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The specific goals of the proposed research have been threefold: (1) to establish a fundamental, mechanistic understanding of the degradation processes that occur in superalloy components with coatings during thermo-mechanical cycling; and (2) to use the experimental information to critically evaluate and further develop models for thermochemical and thermomechanical degradation of the multilayered systems and (3) to more quantitatively define the design space and guide the development of future multilayered systems for Naval applications.
Coating – Substrate Systems for Thermomechanically Durable Turbine Airfoils

1. Summary

In the severe operating environments encountered in Naval ship, aircraft and hypersonic applications, new materials are essential for advances in performance and efficiency. Given the accompanying need for durability and reliability, multilayered materials systems are often required in these complex thermochemical and thermomechanical environments. The design of multilayered systems for aggressive chemical and mechanical environments is challenged by uncertainties in the properties of the constituent layers, limited predictive models for evolution of structure and composition of the layers, lack of information on the properties of the interfaces and incomplete models for prediction of life-limiting failure or degradation mechanisms. This research program has addressed these challenges in metal / intermetallic / ceramic multilayered systems.

The specific goals of the proposed research have been threefold: (1) to establish a fundamental, mechanistic understanding of the degradation processes that occur in superalloy components with coatings during thermo-mechanical cycling; and (2) to use the experimental information to critically evaluate and further develop models for thermochemical and thermomechanical degradation of the multilayered systems and (3) to more quantitatively define the design space and guide the development of future multilayered systems for Naval applications.

Our approach has been to study in detail degradation mechanisms during thermomechanical cycling under isothermal fatigue conditions with sustained compressive holds at high temperature using several different superalloy single crystal substrates coated with β-NiAl, γ – γ' and reactive element-containing bond coatings. Confocal laser-stimulated microscopy has been employed to acquire new information on stresses that develop in the thermally grown oxides that form on both the superalloy substrates and the intermetallic bond coats during cycling. Finite element analyses of the damage growth processes as a function of coating and substrate properties, oxide growth stresses and initial flaw geometry have been conducted. New strategies for the design of damage resistant coating – substrate systems that can substantially improve the durability of turbine airfoils are described.

Major findings of this research program include:

- The presence of coatings and the associated interdiffusion zone influence the fatigue life at 982°C and 1080°C during cycling with 2 min. compressive holds. The presence of the intermetallic coating may either enhance or degrade fatigue life, depending on coating and substrate properties.
- Growth stresses in the thermally grown (alumina) oxide and creep properties of the bond coating and interdiffusion zone strongly influence life.
- Growth stresses in the oxides that form on the base superalloys (René N4, N5 and N6) are inhomogeneous at the dendritic scale and vary substantially among alloys.
- Bond coatings and interdiffusion layers that have high strength at temperatures above 982°C will increase life, particularly for thin sections.
- Finite element models of the damage process demonstrate that the properties of the superalloy substrate have a stronger influence on total life at lower temperatures.
- Thin (30 – 60 μm) bond coats are more favorable for increasing system life if the coating is mechanically soft at high temperatures.
2. Background and Motivation

The increasingly severe operating environments of naval ship, aircraft and hypersonic flight systems require new advanced materials to achieve new levels of performance, efficiency and reliability. Given the complex combinations of high temperatures, monotonic/cyclic stresses along with oxidizing/corrosive environments, nearly every material system requires multiple layers of surface protection. For example, yttria-stabilized zirconia (YSZ) thermal barrier coating systems are applied to nickel-base single crystals to increase the temperature capability of these components [1 - 3]. Since the porous YSZ coatings do not protect the substrate from detrimental oxidizing and corrosive environments, intermetallic interlayers are applied to the nickel-base alloy prior to deposition of the YSZ layer. The intermetallic interlayer, referred to as the bond coat (BC) forms a protective alumina layer beneath the YSZ. The final thin-walled component is then comprised of the substrate and four additional layers: (1) the interdiffusion zone between the substrate and the intermetallic layer, (2) the intermetallic bond coat, (3) the protective alumina layer and (4) the YSZ top coat, Fig. 1. Similar complexity is encountered in higher temperature ceramic matrix composites, where multilayered coatings are essential for environmental protection of the base composite material [4, 5].

