A MECHANISM-BASED APPROACH TO LIFE PREDICTION AND NON-DESTRUCTIVE EVALUATION FOR THERMAL BARRIER COATINGS

Anthony G. Evans, David R. Clarke, and Carlos G. Levi

Materials Department, University of California, Santa Barbara, CA 93106-5050

with the collaboration of

M.Y. He, J.R. Litty, J.B. Pritchard, E.A.G. Shillington,
D. Stave, S.G. Terry and V. Tolpygo (UCSB)
J.W. Hutchinson, D. Mumm and J.S. Wang (Harvard University)

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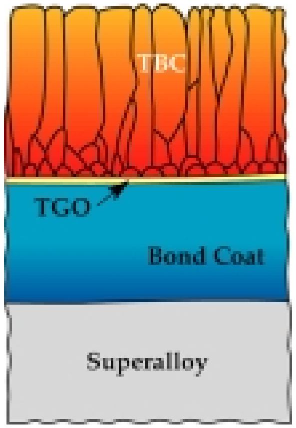


Sponsored by the Advanced Gas Turbine System Research Program

SUMMARY

The overarching goal of this AGTSR program is to develop a mechanism-based strategy to assess and understand the evolution of damage and failure of thermal barrier coatings (TBCs), and to use this strategy as a foundation for a lifing methodology and a related NDE testing protocol. The program involves activities in mechanics modeling, testing, characterization and processing aimed at providing insight into the mechanisms that dictate the life of TBCs for advanced turbine systems. A central element of the approach is a coupled modeling/experimental study of the evolution of spalls from "designed flaws" purposely introduced into the TBC system. The initial emphasis is on TBCs produced by electron-beam physical vapor deposition (EB-PVD) because of their relevance for the more critical airfoil components, with connections to plasma spray (PS) systems drawn as appropriate. Although the program is still in its first year, significant advances have already been made thanks in part to the effective participation of industrial members of the AGTSR consortium. These interactions have led to a more detailed understanding of the TBC experience in the land-based turbine industry, the similarities and divergences with the aeroengine experience and goals, the priorities in performance needs for advanced power generation and industrial gas turbine systems, and the implications for the development of lifing procedures.

A key activity in the program is the development and integration of physical and quantitative mechanics models which will form the foundation of the lifing methodology. The working assumptions are: (i) spalling is the most critical mode of failure limiting life, and (ii) cracks which produce spalling typically initiate from flaws in the thermally

grown oxide (TGO) or its interfaces with the neighboring bond coat (BC) or TBC. For these reasons, much of the initial work has focused on the mechanisms leading to buckling and spallation of the TGO in the absence of a TBC. This initial work has led to the following findings and accomplishments:

- Direct compression tests coupled with optical microscopy imaging have been used to study the initiation and evolution of damage. Details of the separation, buckling and spalling events have been documented, enabling measurement of the TGO/BC interfacial toughness (5-20 $J \cdot m^{-2}$).
- The role of oxide imperfections and other aperiodic features in the TGO as potential sources of dilatation which nucleate separations has emerged prominently. The mechanics of cracks emanating from these features has been modeled for systems with and without TBCs.
- Buckling maps have been developed and used to experimentally assess the role of non-planar features at the interface in accelerating the buckling process. These maps depict the combinations of residual stress, thickness and size of the interfacial separation, and interfacial toughness that are needed for nucleation as well as for stable or unstable propagation of the buckle.
- Studies on a IN939/CoNiCrAlY system have highlighted the detrimental effects of Al depletion in the BC upon extended high temperature oxidation. The TBC adhesion was severely impaired following the TGO transformation from a desirable α-Al_2O_3 scale into a mixture of α-$(Cr,Al)_2O_3$ and a $(Co,Ni)(Cr,Al)_2O_4$ spinel.

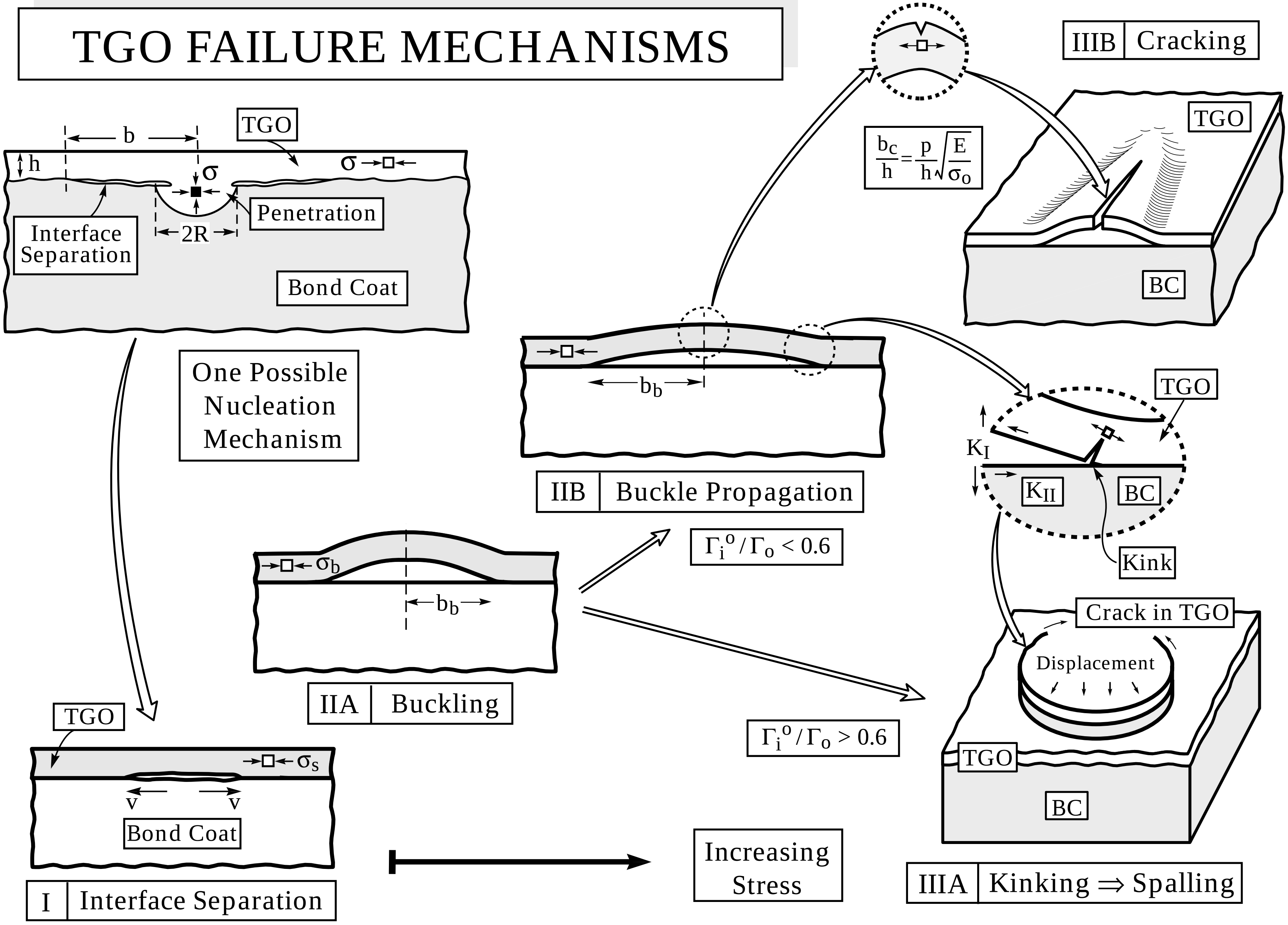
Recent work has shed considerable light on the potential role of the TBC structure and properties in modifying the state of stress and introducing alternate failure mechanisms to the buckling and spalling sequence observed in the TGO alone. The salient findings are noted below:

