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Failure Mechanisms of Thermal Barrier Coatings Exposed to Elevated Temperatures

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EXPOSED TO ELEVATED TEMPERATURES

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ABSTRACT

The failure of a ZrO_2 -8 percent Y_2O_3 /Ni-14 percent Cr-14 percent Al-0.1 percent Zr coating system on Rene 41 in Mach 0.3 burner rig tests has been characterized. High flame and metal temperatures were employed in order to accelerate coating failure. Failure by delamination was shown to precede surface cracking or spalling. This type of failure could be duplicated by cooling down the specimen after a single long duration isothermal high temperature cycle in a burner rig or a furnace, but only if the atmosphere was oxidizing. Stresses due to thermal expansion mismatch on cooling coupled with the effects of plastic deformation of the bond coat and oxidation of the irregular bond coat are the probable life limiting factors. Heat up stresses alone could not fail the coating in the burner rig tests. Spalling eventually occurs on heat up but only after the coating has already failed through delamination.

INTRODUCTION

Plasma sprayed thermal barrier coatings, consisting of an insulating ceramic layer applied over an oxidation resistant metallic bond coat layer, are being developed for gas turbine applications.^{1,2} Significant advances in coating durability have been realized through improvements in coating materials and processing conditions. Future improvements will be greatly facilitated if coating failure mechanisms are more fully understood.

Coating failure is expected to result either from stresses developed upon heating to high temperatures or from stresses developed upon cooling to ambient temperatures. Failure by either mode may be influenced or even controlled by the initial residual stress state of the coating or by the effects of degradation due to thermally activated processes such as bond coat oxidation, oxide and/or bond coat plastic deformation, ceramic sintering, and phase transformations.

According to recent calculations, a rapidly heated coating is in a state of high biaxial compression a few seconds after exposure to a burner rig flame³ or in an idling engine.⁴ Due to temperature gradients in the radial direction, the higher temperature outer "fibers" of the ceramic expand but are rigidly constrained by the cooler inner "fibers". As a result, a state of biaxial compression and radial tension develops. Also, substrate curvature effects the magnitude of the tensile stress. This stress state has been described as one which tends to buckle the coating.⁵ Therefore, thermal fatigue damage could conceivably accumulate after many heating cycles until compressive failure finally occurs.⁶ The same type of stress state could also develop on cooling due to thermal expansion mismatch be-

tween the ceramic and metallic layers. In this case, the expansion mismatch creates maximum compressive stresses at the interface. Failure on cooling is observed on oxide scales which are grown relatively stress free, at high temperatures. The more adherent grown oxides fail within the oxide layer and failure is independent of cooling rate.

Thus, the purpose of the present paper is to describe the results of certain experiments which help to define failure of thermal barrier coatings exposed to a high heat flux, Mach 0.3 burner rig test in terms of the possible thermal stress and thermally activated process failure modes described above.

EXPERIMENTAL

Cylindrical 1.3 cm diameter Rene'41 superalloy test specimens were coated over 7.6 cm of length with 0.01 cm of a Ni-14 percent Cr-14 percent Al-0.1 percent Zr bond coat and 0.04 cm of a ZrO₂-8 percent Y₂O₃ ceramic alloy. (All compositions are expressed in weight percent.) This bond coat was the most durable of those evaluated in reference 8, and this alloy was originally reported in reference 9. The ceramic is taken from the experimentally identified optimum range.¹⁰ Room temperature X-ray diffraction analysis of the coating confirmed that it consisted primarily of a quenched tetragonal phase with minor amounts of the monoclinic and cubic phases. This phase distribution is quite stable for the times and temperatures discussed in this paper.¹¹ Coated specimens were exposed one at a time to the combustion gases of a Mach 0.3 burner rig of the type described in reference 12. The rigs were fired on Jet A1 fuel and combustion air preheated to 260° C.

Specimens were exposed, either in the as-sprayed condition or after various heat treatments, to 30 second, 2 minute, or 1 hour heating cycles. The fuel-to-air weight ratio (F/A) was usually maintained at 0.058 which corresponds to a calculated adiabatic (i.e., theoretical maximum) flame temperature of 1965° C. For two of the heat treatments, F/A was 0.062 (2025° C). Flame temperature downstream at the specimen is about 300° C lower (G. Santoro, NASA Lewis Research Center, personal communication).

