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Mechanisms of Degradation and Failure in a Plasma Deposited Thermal Barrier Coating

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ABSTRACT

Failure of a two layer plasma deposited thermal barrier coating is caused by cyclic thermal exposure and occurs by spallation of the outer ceramic layer. Spallation life is quantitatively predictable, based on the severity of cyclic thermal exposure. This paper describes and attempts to explain unusual constitutive behavior observed in the insulative ceramic coating layer, and presents details of the ceramic cracking damage accumulation process which is responsible for spallation failure. Comments also are offered to rationalize the previously documented influence of interfacial oxidation on ceramic damage accumulation and spallation life.

INTRODUCTION

A thermal barrier coating (TBC) is a thin layer of ceramic insulation applied to the external surface of hollow, internally cooled turbine airfoils and platforms. A TBC provides performance, efficiency, and durability benefits by reducing turbine cooling air requirements and lowering metal temperatures (Ruckle, 1980; Miller, et. al., 1980; Duvall and Ruckle, 1982). Calculations indicate that a 10 mil (250 micron) thick layer of zirconia can reduce metal temperature as much as 300F (about 170C), depending on local heat flux. It is estimated that efficiency gains resulting from the application of a TBC to all high turbine airfoils in a typical modern gas turbine engine could result in annual fuel savings as high as ten million gallons for a 250 aircraft fleet (Sheffler and Gupta, 1988).

Premature spallation of the insulative ceramic layer is a significant concern in the utilization of TBC on gas turbine components (Miller and Lowell, 1982; Grisaffe and Levine, 1979; Ruckle, 1979). Ceramic spallation is caused by cyclic thermal stresses resulting

from differential thermal expansion of ceramic and metal. Fortunately, the amount of cyclic thermal exposure required to cause spallation appears to be deterministically related to the number and severity of applied thermal cycles, and can be predicted quantitatively with the same degree of reliability as metallic failure from creep, fatigue, etc. (Miller, 1984; Miller 1988; Cruse et. al., 1988).

Most current TBC applications use a two layer coating system incorporating an inner oxidation resistant metallic layer and an outer insulative ceramic layer, both applied by the plasma spray process. Examination of failed components indicates that spallation occurs as the result of cracking in the ceramic layer parallel and adjacent to, but not coincident with, the very rough metal-ceramic interface. Phenomenological assessment of factors which cause plasma deposited ceramic spallation indicate two independent but apparently interactive degradation modes (Miller and Lowell, 1982; Miller, 1984; Cruse et. al., 1988). The first involves mechanical damage which is attributed to cyclic inelastic strain in the ceramic. The second appears to involve gradual interfacial oxidation of the metallic coating layer. The purpose of this paper is to comment on the occurrence and possible causes of significant inelastic deformation in a nominally brittle ceramic coating, and to present recent observations which more fully characterize the accumulation of ceramic cracking damage.

COATING SYSTEM DESCRIPTION

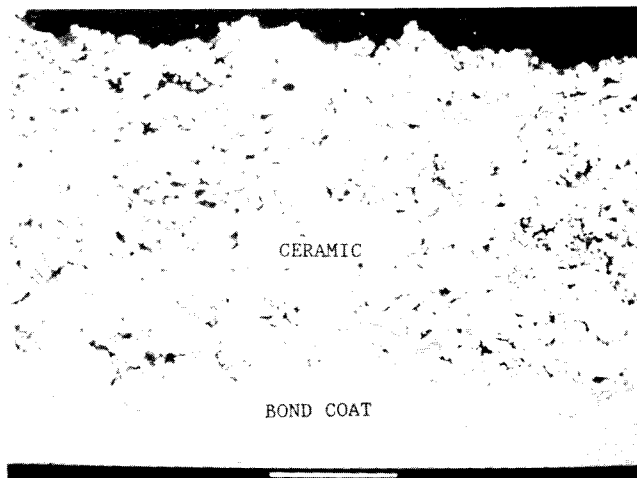
The investigated coating system is used on turbine vanes in several commercial engines, including the JT9D, PW2037, PW4000, and V2500. As shown in Figure 1, it incorporates a nominal 5 mil (130 micron) inner "bond coat" of highly oxidation resistant Low Pressure Plasma Sprayed (LPPS) NiCoCrAlY and a nominal 10 mil (250