As with all multilayered systems that are subject to thermal and mechanical cycling, a multitude of challenges limit the design of robust, compatible layers and the prediction of their performance in the operating environment. Among these challenges are:

- Uncertainties in the properties of the constituent layers and inadequate techniques for measuring or predicting these properties
- Limited predictive models for evolution of structure and composition of the layers
- Lack of information on the properties of the interfaces and the species that degrade interfacial properties in service
- Multiple competing modes of failure or degradation that limit life and incomplete models for relevant failure modes

In the following sections our current understanding of the various failure modes is first reviewed. Following this, new findings regarding the role of coatings in degradation process under cyclic loading conditions are presented. The implications for design of new coatings with improved durability are discussed.

3. Failure Modes in Multilayered TBC Systems

Improved durability of a multilayered system requires that the resistance to multiple competing failure modes be improved by tuning the large suite of material properties that control the thermochemical and thermomechanical processes involved in degradation. For the nickel base single crystal/bond coat/YSZ system, three major intrinsic failure modes have been observed: (1) bond coat rumpling that results in cracking of the YSZ with subsequent spallation, (2) delamination at the TGO interface with either the bond coating or the YSZ and (3) thermomechanically-assisted cracking of the coating with subsequent oxidation-assisted crack growth through the coating and into the substrate.

![Figure 1 - Multilayered system for turbine airfoils consisting of superalloy single crystal, interdiffusion zone (IDZ), bond coating, α-Al2O3 thermally grown oxide (TGO) and yttria-stabilized zirconia thermal barrier layer.](image)
An example of a rumpling-induced failure in a standard René N5 / Platinum Aluminide / 7YSZ multilayered system is shown in Fig. 2. This failure mode is driven by the large compressive stresses and the associated high levels of stored elastic energy in the TGO that are relaxed during thermal cycling to very high temperatures. This energy minimization process results in out-of-plane displacements and an undulating 'rumpled' structure. These displacements are mediated through plasticity in the bond coat, and the rate of displacement is a function of a number of factors, with the temperature dependent creep rate of the bond coat being of central importance. Analytical and numerical models have been developed by Hutchinson and co-workers to describe this phenomenon [6 - 8]. As rumpling proceeds, cracks form at the TGO/TBC interface and within the TBC near the interface. Upon further cycling, these cracks grow parallel to the TBC surface and coalesce, creating a separation large enough for the TBC to buckle [7, 9].

![Figure 2: Cross-sectional SEM micrographs of a Pt aluminide TBC after thermal cycling to failure (320 cycles), with 1 h thermal cycles to a maximum temperature of 1163°C. Extensive bond coat rumpling and cracking in the TBC results in delamination of the YSZ top coat.](image1)

Our recent research [10] demonstrates that when the Pt aluminide layer is replaced with a more creep resistant Ni-5Pd-12Cr-23Al-0.3Hf overlay coating, the failure now occurs at the TGO/BC interface, Fig. 3. In the absence of rumpling, as the thickness of the TGO increases with time at temperature, the stored elastic strain energy increases, eventually exceeding the toughness of the interface. Delamination can either proceed via the propagation of an edge crack [12], or through buckling of the TGO/TBC bilayer [11 - 14]. Both failure modes require initiation sites. For edge cracking this can be manifested through the presence of a free surface, such as the edge of a coupon specimen or a planar vertical crack through the TBC. Furthermore, for the coating to buckle, a large interfacial flaw must develop [12], which is believed to generate through the coalescence of small flaws along the interface via thermal fatigue mechanisms [13]. Time to failure is primarily governed by the growth rate of the TGO and the BC/TGO interfacial toughness, which may evolve during cycling.

