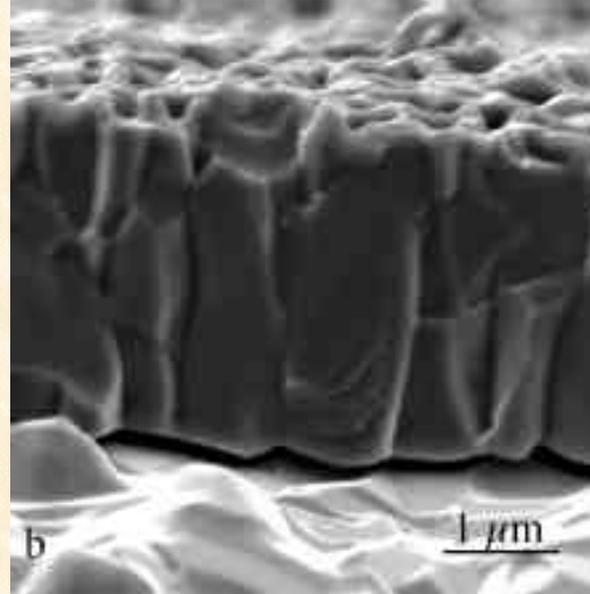
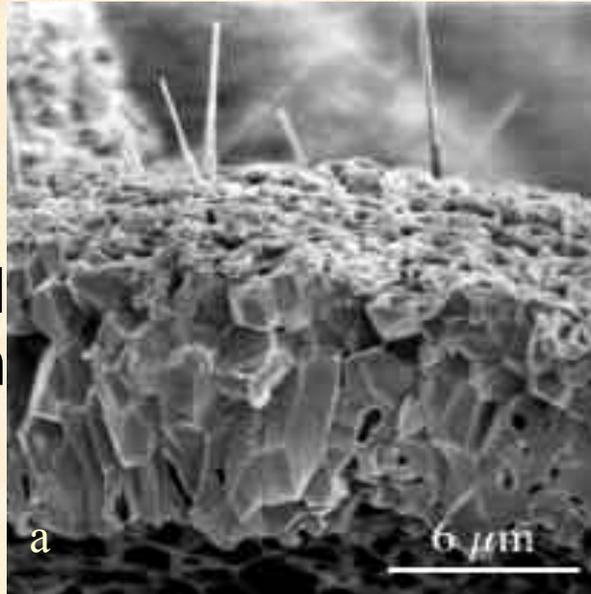


- *Undoped:*—rapid scale spallation
- *Pt:* improved resistance to spallation...for a time
- *RE-doping:*—lower scale growth rate + greatly improved spallation resistance

(Pint, et al., 1998)

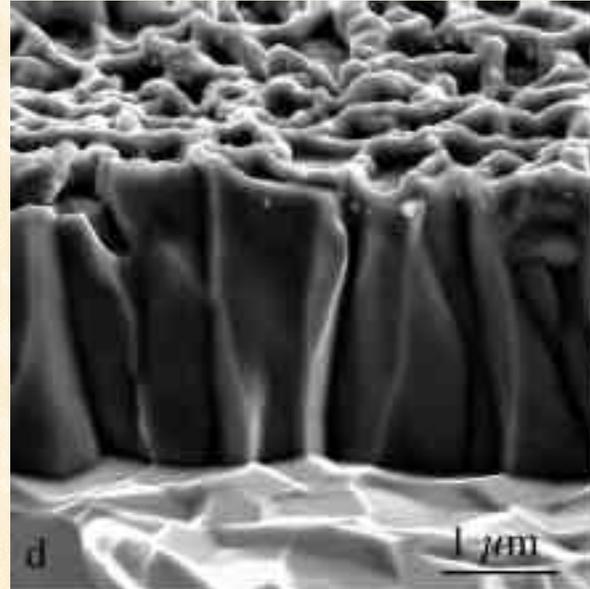
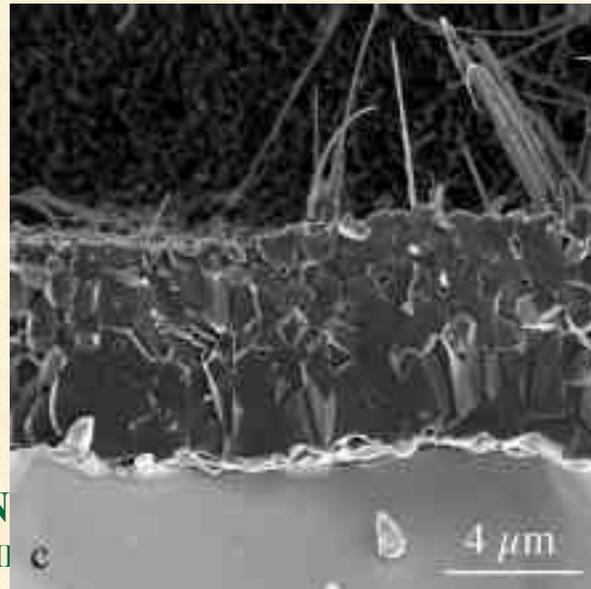
# RE additions modify scale morphology and reduce growth rate; Pt does not (1200°C)