For F/A = 0.058, a steady state surface temperature of about 1200° C was achieved in about 4 minutes (a 55° C optical pyrometer correction factor was used). Because specimens were not internally cooled, metal temperatures were high enough to produce accelerated coating failure rates. After 30 seconds and 2 minutes, surface temperatures were about 1000° C and 1175° C, respectively. When F/A was 0.062, the steady state surface temperature was about 1250° C. The heating rates and steady state temperatures achieved with single specimen are somewhat higher than those achieved when 8 specimens are heated simultaneously as in reference 3. It is important to note that when exposed to 30 second cycles, maximum heating stresses are achieved but thermal degradation is minimal.

Additional cylindrical specimens were also tested. Specimens were subjected to isothermal heat treatments in air and argon atmosphere furnaces at 1250° C. These isothermal treatments assured that any thermo-mechanical damage to the coating would occur upon cooling. Damage would have accrued after a shorter total time at temperature if temperatures had been cycled. However, it would not have been possible to separate heating effects from

cooling effects. One of the specimens treated in Argon was subsequently subjected to 30 second burner rig cycles.

RESULTS

In figure 1, the number of heating cycles before spalling is plotted against the length of the burner rig heating cycle. As shown in the plot, life varies from 1 to over 10 000 cycles demonstrating that coating life is strongly dependent on cycle duration and prior heat treatment. Test conditions were sufficiently severe that when subjected to 1 hour cycles at 1200° C, five assprayed specimens spalled in an average of only 13.4 cycles with a standard deviation of 2.2 cycles. Time lapse and high speed motion pictures revealed that one or two cycles before a coating spalls, the region which is about to spall heats up very rapidly. When tapped with a coin, these locations sounded as if they were detached. In figure 2, a cross sectional scanning electron microscope (SEM) micrograph of one such specimen, which has failed (delaminated) but not yet spalled, is shown. The bond coat of this specimen is significantly oxidized, and from EDS analysis, the oxide appeared to be mostly alumina plus some spinel. Oxides formed on the outer surfaces of the bond coat and at the splat boundaries, and the coating has failed (become detached) within the ceramic just above the bond coat. Thus, it became apparent that failure by detachment preceded spalling.

Spalling is only observed after failure by delamination has already occurred. In figure 3, a frame from a 400 frame per second motion picture of a spalling specimen is shown. Spalling within the detached portion of the coating has begun at 2.4 seconds into cycle 13 which was the second cycle after a hot spot was first observed. Several pieces of ceramic are seen flying from the substrate and the dark spots in the photograph are shadows from spalled pieces. The portions of the hot spot which have not yet spalled are visible, and a large surface crack, more visible in later photographs, has appeared.

On the other hand, when the coating is exposed to 30 second heating cycles, no failure is observed after 10 000 cycles as indicated in figure 1. The thermal stresses, calculated for heating rates somewhat less than observed here, maximize at about 2 seconds into the heating cycle.³ Thus, if heating stresses alone were sufficient to fail the coating, failure would have been observed. However, as shown in Figure 4 which is an SEM micrograph of the 30 second cycle specimen, no delamination has occurred. Oxides are observed at the splat boundaries of the bond coat and the ceramic is microcracked, but these are both characteristics of an as-sprayed coating.

The temperatures reached in the 2 minute exposure cycles were high enough for oxides to form, and spalling was observed in two specimens after 314 and 361 cycles. Preoxidation for 20 hours at 1200° C, which represents greater time at temperature than the failed 1 hour cycle specimen received, caused the curve in figure 1 to be lowered significantly for 2 minute exposure cycles and a lesser amount for 1 hour exposure cycles. However, even after heat treating, failure was still not observed after 10 000 30 second cycles.