![Figure 3 - Cross-sectional SEM micrographs of the 5Pd-12Cr-23Al TBCs after 260 cycles to 1163°C, at failure. Higher magnification images are inlaid showing the exfoliated TBC with the adhered TGO and the bond coat without a TGO.](image2)

Considering the competing failure modes of rumpling and delamination, it is possible to devise a failure mechanism map. Consider first the interfacial delamination failure mode, Fig. 4. Delamination at the BC/TGO interface occurs when the stored elastic strain energy in the TBC system exceeds the BC/TGO interfacial toughness. The stresses in each layer are proportional to $\bar{E}_i\Delta\alpha_i\Delta T$ where $\bar{E}_i$ is the effective elastic modulus of layer $i$ and $\Delta\alpha_i$ is the difference in CTE between

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layer \( i \) and the substrate. The stored elastic strain energy can then be related to the stress in the layer, \( \sigma_i \), through Equation 1, in which \( h_i \) is the thickness of the layer:

\[
U_i = h_i \frac{\sigma_i^2}{2 \varepsilon_i}
\]  (1)

Due to the high elastic modulus and low CTE of \( \alpha\)-Al\(_2\)O\(_3\), the largest stresses are generated in the TGO. Thus, the increase in the total strain energy of the system is primarily influenced by the rate of TGO growth, and, as a first-order approximation, the tendency for delamination can be related to \( U_{TGO} \). Thus, the driving force for delamination increases proportionally with the TGO growth rate, Fig. 4. \( U_{TGO} \) is expressed in terms of exposure time, \( t \), and temperature through an Arrhenius-type expression for oxide growth on the bond coating, Eqn. 2, with \( Q = 135 \) (kJ/mol), \( k_o = 5.89 \times 10^{-2} \) (m\(^2\)-s\(^{0.4}\)), \( n = 0.4 \) [15] and \( E_{TGO} = 427 \) GPa [16]:

\[
U_{TGO} = 0.5k_o \exp \left( \frac{Q}{RT} \right) t^n (\Delta \alpha \Delta T)^2 E_{TGO}
\]  (2)

Prediction of the number of cycles to failure requires several material properties (Eqn. 2), including the BC/TGO interfacial toughness, which is in most cases unavailable due to the difficulty of measuring this property. Here we assume that the BC/TGO interfacial toughness decreases with exposure time, as impurities segregate to the interface and imperfections grow [17]. Sulfur segregation occurs rapidly at high-temperature and in most cases the interface is saturated in less than 50 hours [17 - 19]. The interfacial toughness expected for a BC/TGO system with strong (representing low S) and weak interfaces (high S) are also plotted in Fig. 3. The intersection of the delamination driving force curve with the interfacial toughness curve denotes the time-to-failure of the system [20, 21]. From Fig. 4, it is apparent that variations in interfacial toughness and its evolution with time can easily influence failure times by factors of 2 to 10. As discussed in more detail in the proposed research section below, we will employ a new method for measurement of interfacial toughness in order to more quantitatively predict failure times.