- Edge delamination has emerged as a potential failure mechanism for TBC systems. Modeling suggests the existence of a fail-safe regime—for certain combinations of TBC thickness and elastic anisotropy —between the buckling and edge delamination conditions.
- The above results have brought to light the relevance of the graded compliance inherent in the EB-PVD systems. To address this issue, efforts have been initiated to characterize the TBC compliance as a function of coating thickness, taking advantage of the capability for producing a wide range of controlled TBC thicknesses using the EB-PVD facility at UCSB.
- Preliminary compression tests performed on substrates with and without TBCs have indeed revealed differences in failure mechanisms, as suggested by the modeling work. Related efforts to measure stress redistribution via piezospectroscopy and for monitoring damage evolution in TBC coated specimens using thermal imaging is underway.

Significant progress has also been made in the development of potential NDE tools for the monitoring of stresses and damage evolution in TBCs. Most of the emphasis has been placed on fluorescence-based piezospectroscopy, but work has already been initiated on thermal imaging as a potential tool for assessing damage evolution through the TBC. Salient accomplishments are:

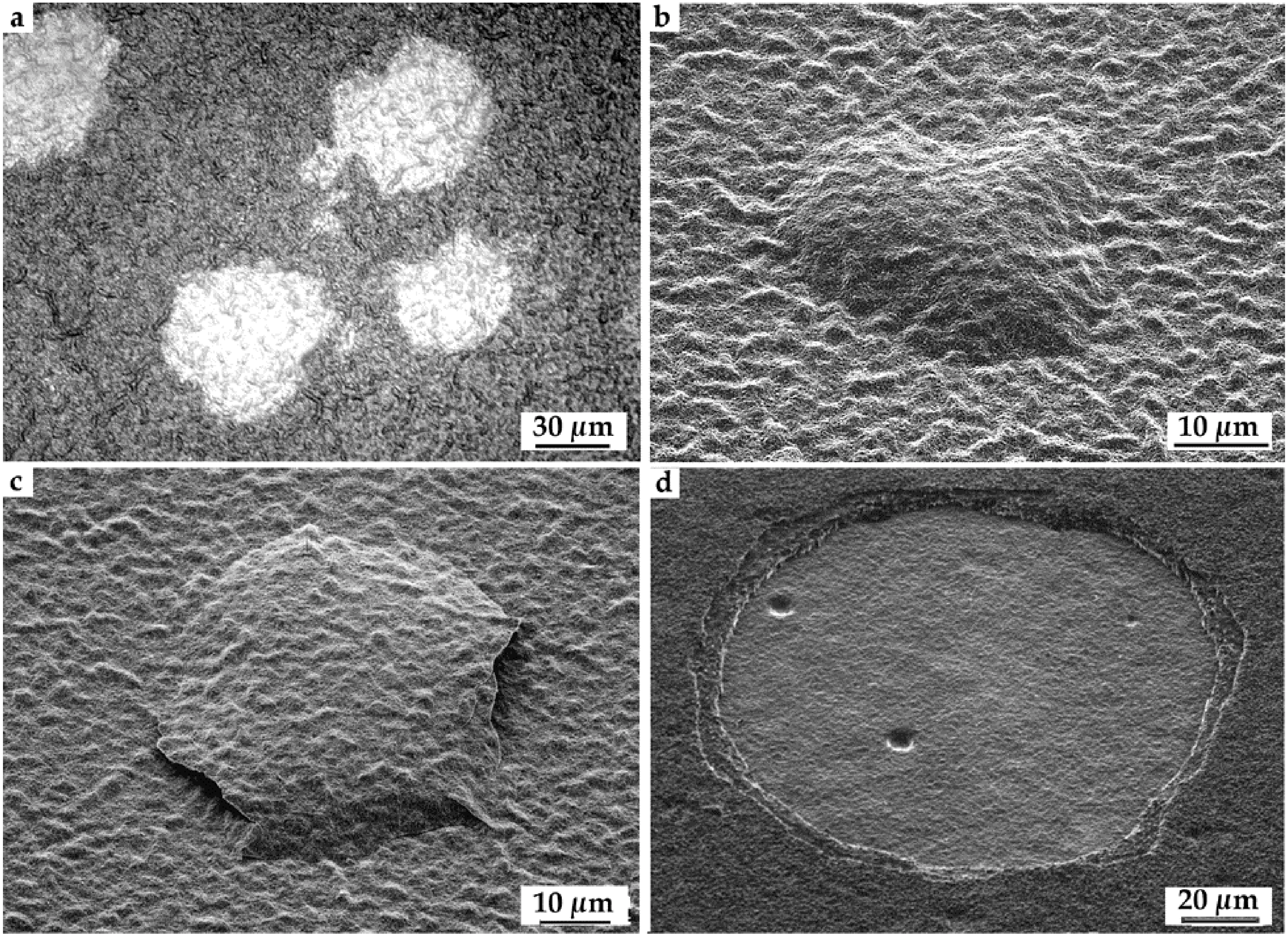
- The potential of the piezospectroscopic technique to characterize the stresses in the TGO under a TBC has been amply demonstrated. Recent work has extended the technique to study stress redistribution near edges and in the vicinity of geometric features such as small holes.
- The study on the IN939/CoNiCrAlY system cited above revealed the sensitivity of the fluorescence spectroscopy technique to changes in the TGO chemistry and phase composition. Significant Cr incorporation into the TGO was manifested in a marked attenuation of the signal and accompanied by the onset of small spalling events preceding generalized TBC detachment . In principle, this effect could be used as a warning of excessive Al depletion from the bond coat and the impending de-stabilization of the α-Al_2O_3 scale.
- The above study also revealed the complications associated with measuring stresses in TGOs wherein roughness may give rise to significant out-of-plane stresses. The implications for the NDE application of this technique are under investigation.
- Images of edge delaminations have been produced using thermal imaging.

