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**HOT CORROSION OF CERAMIC-COATING MATERIALS
FOR INDUSTRIAL/UTILITY GAS TURBINES**

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ABSTRACT

Furnace hot corrosion tests of yttria-stabilized zirconia (YSZ) and other candidate ceramic coating materials were run under combinations of temperature, salt deposits, and gaseous environments known to cause severe hot corrosion of state-of-the-art metallic coatings for industrial/utility gas turbines. Specimens were free-standing ceramic coupons and ceramic-coated IN 792. Post-test analyses by such techniques as visual inspection, weight changes, X-ray diffraction and fluorescence, scanning microscopy of exposed surfaces, and microscopy of polished cross sections were carried out to establish useful methods for characterizing the hot corrosion behavior of ceramics and determine if a consistent and interpretable dependence of severity of attack on temperature, SO_3 pressure, and salt composition could be observed.

X-ray fluorescence and diffraction data on free-standing YSZ coupons showed surface yttrium loss and cubic-to-monoclinic transformation as a result of exposure to liquid salt and SO_3 . Greater destabilization was observed at the lower of two test temperatures (704 and 982°C), and destabilization increased with increasing SO_3 pressure and V-containing salt deposits. Although the mechanism of yttrium loss is not understood, the data suggest that hot corrosion of YSZ can occur by a type of acidic dissolution of Y_2O_3 from the ZrO_2 solid solution.

In spite of the greater surface destabilization at 704°C, the bond coat and substrate of YSZ-coated IN 792 were not attacked at 704°C but severely corroded at 982°C. These results show that degradation of ceramic-coated metallic components can be more strongly influenced by the porosity of the microstructure and fluidity of the liquid salt than by the chemical stability of the ceramic coating material in the reactive environment.

Other ceramic materials (SiO_2 , Si_3N_4 , ZrSiO_2 , and mullite), concurrently exposed to the same conditions which produced significant destabilization of YSZ, showed no evidence of reaction at 704°C but noticeable corrosion at 982°C. Also, the high temperature corrosion was greater in air than in SO_3 -containing gases. These trends suggest that hot corrosion of the silicon-containing ceramics was basic in nature, and such materials have potential for good resistance to chemical decomposition under the acidic conditions characteristic of industrial/utility gas turbines.

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HOT CORROSION OF CERAMIC COATING MATERIALS FOR INDUSTRIAL/UTILITY GAS TURBINES

INTRODUCTION

Ceramic coatings are of interest for industrial/utility gas turbines both as thermal barriers and as corrosion resistant materials, a particular incentive for such applications being the fact that several types of environmentally induced degradation (e.g. vanadium hot corrosion, chloride effects, high SO_3 pressures, erosion-hot corrosion interactions) anticipated in alternate fuel capable industrial engines are very difficult to inhibit in metallic systems. While ceramics are by no means immune to attack in these environments, the mechanisms responsible for the rapid consumption of metals and metallic coatings in the propagation stage of hot corrosion are precluded by the already oxidized state of the ceramic cation. Ceramic coatings thus offer the potential for good resistance to combinations of component temperature, gas/salt chemistry, and particle-laden gas streams which severely limit the durability of metallic alloys and coatings.

Ceramic coatings have long been used in aircraft gas turbines as thermal barriers. Unfortunately the porous, low density microstructure of these coatings is pervious to gaseous oxidants and liquid salt, and burner rig testing suggests that the stabilized or partially stabilized zirconia-base ceramics which perform satisfactorily in the combustion products of clean, aircraft-grade fuels may be susceptible to salt-induced spallation when exposed to industrial fuels of higher impurity content. The potential for alleviating this problem lies primarily in new concepts and improved processing technology which will permit better control of the density and microstructure of ceramic coatings. Feasible with advanced plasma spray and electron beam coating techniques, for example, are thermal barrier coatings with a highly uniform, well-controlled distribution of pores and microcracks to promote adherence but sealed against penetration of liquid salt by a high density surface layer. Also being considered - primarily for their corrosion resistance rather than the thermal barrier effect - are thinner coatings with less insulating ability but better adherence.*

*Several programs concerned with the development and hot corrosion behavior of ceramic coatings are reviewed in the Proceedings of the First Conference on Advanced Materials for Alternative Fuel Capable Directly Fired Heat Engines, CONF-790749, J.W. Fairbanks and J. Stringer, Eds., NTIS, Springfield, VA 22161.