The maps can be further developed to analyze the competition between the rumpling and delamination failure modes. When a bond coat rumples out-of-plane stress develop, in addition to the in-plane stress present in the planar TBC multilayer. Evans and co-workers have characterized the development of these out-of-plane stresses, finding compression above peaks and tension above valleys in the wavy interface [1, 22, 23]. Cracks form in the TBC in the regions under tension (above valleys) and these cracks extend toward the adjacent region under compressive stress. Crack growth is halted by the compressive stress until the rumpled interface evolves such that compressive stresses are sufficient to extend the cracks in a primarily Mode II manner. When the driving force for Mode II propagation is reached, the crack can grow unstably and link with adjacent cracks growing above nearby rumpled regions. When a sufficient number cracks coalesce, the TBC fails by buckling. Xu et al. [24] analyzed this problem using a combined numerical and analytical approach and calculated influence of material properties and thermal history on the propagation of mode-II cracks. The cycle-number, \( N \), dependence of this driving force, \( G_{TGO,TBC} \), is most strongly influenced by elevated
temperature bond coat strength and the growth stress in the TGO [24] and is shown in Fig. 5. Unlike fracture at the BC/TGO interface, the toughness of the TBC, through which the cracks will propagate, is not expected to degrade significantly with time and a constant toughness is plotted on Fig. 5. By analogy to the BC/TGO failure, time to failure can be denoted by the intersection of the rumpling delamination driving force curve with the TBC toughness curve. With both mechanisms represented in Fig. 5, it is apparent that the failure mechanism can easily change as the level of the BC/TGO interfacial toughness changes, with failure occurring at the BC/TGO interface for a low interfacial toughness, but at the TGO/TBC interface with higher BC/TGO toughness. Again, knowledge of the BC/TGO interface toughness, elevated temperature bond coat strength and oxide growth stresses are critical for predicting coating failure mode and total cyclic life for both failure modes.

The third intrinsic failure mode has been the focus of our most recent research, since it has become a limiting factor in the development of new alloy and coating systems and the design of turbine airfoils [25]. In these multilayered airfoil systems, the superposition of centrifugal and vibratory stresses with thermal stresses that arise due to internal air cooling [26] result in a degradation process that initiates cracks in the surface coating(s). The impingement of hot gases on the surface of the airfoil and the constraint caused by the cooler inner surfaces typically results in surface compressive stresses [27 - 29]. Under these conditions, the failure of nickel-base single crystals subjected to thermomechanical fatigue cycling typically occurs by surface crack initiation and subsequent propagation inward through the coating into the substrate [25]. This damage growth process is influenced by the simultaneous oxidation of the intermetallic coating and/or the superalloy substrate [27 - 37]. When a thermal barrier coating is present, these processes often occur following local spallation of the YSZ, leading to “conservative” maximum design temperatures for the TBC. Material degradation is further accelerated by sustained compressive holds present in the fatigue cycle [25, 34]. We have focused on the most severe loading scenario involving fatigue cycling with compressive holds, which is referred to as Sustained Peak Low Cycle Fatigue (SPLCF). During the compressive hold, creep deformation occurs, resulting in tension upon returning to zero strain, Fig 6.

The SPLCF failure mode has been the focus of the research conducted in this program. This mechanism of degradation has been studied in detail with an emphasis on identification of the properties of the multilayered system that most strongly influence cyclic life. Major results are summarized in the following sections.

4. Modeling of System Behavior under SPLCF Cycling Conditions
During cycling under the conditions shown in Fig. 6, cracks, if present, open during the tension part of the cycle, permitting oxidation along the crack faces and at the crack tip. Fig. 7 shows the early stage of the
formation of a crack during SPLCF cycling of René N5 single crystal superalloy at 1093°C, where the TGO is cracked and intruding into the superalloy substrate.

**Figure 6** - Schematics of the applied straining conditions associated with sustained peak load cyclic fatigue. (a) The compressive strains imposed and trends in the stresses induced as cycling proceeds. (b) The hysteresis loops and their evolution with cycling.

With the presence of an intermetallic bond coating, Fig. 8, as cycling continues, oxidation-assisted crack growth occurs through the bond coating (Stage I), interdiffusion zone (Stage II) and into the nickel-base substrate (Stage III) occurs. This degradation process is linked to the rumpling process (that occurs during thermal cycling only) in that the oxide growth stresses provide a driving force for the extension of the oxide-lined crack through the multiple layers into the substrate.

To date, cycling experiments on β-NiAl based coatings on René N5 single crystal substrates have demonstrated that the presence of an aluminide coating can either extend or reduce cyclic life compared to bare, uncoated specimens. These cracks grow through the coating, interdiffusion zone and into the single crystal substrate during cycling. The creep deformation that occurs during the compressive hold relaxes compressive stresses and results in tensile stresses upon return to zero strain, opening the cracks and permitting oxidation of crack faces. This rate of degradation is sensitive to the mechanical properties of the substrate and coating as well as on the presence of growth strains in the oxides formed on samples surfaces and along the crack faces.