TGO FAILURE MECHANISMS



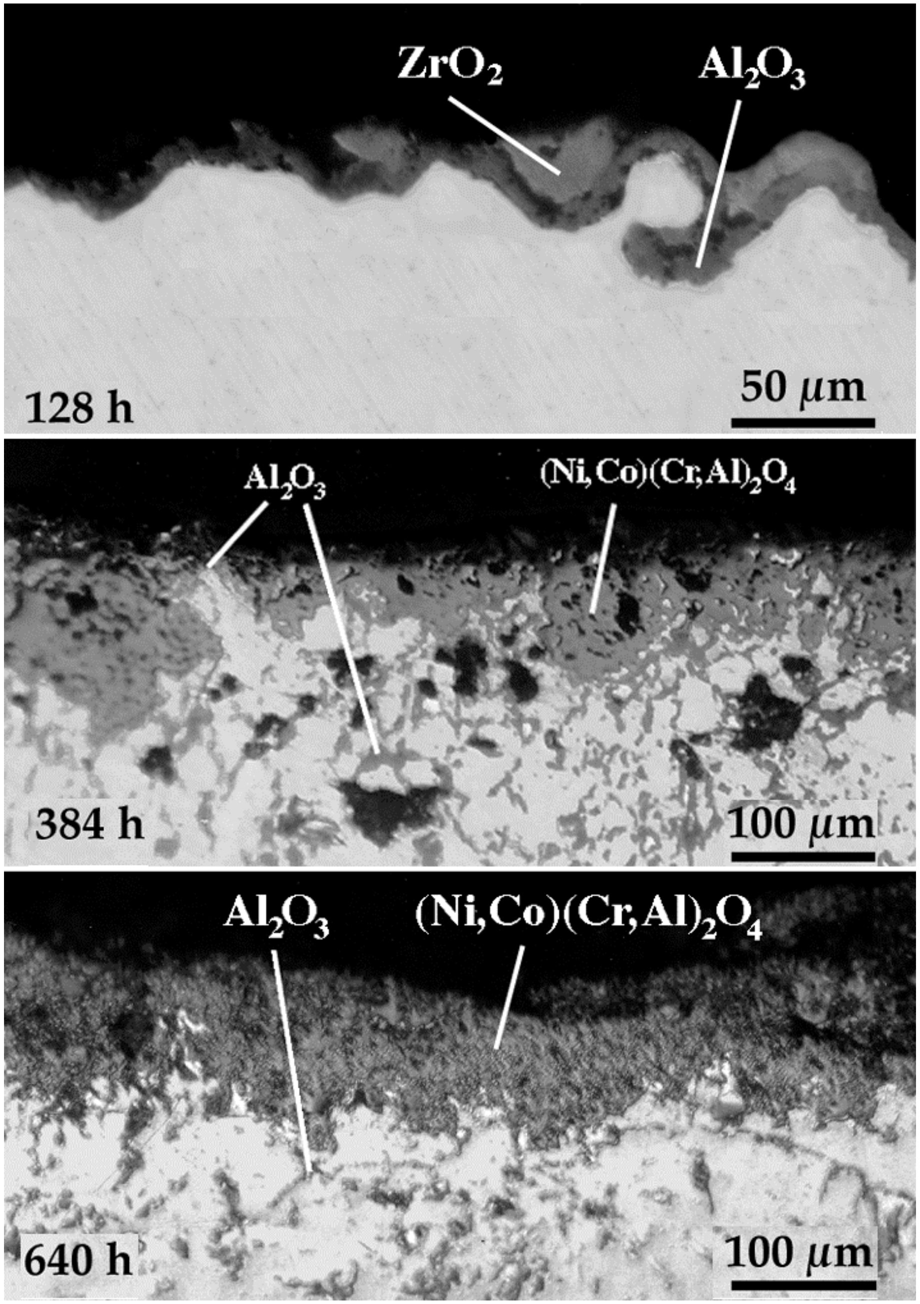
FAILURE MECHANISMS IN THE THERMALLY GROWN OXIDE

- Predominant failure mechanism is spalling driven by residual compressions (~4GPa) in the TGO.
- Spalling initiates by the nucleation of interface separations (I), typically at defects in the TGO and assisted by impurity segregation. Nucleation requires normal stresses along the interface which arise from the redistribution of the residual compression due to the non-planarities in the TGO. Likely nucleation sites are provided by oxide penetrations which represent local sources of dilatation.
- The separation thus formed grows until it meets a buckling criterion (IIA). The buckle expands (IIB) until the associated increase in the mode mixity angle causes the interface crack to kink into the TGO (IIIA), whereupon a spall develops and detaches a region of the TGO.
- Bending within the buckle induces tensile stresses in the TGO upper surface. In some cases, e.g. highly elliptical buckles, these stresses can cause cracking before the onset of spalling (IIIB). Cracks allow rapid oxygen ingress and the evolution of locally thick oxide layers. These defective regions then degrade the entire system.
- Buckle propagation is motivated by the strain energy density in the TGO and resisted by the fracture toughness of the TGO/BC interface. The extent of propagation before failure depends on the relative toughnesses of the TGO (Γ_o) and the interface (Γ_i^o).


a
30 μm
b
10 μm
c
10 μm
d
20 μm

OBSERVATIONS OF TGO SPALLING

- Formation of interfacial separations can be detected optically by a change in reflectivity of the oxidized surface (a). These particular separations are initiated at the apex of wrinkles in the TGO formed on a Fe-Cr-Al alloy after 10h at 1000°C.
- Buckle formation (b) and edge cracking (c) can be readily observed by SEM in the same sample. Note the scale of the wrinkles is much smaller than that of the buckles.
- Spalls may exhibit a circular shape (d) and in other cases a "telephone-cord" morphology. This particular sample was oxidized 25 h at 1200°C. Note the imprints of heterogeneities in (d) that may have acted as initiation sites for the initial separation.
- The exposed bond coat surface typically exhibits an imprinted morphology of the TGO grains, with no definitive evidence of plastic deformation (e.g. slip lines). This suggests brittle failure of the TGO/BC interface with minimal plastic dissipation, a behavior often associated with interfaces embrittled by segregation.