micron) air plasma deposited outer layer of seven percent yttria partially stabilized zirconia. X-ray diffraction analysis indicates 55 to 60 volume percent (v/o) tetragonal, 40 to 45 v/o cubic, and no detectable monoclinic phase in the as-deposited ceramic. This non-equilibrium phase distribution results from very rapid solidification in the deposition process (Miller, et.al., 1983). The ceramic structure is porous and extensively microcracked (Figure 1c). This contributes significantly to the unusual ceramic mechanical behavior described in the following section. The interface between ceramic and metal possesses a very complex topology characteristic of the original LPPS NiCoCrAlY surface. As shown in Figure 1b and Figure 2, this surface includes many small, almost free-standing "peninsular" metal deposits which penetrate relatively deeply into and are almost completely surrounded by ceramic. This feature creates many re-entrant angles and pockets which promote mechanical interlocking between ceramic and metal. This interface also has a high specific surface area. Because of the high degree of interpenetration and interlocking, the ceramic-metal interface can be viewed as a narrow "graded zone" about one mil (25 microns) thick. This concept of a graded zone of extremely high metal surface area, incorporating many almost free-standing peninsular surface deposits, is important to subsequent interpretation of the relationship between oxidation and ceramic cracking.

CERAMIC MECHANICAL BEHAVIOR

Because spallation occurs by cracking in the ceramic layer, substantial effort was devoted to characterization of ceramic mechanical behavior. Four point bend, uniaxial tensile, compression, creep, and pseudo-tensile disk fatigue tests (Shaw, et. al., 1973) were conducted on specimens machined from bulk plasma deposited ceramic. Loads were applied in a direction to produce maximum principal stress in the plane of the splat structure. Deposition parameters were the same as those used to deposit TBC and produced essentially identical microstructure. Some of these data are reported by Cruse, et.al. (1988); details of the ceramic microstructure and test methods are reported by DeMasi et.al. (1989).

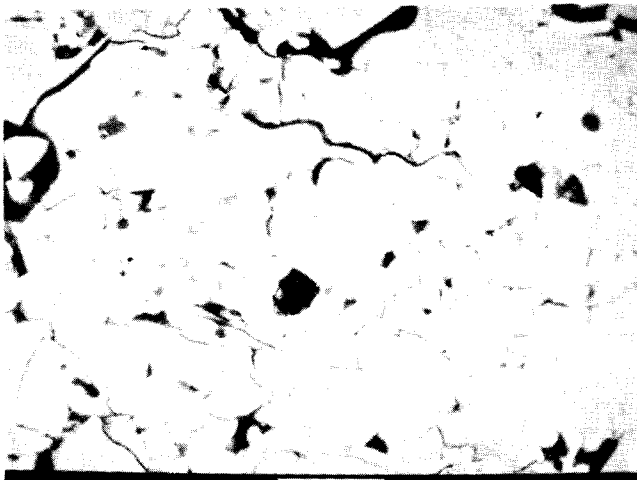
The most significant finding of this work is the observation of substantial reversed inelastic deformation at all temperatures investigated (ambient to 2200F/1204C). This is very unusual behavior for a ceramic material. Most ceramics are brittle, exhibiting only linear elastic deformation at low and intermediate temperatures. The excellent cyclic thermal durability of plasma deposited ceramic is attributed primarily to this unusual reversed inelasticity. As shown in Figure 3a, uniaxial tensile curves for the plasma deposited ceramic are non-linear even at very low stress levels, with no clearly definable elastic segment. Ultimate tensile strength and fracture strain are quite low, on the order of 7 KSI (48 MPa) and 0.25 percent respectively. Fracture toughness also is quite low, on the order of 0.5 KSI root-inch (0.55 MPa