**Figure 7** - Cracks in the surface oxide extending into the nickel-base superalloy during fatigue cycling with compressive holds at 1093°C.

To more quantitatively assess the influence of the properties of the oxide and other constituent layers on lifetime, detailed finite element analyses of the damage growth process have been conducted and validated with parallel experiments [27, 38].
Modeling of the SPLCF Degradation Mechanism

Finite element models for each stage of the SPLCF process, Fig. 8, have been developed to address the properties of the coating, interdiffusion zone, thermally grown oxide (TGO) and superalloy substrate that most strongly influence the failure process at each stage. To critically examine the quantitative predictions of the model we have also modeled the SPLCF process for uncoated René N5, Fig. 9, since the relevant properties (modulus, CTE, oxide growth strains, creep resistance) for the single crystal substrate are well understood, compared to the coatings, which are not as well characterized.

Figure 10 shows the predicted fatigue hysteresis loops assuming that relaxation during the compressive hold is governed by steady state and transient creep, respectively. Good agreement with experimentally measured hysteresis loops is observed when including the transient creep response. Using this form of the model, energy release rates at the crack tip and the associated stress intensities were calculated. When the calculated stress intensities exceeded the threshold cyclic crack threshold, then crack advance was then calculated by a conventional fracture mechanics approach.

Figure 9 - (a) SPLCF Finite element model showing the oxide (red) with TGO thickness h and crack depth a and (b) schematics of the meshes used to simulate damage growth at each of the three stages of crack penetration into the substrate.
Steady State Creep Rate

Creep, no Plasticity, $h=1\mu m$, $\sigma_{\gamma}^{\text{sub}}=300\text{ MPa}$, $a=100\mu m$

uncoated, $\frac{ds}{dt} = 4 \times 10^{-9} \frac{(a/a_0)^{1/2}}{s}$, $\sigma_{\gamma}^{\text{sub}}=100\text{ MPa}$

$\varepsilon_a = 0.16\%\text{/cyc}$, $\Delta u/L=0.4\%$

Figure 10 - Modeled hysteresis loops for SPLCF cycling of uncoated René N5, showing that importance of transient creep. The evolution of stress/strain loops predicted for coated samples with the yield strength of the coating $\sigma_{\gamma}^{\text{coat}} = 20\text{ MPa}$, and $\sigma_{\gamma}^{\text{sub}} = 100\text{ MPa}$, $\sigma_{\gamma}^{\text{sub}} = 300\text{ MPa}$, $\varepsilon_{\text{growth}} = 0.4\%\text{/cycle}$, $\varepsilon_{\text{appl}} = 0.4\%$ The creep rate coefficient for the superalloy: $\frac{ds}{dt} = 4 \times 10^{-9} \frac{(a/a_0)^{1/2}}{s}$; crack depth (a) $a/h = 30$, (b) $a/h = 100$.

Transient Creep Included

Creep, no Plasticity, $h=1\mu m$, $\sigma_{\gamma}^{\text{sub}}=300\text{ MPa}$, $a=100\mu m$

uncoated, $\frac{ds}{dt} = 4 \times 10^{-7} \frac{(a/a_0)^{1/2}}{s}$, $\sigma_{\gamma}^{\text{sub}}=100\text{ MPa}$