FAILURE DUE TO ALUMINUM DEPLETION

- Al depletion in the BC can impact the phase stability of the TGO and lead to embrittlement, similar to that produced by segregants.
- When a standard CoNiCrAlY (CT102) is applied to IN939, a superalloy with a relatively lean Al content, and oxidized at 1200°C for the times indicated, the initial Al_2O_3 scale is seen to transform over time into a mixture of α-$(Cr,Al)_2O_3$ and the spinel $(Ni,Co)(Cr,Al)_2O_4$, causing massive spalling of the TBC.
- Thermodynamic arguments indicate that the transformation is a consequence of Al depletion in the bond coat aggravated by interdiffusion with the substrate.
- Future research will examine the behavior of this BC on CMSX-4, a substrate with much higher Al content than IN939.

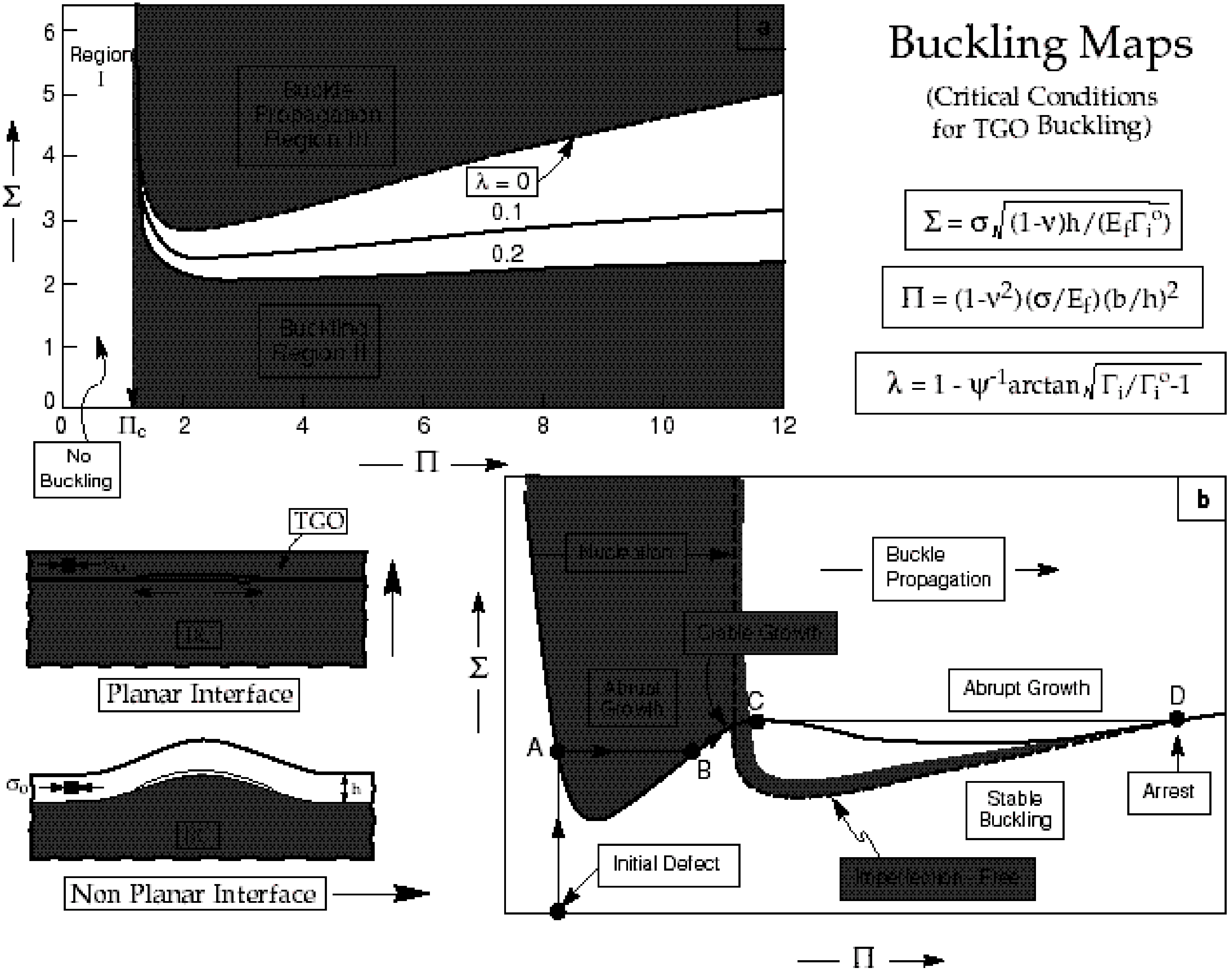
Buckling Maps

(Critical Conditions for TGO Buckling)