Anticipating advances in coating adherence and resistance to the mechanical and microstructural aspects of salt-induced coating spallation (i.e. penetration of salt along microstructural discontinuities), the chemical stability of the ceramic coating material in the high temperature reactive environment becomes a major factor in coating durability. The current program was therefore carried out to examine the corrosion behavior per se - meaning, as far as possible, the degradation of ceramic materials by a chemical reaction with the liquid salt as opposed to porosity-induced ceramic layer spallation - of state-of-the-art and candidate ceramic coating materials. Furnace testing was used to provide optimum control of the reactive environment and minimize the thermal cycling damage and temperature gradient effects which would complicate interpretation of burner rig test results. Most of the furnace tests were run under conditions known to cause severe hot corrosion of the metallic coatings currently used in industrial gas turbines, and conditions were varied to determine if a consistent and interpretable dependence of severity of attack on temperature, SO_3 pressure, and salt composition could be observed. Post-test evaluation was attempted by various techniques (visual inspection, X-ray diffraction and fluorescence, scanning microscopy of exposed surfaces, optical and scanning microscopy of polished cross sections) to determine the most useful methods for characterizing the hot corrosion behavior of ceramic materials and judge the extent to which corrosion processes are likely to be a factor in salt-induced spallation of ceramic coatings.

EQUIPMENT AND PROCEDURE

Except for several tests in air to demonstrate the effect of SO_3 in the gaseous environment, all of the experiments for this program were performed in the horizontal tube furnace shown in the schematic diagram of Figure 1. The furnace environment was controlled by mixing bottled SO_2 and O_2 ; oxidation of SO_2 to SO_3 was catalyzed by sputtered platinum on DuPont Torvex[®] honeycomb alumina. The catalyst was maintained at the same temperature as the specimens, and equilibrium SO_3 pressure at the test temperature was calculated from data in the JANAF tables. The ceramic specimens were coated with approximately 1 mg/cm^2 of a selected salt deposit (Na_2SO_4 in the initial experiments; mixed sulfates for comparison with pure Na_2SO_4 in later tests), suspended on platinum wires in the center of the hot zone, exposed for 20 hours, water washed, and recoated with fresh salt for continued testing. Total exposure times of 100 hours were found sufficient to demonstrate relative performance of various ceramics and dependence of severity of attack on temperature and gas/salt chemistry.

Fig. 1. Schematic diagram of horizontal tube furnace for hot corrosion testing with SO_3 gas and/or NaCl vapor in the atmosphere. For experiments with NaCl vapor, the separate input of O_2 and $\text{SO}_2:\text{O}_2$ mixture is necessary to avoid reaction of the SO_2 with solid NaCl prior to reaching the catalyst and the specimens.

TEST CONDITIONS

One of the factors complicating a fundamental understanding of burner rig hot corrosion of ceramic coatings is the continuous variation in corrosion-controlling thermodynamic parameters due to the high temperature gradient the coating is designed to maintain between the surface of the outer ceramic layer and the underlying MrAlY bond coat. Thus if a ceramic material tends to degrade by acidic processes, it is conceivable that low temperature subsurface corrosion could contribute to salt-induced coating spallation even if the high temperature surface suffers minimal reaction with the liquid salt. To detect the susceptibility of ceramic coating materials to failure by such mechanisms, the following combinations of temperature and SO_3 pressure include those known to favor low temperature acidic mechanisms as well as high temperature corrosion:

Table 1

Temperature and gas compositions used in tube furnace hot corrosion testing of various ceramic materials

704°C (1300°F)		982°C (1800°F)	
input $\text{SO}_2:\text{O}_2$ ratio (volume fraction)	equilibrium SO_3 pressure (atmospheres)	input $\text{SO}_2:\text{O}_2$ ratio (volume fraction)	equilibrium SO_3 pressure (atmospheres)
0.0010	7.1×10^{-4}	0.0049	7.1×10^{-4}
0.0100	7.1×10^{-3}	0.0100	1.4×10^{-3}

Since it is generally agreed that NaCl vapor is capable of increasing the severity of sulfate-induced hot corrosion, it was planned to run all tests with a gaseous salt concentration of 30 ppm, introduced from a salt-filled boat as shown in Fig. 1. The 704°C experiments were run in this manner as planned. However in the initial test at 982°C, the presence of the chloride vapor was found to cause complete removal of the liquid Na_2SO_4 salt deposit during the 20-hour exposure cycle (presumably by a reaction of the form $2\text{NaCl} + \text{SO}_2 + \text{O}_2 \rightleftharpoons \text{Na}_2\text{SO}_4 + \text{Cl}_2$ being driven to the left at a significant rate by the combination of thermodynamic parameters and reaction kinetics). The 982°C experiments were therefore performed without gaseous chloride in the environment.