A) OVERVIEW



B) MAGNIFIED VIEW OF INTERFACE SHOWING METAL SURFACE DEPOSITS SURROUNDED BY CERAMIC



C) MAGNIFIED VIEW OF CERAMIC POROSITY AND MICROCRACKING

FIGURE 1 - PLASMA DEPOSITED THERMAL BARRIER COATING MICROSTRUCTURE

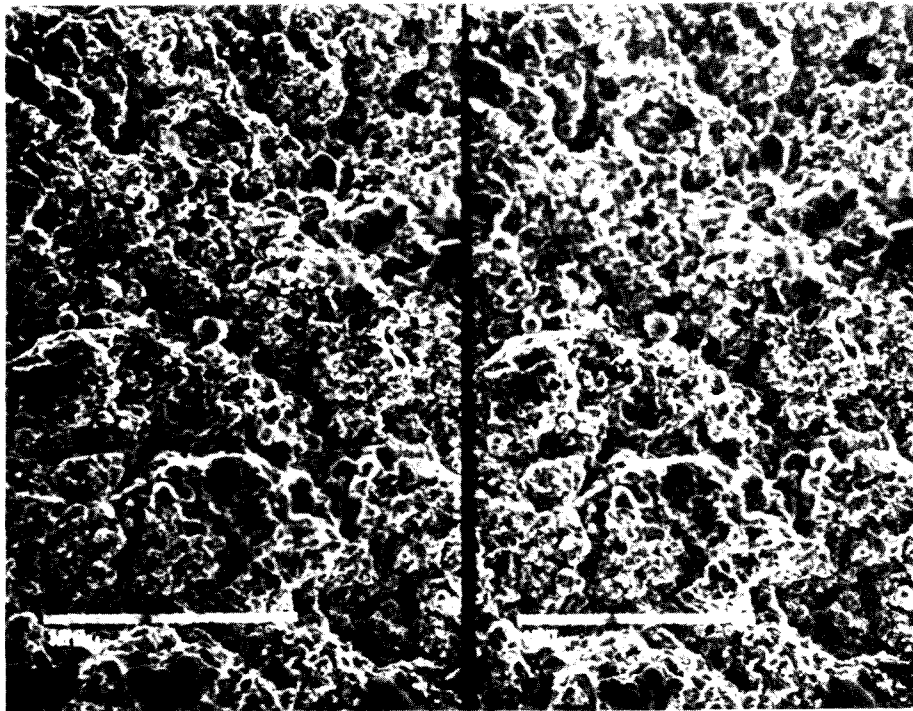


FIGURE 2 - STEREOGRAPHIC PAIR OF PHOTOMICROGRAPHS OF AS-DEPOSITED MCrAlY BOND COAT SURFACE. NOTE THAT A SPECIAL VIEWER IS REQUIRED TO OPTICALLY SUPERIMPOSE THESE IMAGES FOR TRUE THREE-DIMENSIONAL VIEWING.

root-meter). Only a slight decline of strength is seen between ambient temperature and 1800F (982C), with an apparent slight increase of strength at 2000F (1094C) (Figure 4). Above this temperature, strength starts to decline rapidly. Uniaxial compression exhibits a combination of linear and non-linear behavior, with significantly higher strength than in tension (Figure 3b). Substantial permanent offset was measured on a strain gaged four point bend specimen from which load was removed prior to failure. No visually observable cracking was seen on the tensile face of this specimen, indicating that the curvature in Figure 3 represents truly inelastic behavior. A hysteresis loop obtained by reversing the orientation of this specimen at zero load exhibits significant reversed inelastic strain (Figure 5). Evidence of significant creep at 1800F (982C) and above, and of exceptionally stress sensitive fatigue behavior (stress exponent on the order of 50) also are found.

The proposed explanation for the metal-like behavior described above is based on the nature of the plasma deposited ceramic structure shown in Figure 1. The development of this plasma splat structure is nicely illustrated by Herman (1988). It can be idealized as an assembly of independent segments which are mechanically interlocked in an interpenetrating network almost analogous to a three dimensional jig-saw puzzle. A better appreciation of this layered, interpenetrating "puzzle structure" is provided by a fractograph obtained from the tensile face of a four point bend failure (Figure 6). This fractograph also shows a columnar substructure within the splats.

Microcracking has been known to induce non-linear stress-strain behavior in ceramics (Fu and Evans, 1984). In the present investigation, it is hypothesized that reversed inelastic deformation results from a form of stick-slip behavior between adjacent interpenetrating elements of the microcracked ceramic structure. This stick-slip behavior results in turn from an attempt of surfaces which are rough on a very fine scale to slide past one another, which requires them to be forced very slightly apart. As shown by the transmission electron micrograph in Figure 7, microcracks in the plasma deposited ceramic are inherently rough on the submicron scale as a result of the intergranular crack morphology.

The stick-slip concept is illustrated schematically in Figure 8. As force is initially applied, surfaces with very small asperities slide first at very low stresses. As stress increases, surfaces with progressively larger asperities slide to a new "stuck" position. This progressive increase of cumulative amount of sliding with increasing stress accounts for the shape of the tensile curve shown in Figure 3. Behavior in compression is analogous, except that stresses required to cause relative movement across adjacent shear boundaries is much greater because movement of these boundaries is restrained by direct abutment of interfaces normal to the maximum principal stress. Hence relative movement of adjacent structural elements requires substantial elastic deformation of abutting segments before sufficient strain is accumulated to permit discontinuous displacement of adjacent shear surfaces. The occurrence of reversed inelasticity is easily accounted for by this

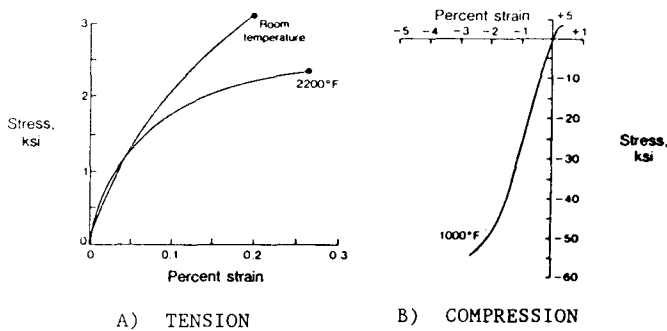


FIGURE 3 - UNIAXIAL TENSILE AND COMPRESSIVE DEFORMATION OF BULK PLASMA DEPOSITED CERAMIC AT VARIOUS TEMPERATURES.