$\varepsilon_a = 0.16\%\text{/cyc}$, $\Delta u/L=0.4\%$

Fig. 11 shows the crack length as function of the number of cycles for the uncoated material for the model calculation compared to the experimental measurement, with good agreement. Note also that when the maximum tensile stresses in the cycle are 150 - 200 MPa that more than half of the life is consumed before the crack length exceeded the cyclic threshold stress intensity. This is consistent with experimental observations [25]. Since the model provided very good predictions for the uncoated material, it has been used to assess the role of coating properties. For example, the influence of soft, intermediate and hard bond coats on the total cyclic life is predicted. It is important to note that the presence of even a soft bond coat extends the SPLCF life relative to the uncoated material, while stronger bond coats (50 MPa) could improve life by more than a factor of 5. This motivates the development of stronger bond coat compositions.
Finally, the growth strains in the oxide play a very significant role in the damage growth process. Fig. 12 shows the oxide penetration rate through the coating during Stage I, with growth strains as small as 0.03% accelerating the TGO penetration rate by a factor of 4.

5. Oxide Growth Strains
Modeling shows an important role for the substrate and/or bond coat oxide growth strains in the rumpling and the SPLCF processes. Unfortunately these growth strains are not well understood for the TGO that forms on either the superalloy substrate or the intermetallic coatings. In general, the growth stresses/strains are thought to develop during steady state oxidation at high temperature, as new α-Al2O3 forms at the surface of the intermetallic by inward diffusion of oxygen and at transverse grain boundaries due to an additional outward counter-flux of Al from the substrate [47, 48]. The alumina formed on the grain boundaries is accommodated by lateral straining and creep of the neighboring oxide grains [49 - 51], with an oxide growth stress that persists during continued growth [52, 53]. The magnitude of this stress has been measured in-situ for the oxide that forms on several different intermetallic coatings and the magnitude of these growth stresses during oxidation above 1000°C is of the order $\sigma_{\text{growth}} \approx -200$ to $-300$ MPa [52 - 54].

Motivated by the SPLCF modeling problem described in the previous section, we have focused on the measurement of growth stresses that develop in single crystal substrates (René N4, N5 and N6) in comparison to earlier measurements on various bond coats [52 – 54, 57 – 59]. Stresses within the oxide following isothermal oxidation were measured at room temperature in a laser scanning confocal microscopy (LSCM) system with capabilities for topographic imaging, photo-stimulated luminescence imaging and Raman spectroscopic imaging, in collaboration with Case Western University [56]. Several interesting observations emerge from these initial measurements. First, the growth strains on the single crystal superalloys measured at room temperature (and adjusted to account for thermal expansion mismatch during cooling) are a factor of 5 to 10 higher than those observed on NiAl, platinum aluminate and MCrAlY coatings, as measured directly in-situ via high temperature X-ray diffraction or indirectly (similar to the present experiments) by piezospectroscopy at room temperature [52 – 54, 57 – 59]. Second, the stresses also vary substantially among the three single crystal alloys, Fig 13. Finally, there are substantial spatial variations in the magnitudes of the growth stresses. For the single crystal alloys the wavelength of the spatial inhomogeneities observed were of the order of 200 - 300 µm, which is also of the order of the primary dendrite arm spacing. At the scale of dendrites there is substantial enrichment of W and Re (if present) in the cores of the dendrites and Ta and Al in the interdendritic regions [60, 61]. There were also significant spatial variations in the stresses measured in the oxide that grows on a platinum aluminate bond coating deposited on René N5 (Fig. 13, note at longer annealing times with thicker oxide). The origins of these spatial variations are likely to be very important to the failure process, since they exhibit compressive stresses upon cooling that are as high as 6 – 7 GPa over local regions of similar size as the potential size of the critical buckling radius for the oxide.
6. SPLCF Experiments

Building on our prior experimental work, degradation mechanisms have been studied experimentally via sustained peak low cycle fatigue (SPLCF) cycling experiments on uncoated single crystal substrates as well as on substrate materials with three different coatings, including β and γ - γ' coatings. In strain-controlled fatigue cycling at 1080°C with $R = \infty$ and a 120s compressive hold. The straining cycle was selected in collaboration with GE Aviation, since this cycle is a key materials/coatings design and selection metric [25].