Two other specimens were exposed to more severe aging: 1250° C for 23 and 50 hours. As shown in the SEM micrograph in figure 5, at room tempera-

ture a large crack has formed in the ceramic near the interface with the bond coat. Therefore, this exposure is sufficient to fail (i.e., cause delamination of) the coating on cooling. As indicated in figure 1, when subsequently exposed to a $F/A = 0.058$ flame, the failed coating spalls on first heat up. Delamination was so extensive that the heating rate was sufficiently high for spalling to occur after only 0.4 seconds of exposure, according to high speed photography.

The conditions leading to coating failure after a single isothermal cycle were further explored in furnace tests. Specimens heated for 5 or more hours at 1250°C in air delaminated after they were slowly cooled to room temperature. When given a 20 hour treatment in an inert, argon atmosphere, no failure was observed. Thus, degradation through oxidation, superimposed on any damage that may have been due to other thermally activated processes, caused these specimens to fail. One of the specimens which had been annealed in argon at 1250°C did not subsequently fail after being subjected to 5000 30 second burner rig cycles at $F/A = 0.058$.

DISCUSSION

The results of the 30 second exposure tests demonstrate that the stresses developed as an advanced thermal barrier coating system is heated in a Mach 0.3 burner rig flame are not sufficient to cause failure in an as-sprayed coating or a coating previously treated in an inert environment. Those coatings which eventually spall do so early in the heating cycle, but only after failure has already occurred through delamination. The mechanisms leading to delamination are what must be addressed.

The observation in this study that coatings fail near the interface on cooling from high temperature, isothermal exposure in air, even when the cooling rate is very slow, suggests that stresses arising from metal/ceramic thermal expansion mismatch and not thermal shock contribute to failure. In furnace and burner rig tests, coating life generally increases as thermal expansion mismatch between different coatings or substrates decreases.^{13,14,15} Under certain conditions, such as when dense coatings are tested,¹⁶ stresses developed on cooling can lead to spalling. The authors have also observed spalling on cooling when a coating has been plasma sprayed onto an excessively hot substrate. The observation that the coatings spall or at least crack within the ceramic near the interface has also been reported for furnace tests,^{10,17} rig tests,^{8,17} and engine tests.¹⁸ An expression for the thermal expansion mismatch stress, using a balanced biaxial stress state approximation and assuming a thin coating, is⁵

$$\sigma_{\Delta T} = \frac{\Delta T \Delta \alpha E}{1 - \mu}$$

where ΔT is the difference between the temperature after cooling and the stress free reference temperature, $\Delta \alpha$ is the difference in coefficients of thermal expansion between the metal and the ceramic, E is the elastic modulus of the ceramic, and μ is the Poisson ratio. Initially, the reference temperature (or stress free temperature) may be as high as 400°C ,^{4,16} i.e., approximately the bond coat temperature when the ceramic is applied. The value of $\Delta \alpha$ ¹⁴ is about $5 \times 10^{-6}^{\circ}\text{C}^{-1}$, and estimates of E and μ are $4.8 \times 10^4 \text{ MPa}$ and 0.25, respectively.³ Thus, the stresses encountered at the interface on cooling to room temperature from temperatures greater or equal to the stress free temperature are approximately $\sigma_{375} = -120 \text{ MPa}$.

This stress must not be large enough to fail a coating or else failure would be observed on cycling to a metal temperature of 400° C.

Subsequent heating stresses tend to counteract compressive residual cooling stresses near the interface where failure ultimately occurs. Cooling stresses are most compressive at the interface and diminish toward the surface. Heating stresses are most compressive at the surface and are tensile with respect to the assumed residual stress at the interface.

Cooling stresses will increase if the reference temperature increases, which will be the case if stress relief occurs at high temperatures. A probable mechanism for stress relief is flow of the bond coat. The bond coat begins to become ductile at temperatures of about 600° C.^{4,17} Therefore, the bond coat should, after a suitable period of time at high temperature, flow to match the stress free length of the ceramic at their common interface. This effectively raises the stress free temperature. Stress relaxation is also expected for single layer NiCoCrAlY coatings.¹⁹