Undoped NiAl, 200h



NiAl+Hf, 100h

PtAl, 100h



NiPtAl+Hf, 100h

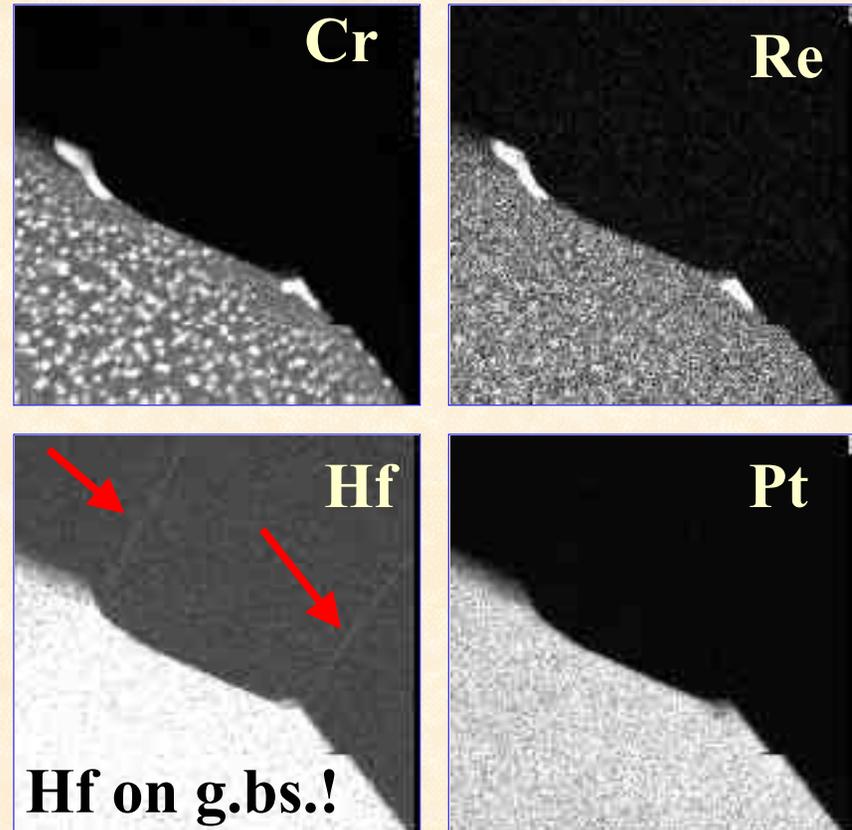
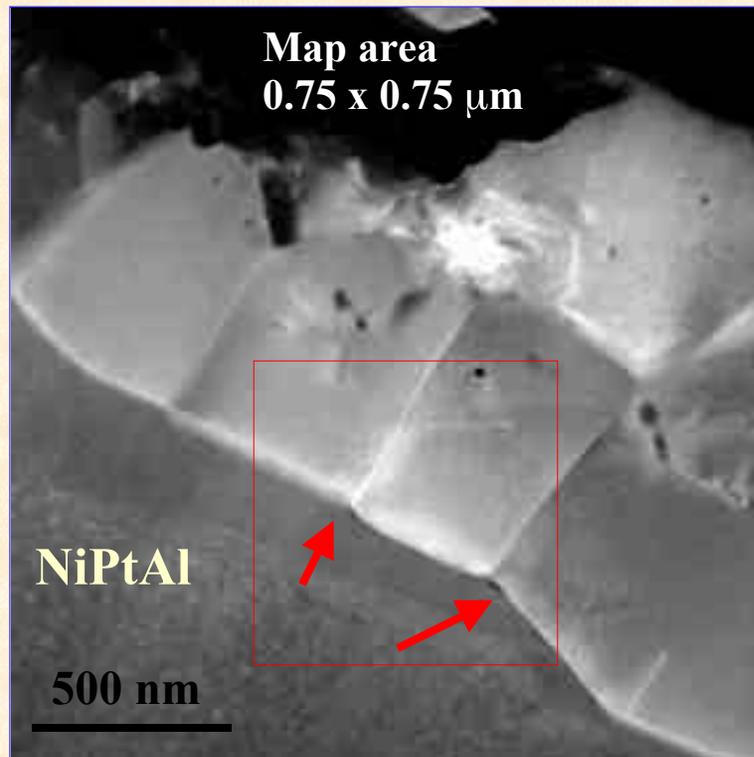
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Pint et al., 1998



# STEM/EDS Mapping of Alumina Scales on (NiPt)Al

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



More, et al., 2001

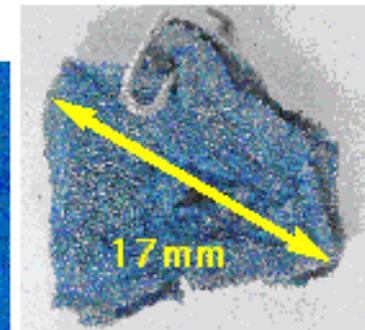
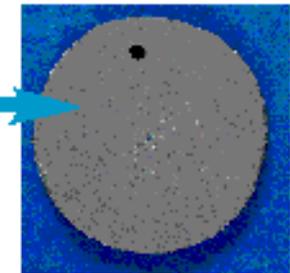
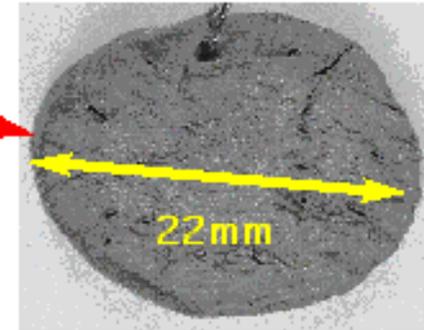
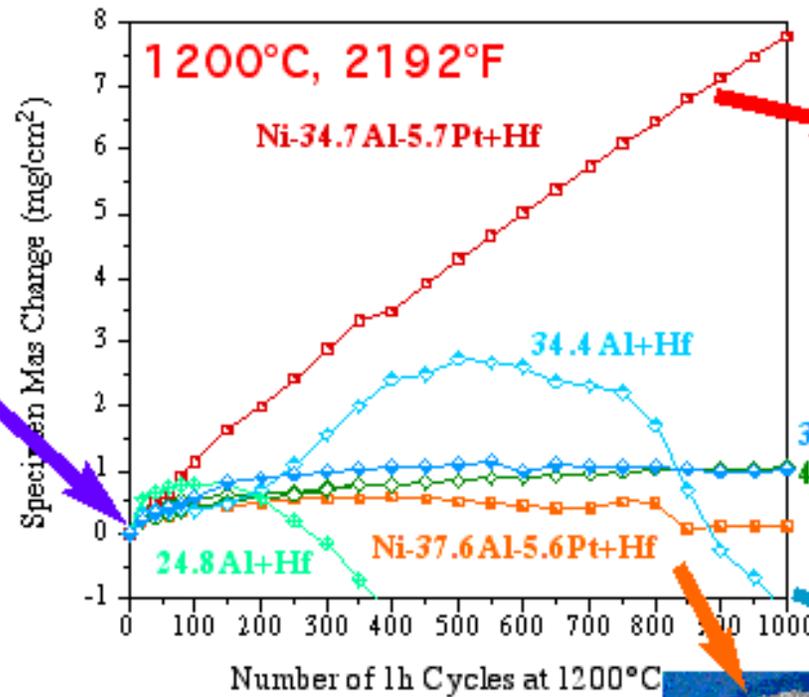
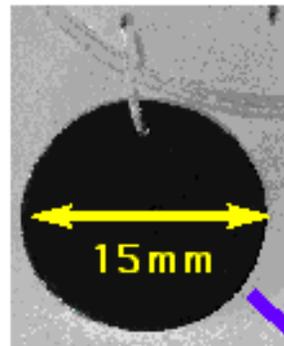
- Hf from the Rene N5 substrate was detected on the columnar oxide grain boundaries of NiPtAl, but not in the equiaxed outer grains.
- No Hf was detected on oxide grain boundaries on NiAl.
- Apparently, Hf diffused more rapidly through NiPtAl than NiAl.

