



Interdiffusion and High Temperature Coatings for Gas Turbine Applications

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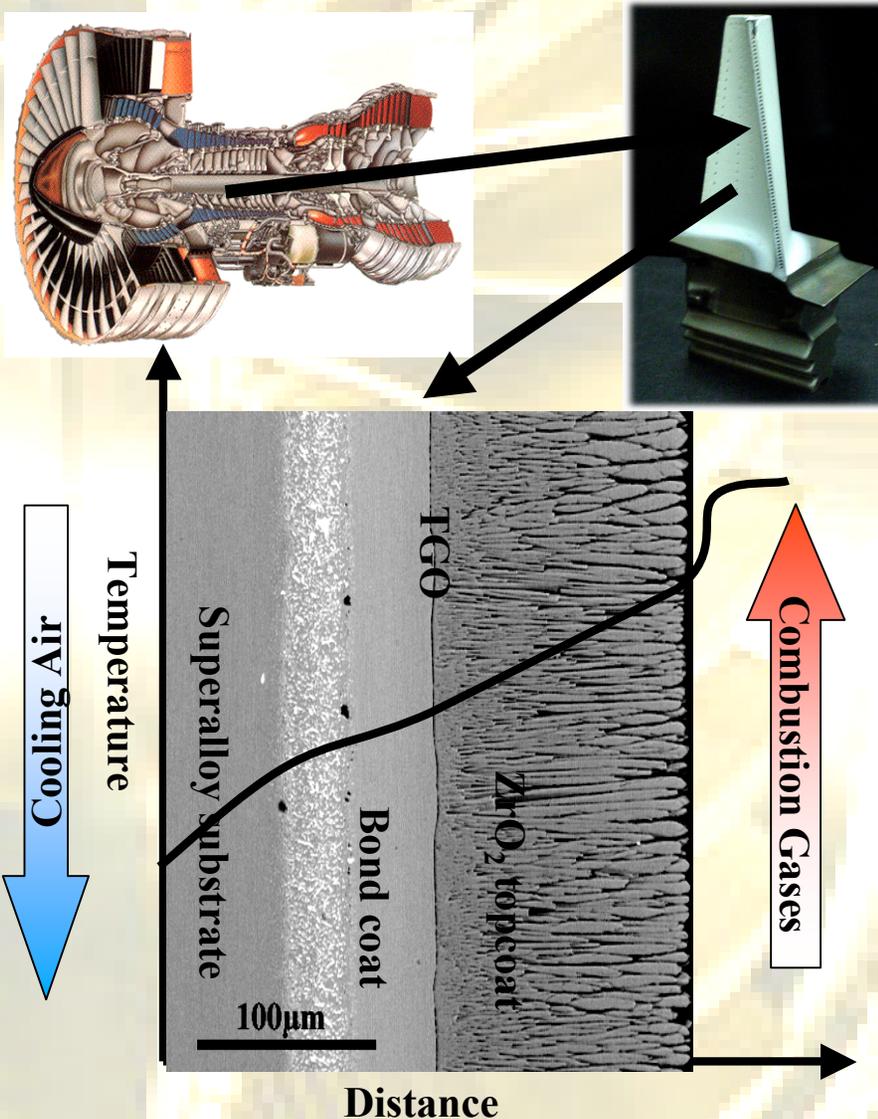
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***TMS Annual Meeting and Exhibition,
February 13-17, 2005 • San Francisco, California, USA.***

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High Temperature Coatings for Gas Turbine Applications



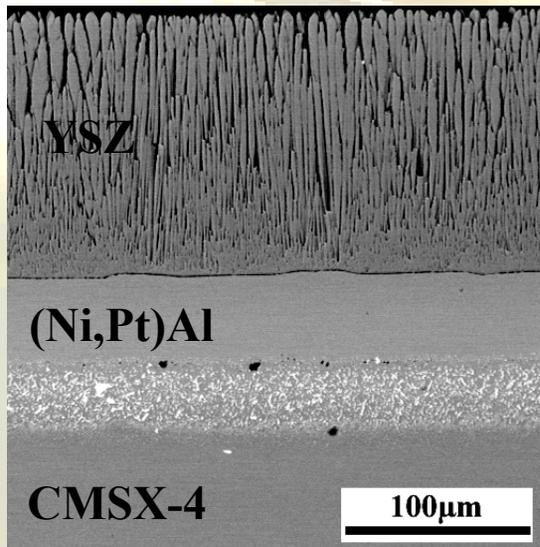
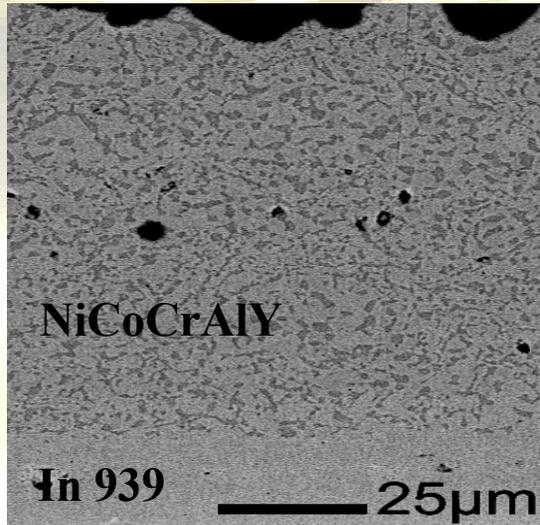
- **Coatings Provide Protection of Hot Components in Advanced Gas Turbine Engines**

- Increase in Performance, Efficiency, Reliability and Maintainability.
- Reduction in Emission and Life Cycle Costs.

- **Processing, Lifetime Prediction and Failure Mechanisms of High Temperature Coatings Requires Knowledge in Multicomponent - Multiphase Diffusion.**



Gas Turbine Needs: Oxidation Resistant and Thermal Barrier Coatings (TBCs)



Oxidation Resistant Overlay Coatings

- Formation of Protective Oxide Scale
- NiAl or MCrAlY overlay Coatings
- Substrate

Thermal Barrier Coatings: Provides Insulation to the Hot Components such as Blades and Vanes in Advanced Turbine Engines.

- Ceramic Top Coat: ZrO_2 -7~8wt.% Y_2O_3 (YSZ)
- Thermally Grown Oxide (TGO)
- Bond Coat: MCrAlY (M \equiv Ni, Co, or Both) or Aluminide, (Ni,Pt)Al
 - Al Reservoir for Oxidation Resistance
 - Enhanced Adherence
- Superalloy Substrate



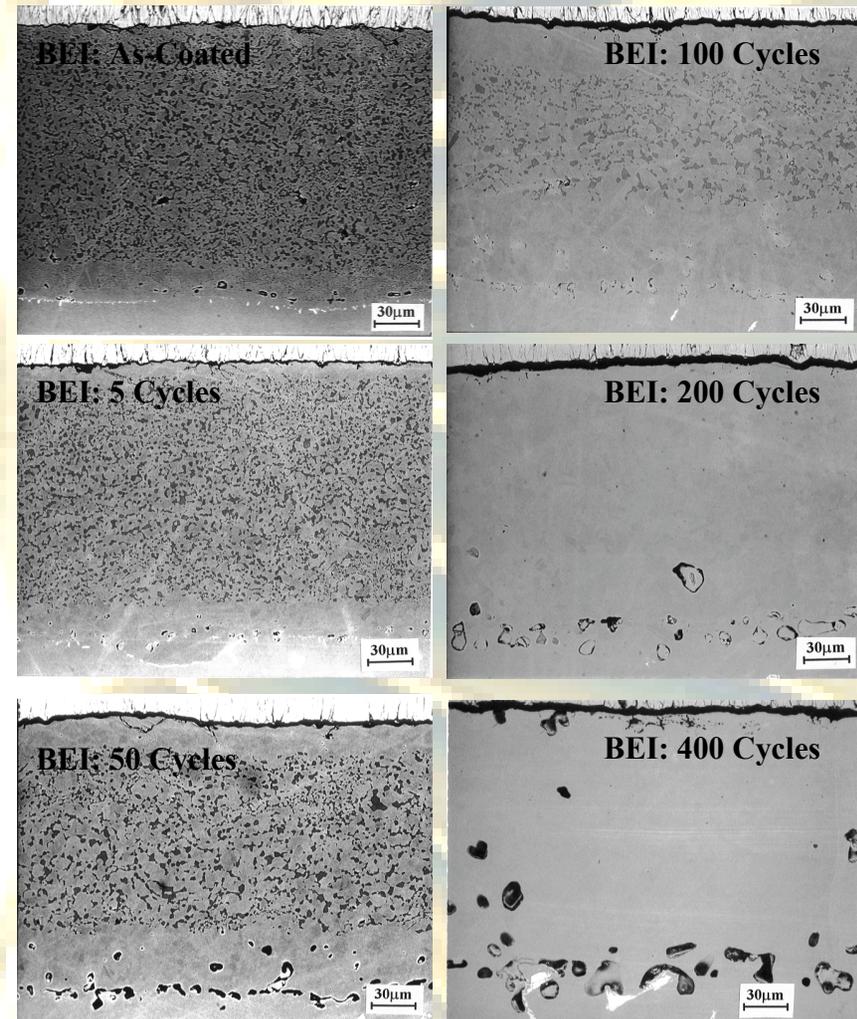
Multicomponent-Multiphase Diffusion in High Temperature Coatings