$$\Sigma = \sigma\sqrt{(1-\nu)h/(E_f\Gamma_i^o)}$$

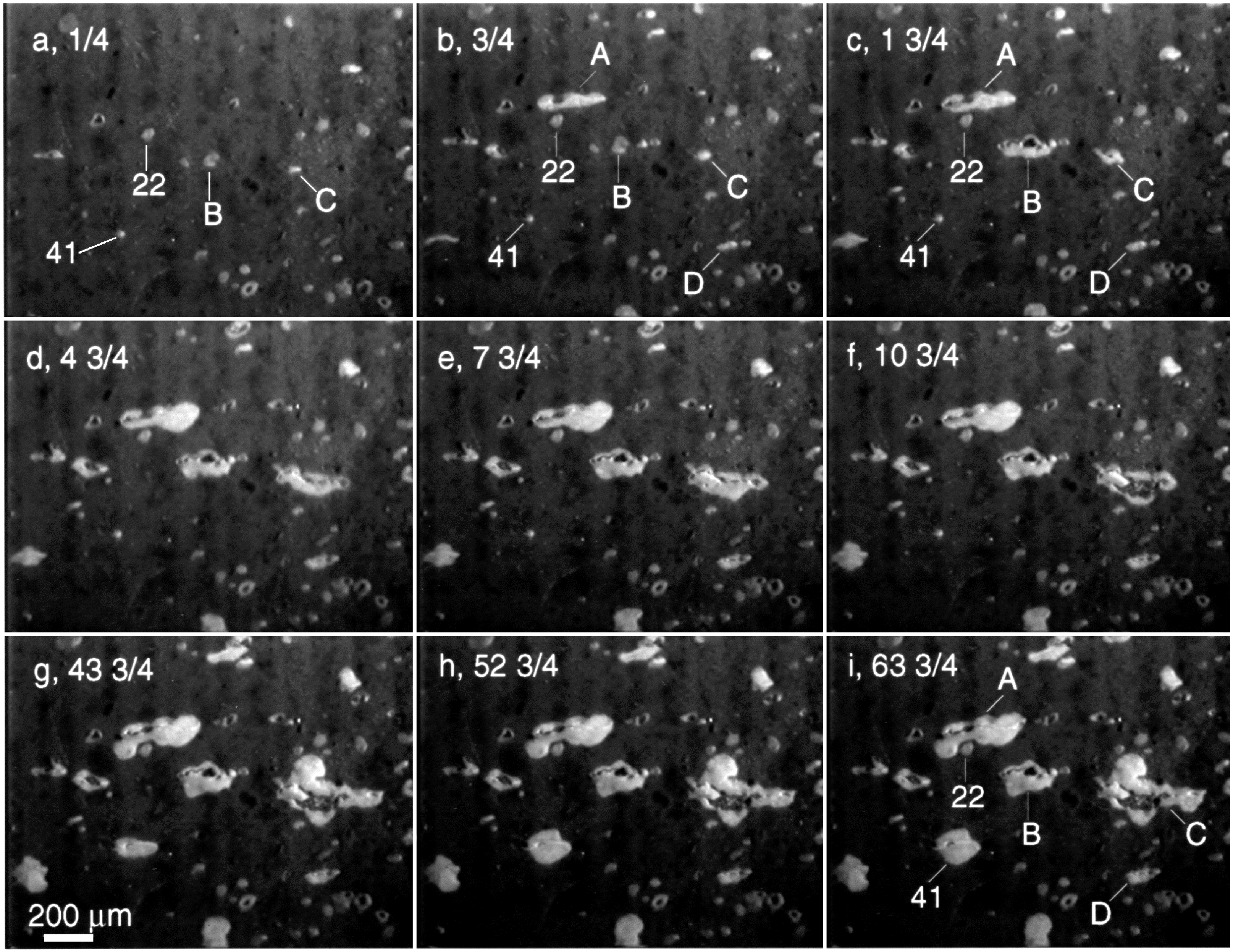
$$\Pi = (1-\nu^2)(\sigma/E_f)(b/h)^2$$

$$\lambda = 1 - \psi^{-1}\arctan\sqrt{\Gamma_i/\Gamma_i^o - 1}$$



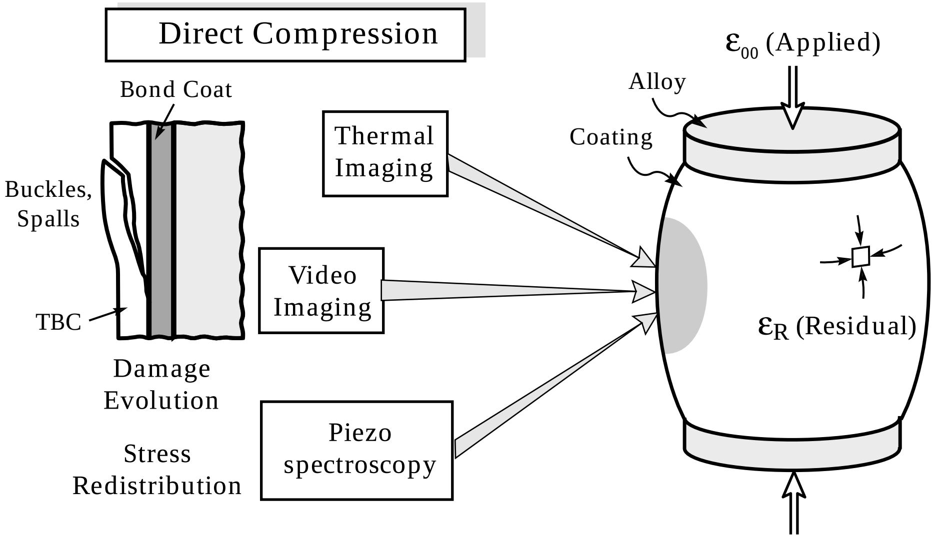
BUCKLING MAPS

- Established mechanics of compressed thin films can be used to calculate buckling maps. The behavior is represented in terms of three dimensionless indices: an adhesion index Σ, a buckling index Π, and a mode mixity index λ (see figure). In these indices σ is the residual compression in the TGO, h its thickness, E_f its Young's modulus, ν its Poisson ratio, b the separation (buckle) radius, Γ_i^o the mode I adhesion energy, Γ_i the mixed mode interfacial toughness and ψ is the mixity angle,
- The buckling map for separations in a planar interface identifies three regions:
  ⇒Region I: stable separations exist because the buckling condition is not satisfied.
  ⇒Region II: the buckling condition is satisfied, but the energy release rate is too low to cause additional buckle propagation.
  ⇒Region III: the energy release rate exceeds the interface fracture energy. At fixed mode mixity, the buckle enlarges stably as the adhesion index increases.
- For non-planar interfaces the buckling condition is satisfied at lower stresses and/or separation sizes.



a, 1/4
22
B
C
41
b, 3/4
A
22
B
C
41
D
c, 1 3/4
A
22
B
C
41
D
d, 4 3/4
e, 7 3/4
f, 10 3/4
g, 43 3/4
200 µm
h, 52 3/4
i, 63 3/4
A
22
B
C
41
D