# BC-Superalloy Interdiffusion

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

# NiAl+Hf: critical effect of Al content

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

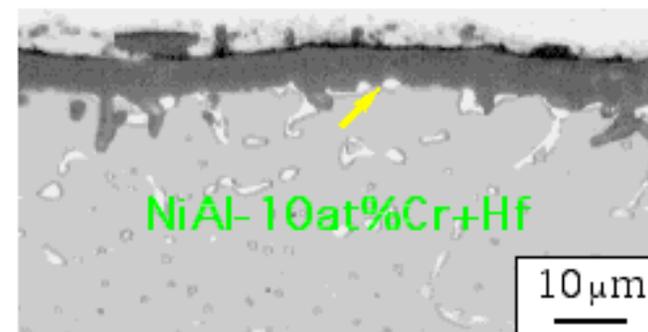
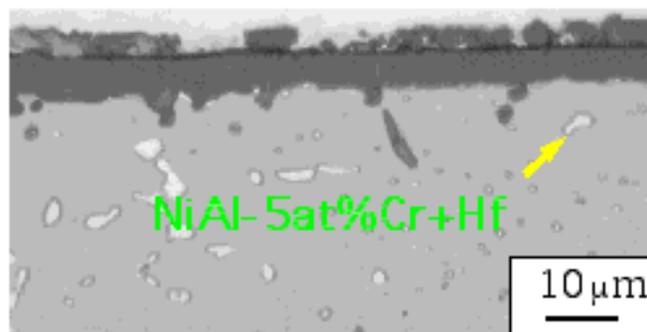
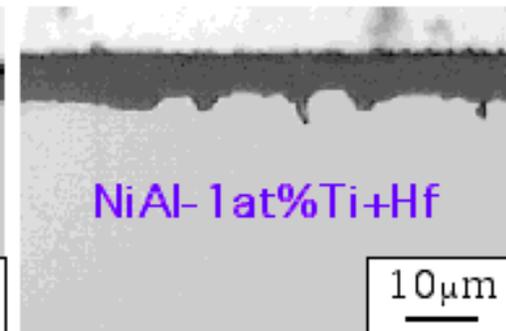
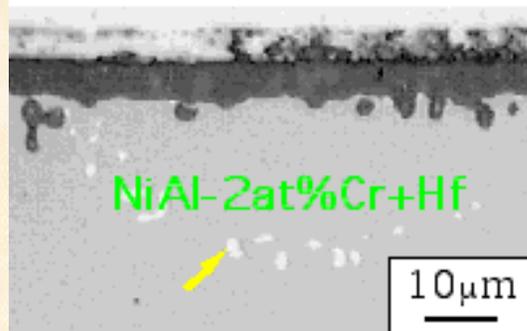
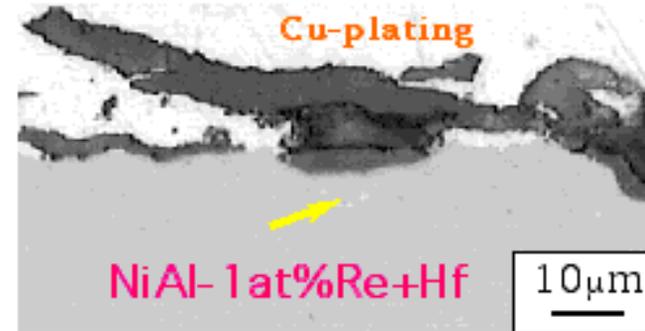
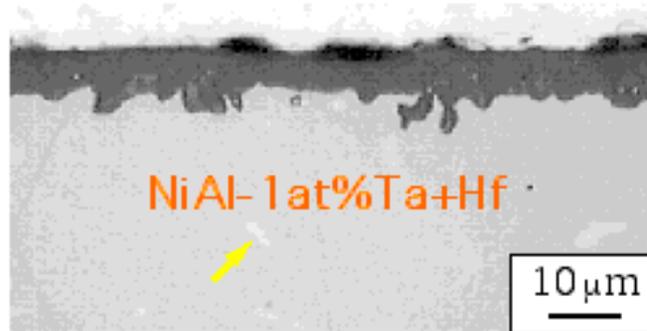


Critical range: 35-37.5%  
two phase vs. one phase?

- 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 1000x1 h at 1150°C in O<sub>2</sub>



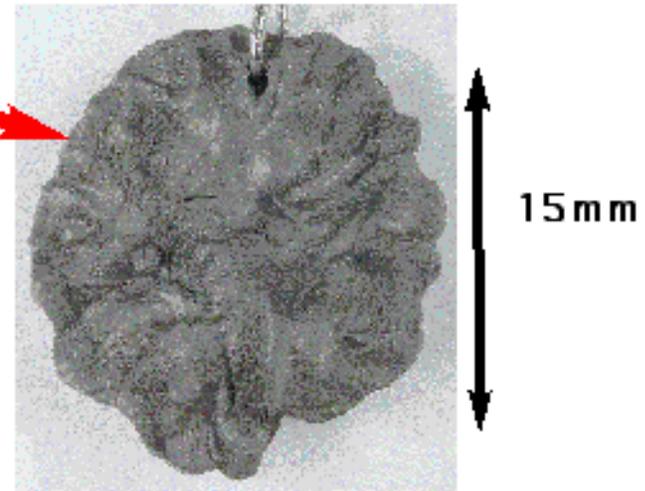
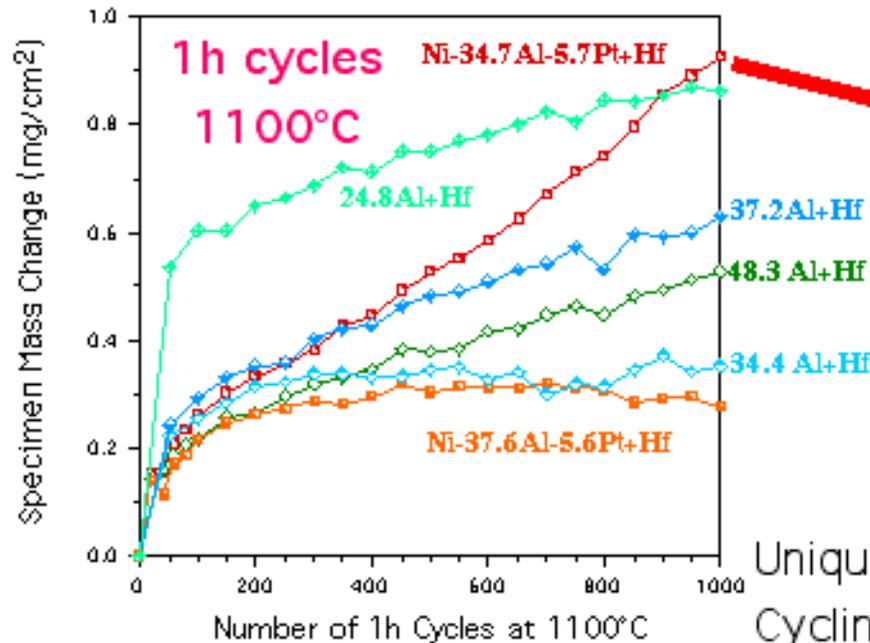
All additions accelerate scale growth rate compared to NiAl+Hf