- **Multicomponent - Multiphase Diffusion Plays a Critical Role in Degradations and Failure Mechanisms of High Temperature Coatings.**
- **Oxidation and Coating-Substrate Diffusion.**
- **Formation of Kirkendall Porosity at Critical Locations.**
- **Phase Transformations in Coatings and Thermally Grown Oxide.**
- **Internal Oxidation.**



Oxidation and Coating-Substrate Diffusion

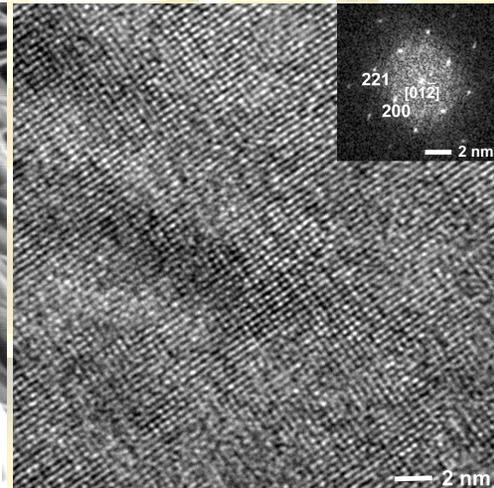
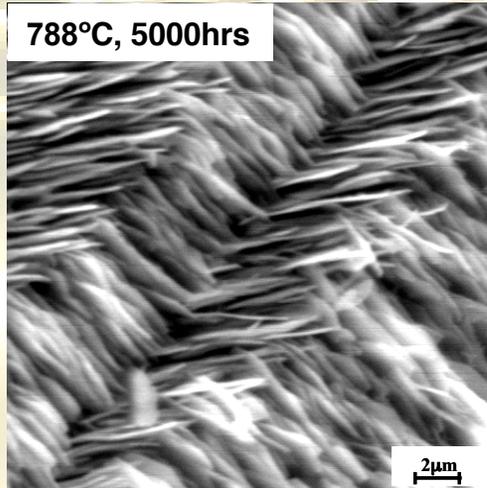
- **Al Diffuses Out to Form Al_2O_3 Scale.**
 - **Polymorphic Transformation of Al_2O_3 Scale.**
- **Al Diffuses into the Substrate:**
 - **Dissolution of High Aluminum β phase (Al-Reservoir).**
 - **Formation of Deleterious Oxide Scale Rich in Ni, Co and Cr.**
 - **Formation of Kirkendall Porosity.**
- **Elements Added to the Substrate for High-Temperature Strengthening Diffuse into the Coating:**
 - **Affect Near-Surface Mechanical Properties of a Component.**
 - **Impair the Formation or Adherence of the Protective Oxide Scale.**



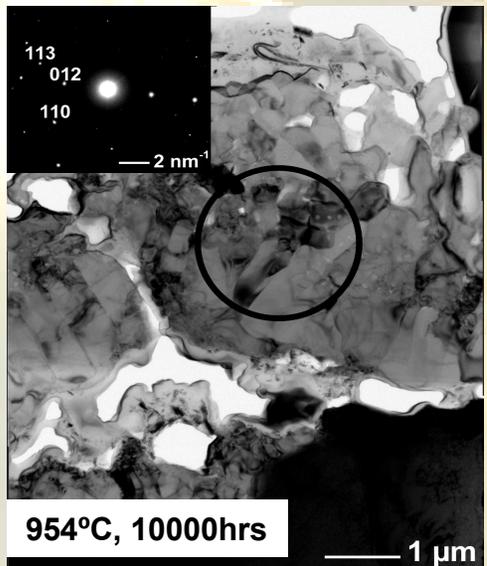
Backscatter electron micrographs of NiCoCrAlY-IN738 illustrating dissolution of β -phase as a function of thermal cyclic oxidation at 1121°C



Polymorphic Transformation of Al_2O_3 Scale



- Oxidation with Outward Diffusion of Aluminum through the TGO Scale:
 - Needle-like whisker TGO morphology
 - Metastable γ - and/or θ - Al_2O_3

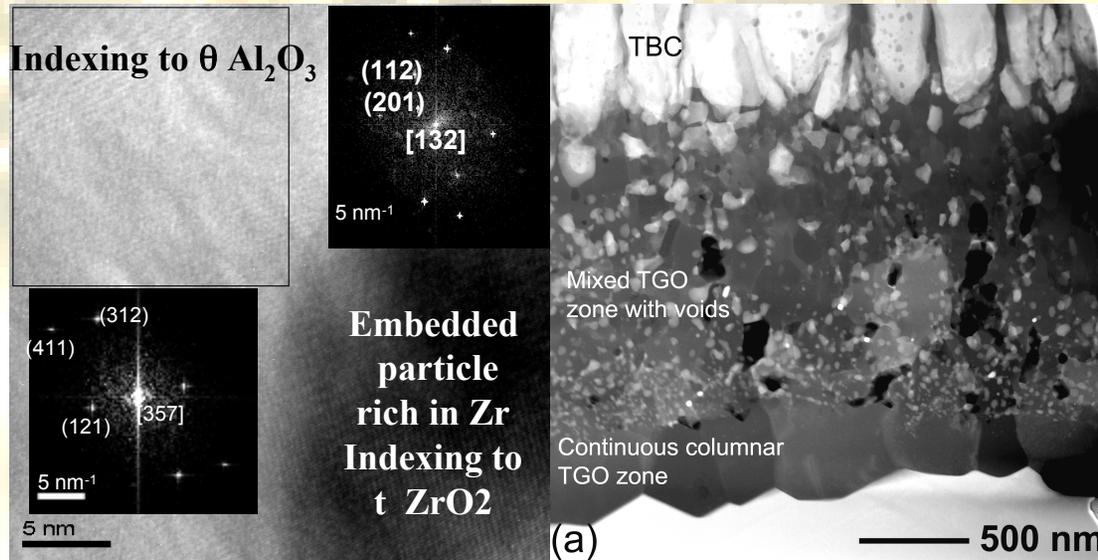


- Oxidation with Inward Diffusion of Oxygen
 - Columnar or Equiaxed TGO Grains
 - Equilibrium α - Al_2O_3
- Polymorphic Transformation within the Al_2O_3 Scale Influence
 - Formation of Voids due to Volume Contraction

N. Mu, Y.H. Sohn, I. Nava, SCT, 2004.



Polymorphic Transformation and Formation of Voids



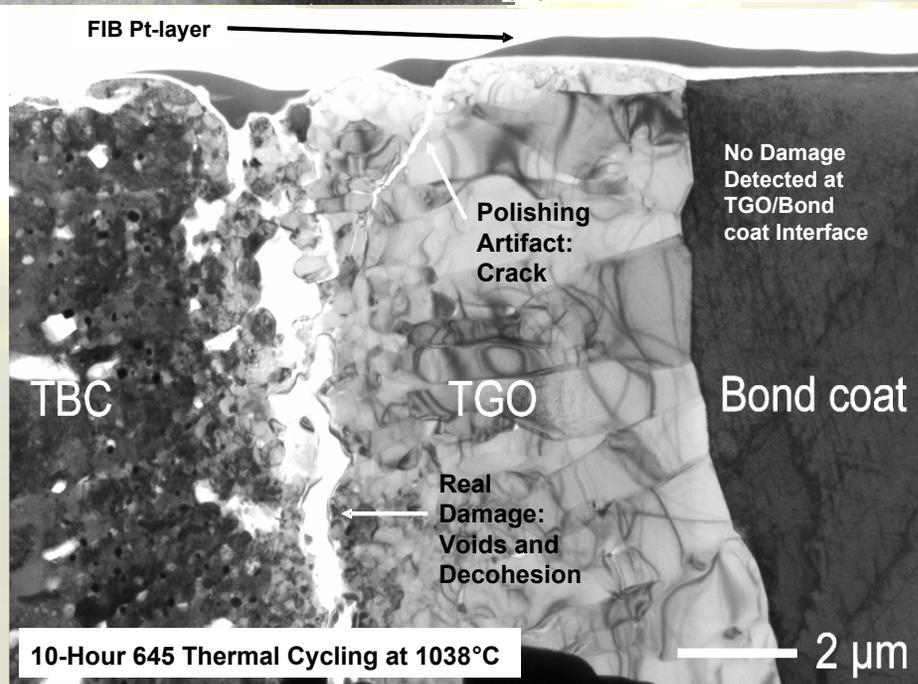
MetaStable Al_2O_3 and Mixed Oxide Zone:

⊞ Initially a Mixture of ZrO_2 and $\theta\text{-Al}_2\text{O}_3$ Transforming to $\alpha\text{-Al}_2\text{O}_3$ with Thermal Cycling.