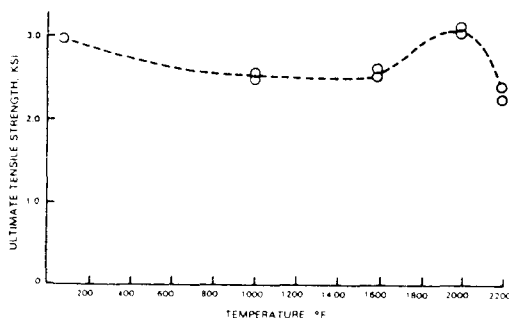


FIGURE 4 - INFLUENCE OF TEMPERATURE ON TENSILE STRENGTH OF BULK PLASMA DEPOSITED CERAMIC.

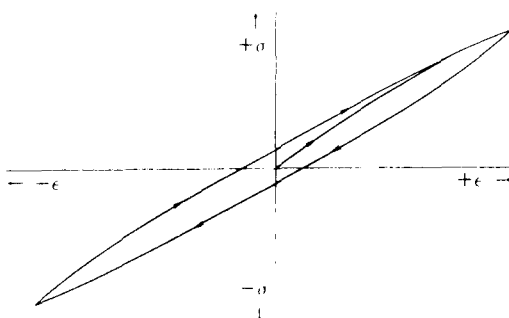


FIGURE 5 - AMBIENT TEMPERATURE HYSTERESIS LOOP OBTAINED BY SUCCESSIVE REVERSAL OF STRAIN GAUGED BEND SPECIMEN.

model, and in fact the non-linear nature of the unloading and compressive reloading curves can be rationalized by an argument identical to that put forward to account for initial tensile non-linearity. Further refinements can be formulated to account for the cyclic strain "softening" seen with repeated strain cycling. These refinements might involve localized fracture of smaller asperities, which would permit adjacent surfaces to slide more freely on subsequent cycles.

There are several lines of further investigation which might be pursued to gain additional understanding of the proposed deformation mechanism. The use of internal friction and/or acoustic emission are proposed, as is more detailed phenomenological characterization, including additional studies of cyclic strain softening behavior and strain rate sensitivity. The influence of microcrack

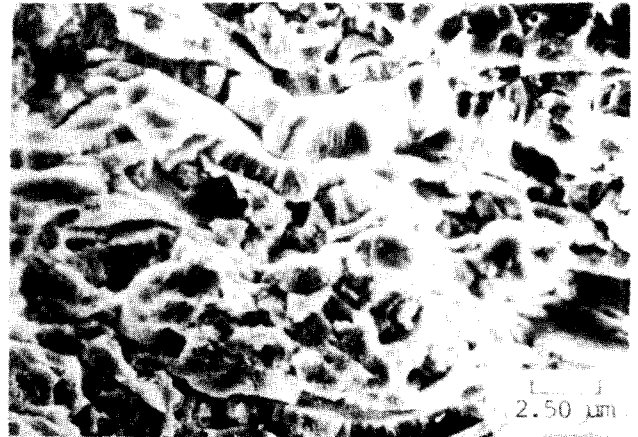


FIGURE 6 - TENSILE FRACTURE SURFACE OF BEND TEST SPECIMEN.

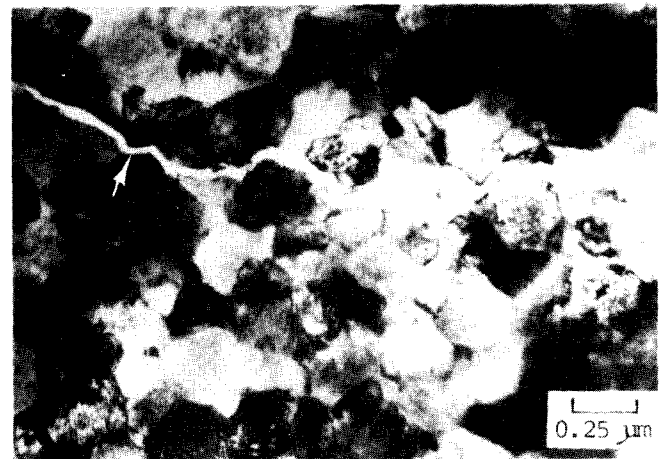


FIGURE 7 - TRANSMISSION ELECTRON MICROGRAPH SHOWING SUB-MICRON SCALE CRACK SURFACE ROUGHNESS PRODUCED BY MICROCRACKING AT GRAIN BOUNDARIES (ARROWS). PLANE OF MICROGRAPH IS PARALLEL TO PLANE OF COATING.