Problems with scale adhesion with Cr and Re -> precipitates

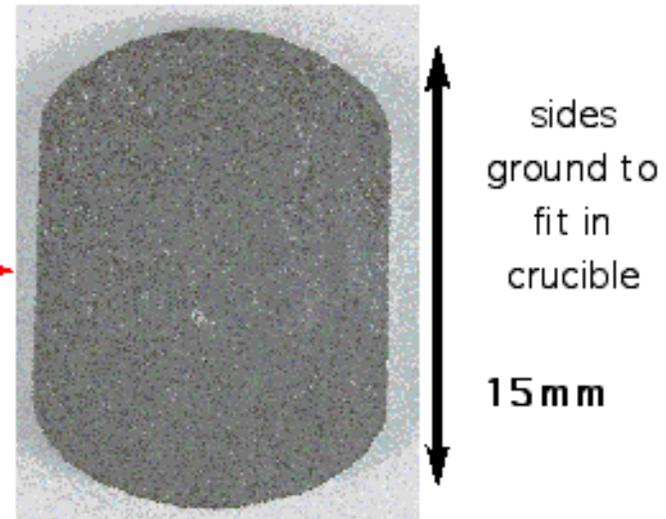
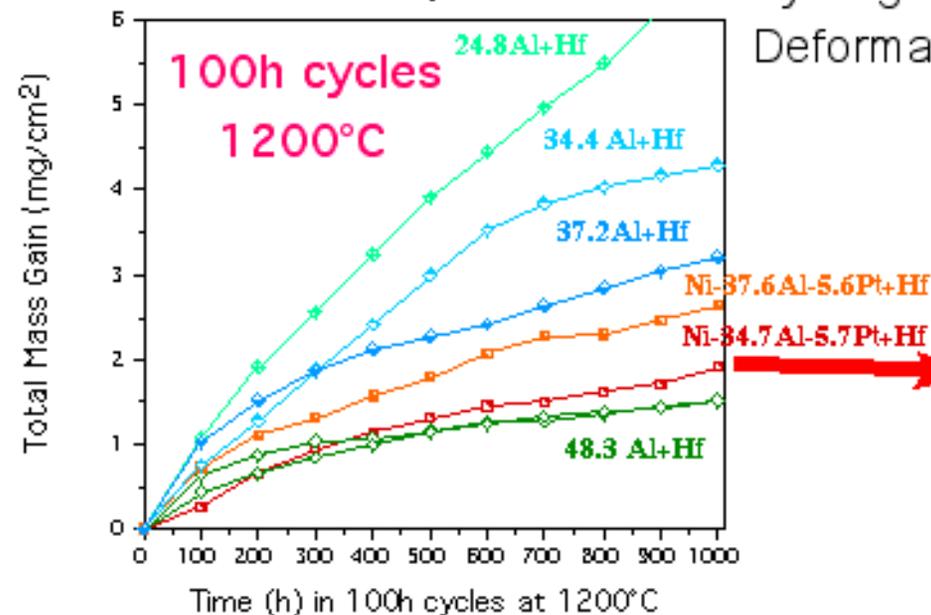
# Cyclic Operation Issues

- 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
- How detrimental is thermal cycling?
  - long cycles: more oxide growth between cycles, but increased opportunity for stress relief-localized rather than massive damage?
  - short cycles: more cycles/unit time

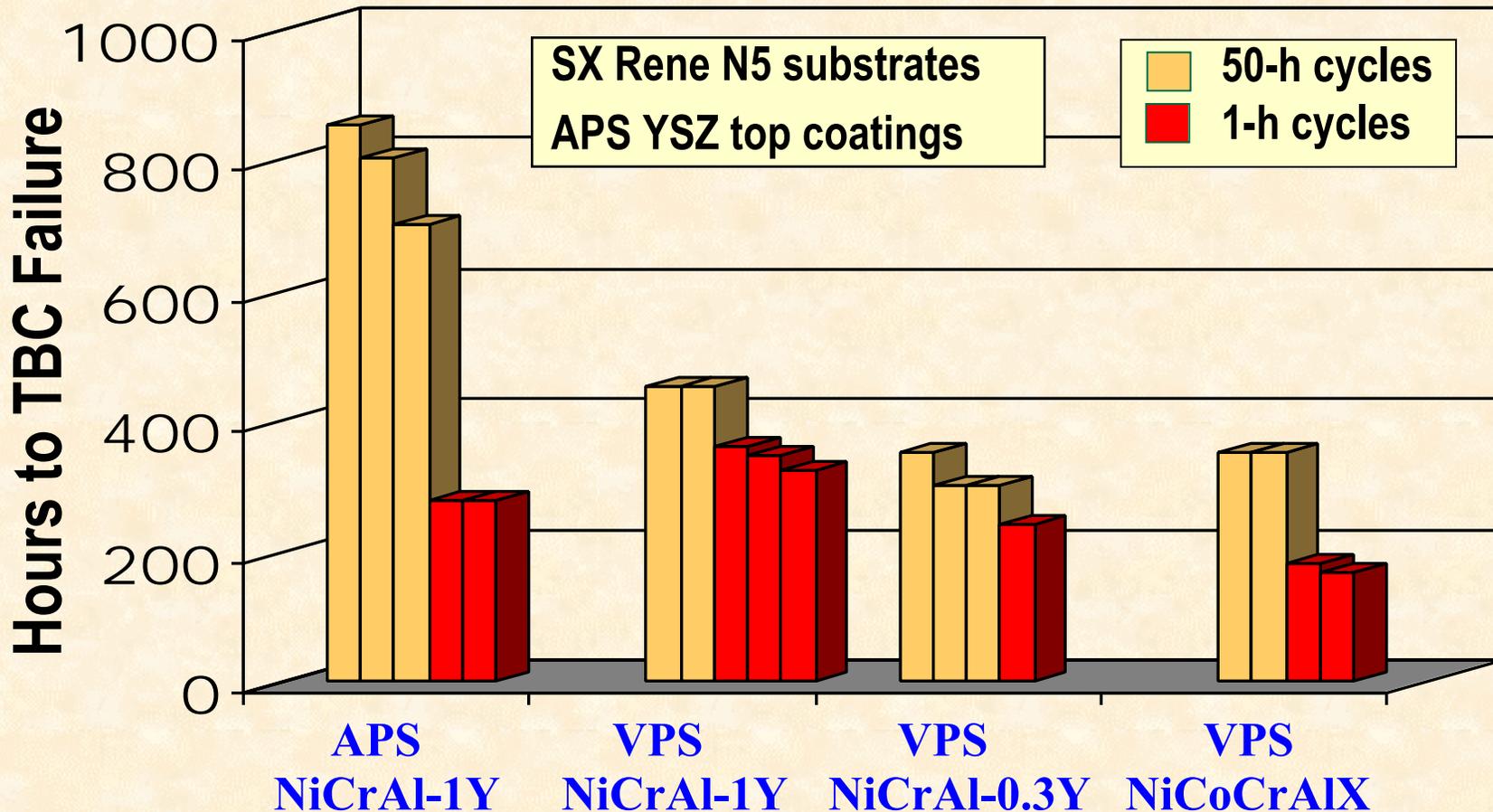
# Deformation of BC: depends on T & cycle frequency