Still, it must be remembered that coatings only failed after the bond coats had oxidized. In previously reported laboratory tests, which are generally conducted at lower temperatures, coating durability correlates very well with the oxidation resistance of the bond coat.^{8,20} Also, in reference 17, the authors felt that environmental effects including oxidation were life limiting. In an engine test failure correlated best with regions of high temperature where oxidation as well as other processes would be accelerated, and less well with regions experiencing high heat fluxes resulting in excessive compressive heating stresses.⁴ The fact that coatings that failed in 13 1-hour cycles did not fail in one 20 hour isothermal cycle suggests that failure is sensitive to both the number of cycles and the time at temperature. Cycle dependence has been reported elsewhere.³ There it was discussed in terms of failure on heating. However, failure on cooling would also show a cycle dependence.⁷

Bond coat oxidation may affect coating durability in several ways. The oxide that forms on the bond coat may spall. Specks of bond coat oxide generally remain attached to the underside of spalled ceramic pieces. However, since failure occurs mainly in the ceramic, this probably has only a secondary effect. Oxidation could decrease bond coat ductility through the formation of additional oxides at the splat boundaries or cause it to increase through aluminum depletion. This could effect the value of the stress free temperature. Nickel oxide growths projecting into the ceramic from a severely oxidized Ni-16 percent Cr-6 percent Al-0.3 percent Y bond coat have been reported.²¹ This does not appear to be important for better bond coats where failure occurs well before any NiO forms.

Oxidation is known to play a dominant role in the failure of graded thermal barrier coatings (T. Strangman as cited in reference 4). With graded coatings, there is an intermediate layer consisting of mixed bond coat alloy and ceramic. This layer is intended to mitigate the effects of thermal expansion mismatch stresses. However, at high temperatures, the metal particles in the graded zone oxidize significantly. As the particles oxidize, they expand thereby creating buckling stresses in the coating. These "growth" residual stresses add to thermal stresses imposed by cycling,

and this results in the formation of cracks parallel to the surface in the graded zone and subsequent spalling.

With the two layer thermal barrier coatings described in this paper, the surface of the bond coat is very rough and irregular. That morphology is required for coating attachment.^{14,22,23} However, the presence of these irregularities (or asperities) may also lead to coating failure. Even in the absence of oxidation, they could act as stress concentrators.¹⁴ When the bond coat oxidizes, each asperity expands thereby partially filling in the "basins" between them. The additional strains in the ceramic resulting from perhaps an additional micron of growth should be considerable. Such strains may precipitate failure, but only if the remaining metallic portion of each asperity does not flow enough to relieve all of this additional stress.

Other properties of the ceramic notably fracture toughness, phase stability, structure,¹⁶ and density^{22,24} should influence the propensity toward cracking in the ceramic. In fact, in reference 13 it was shown that zirconia-yttria composition has a greater effect on coating life than that which may be accounted for by changes in the coefficient of thermal expansion.

After failure, the delaminated region heats up much more rapidly than the surrounding ceramic. Since, the delaminated region is constrained, a stress corresponding to the ΔT between the delaminated region and the surroundings develops. Replacing $\Delta\alpha$ in the stress expression by α of the ceramic (about $10^{-5} \text{ } ^\circ\text{C}^{-1}$) and assuming that ΔT is roughly 700°C gives a biaxial compressive stress of -450 MPa .

Additional investigations are required to further characterize failure in thermal barrier coatings. Further work is expected to continue to show that a variety of factors can influence thermal barrier coating life. Thus, an important task is to characterize the conditions under which any of the various possible modes may contribute significantly to failure. Additional experiments in higher heat flux burner rigs and engines and testing under less accelerated thermal conditions will be especially valuable. Testing of air cooled specimens would also be valuable to determine whether phase transformations, sintering, and creep at the hot outer ceramic surface contribute to coating failure. Measurements of ceramic thermal expansion as a function of aging time are also needed. Finally, a detailed finite element analysis of the stresses encountered in thermal cycling is required to build on currently available analyses and to guide future experimentation. Such a study should be designed to determine the sensitivity of coating system response to changes in mechanical and environmental parameters and should also include the effects of the irregular interface.