MATERIALS

Plasma sprayed yttria-stabilized zirconia (YSZ) with 12, 20, and 35 wt% yttria was supplied by Metco, Inc. The specimens were prepared by state-of-the-art processing techniques in the form of 3 cm square by 2 mm thick coupons of free-standing material.

Coupons of bulk SiO_2 , ZrSiO_4 , and Si_3N_4 were cut from 1-inch hot pressed rounds supplied by Haselden Company; certified purity level was at least 99.8%. Results of a semi-quantitative emission spectrographic analysis were as shown in Table 2.

Table 2

Semi-quantitative emission spectrographic analyses of impurity levels (weight %) in Haselden materials

SiO_2	ZrSiO_4	Si_3N_4
0.001 - 0.01 Al	0.1 - 1 Ti	0.5 - 5 Mg
0.001 - 0.01 Ni	0.05 - 0.5 Al Ca	0.1 - 1 Ca
	0.05 - 0.5 Y	0.05 - 0.5 Al
	0.01 - 0.1 Fe, Hf	0.01 - 0.1 W
	0.005 - 0.05 Mg, Cr	0.005 - 0.05 Fe, Cr
	0.005 - 0.05 Ni, Co	0.005 - 0.05 Ni, Co
		0.001 - 0.01 Mo, Ti

Other materials evaluated were Lucalox[®] and single crystal alumina (obtained from Union Carbide Crystal Products Division), Norton NC 132 silicon nitride, and McDaniel MV30 mullite. Emission spectrographic test results were:

Table 3

Semi-quantitative emission spectrographic analyses of impurity levels (weight %) in other ceramic materials

Lucalox	NC 132 Si_3N_4	Mullite
0.05 - 0.5 Mg	0.1 - 1 Fe, Mg, W	0.1 - 1 Fe, Ti
0.01 - 0.1 Fe	0.1 - 1 Al, Co	0.05 - 0.5 Mg
0.005 - 0.05 Ni, Si	0.05 - 0.5 Mn, Ti	0.001 - .01 Cr, B, Co
	0.01 - 0.1 Cr	0.005 - 0.05 Ni, Cu
	0.005 - 0.05 B, Ni	0.005 - 0.5 Mu, V
	0.005 - 0.05 Mo, V, Cu	0.01 - 0.1 Cu

The bulk ceramic specimens cut from the hot pressed rounds were polished with 600 grit SiC paper prior to testing. The surface of the YSZ coupons in contact with the back-up plate during plasma spraying was also polished on 600 grit paper to remove impurities and provide uniformity of pre-test surface condition.

Ceramic coated IN 792 coupons with NiCoCrAlY bond coats and various thicknesses (<1 to >6 mils) of 20% YSZ overlayers were prepared by standard plasma spray coating techniques and tested in the same manner as the free-standing ceramic materials.

TECHNIQUES FOR STUDYING HOT CORROSION OF CERAMICS

Various analytical procedures, such as visual inspection, weight changes, chemical analysis of reaction products (by wet chemistry, X-ray diffraction, electron probe microanalysis), scanning microscopy of corroded surfaces, and microscopy of polished cross sections, have been widely and successfully used to study the hot corrosion behavior of metallic materials. In principle, they are equally applicable to characterizing the hot corrosion of ceramics, although several practical difficulties immediately present themselves.

In the case of hot corrosion of metals, visual inspection alone is a simple but highly useful source of information. Since the distinction between unaffected metal and corrosion products is obvious, the onset of hot corrosion and a semi-quantitative determination of the nature and severity of attack (e.g. localized versus general surface degradation, adherent versus non-adherent scales, etc.) are readily apparent. Except for the case of spallation of a ceramic coating (which is often due to factors other than ceramic corrosion per se), degradation of ceramic materials is likely to be much less obvious on visual inspection.