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

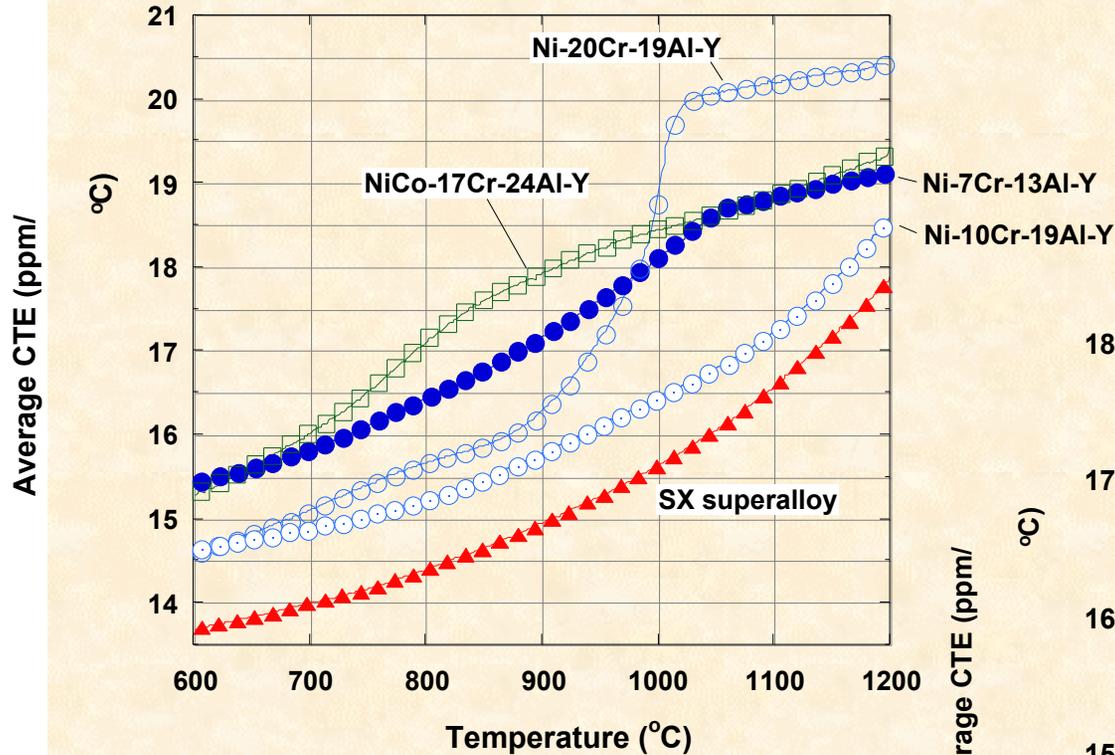


# TBC lifetimes are influenced by the length of thermal cycles



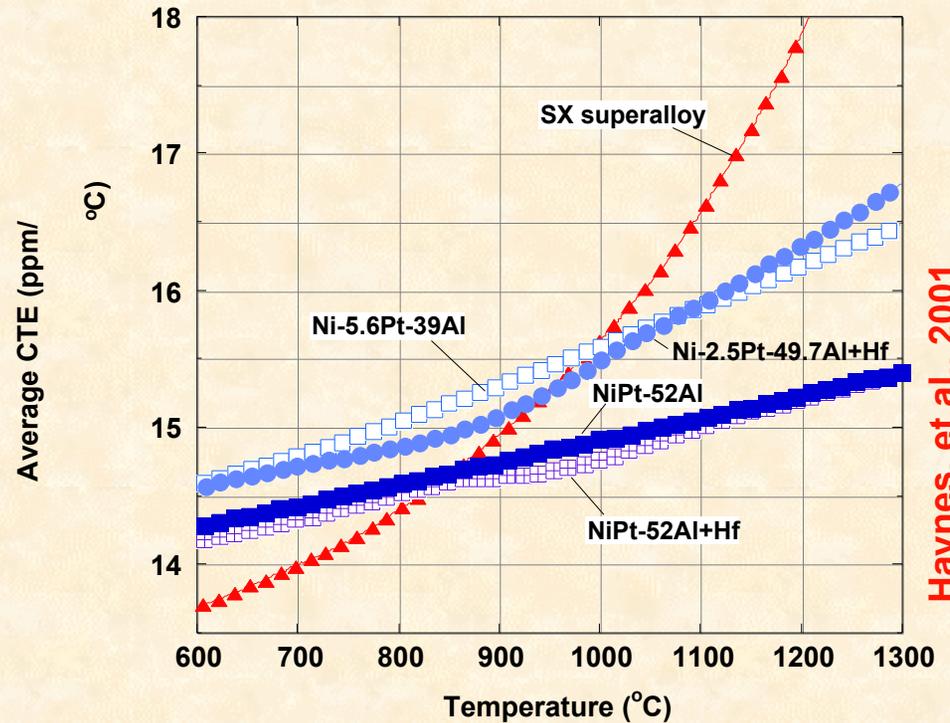
- For PS TBCs: lifetimes longer for longer cycles (at 1150°C)
- Suggests MCrAlX CTE more dominant than oxidation-related factors?