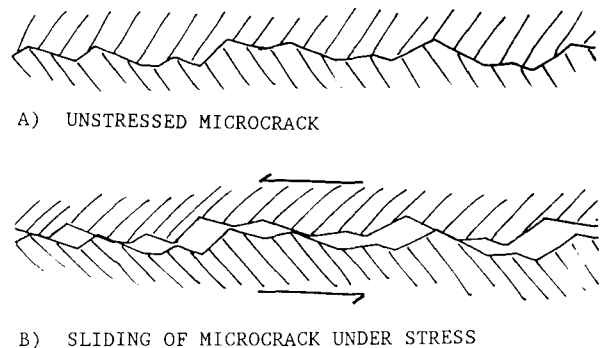


FIGURE 8 - ILLUSTRATING HYPOTHESIZED STICK-SLIP SLIDING BEHAVIOR OF ROUGH MICROCRACK SUCH AS SHOWN IN FIGURE 7.

roughness level, which could be varied by manipulation of deposition parameters and hence crystalite size, would be of great interest in the above studies. Additional microstructural characterization is needed, especially fractography of fatigue crack surfaces to search for evidence of abrasion damage.

Behavior of the ceramic above 1800F is attributed to the presence of glassy phase(s) at splat and possibly grain boundaries. The classic indication of this phase is the reduction of strength above the temperature where softening and consequent boundary sliding initiate. Typically, at the temperature where the phase just becomes viscous, there is an initial increase in strength and toughness resulting from crack blunting. Such an increase has been observed in many systems (Tsai and Raj, 1981). While a similar strength vs. temperature increase has been attributed to aging effects in partially stabilized zirconia (Hannink and Swain, 1986), specimens in the present study were at temperature for less than one hour, which is not sufficient time to experience aging at the investigated temperatures (Miller, et.al., 1981). To demonstrate this, furnace exposed specimens were examined by x-ray diffraction. These specimens showed very little change from the as-deposited phase distribution for times up to sixty hours at 2200F (1204C). The apparent slight increase in strength seen in Figure 4 near 2000F thus is attributed to glassy phase(s) arising from the presence of glass forming impurities in the original spray powder, which was analyzed to contain 0.53 percent silica. The decline of strength above this temperature is attributed to further softening of the hypothesized boundary phase(s). Additional transmission electron microscopy will be required to confirm the presence of this phase.

To summarize, reversible, nonlinear, inelastic behavior is observed at ambient and elevated temperatures in plasma deposited seven percent yttria partially stabilized zirconia. This reversible inelasticity is attributed to a form of "stick-slip" behavior in the heavily microcracked plasma splat structure. This stick-slip behavior involves the accumulation of discrete, discontinuous displacements across adjacent shear loaded surfaces in the interpenetrating, mechanically interlocked microcrack structure, as illustrated schematically in Figure 8. Above 1800F (982C), glassy boundary phases soften, leading to strength reduction and creep.

CERAMIC DAMAGE ACCUMULATION

Results of stress analyses based on the above constitutive properties indicate that thermal cycling of the TBC on gas turbine airfoils produces substantial reversed inelastic deformation in the ceramic coating layer (Cruse, et. al., 1988). To determine the influence of this reversed inelastic strain cycling on the nature and accumulation of ceramic damage, interrupted laboratory thermal cycling tests were conducted in a jet fueled burner rig (details reported elsewhere by DeMasi, et. al., 1989). Behavior of the ceramic in this test correlates well with engine behavior.