CONCLUSIONS

The failure of thermal barrier coatings exposed to relatively high heat flux Mach 0.3 burner rig flames, at gas and metal temperatures high enough to accelerate failure rates, has been characterized. The coatings fail by delamination prior to visible surface cracking or spalling. Thermal stresses on heating do not cause this failure. Under certain conditions, cooling stresses after only a single isothermal heat treatment in an oxidizing envi-

ronment can cause failure. The failure mechanism is presumed to involve cooling stresses arising from thermal expansion mismatch between the ceramic layer and the bond coat, and it appears to be influenced by flow and oxidation of the bond coat at the irregular bond coat/ceramic interface. A few cycles after delamination is observed, the rapidly heated unattached portion of the coating spalls on heat up. Also, coating life is both time and cycle dependent in agreement with previous studies.

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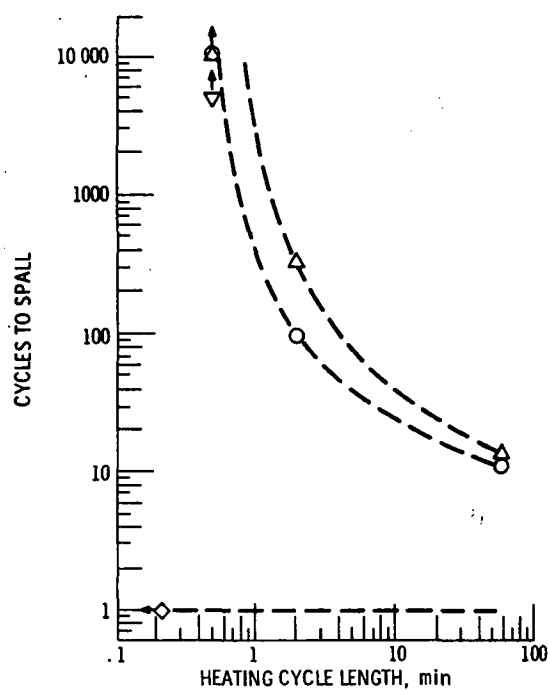


Figure 1. - Effect of heating cycle duration and prior heat treatment on cycles to spalling of $ZrO_2 - Y_2O_3/NiCrAlZr$ thermal barrier coating system in Mach 0.3 burner rig at $F/A = 0.058$. Prior heat treatments: (Δ) none, (\circ) 20 hr at $1200^\circ C$ in rig, (\diamond) 23 hr at $1250^\circ C$ in rig, and (∇) 20 hr at $1250^\circ C$ in Argon furnace; also: (\uparrow) did not spall, (\leftrightarrow) spalled at 0.4 sec.

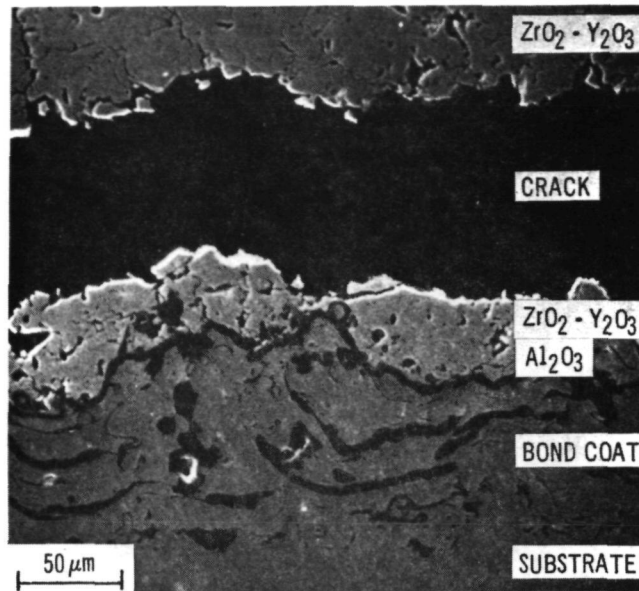


Figure 2. - SEM photomicrograph of the cross section of a thermal barrier coating system after exposure to 12 one hour rig cycles at $F/A = 0.058$. Specimen has failed (delaminated) but not yet spalled.