# CTE of NiCrAl > aluminide BC alloys



(Ni,Pt)Als: CTE straddles that of the SC superalloy

- compression to tension during heating
- tensile creep at T?
- on cooling, into compression then tension



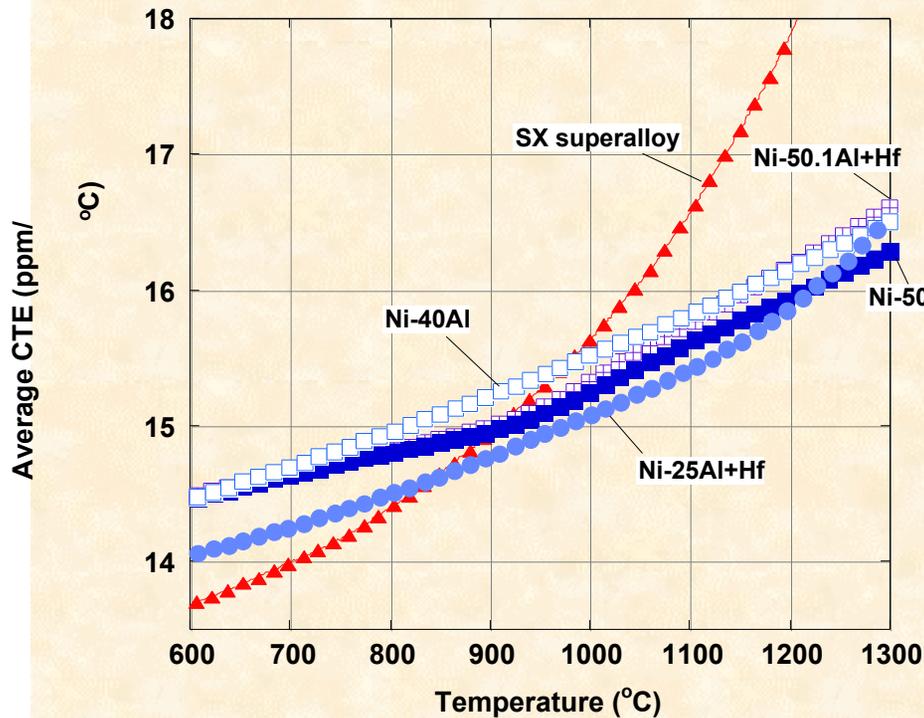
Haynes, et al., 2001

MCrAlYs: CTE > SC Superalloy

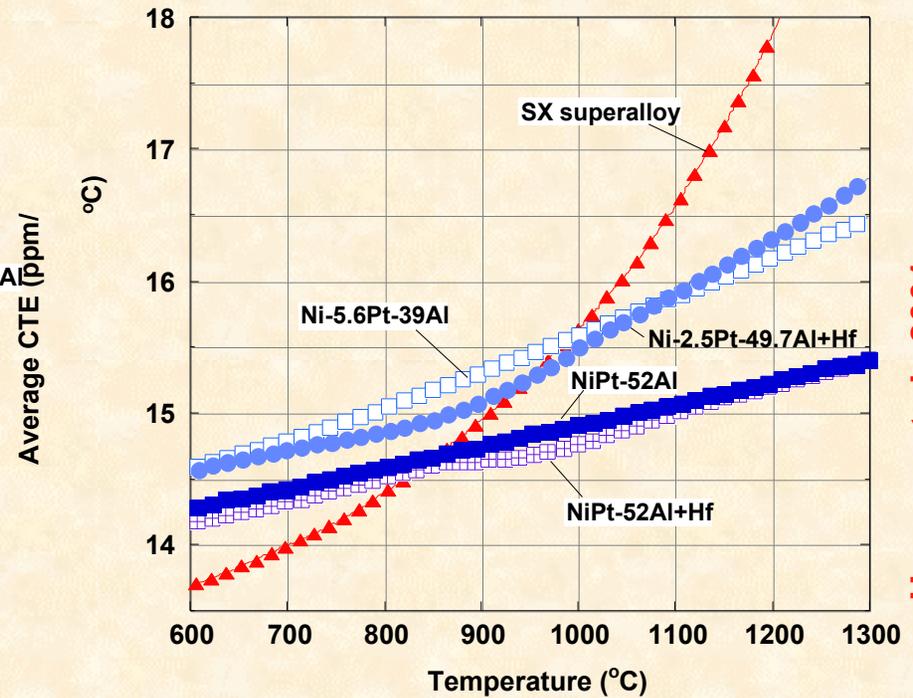
- BC in compression during heat-up
- compressive creep at T?
- in tension during cooling

# Pt lowers CTE of of Al-rich aluminide BC 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

- Pt reduces CTE for Al-rich (Ni,Pt)Al alloys, but  $\pm$ no effect for lower (relevant) Al contents
- No great difference in  $\Delta$ CTE with superalloy that would suggest positive effects for scale adherence