Ceramic cracking damage found in selected specimens removed from test at various fractions of the cyclic thermal spalling life is shown in Figure 9. It is clear from these

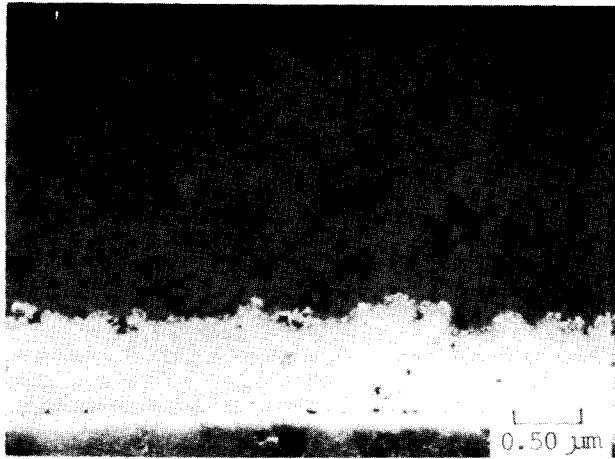
and other fractionally exposed samples that ceramic cracking commences early, on the order of one-quarter to one-third of the total exposure required to spall the coating. Careful examination of crack morphology at successively increasing life fractions suggests that ceramic spallation may result from progressive link-up of adjacent sub-critical cracks, rather than from subcritical growth of a single dominant crack. Quantitative measurement of average crack length shows a progressive increase with increasing exposure. "Young" specimens contain cracks on the order of 2 to 3 mils (50 to 80 microns); longer exposure times yield average crack lengths of about 6 to 10 mils (160 to 250 microns). The number of cracks also appears to increase with exposure time. "Old" specimens exhibit large isolated cracks on the order of 13 mils (330 microns) together with shorter cracks about 2 to 3 mils (50 to 80 microns) long. The "oldest" unfailed specimen examined (90% life) showed one major crack 38 mils (970 microns) long and several shorter cracks (about 7 mils/180 microns).

An observation that is consistent with the stick-slip hypothesis proposed earlier is the presence of detectable monoclinic phase on the surface of spalled coating chips. X-ray diffraction analysis of failed specimens indicates very little change of "bulk" coating phase distribution, with essentially no monoclinic phase detectable in the bulk ceramic coating after cyclic thermal exposure. However, analysis of the spalled surfaces does indicate small but detectable quantities of monoclinic. Strain induced transformation from tetragonal to monoclinic has been observed on abraded surfaces of bulk partially stabilized zirconia (Reed and Lejus, 1977). While the importance of this effect is not well understood for plasma sprayed zirconia, it seems reasonable to expect that sliding surfaces in the stick-slip model might exhibit detectable monoclinic content.

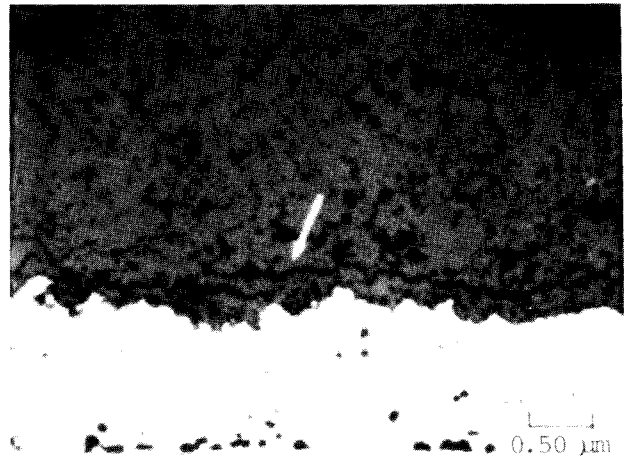
To summarize, the accumulation of ceramic damage occurs by progressive cracking directly adjacent to the ceramic-metal "graded zone". Significant cracking is seen as early as one-fourth of the spallation life, and seems to accumulate by a mechanism of multiple crack link-up rather than by monotonic propagation of a single dominant crack. The issue of crack initiation is addressed in the following section.

THE ROLE OF OXIDATION

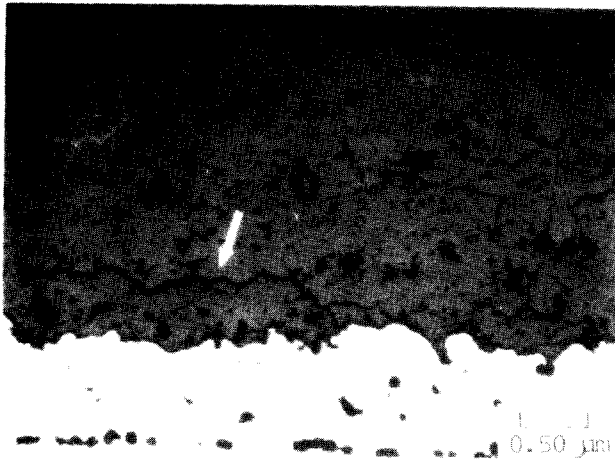
As noted in the introduction, previously published phenomenological evidence clearly demonstrates a significant influence of oxidation on spallation life. Based on this evidence, substantial effort was devoted to investigation of the relationship between ceramic cracking and the growing oxide scale. This scale can be discerned in Figures 9b-d as a very thin dark layer at the ceramic-metal interface. Because of the very rough nature and high specific surface area of the interface, this oxide layer is highly irregular, with numerous accumulations of uncharacteristically