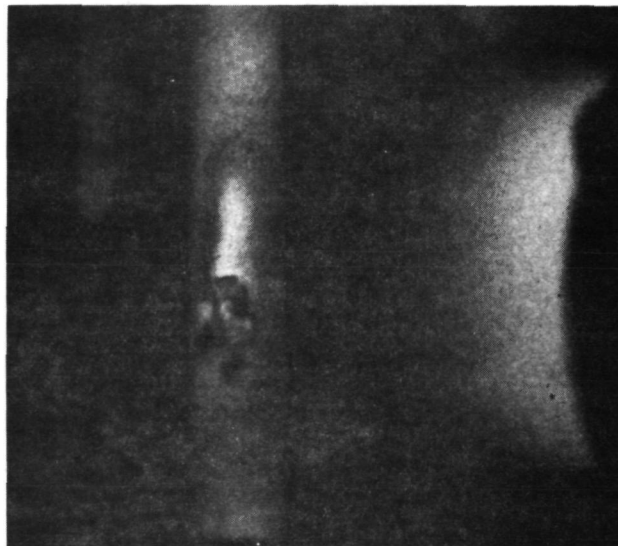


Figure 3. - Frame from a 400 frame per second motion picture showing a previously failed (delaminated) specimen as it begins to spall at 2.4 seconds into heat up.

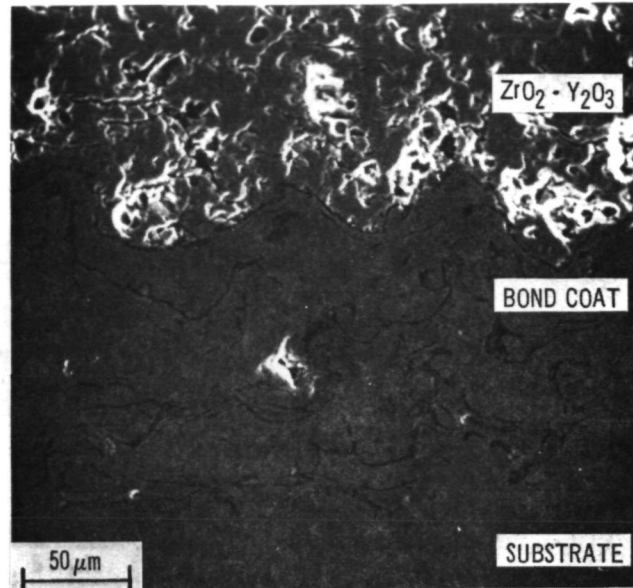


Figure 4. - SEM photomicrograph of the cross section of a thermal barrier coating system after exposure to 10,000 30 second cycles in a Mach 0.3 burner rig at $F/A = 0.058$. Features are equivalent to an as-sprayed specimen.

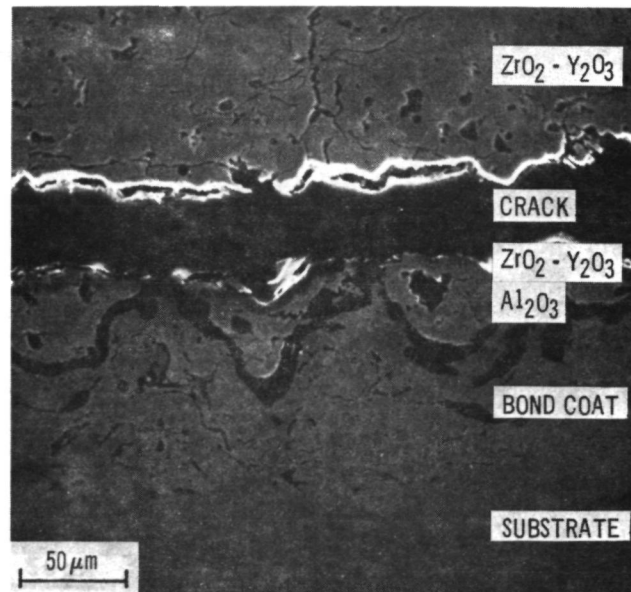


Figure 5. - SEM photomicrograph of the cross section of a thermal barrier coating system after 50 hours of isothermal Mach 0.3 burner rig exposure at $F/A = 0.062$. Specimen has failed (delaminated) on cooling. Spalling would occur on subsequent heat up.

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