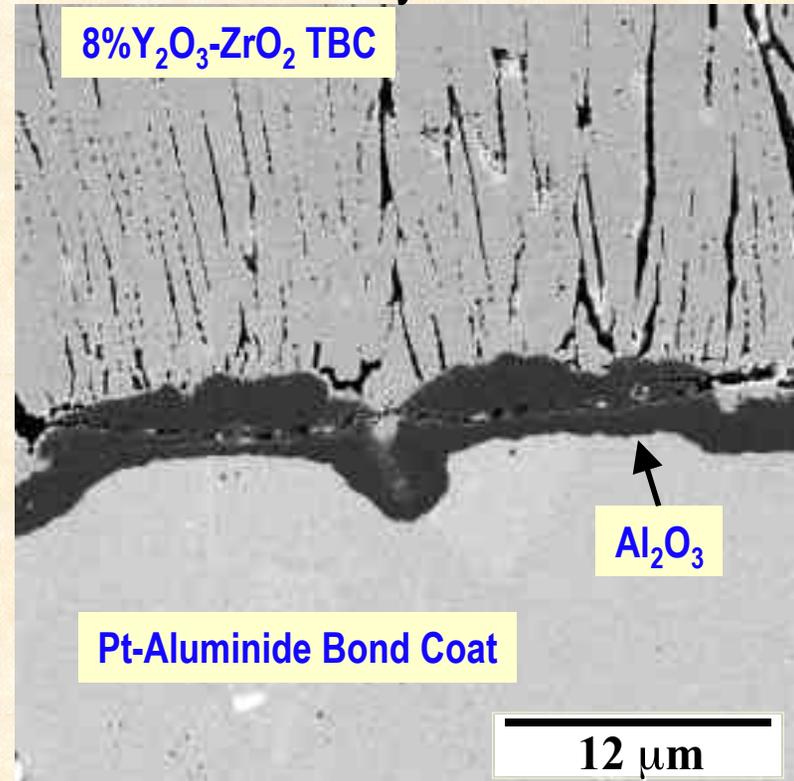
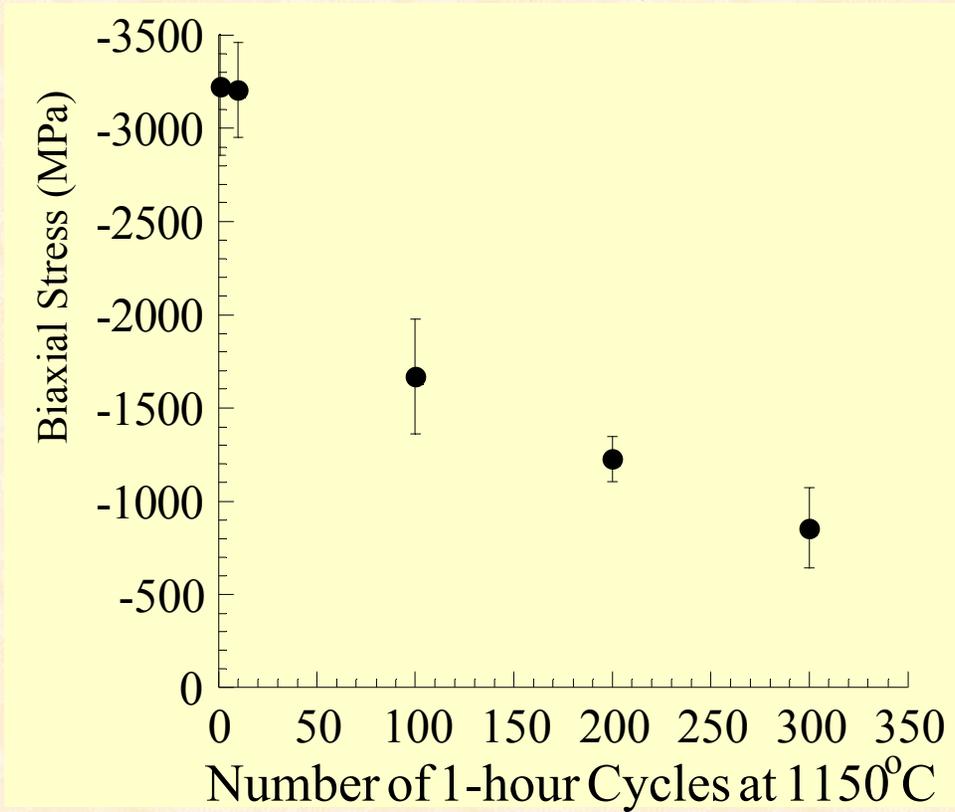
# Does CTE correlate directly with oxidation life?

- Comparisons are complicated by other influences:
  - RE doping (optimized vs nominal)
  - substrate strength
- Our data show:
  - Ni-7Cr-13Al: lifetime of 100 h in 1-h cycles at 1150°C ( CTE vs Al<sub>2</sub>O<sub>3</sub> = 10.2 ppm°C<sup>-1</sup>)
  - Ni-7Cr-13Al+Y (same CTE): lifetime of 625 h
  - René N5 (optimized RE, stronger, CTE = 7.1): lifetime of 1,000 h
  - NiAl+Hf, Ni(Pt,Al)+Hf ( CTE = 5.9-6.0): lifetime 10,000h, but
  - Ni<sub>3</sub>Al+Hf; Ni<sub>3</sub>Al+Y<sub>2</sub>O<sub>3</sub> (lower Al, CTE = 5.5): 820 and 250h, resp<sup>y</sup>
- Maybe RE > CTE > substrate strength? But it is difficult to separate the interactions...