Weight change data are often compromised by breakage of ceramic specimens in handling, and the same inherent brittleness of ceramics renders preparation of polished cross sections for microscopic examination very difficult. Techniques such as chemical analysis and scanning microscopy present no conceptual problems, although the detection, characterization, and interpretation of relatively slight attack of ceramic materials may not be straightforward.

As shown by the data and comments in the following section, no single analytical technique proved as useful and valuable as in the same type of hot corrosion testing with metals. However the combination and correlation of several methods of post-test analysis of the corroded specimens was found to be informative.

RESULTS AND DISCUSSION

Na₂SO₄ - SO₃ Hot Corrosion of Yttria-Stabilized Zirconia

Expected from basic principles and observed in service useage is that stabilized zirconia-base ceramic coatings can degrade via chemical alteration of the more reactive stabilizing compound (MgO, CaO, or Y₂O₃). To determine if this tendency could be meaningfully related to hot corrosion parameters and suppressed by higher concentrations of the stabilizer, corrosion coupons were prepared with 12, 20 and 35% Y₂O₃.

Specimens were exposed for 100 hours at each of the four conditions listed in Table 1. In characterizing the hot corrosion attack as discussed on p. 7, consideration of X-ray flourescence and X-ray diffraction results as a function of temperature, SO₃ pressure, and yttria content of the starting material proved the single most useful indication of the nature of degradation of the material and its dependence on corrosive conditions.

The X-ray flourescence data in Table 4 were obtained by irradiating a 1 cm² area with 50 KV white radiation; the surface yttria contents of the tested samples are the uncorrected ratios of yttrium X-ray intensities to those of the as-received starting materials. Although the limitations of the relatively unsophisticated (but rapid and low cost) analytical technique are recognized; a consistent

Table 4

Yttria content of plasma sprayed surface after cyclic hot corrosion testing for 100 hours with 1 mg/cm² Na₂SO₄ salt. Values were determined by X-ray fluorescence using as-received materials as standards.

% Y ₂ O ₃ as sprayed	704°C .0007 SO ₃	982°C .0007 SO ₃	704°C .0071 SO ₃	982°C .0013 SO ₃
12	9	11	2	11
20	15	19	9	18
35	19	33	16	31

dependence of surface yttrium loss on temperature and SO_3 pressure is apparently established. At fixed SO_3 pressure, the samples suffered greater yttrium loss at 704 than at 982°C, and at each temperature, higher SO_3 pressure caused greater yttrium loss. Especially dramatic is the difference between the large yttrium losses at 704°C and the much smaller effect at the higher temperature.

Results of X-ray diffractometer scans of the YSZ corrosion coupons are listed in Table 5. Although the numbers cannot be quantitatively rationalized by thermodynamic or bulk diffusion considerations, a consistent dependence on temperature and SO_3 pressure is again evident, and the trends - especially the substantial transformation at 704°C in comparison with the minimal destabilization at 982°C - are the same as implied by the X-ray fluorescence results.

Table 5

Volume percent cubic (stabilized) zirconia determined by X-ray diffraction of plasma sprayed surface after cyclic hot corrosion testing for 100 hours with 1 mg/cm² Na_2SO_4 salt.

% Y_2O_3 as sprayed	as sprayed	704°C .0007 SO_3	982°C .0007 SO_3	704°C .0071 SO_3	982°C .0013 SO_3
12	> 98	98	98	65	97
20	> 98	93	98	52	98
35	> 98	73	98	22	90*

*Also detected about 5 vol% hydrated sodium yttrium sulfate, $\text{Na}_2\text{Y}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$

The selective removal of yttrium indicated by the XRF and XRD data was independently implied by wet chemical analysis of the 25-ml wash solutions used to remove spent salt after each 20-hour exposure cycle. Concentrations of the order of 50 to 100 $\mu\text{g}/\text{ml}$ of dissolved yttrium but <1 $\mu\text{g}/\text{ml}$ of zirconium were detected in these solutions. Scatter in the data, however, masked any systematic effect of temperature, SO_3 pressure, or yttrium content of the starting material, except that the role of SO_3 was confirmed by the negligible Y content of solutions from salt-coated coupons exposed in sulfur-free air.