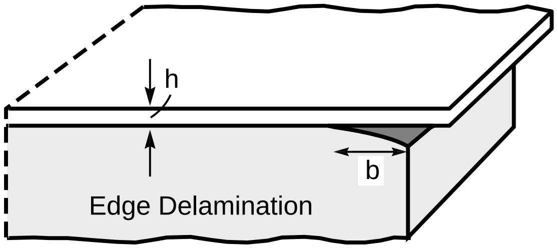
BUCKLING OBSERVATIONS

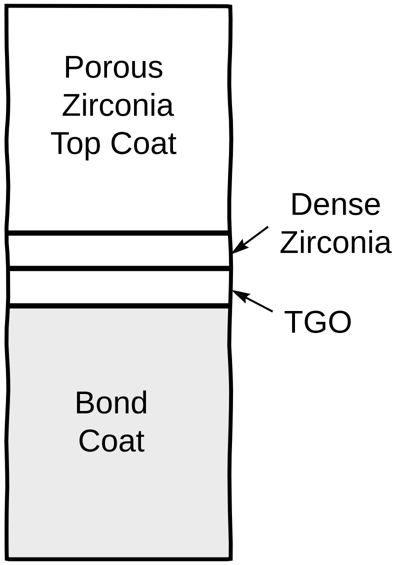


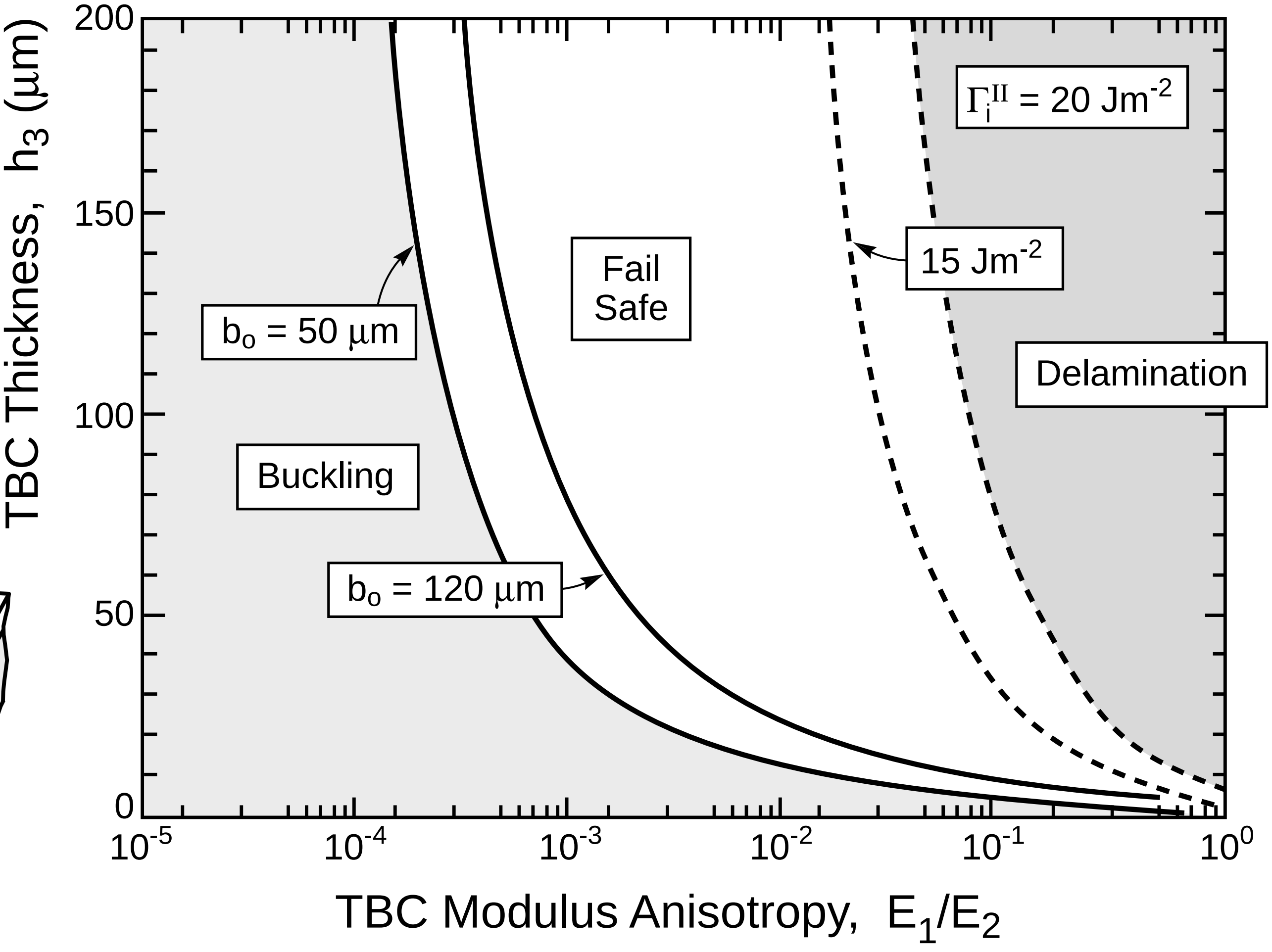
- Buckling and spalling events in the TGO can be detected by optical imaging of a specimen under compression.
- Subcritical separations formed during pre-oxidation grow and eventually buckle under imposed cyclic stress.
- The buckles expand during each cycle until they become large enough to either crack or spall (cf. e and f above).
- Observations are consistent with buckling mechanics and interface crack growth phenomena. Basic parameters such as the interfacial toughness can be assessed in this manner.
- Evidence suggests that the buckles interact with oxide heterogeneities, manifest as dark "spots" in figure above. Some buckles may initiate from these heterogeneities whereas others appear to be arrested by them. Investigation of mechanisms is in progress.
- Testing approach to be extended to TBC systems by using thermal imaging and piezospectroscopy.

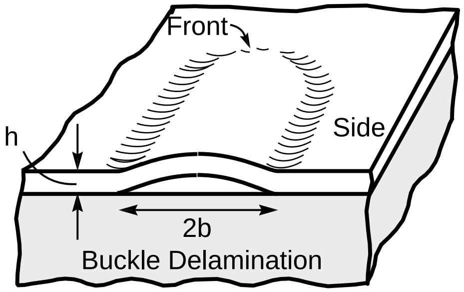
Failure Mode Competition in TBC Systems

(based on work by Choi and Hutchinson)