❖ Formation of Voids Near YSZ/TGO Interface.

❖ A Significant Amount of Decohesion at the YSZ/TGO Interface.

❖ The Degradation of YSZ/TGO Interface Can Influence the Overall Thermo-Mechanical Behavior of TBCs.

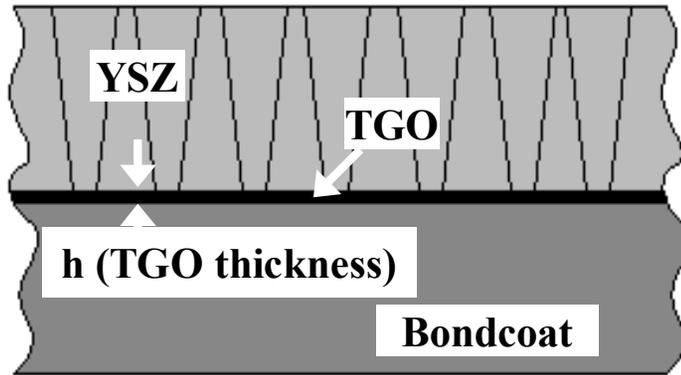


S. Laxman, Y.H. Sohn, K.S. Murphy, SCT, 2004.

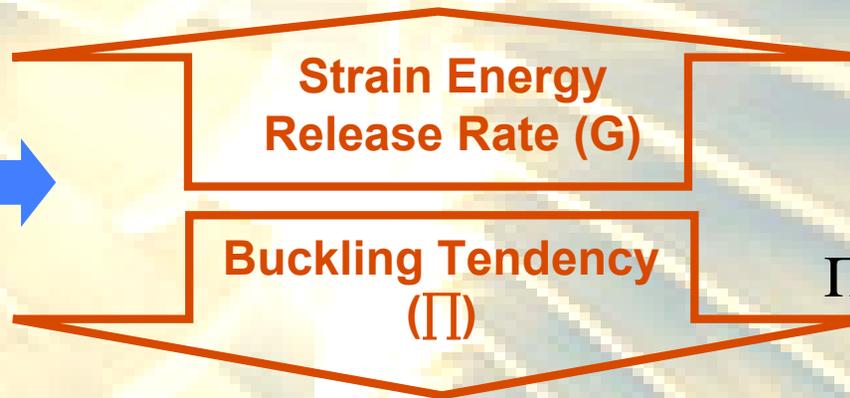
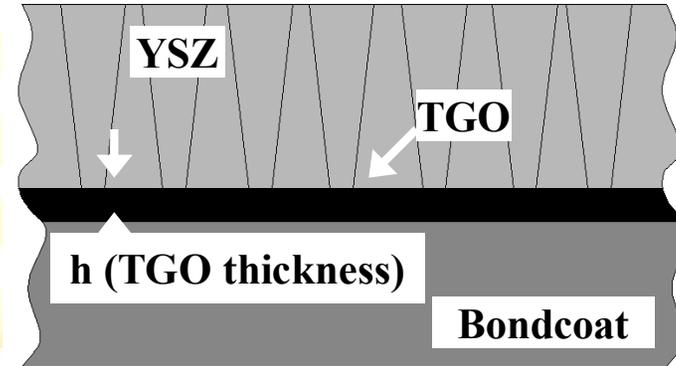


Effective Thickness of Oxide (YSZ and TGO) Governing the Failure of TBCs

As-Coated



After Thermal Cycles



$$G = \frac{Z\sigma^2 h(1-\nu^2)}{E} *$$

$$\Pi = (1-\nu^2) \left(\frac{\sigma_0}{E_0} \right) \left(\frac{b}{h} \right)^2 *$$

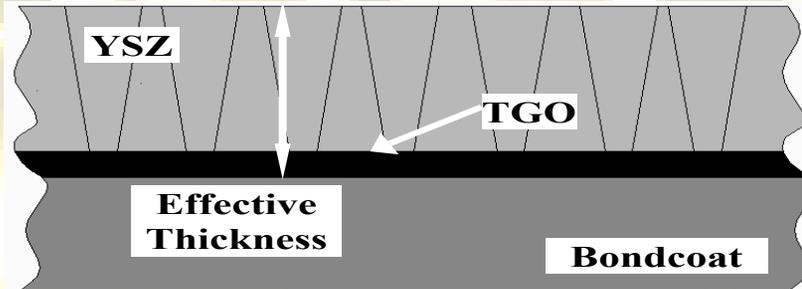
Z = Geometry Constant for the TGO; E = Young's Modulus of Al_2O_3 ; ν = Poisson's ratio; h = TGO Thickness; G = Strain Energy Release Rate; σ or σ_0 = In-Plane Compressive Stress (due to Thermal Mismatch); Π = Buckling Index; b = Crack Width.

*A.G.Evans et al, Progress in Materials Science 46 (2001) 505-553;
M.C.Shaw Design of Power Electronics Reliability.

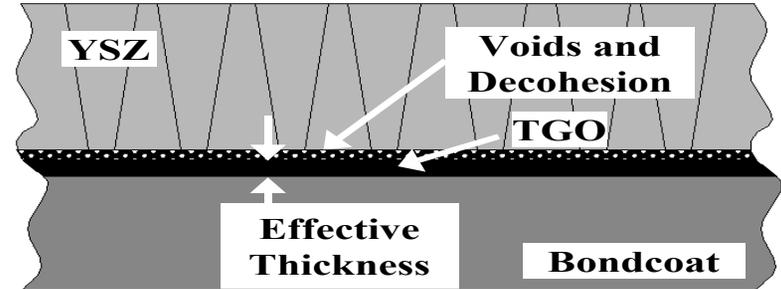


Effective Thickness of Oxide (YSZ and TGO) Governing the Failure of TBCs

Situation I



Situation II

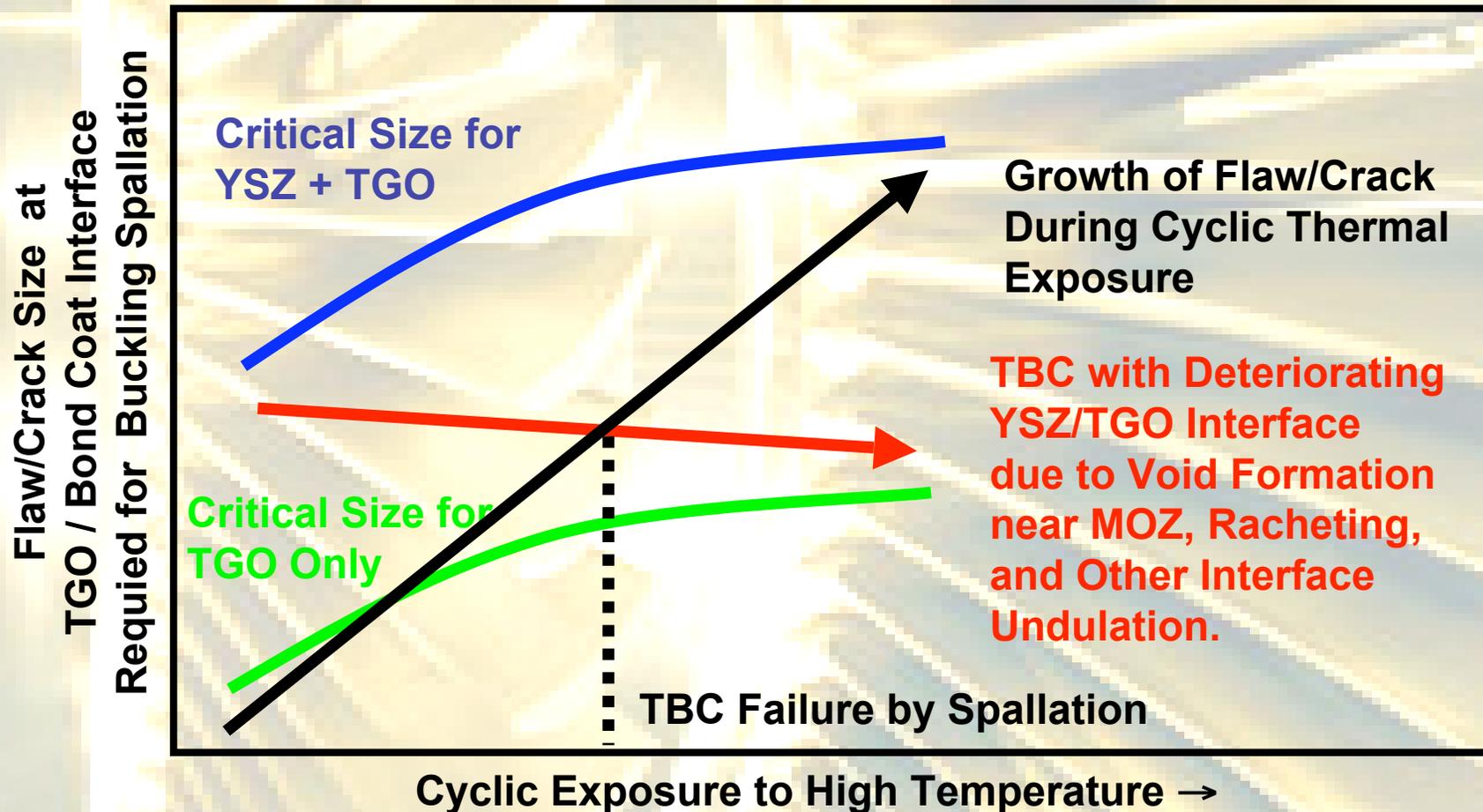


Situation	TGO/YSZ Interface or TGO Near YSZ	Effective Thickness for Resisting Buckling	Strain Energy Release Rate (G)	Buckling Tendency (II)	Results
I	Good	YSZ + TGO	Similar	Low	Difficult to Fail
II	Flawed	TGO + Partially YSZ		High	Easy to Fail

- The Thickness Governing the Buckling Failure May Include that of TGO and YSZ Combined.
- The Microstructure at or near the YSZ/TGO Interface May Play a Significant Role in Thermo-Mechanical Behavior of Thermal Barrier Coatings During Thermal Cycling.