# 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

# How can understanding of oxidation behavior contribute to TBC condition monitoring?

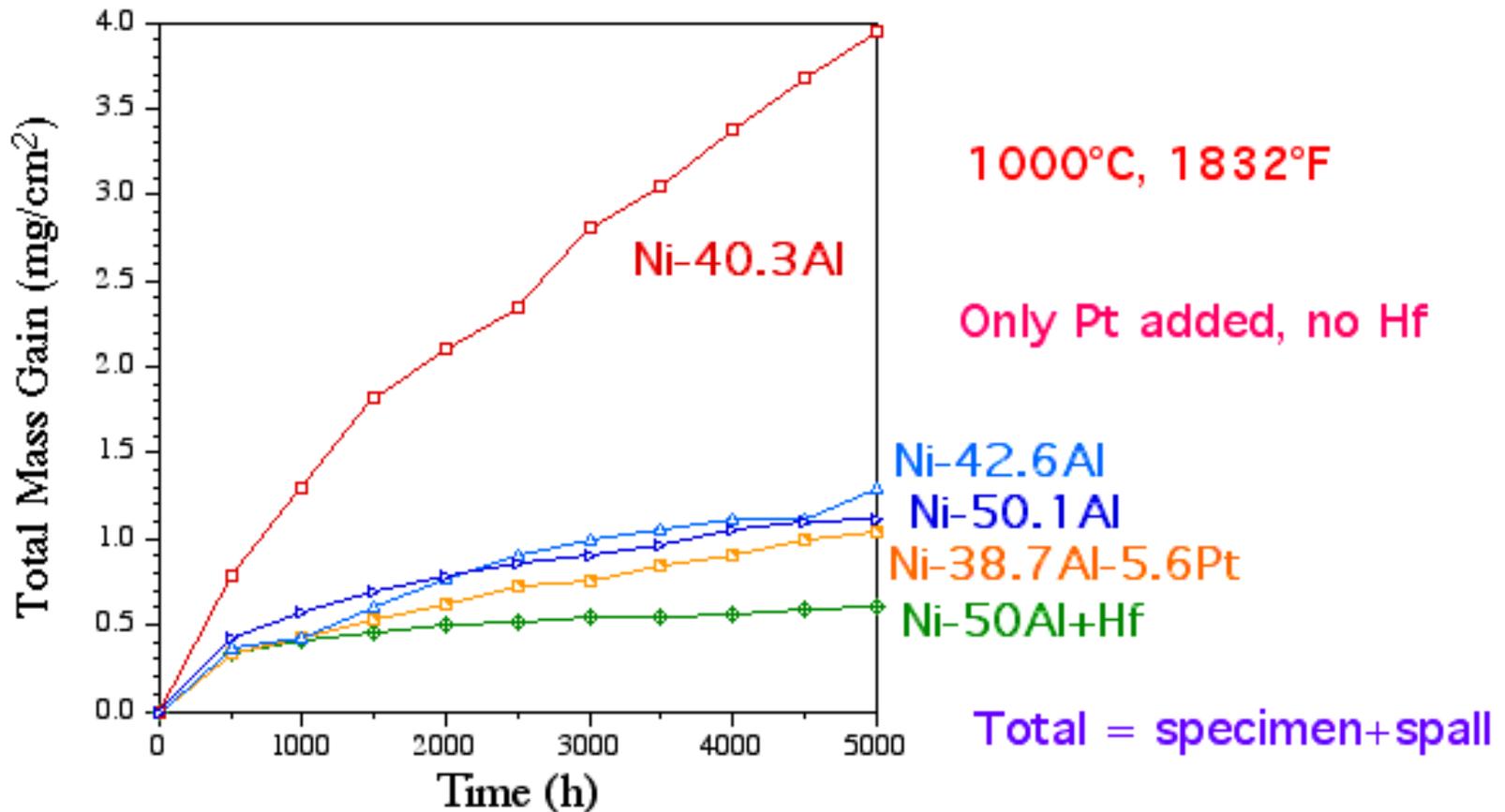
- IR imaging (Siemens Westinghouse; ORNL)
  - hot spots/debonding
- Laser flash (ANL)
  - oxide-BC interface roughness
  - thermal properties
- PSLS (UCSB; UConn; Howmet; ORNL; NPL and Imperial College, UK; Universita' di Trieste, Italy)
  - stress levels in BC oxide layer
  - phase content of oxide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

# 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

# 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

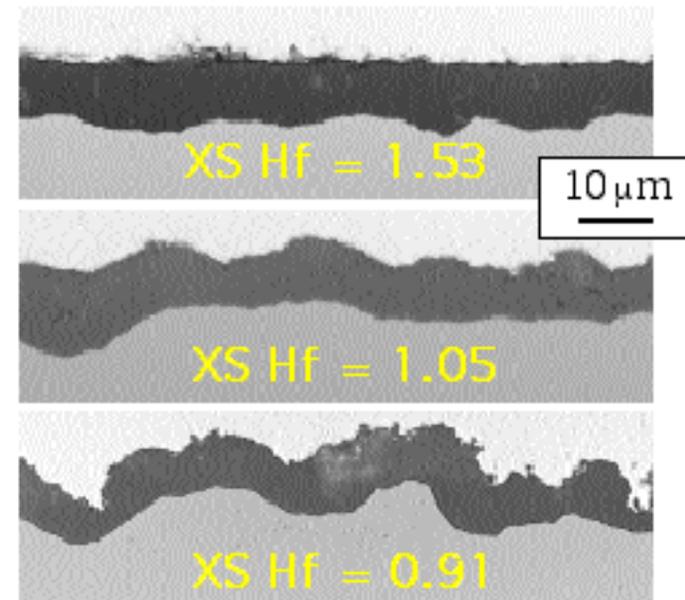
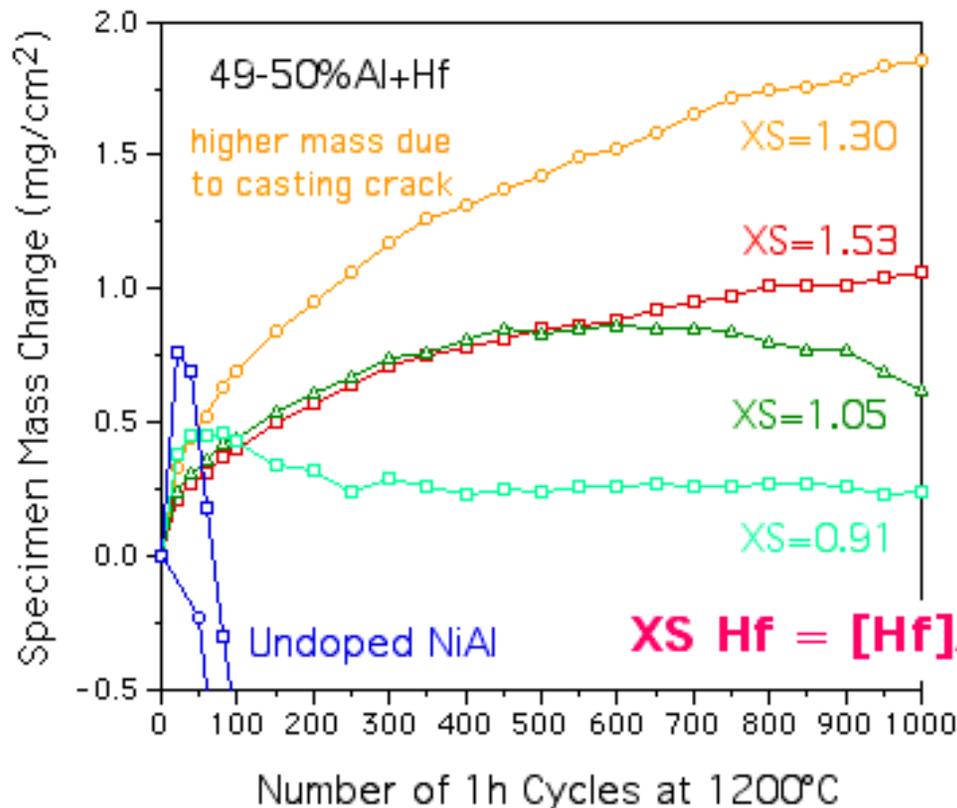
Ni-42.6Al & Ni-50.1Al - undoped alumina growth + some spallation

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



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

after 100h at  
1200°C

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?**