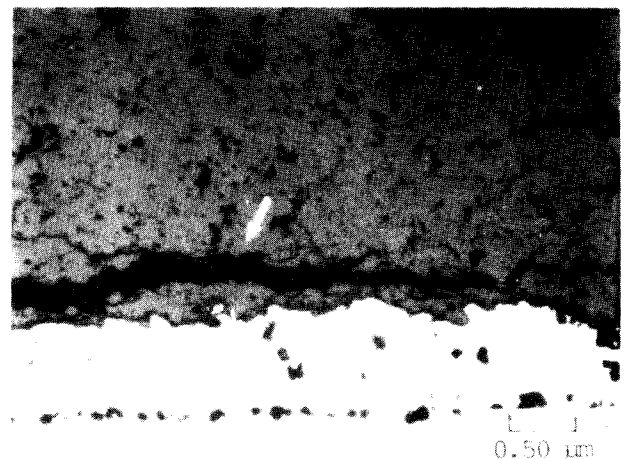
A) 0%



B) 33% (60 Hrs.)



C) 66% (120 Hrs.)



D) 100% (180 Hrs.)

FIGURE 9 - CRACKING DAMAGE IN SPECIMENS SUSPENDED FROM TEST AT VARIOUS FRACTIONS OF SPALLATION LIFE.

thick oxide build-up resulting from partial or total oxidative consumption of the previously noted peninsular metallic surface deposits (Figure 10). As discussed earlier, most ceramic cracking occurs parallel and very close to the interface, touching the tops of the highest metallic protrusions (Figure 9b-d).

Considerable effort was devoted to identification of ceramic crack initiation sites. Based on the clear phenomenological link between oxidation and life, it seems reasonable to speculate that the swelling associated with oxidation, especially of the peninsular deposits, might directly initiate cracking. Electron microscope examinations did find a few isolated cases of what might be interpreted as scale initiated cracking. However, these examples were sufficiently infrequent as to lead to the conclusion that this is not the major initiation mode. Scale initiated cracking was easier to find in "older" specimens, occurring in the same structure together with larger numbers of well developed

longer cracks which appear, at least in the two dimensional section, to be isolated from the interface. This observation would suggest that the thicker oxide scale developed at longer exposure times can initiate cracks, but that this is not the critical damage mode in the sense that these are not the cracks which link and propagate to failure.

Based on the above observations, it is hypothesized that "initiation" really is a process involving near-threshold growth of pre-existing microcracks. It is further hypothesized that this near-threshold growth is facilitated by the accumulation of abrasion damage resulting from the previously discussed stick-slip behavior. Additional quantitative metallographic studies of specimens with very small exposure times will be required to confirm this hypothesis. Also of value would be fractographic studies to characterize abrasion damage on spallation crack surfaces.

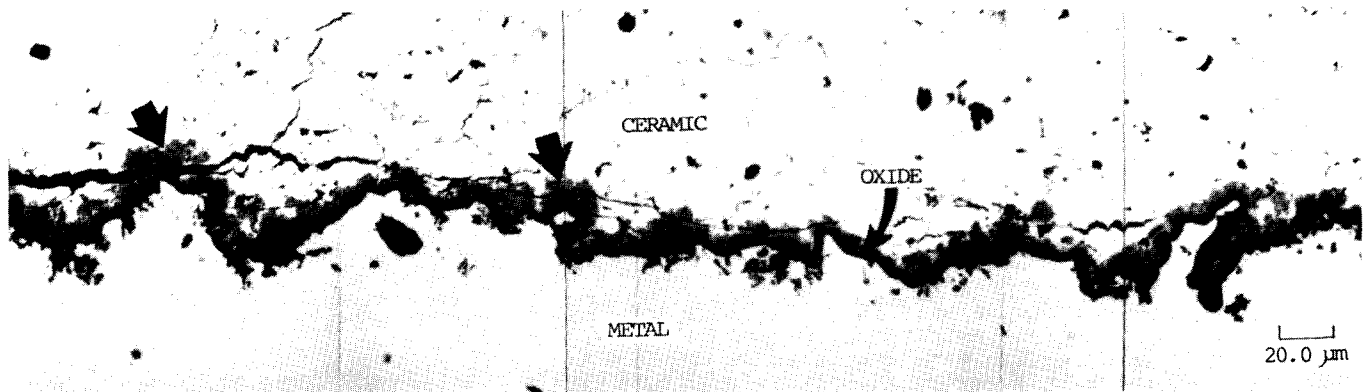


FIGURE 10 - MORPHOLOGY OF INTERFACIAL OXIDE. NOTE SUBSTANTIAL LATERAL GROWTH AT SIDES OF OXIDIZED "PENINSULAR" SURFACE DEPOSITS (ARROWS).