Buckling Failure Mechanisms of TBCs* (Incorporating SEM/TEM/STEM Observations)

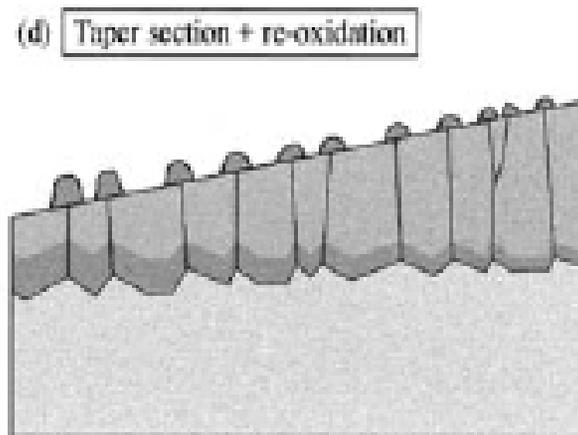
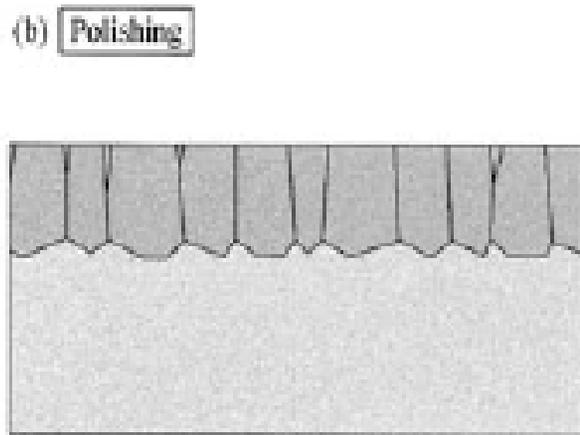
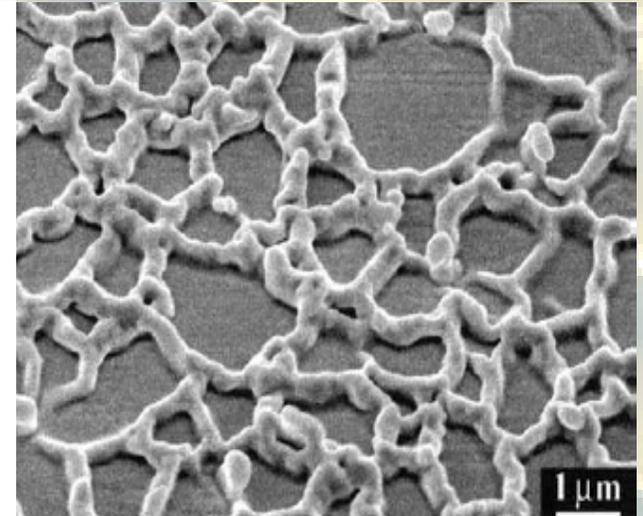
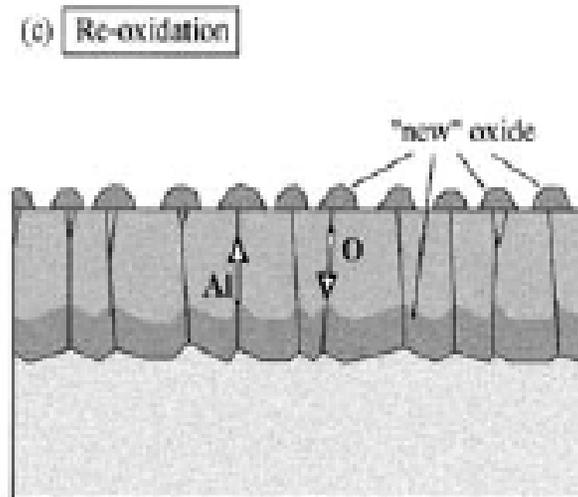
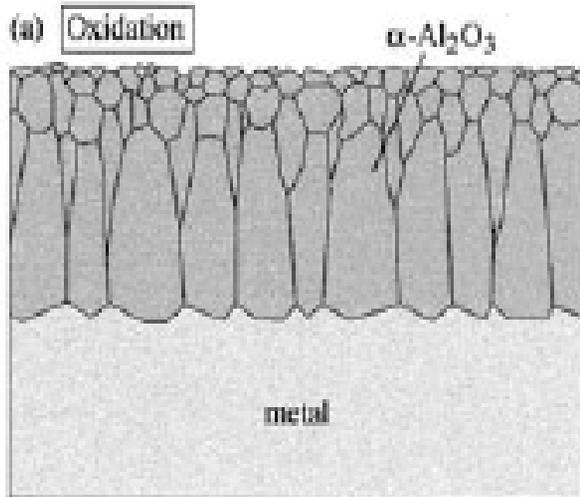


*Y.H. Sohn, B. Jayaraj, S. Laxman, B. Franke, J. Byeon, A.M. Karlsson, *Journal of Metals*, October (2004) 54.



Al Outward Diffusion along Grain Boundaries

Fe-Cr-Al Alloy
Oxidized @ 1100-1200°C



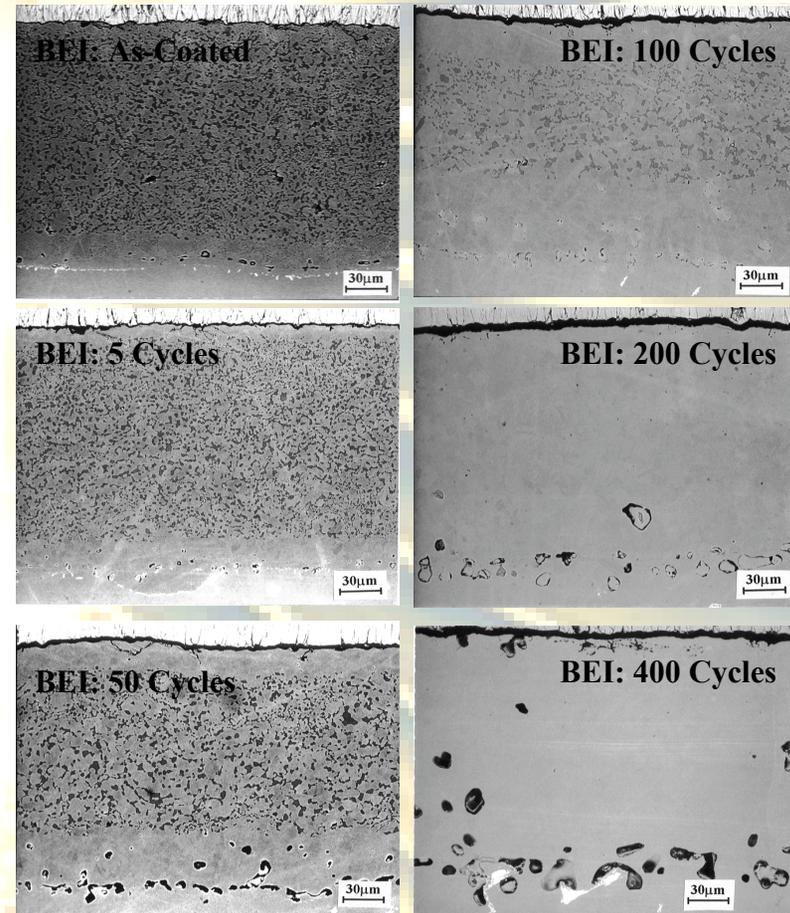
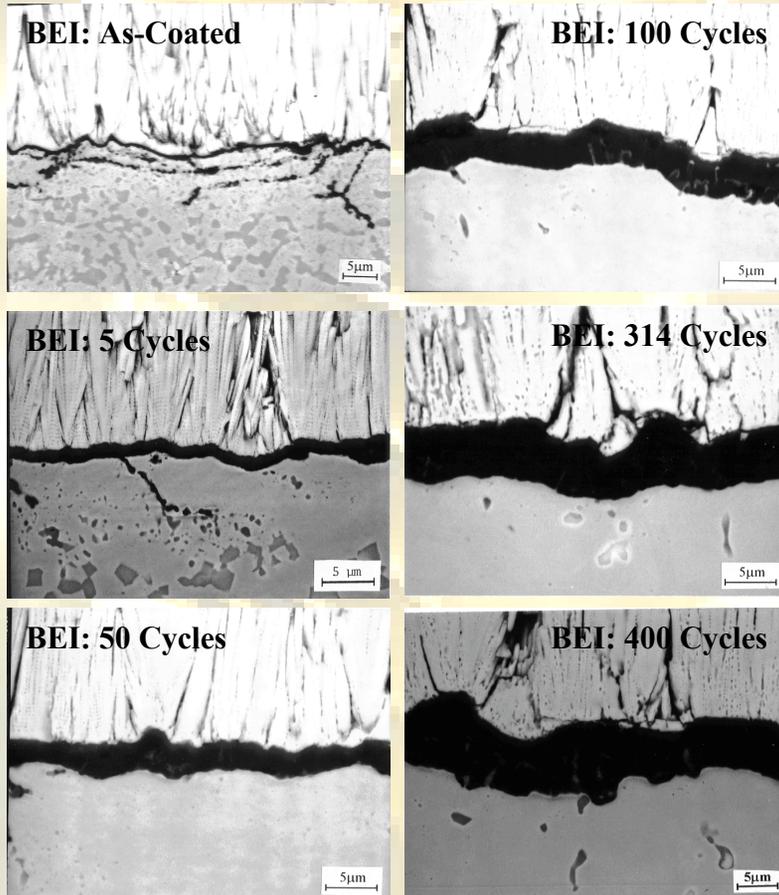
- Al Outward Diffusion through Grain Boundaries and from New Oxides above the Existing Scale.