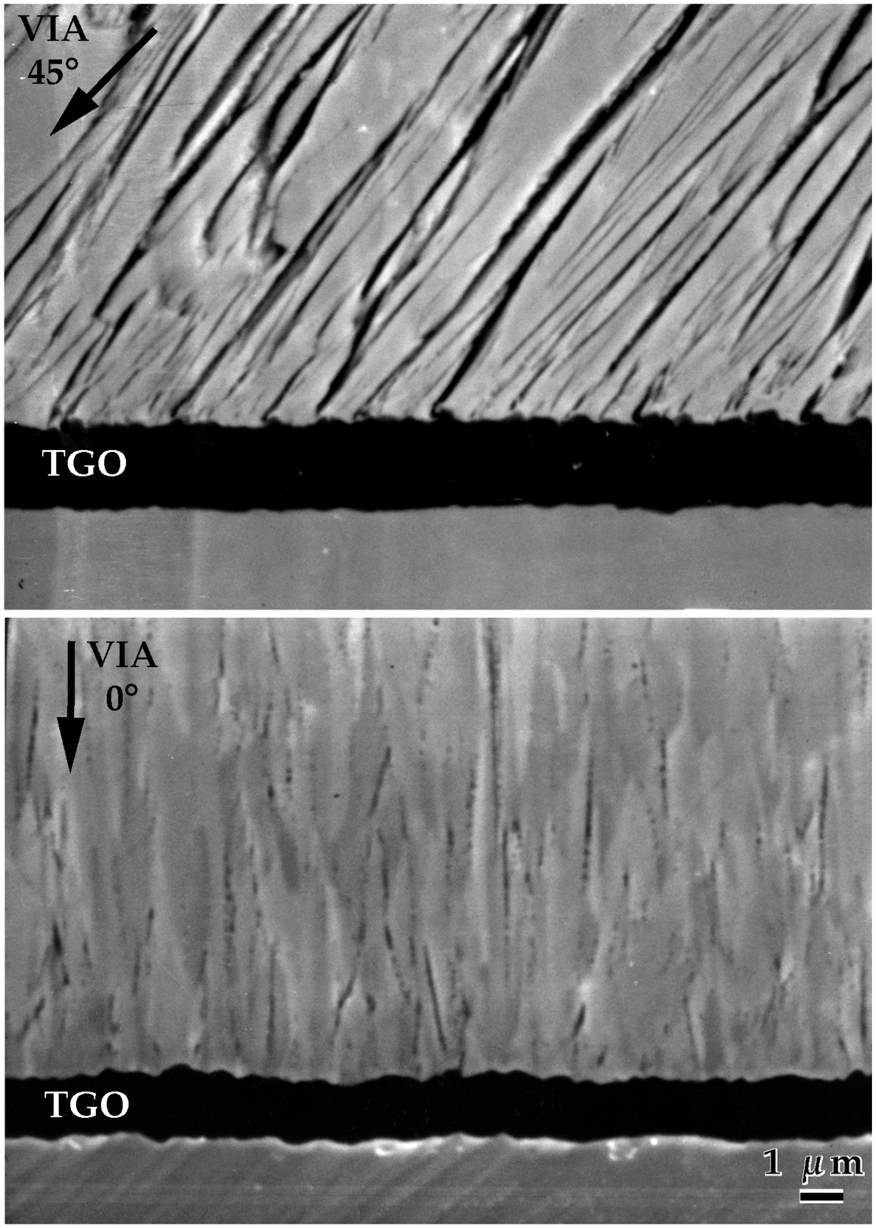




FAILURE MECHANISMS IN THE TBC

- The starting hypothesis is that TBC systems fail by a similar sequence of events as the uncoated TGO, albeit with key differences introduced by the presence of the TBC.
- The residual stress in the TGO and the associated strain energy density are still considered as the primary driving potential for failure.
- The stiffness of the superposed TBC suppresses wrinkling and buckling of the TGO. A high area density of separations and microcracks develop around the TGO well before actual TBC failure, forming preferentially at imperfections such as oxide heterogeneities. The interface remains attached at regions between separations until the latter merge and produce a sufficiently large detached area to induce spall failure. Accordingly, unlike TGO failure, TBC life is dominated by considerations of crack growth and coalescence rather than nucleation.
- As buckling is suppressed competing mechanisms emerge, notably edge delamination. In EB-PVD systems, where the compliance varies through the thickness, the dominant mechanism is determined by the relative magnitudes of the in-plane modulus of the columnar structure and the modulus of the denser layer near the substrate.
- Modeling scenarios suggest that there is a fail-safe region against spalling by either mechanism for combinations of the TBC thickness and the modulus anisotropy ratio (see figure above).