In the absence of clear evidence for oxide initiated cracking, the question naturally arises as to the mechanism by which interfacial oxidation accelerates the accumulation of ceramic fatigue damage. Following the lead of other investigators, it is assumed that oxidation affects spallation life by altering ceramic stress state in the region where cracking occurs (Miller and Lowell, 1982; Miller, 1984). This region is not easily defined, but appears to be coincident with a hypothetical boundary between the ceramic and the thin "graded layer" created by interpenetration. It is suggested that this boundary zone stress state modification is due not just to the roughness of the interface, but to the nature of the roughness, which includes many highly interpenetrating peninsular surface deposits that produce a large specific interfacial area. It is further suggested that it is the swelling of this graded layer, which is significantly greater than might be expected of a flat interface, and especially the swelling of the peninsular surface deposits directly adjacent to the boundary zone (Figure 10), which alters the ceramic stress state to accelerate cracking.

To demonstrate the strength of the forces which can be induced by oxidative expansion of a graded ceramic-metal layer, a previously reported experiment (Duvall and Ruckle, 1982) is reproduced in Figure 11. A flat sheet metal panel with intentionally created grading was thermally exposed for sufficient time to cause significant oxidation of the metal component in the graded layer. The photograph in Figure 11 shows the severe distortion caused by oxidation. While the oxidatively induced expansion force can be relieved by curling of a sheet metal panel, oxidation must result in the build-up of significant ceramic stress on a more rigid substrate such as a turbine airfoil, which is not free to distort.

Also included in the previously reported experiment were non-graded panels with rough ceramic-metal interfaces. While much less dramatic than Figure 11, noticeable curvature is apparent on careful observation of these panels (Figure 2 in Duval and Ruckle, 1982). A suggested approach to quantify the magnitude of

ceramic stress produced by interfacial oxidation would be to measure the amount of distortion produced with varying times, temperatures, and substrate thicknesses.

Other investigators have used highly idealized sinusoidal finite element models of the ceramic-metal interface to study the effect of interfacial oxidation on the ceramic stress state (Chang, et. al., 1987). Results show that simulated oxide growth at the interface can significantly alter stress.

SUMMARY

Failure of a two layer plasma deposited thermal barrier coating is caused by cyclic thermal exposure and occurs by spallation of the outer ceramic layer. Spallation life is quantitatively predictable, based on the severity of cyclic thermal exposure. This paper describes and attempts to explain unusual constitutive and cracking behavior observed in the insulative ceramic coating layer. Reversible, non-linear, inelastic ceramic deformation is attributed to a stick-slip type of behavior in the heavily microcracked, mechanically interlocked plasma deposited splat structure. Elevated temperature strength reductions and creep are attributed to softening of grain boundary glassy phase(s). Ceramic spallation is shown to result from progressive accumulation of ceramic cracking damage parallel and directly adjacent to a narrow (about 1 mil/25 micron) pseudo-graded zone created by interpenetration of ceramic and metal at the very rough interface. Cracking

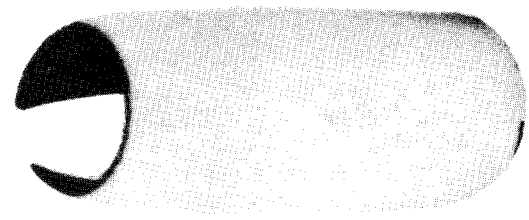


FIGURE 11 - SEVERE CURLING RESULTING FROM THERMAL EXPOSURE OF AN INITIALLY FLAT PANEL WITH AN INTENTIONALLY GRADED METAL-CERAMIC INTERFACE.

damage is seen as early as twenty-five percent of life, and appears to accumulate by progressive link-up of multiple small cracks rather than by monotonic propagation of a single dominant crack.

Previously published work has shown a strong influence of interfacial oxidation on spallation life. Extensive metallographic examination failed to show evidence of significant direct oxide induced ceramic crack initiation. It is thus hypothesized that crack "initiation" really is a process of near-threshold growth of pre-existing microcracks which are intrinsic to the plasma deposited structure, possibly by a process related to the stick-slip deformation behavior mentioned above. Rationalization of the known influence of interfacial oxidation on spalling life is based on the effect of swelling of the pseudo-graded layer on ceramic stress state. Evidence is provided to show that the swelling effect can be dramatic in thick graded layers.

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