Oxidation and Interdiffusion: Recession of ($\beta+\gamma$) in NiCoCrAlY

Parabolic Growth of TGO
 $K_p = 6.3 \times 10^{-3} \mu\text{m}\cdot\text{sec}^{1/2}$

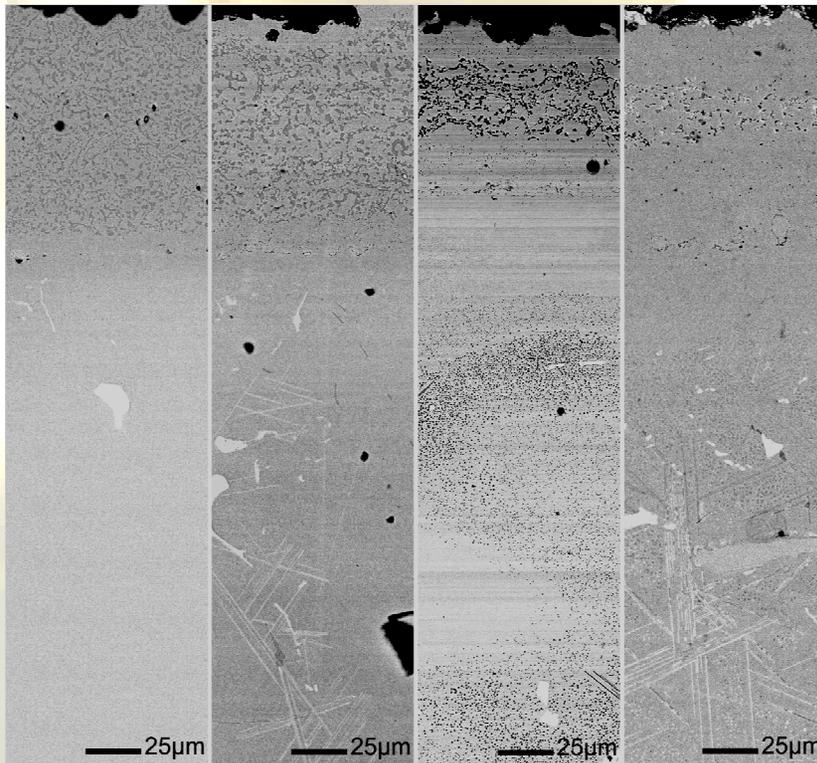
Depletion Zone: $D^{\text{eff}} = 3.4 \times 10^{-15} \text{m}^2/\text{sec}$
Interdiffusion Zone: $D^{\text{eff}} = 9.3 \times 10^{-15} \text{m}^2/\text{sec}$



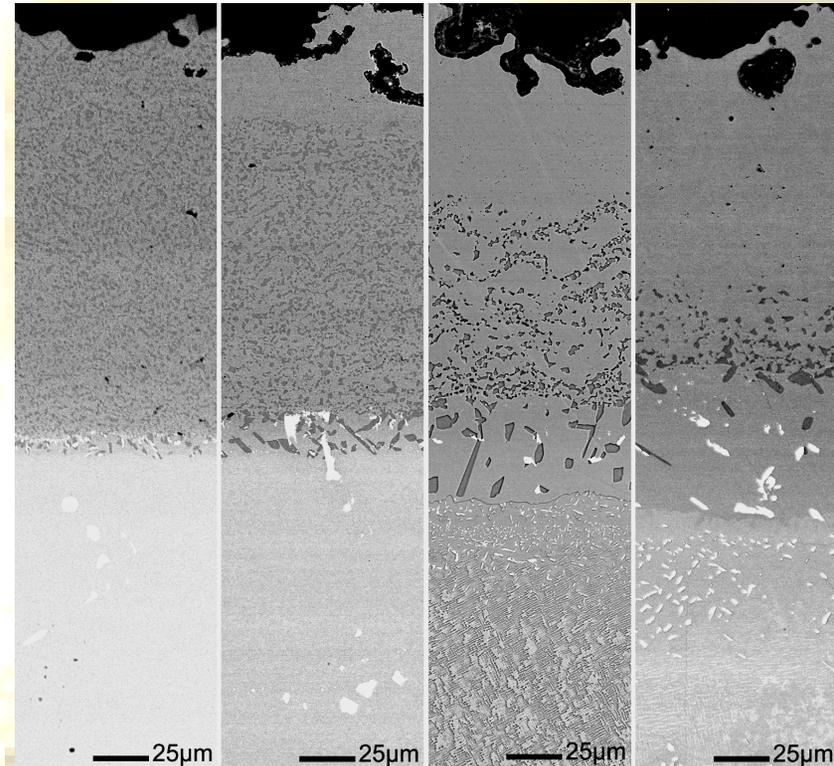


Interdiffusion and Lifetime of Oxidation Resistant Coatings

- **3X in Lifetime (Measured by Stability of Al-Rich β -NiAl Phase) Can be Achieved by Appropriate Selection of Substrate Composition (Given a Coating Composition).**



Isothermal Exposure Time, t



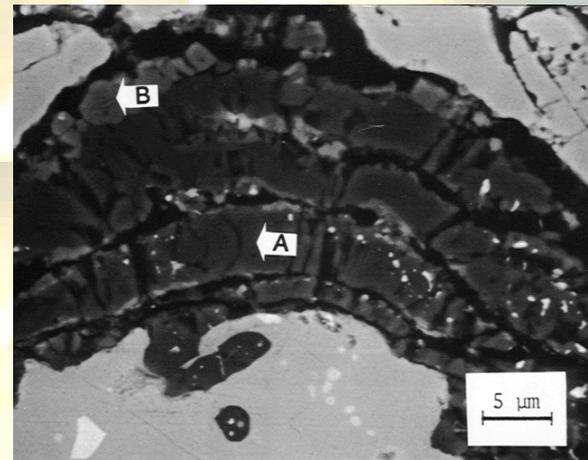
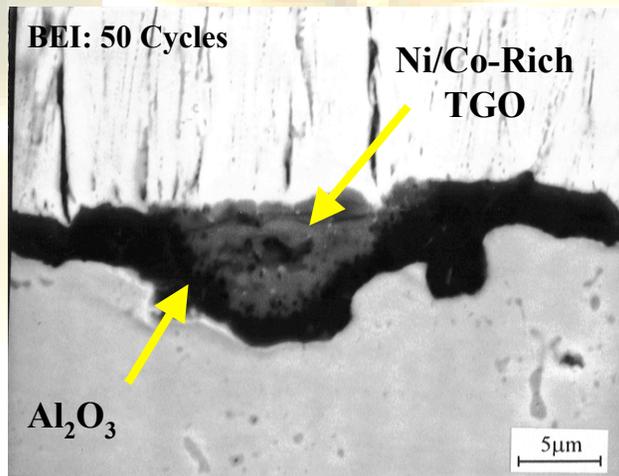
3 x Isothermal Exposure Time, $3t$

E. Perez, Y.H. Sohn, Unpublished Research.

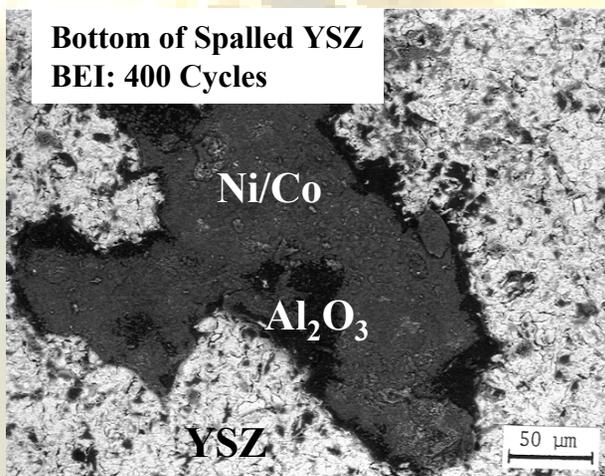


Dissolution of Al-Rich β Phase and Formation of Deleterious Oxide Scale

Lifetime of Oxidation Resistant Coatings and TBCs is Significantly Affected by the Formation of Oxide Scale Rich in Ni, Co and Cr.