Figures 14 and 15 shows the surface crack length and crack growth rate as a function of the number of SPLCF cycles at 1093°C for the NiAl(Cr, Zr) coating, and EQ coating deposited by NIMS in Tsukuba, Japan, and a vapor phase NiAl aluminide coatings, in comparison to bare René N5. Interestingly, relative to the uncoated sample the vapor phase aluminide increased the total life, while the NiAl(Cr, Zr) decreased the cyclic life by about a factor of 2. Relative to the vapor phase aluminide coatings, the oxide-filled cracks in the NiAl(Cr, Zr) coating penetrated through the coating and interdiffusion zone more rapidly (within 2000 cycles). Additionally, without the constraint of a TBC, the NiAl(Cr, Zr) coating experienced extensive rumpling, suggesting a relatively low creep strength at the testing temperature. While the EQ coatings did not rumple to any significant degree and likely have a higher creep strength, these coatings did not increase system life beyond the bare René N5. Oxide filled cracks are apparent in all of the tested coatings, Fig. 15. The vapor phase aluminide provides the best performance of all of the coatings examined. We hypothesize that this is due to low growth strains in both the coating and IDZ; this aspect on the coating behavior remains under investigation.
Figure 14 - Rate of damage growth as a function of number of SPLCF cycles in uncoated, vapor phase NiAl aluminide and NiAl(Cr,Zr) coated Rene N5 samples cycled at 1093 °C with $\Delta e = 0.35\%$.

Figure 15 - Cross sections of cracks that penetrate through the coating and IDZ in each of the experimentally examined coatings on Rene N5 substrates and the maximum crack length as a function of the number of imposed cycles, up to failure.

7. Implications for the Design of Coating – Substrate Systems

The design of multilayered coating systems is a complex challenge, given the large suites of material properties and the multiple modes of degradation that are operative. Experiments on bare Rene N5, where the thermal and mechanical properties of the material are well known are in good agreement with the finite element models for the SPLCF crack growth mechanism. The complete property set for the
coatings is difficult to obtain due to the fact that they are deposited as thin layers. Nevertheless, differences in the coating properties are responsible for the varying cyclic lives observed. Thus models of the multilayered system are useful for exploration of the design space and for focusing the search for new coatings.

For all three modes of degradation: (1) delamination, (2) rumpling and (3) SPLCF, the role of the thermally grown α-Al₂O₃ (TGO) has proven to be very critical, as it stores high levels of strain energy and is the layer essential for maintaining environmental protection. Based on the experiments and models described above, important priorities for design of the multilayered system emerge and will guide our future research:

- **Low growth stresses in the TGO**
  The relaxation of the growth stresses in the TGO that develop due to the counter-flux of ions along the TGO grain boundaries [39] drives the development of the undulations during the rumpling process and the extension of the TGO-lined crack through the coating layers into the substrate in the SPLCF process [38]. As will be discussed in the next section, there are still many uncertainties about the dependence of these growth stresses on coating/substrate chemistry, structure and their evolution at elevated temperatures.

- **Higher interfacial BC/TGO toughness**
  Multilayered systems have a strong tendency to failure along interfaces, which may contain defects, serve as sites for segregation of detrimental chemical species and must bond together disparate metallic/intermetallic/ceramic layers. Also, while the interfacial toughness is thought to decay with exposure time at elevated temperature, the difficulty of measuring interfacial toughness [40] is a barrier to improving the interfaces. A new method for measuring interfacial toughness will be further developed in the proposed program.

- **Higher strength bond coatings**
  In both the rumpling and the SPLCF processes, the bond coating undergoes significant plastic (creep) deformation at elevated temperatures during thermal and mechanical cycling. Suppression or reduction of the degree of bond coat deformation will substantially extend life across a wide range of thermal and thermomechanical cycling conditions. In general this may require that coatings be constituted of phases other than the ordered NiAl-based B2 β phase, which has not shown any improvements in high temperature strength or rumpling resistance with alloying [41].

7. References


8. Personnel

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9. Publications