TBC Cross Section across Columns

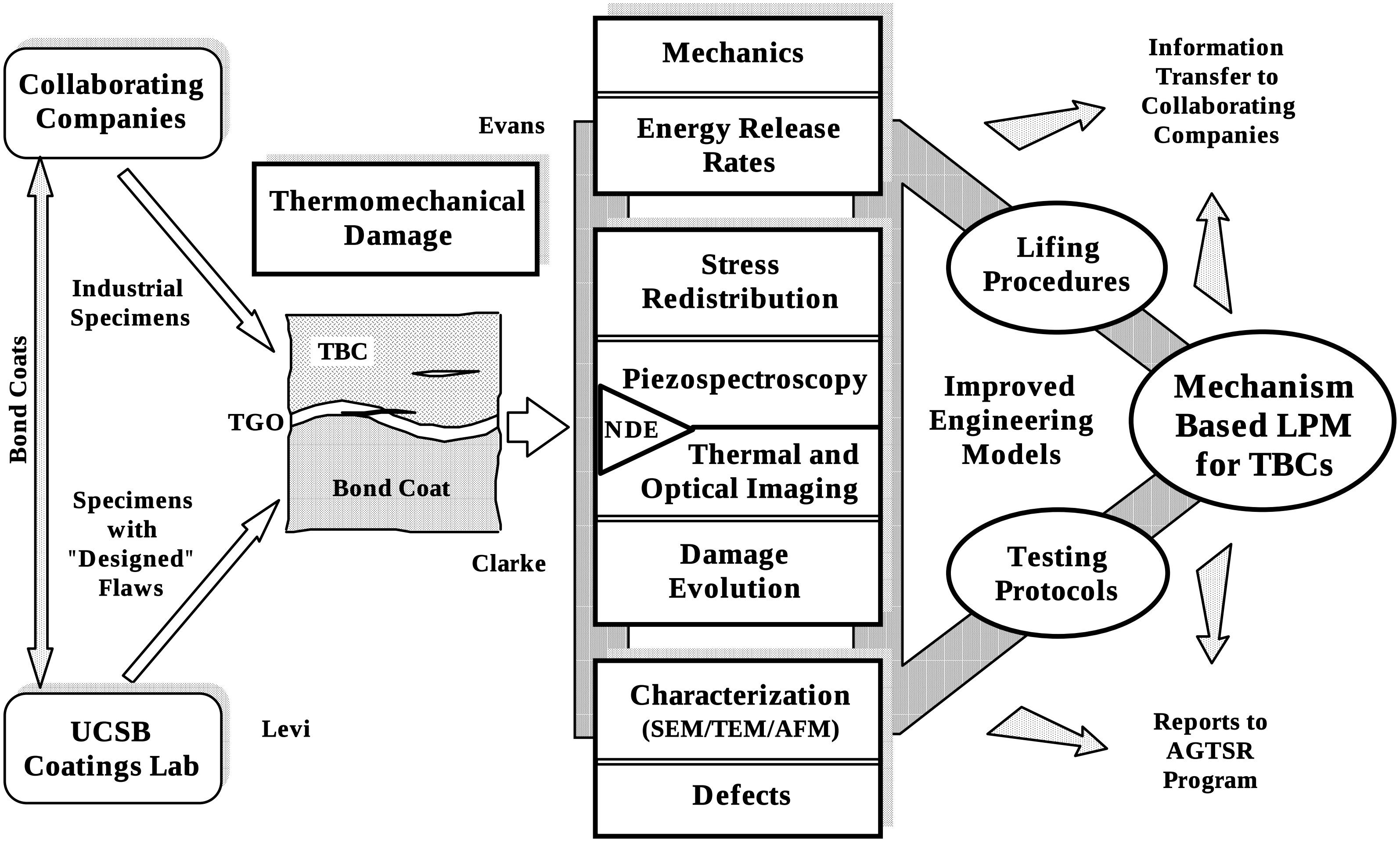


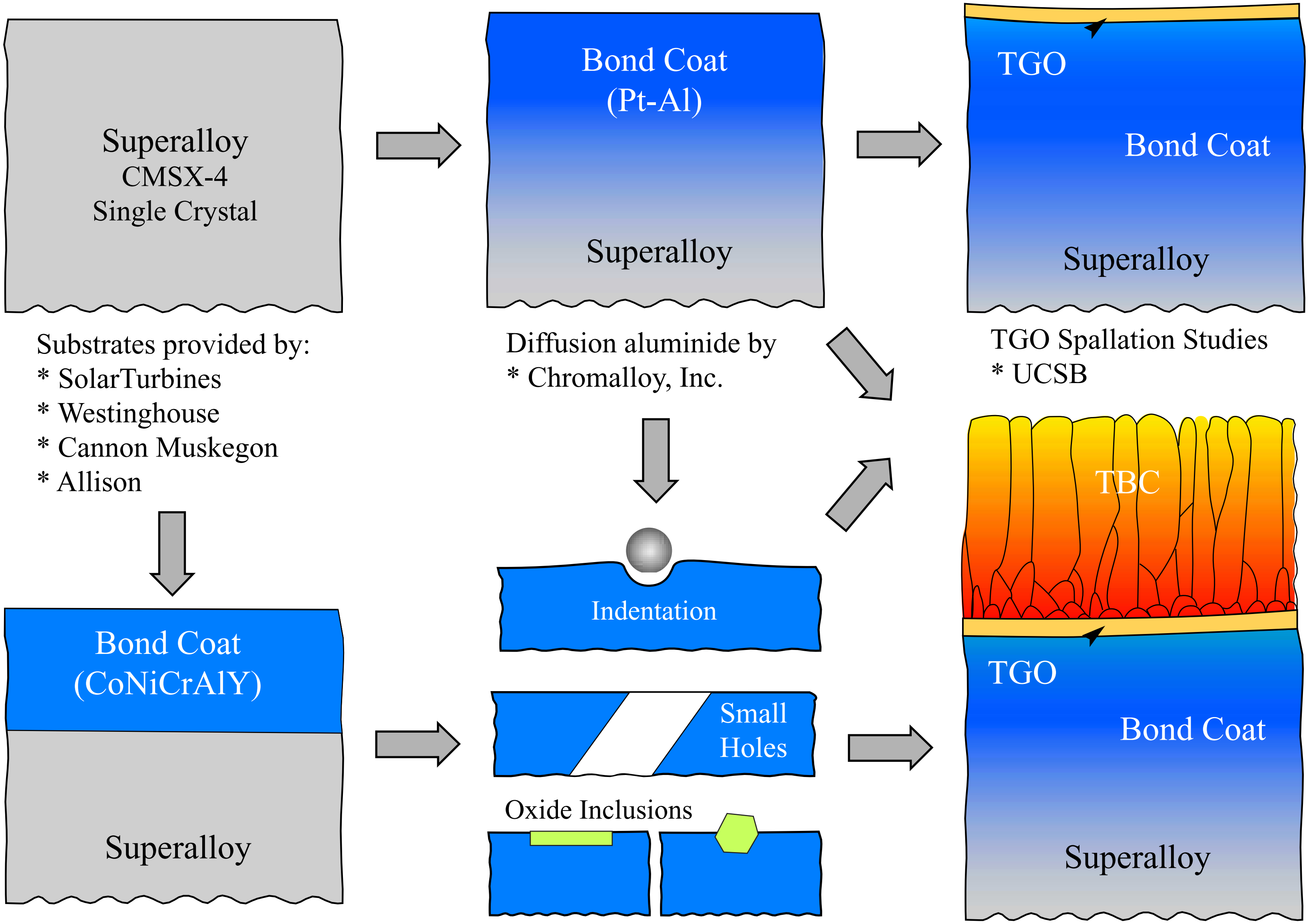
Structure of Near-Substrate Layer

EFFECT OF TBC STRUCTURE ON COMPLIANCE

- EB-PVD TBCs are naturally graded structures, with a compliance that increases with deposition thickness. This structure can be used advantageously to tailor the coating anisotropy to optimize its role in avoiding spalling failures.
- Studies are underway to characterize the variation of compliance with thickness. The figure above shows microstructures for EB-PVD TBCs deposited at 1100°C on stationary FeCrAlY substrates with different vapor incidence angles (VIA).
- The image on the left shows the strong change in porosity scale (and probably volume fraction) with distance away from the substrate. The effect is enhanced because the coating was deposited without rotation but at a high VIA (45°). It is also noted that the distribution of porosity, and hence the compliance, is anisotropic. This is a result of shadowing of the vapor flux by the column tips in only one direction.
- The images on the right show the dramatic effect of VIA on the structure of the near substrate layer, which is normally assumed to be dense.
- Specimens like these, as well as samples produced with rotation and tilting, will be used to establish relationships between compliance and microstructure. These will be used to further improve the mechanics models and the understanding of the effects of the TBC on the failure mechanism.

UCSB-AGTSR Program on Thermal Barrier Coatings





Substrates provided by:
* SolarTurbines
* Westinghouse
* Cannon Muskegon
* Allison

Diffusion aluminide by
* Chromalloy, Inc.

TGO Spallation Studies
* UCSB

LPPS Bond Coat by
* Chromalloy, Inc.

"Designed" Flaws by
* UCSB

TBC deposition at
* Chromalloy, Inc.
* UCSB

COLLABORATIONS WITH COMPANIES

- The program relies on an active and open collaboration with the participating companies, which have been extremely supportive both in terms of providing specimens as well as sharing their experiences and advice.
- A key feature of the program is the generation and study of specimens containing "designed" flaws, whose propagation under different loading conditions can be monitored and used to develop a better understanding of the damage evolution and failure processes. These are then compared with observations on the oxidation and failure behavior of specimens typical of commercial practice.
- The core of future work is based on CMSX-4, kindly provided by Siemens-Westinghouse Power Systems, Solar Turbines and Cannon-Muskegon/Allison Engine Co.
- Bond coats selected for study are platinum-modified aluminides and a standard CoNiCrAlY. Pt-Al bond coats have already been applied by Chromalloy, Inc.
- A fraction of the bond-coated specimens will be applied with a TBC at a commercial source. The rest are returned to UCSB for three major activities:
  - Incorporation of "designed flaws" in various shapes and size scales, followed by subsequent coating at the UCSB EB-PVD facility;
  - Oxidation and spallation studies of the bond coat without a superposed TBC, characterized extensively by piezospectroscopy and optical imaging; and
  - Growth of TBCs under different conditions to characterize the effects of processing on the graded mechanical properties of the coating.