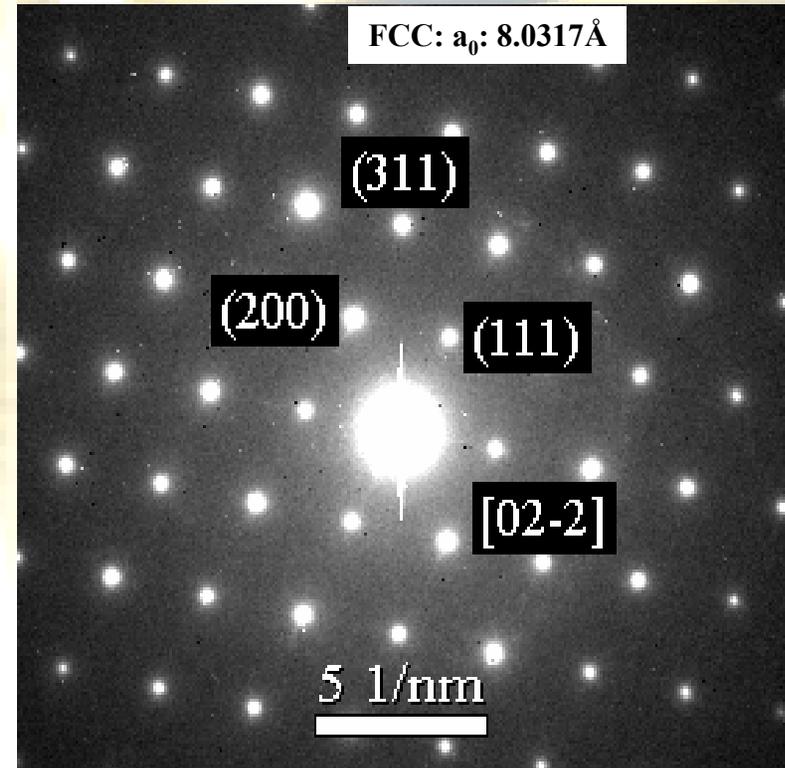
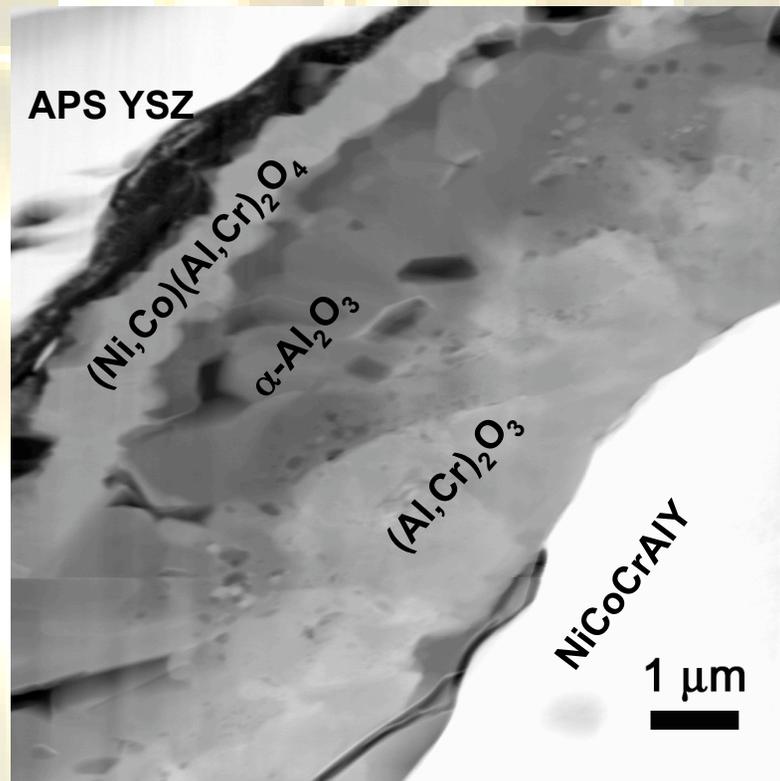


Ni, Co and Cr Rich Oxides Form When Al-Rich $\beta(B_2)$ Phase is Depleted from the NiCoCrAlY Coatings (or Bond Coats) Which Initially Consists of $\beta(B_2) + \gamma(fcc)$.





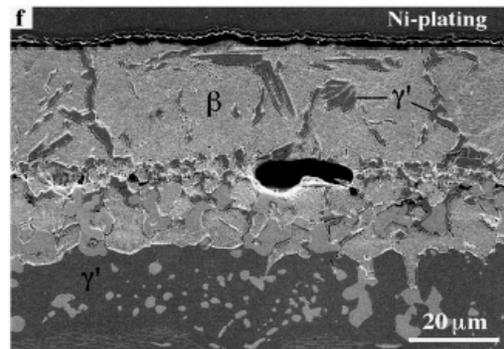
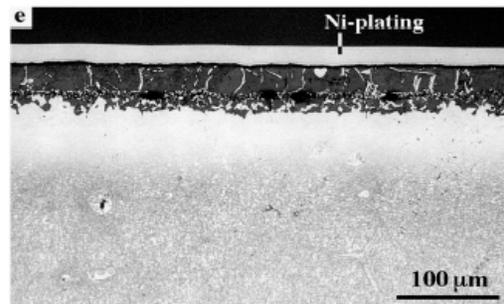
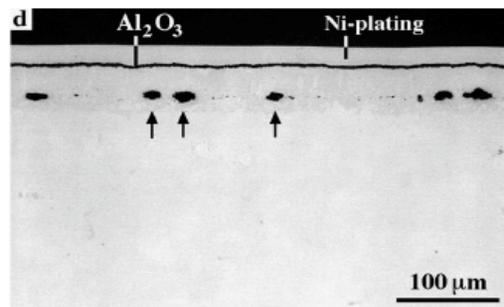
Dissolution of Al-Rich β Phase and Formation of Deleterious Oxide Scale



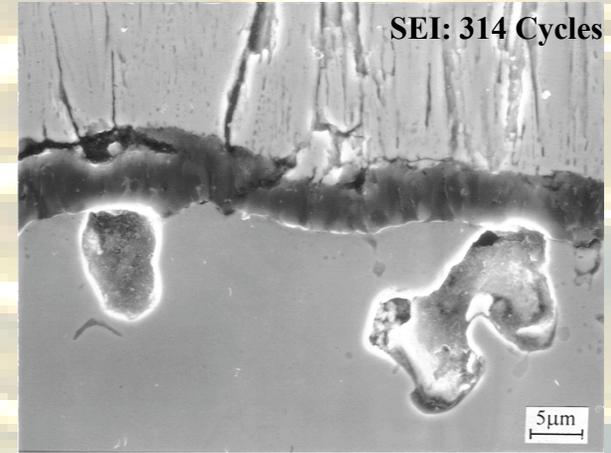
- **(Ni,Co)(Al,Cr)₂O₄ Oxide Layer Near the YSZ/TGO Interface with a Spinel Structure and Lattice Parameter of 8.0317Å.**
- **Result of an Interplay between Thermodynamics and Diffusion in Multicomponent System.**



Formation of Kirkendall Porosity at the Coating/Substrate Interface



- During Isothermal Oxidation, Internal Cavities Form at the Interface Between the (Ni,Pt)Al Coating and the Substrate.
- After Prolonged Cyclic Oxidation, Cavities Form at the Interface Between the NiCoCrAlY Coatings and Thermally Grown Oxide Scale.

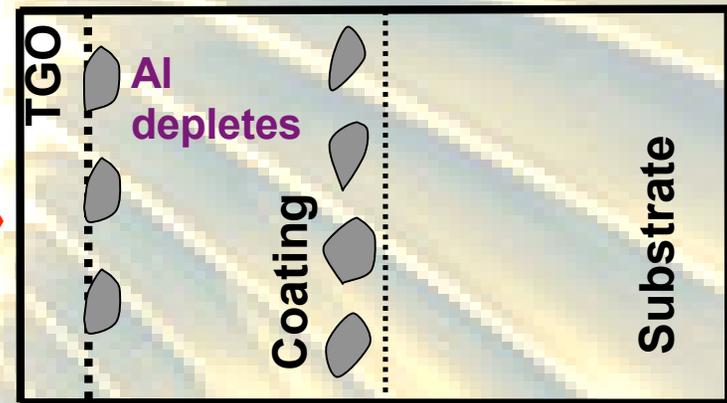
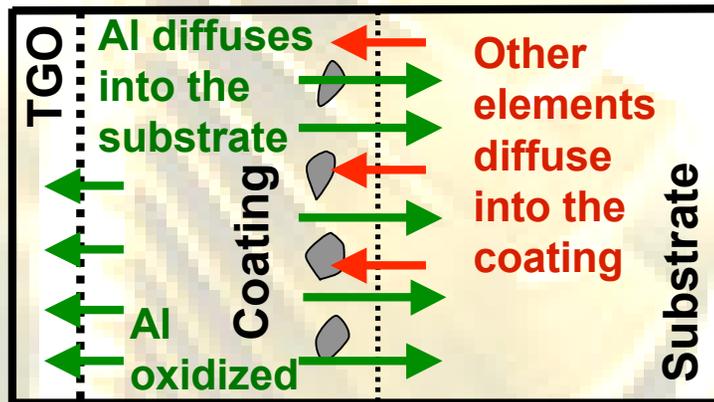
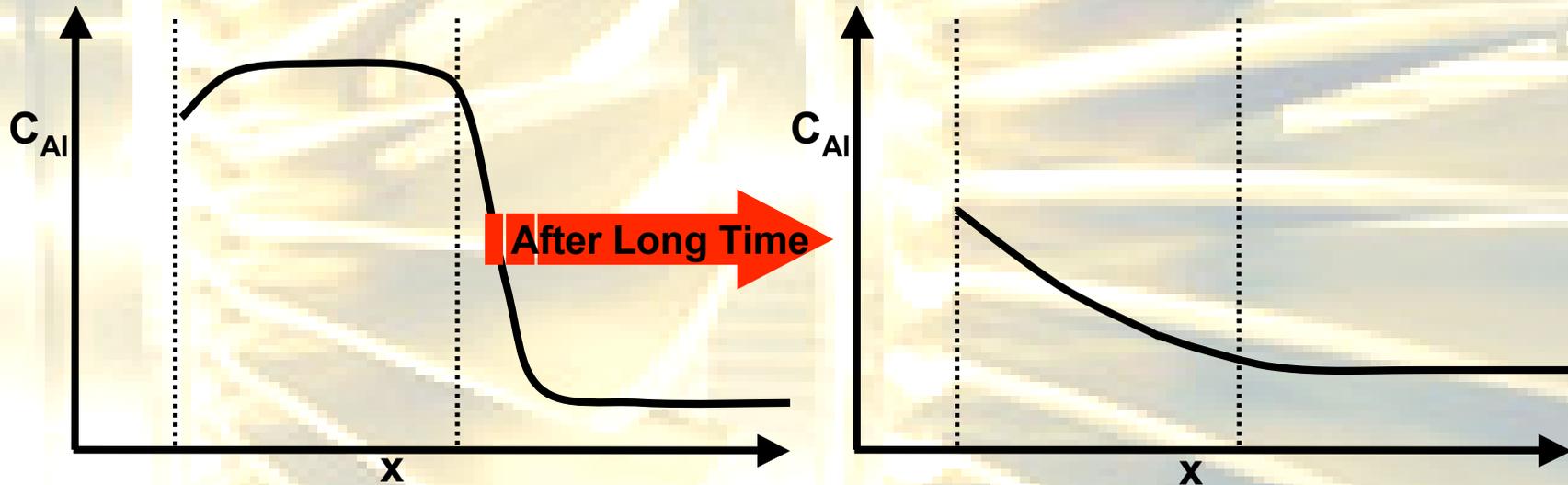


*V. K. Tolpygo and D. R. Clarke
Acta Mater. 48 (2000) 3283-3293.

Y.H. Sohn et al., *Surf. Coat. Technol.*,
146-147 (2001) pp. 70-78.



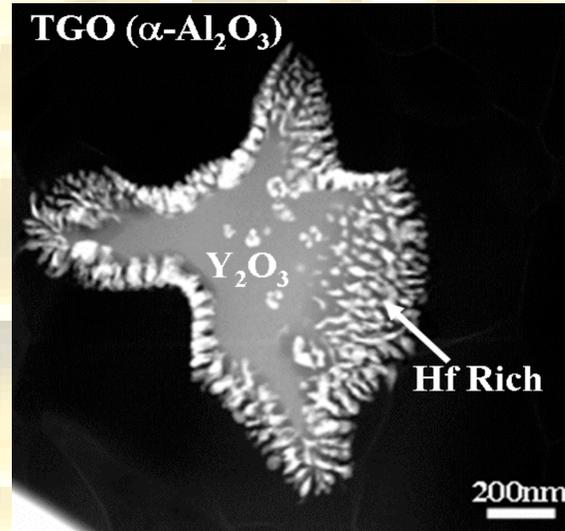
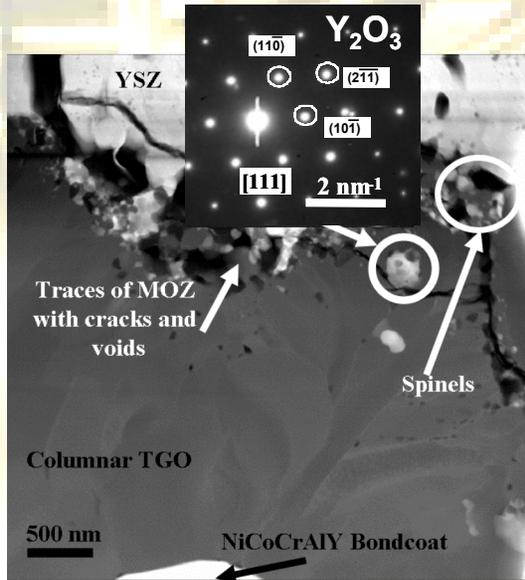
Intrinsic Diffusion of Al and Formation of Kirkendall Porosity





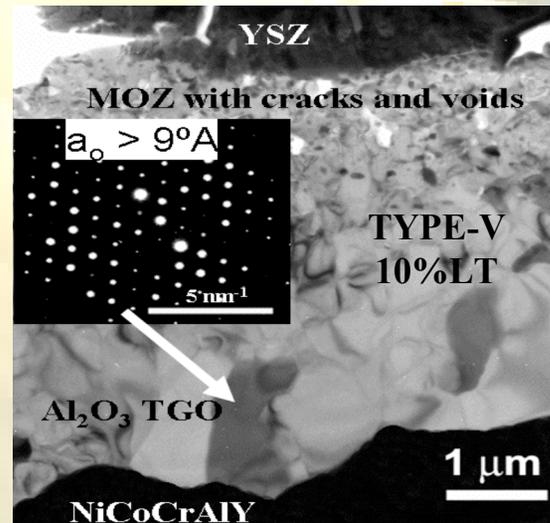
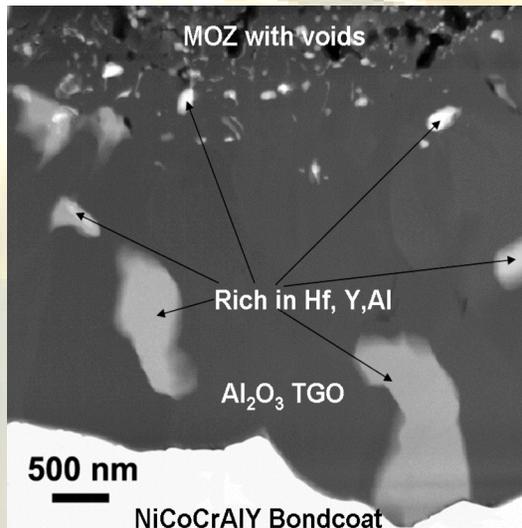
Diffusion Between Coating and Substrate

Oxide Stringers / Inclusions



Y-Rich Oxide:

- Observed as Y_2O_3 on Several TBC Specimens of Different NiCoCrAlY Bond Coats.

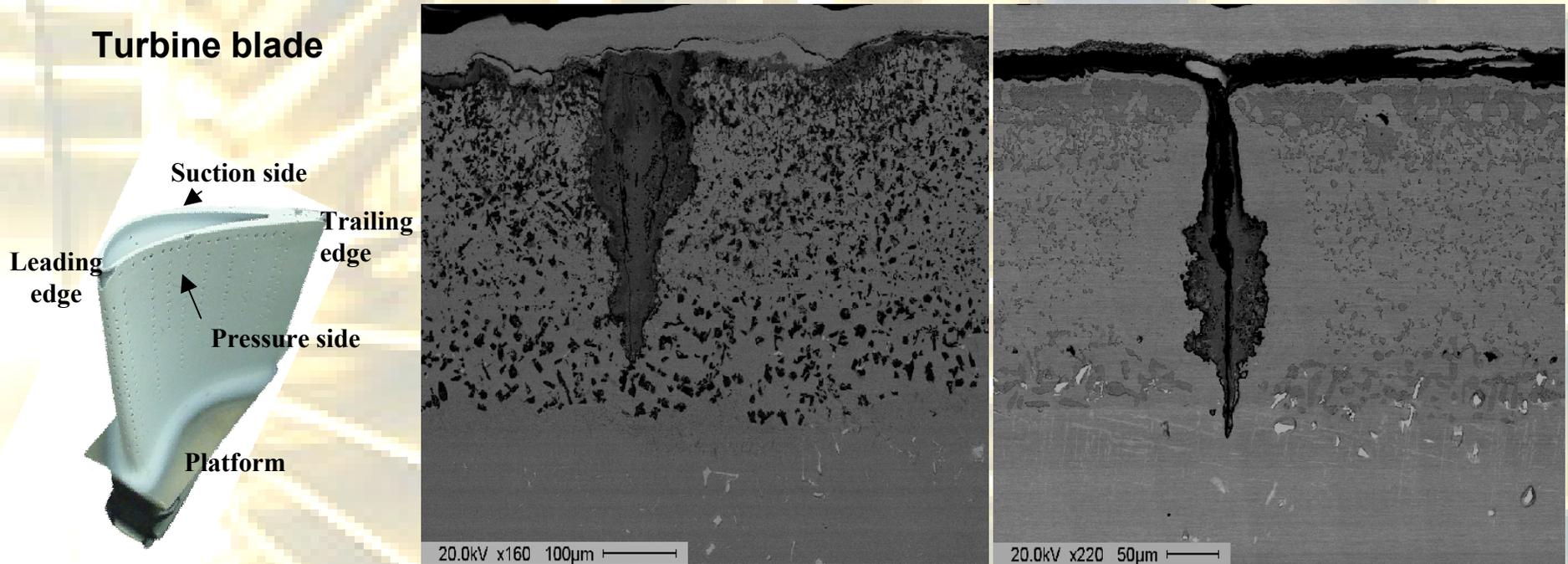


Hf-Rich Oxide:

- Hf rich Particles Exhibits Lattice Parameter $> 9\text{\AA}$.
- $(HfO_2)_{1-x}(Al_2O_3)_x$ with "Pmnb" Structure and Ordered Oxygen Lattice.



Internal Oxidation of NiCoCrAlY Coatings



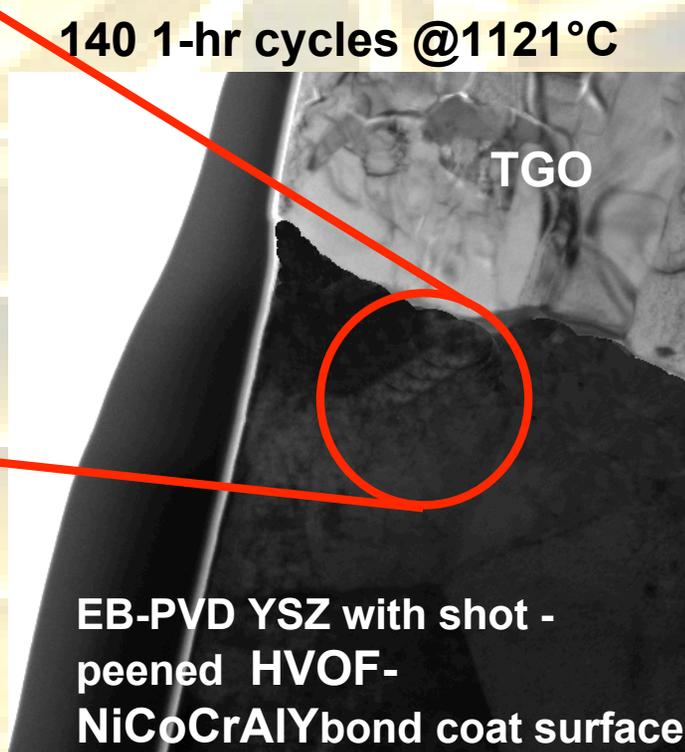
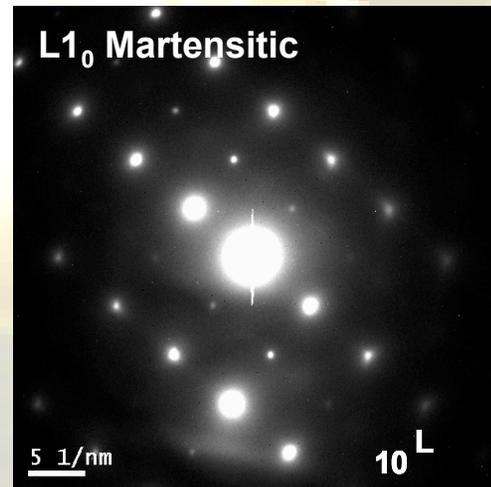
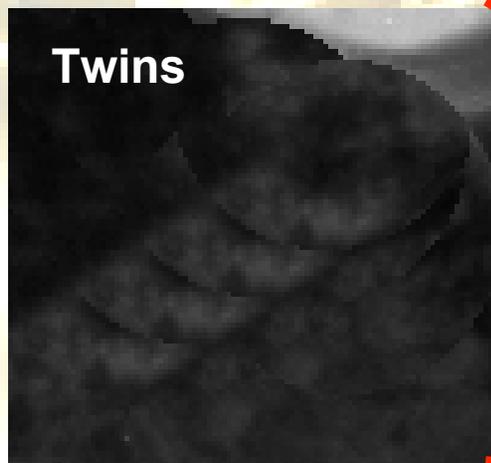
Suction Side of A Turbine Blade

Pressure Side of A Turbine Blade

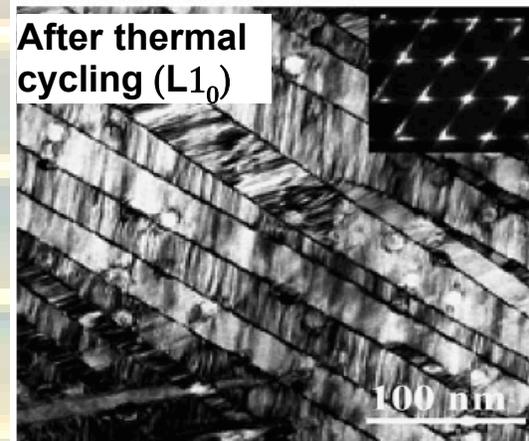
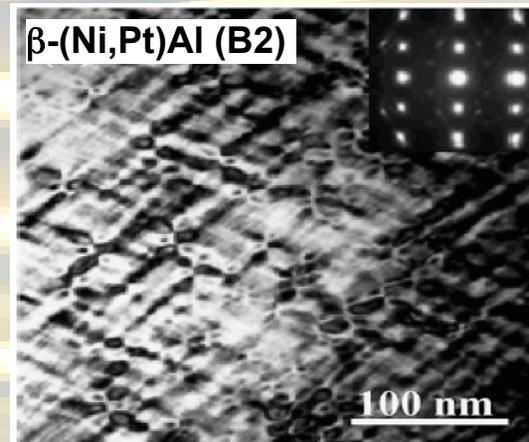
- **At the Suction Side, Internal Oxidation is Predominant. Diffusion of Oxygen into the Alloy Form Numerous Small Al_2O_3 Islands Distributed Evenly in the Coatings.**
- **At the Pressure Side, β -phase Depleting Took Place instead of Internal Oxidation.**



Martensitic Phase Transformations in (Ni,Pt)Al and NiCoCrAlY Coatings



140 1-hr cycles @1121°C



● The Al Content within The β (B2) Phase Decreases with Thermal Exposure and The β (B2) Phase Transforms to L1₀ During Cooling.

* D. Pan et al. Acta Materialia 51 (2003) 2205-2217.

© L1₀ with Twin Microstructure due to Martensitic Transformation



Summary

- **Multicomponent - Multiphase Diffusion Plays a Critical Role in Degradations and Failure Mechanisms of High Temperature Coatings.**
- **Oxidation and Coating-Substrate Diffusion.**
- **Formation of Kirkendall Porosity at Critical Locations.**
- **Phase Transformations in Coatings and Thermally Grown Oxide.**
- **Internal Oxidation.**



Acknowledgements

● Financial Support:

- National Science Foundation (NSF) CAREER (DMR-0238356).
- USDOE University Turbine Systems Research (UTSR); No. 02-01-SR103.
- USDOE Advanced Gas Turbine Systems Research (AGTSR); No. 01-01-SR091
- Siemens-Westinghouse Power Corporation, Orlando, FL.
- General Electric Global Research Center, Schenectady, NY.
- Solar Turbines Incorporated, San Diego, CA.

● Partnership Through Specimen Preparation and Technical Assistance:

- General Electric Aircraft Engines, Cincinnati, OH.
- General Electric Power, NC
- Siemens-Westinghouse Power Corporations, Orlando, FL
- Solar Turbines Incorporated, San Diego, CA.
- Howmet Research Corporation, Whitehall, MI.
- Pratt & Whitney, East Hartford, CT.