Weight changes in the two experiments at 0.0007 atm SO_3 pressure were negligibly small, and post-test scanning microscopy showed no apparent changes in surface condition. At higher values of SO_3 pressure, all specimens showed a weight gain after the initial 20-hour exposure cycle, and the weight changes were greater at the higher yttrium contents (Figure 2). Presumably the initial weight gain reflects a reaction between the SO_3 -containing salt and the Y_2O_3 of the ceramic; the subsequent weight loss may be due partly to leaching of the Y-containing

Fig. 2. $\Delta M/A$ versus time for 12, 20, and 35% YSZ coupons tested at indicated conditions. Weight changes at lower SO_3 pressures were negligible.

reaction products by water washing and partly to undercutting and mechanical removal of the globular plasma-sprayed particles which were evident on the as-received material but not in the post-test SEM photomicrographs of the specimens which experienced measureable weight losses (Figure 3).

Also discernable in Fig. 3 is fine porosity in the 704°C specimen but not in the material tested at the higher temperature. Considered in conjunction with the X-ray fluorescence, X-ray diffraction, and weight change results, this

(a) 20% YSZ, as-sprayed

(b) 35% YSZ, as-sprayed

(c) 20% YSZ, 100h at 704°C, $p_{\text{SO}_3} = 0.007$

(d) 35% YSZ, 100h at 982°C, $p_{\text{SO}_3} = 0.0014$

Fig. 3. Typical surface features of as-sprayed YSZ coupons (top), and post-test surface condition of samples which experienced measureable weight losses at 704 and 982°C respectively.

comparison suggests the fine porosity is indeed corrosion-induced; i.e. it results from a chemical reaction between the bulk ceramic material and the liquid salt. The absence of such porosity in the 982°C samples suggests the corrosion reaction was favored by the lower test temperature.

Polished cross sections of the samples of Fig. 3 (and other material tested later in the program) were examined in detail for evidence of the corrosion reaction implied by the surface condition. These examinations, including scanning microscopy at magnifications up to 3000X, did not reveal cross sections of the fine pores observed on characterizing the as-corroded surface. Apparently the pores are of very shallow depth and extremely fine in comparison with the porosity and microcracking typical of the plasma sprayed YSZ microstructure.

The trends suggested by all of the analytical techniques are consistent with a proposal that hot corrosion of YSZ can occur by a type of acidic dissolution or leaching of Y_2O_3 from ZrO_2 ; i.e. by a reaction of the form

The rate of this reaction would be expected to increase with increasing SO_3 pressure and as the activity of Y_2O_3 in ZrO_2 is increased (hence the consistently greater weight gains in the higher yttria samples in Fig. 2). On cooling from the test temperature, the ions in the liquid salt react to form the hydrated sodium-yttrium double sulfate (identified by x-ray diffraction of one of the specimens) which is presumably the source of the yttrium dissolved in the wash solutions.

$Na_2SO_4 - SO_3$ Hot Corrosion of Other Candidate Ceramic Coating Materials

Furnace tests under the same conditions as those used to characterize the hot corrosion behavior of YSZ were run on bulk specimens of other ceramic materials (Lucalox® and single crystal alumina, SiO_2 , Si_3N_4 , $ZrSiO_4$, mullite) which might be considered for advanced plasma sprayed or vapor deposited ceramic coatings.

In the initial test at 704°C and 0.0007 atm SO_3 , no effect on any of the specimens except a slight dulling of the surface finish of the highly polished Luca-lox alumina was observed. At 982°C, weight changes were negligibly small, but easily detectable corrosion products were observed by SEM and optical microscopy of polished cross sections of SiO_2 and Si_3N_4 (Figure 4). Attack of mullite was clearly discernable by scanning microscopy of the surface (Figure 5), although

Fig. 4. Hot corrosion (100 hours at 982°C, 0.0007 atm SO_3) of SiO_2 (top) and Si_3N_4 as shown by SEM characterization of as-polished versus post-test surface features and corresponding metallography of cross sections.

Fig. 5. As polished (left) and post-test surface condition of mullite coupon exposed 100 hours at 982°C, $p_{\text{SO}_3} = 0.0007$ atm.

degradation was not evident in a metallographically polished cross section. In each case the nature and severity of the hot corrosion attack was difficult to define because of surface damage resulting from the pre-test mechanical polishing.

Characterization of the ZrSiO_4 sample by scanning microscopy showed no discernable effect of exposure to the liquid salt.

X-ray diffraction of the relatively impure Haselden Si_3N_4 gave a very complex pattern which could not be readily solved. Conversely and somewhat surprisingly, the diffraction pattern of the SiO_2 showed only a mixture of α -quartz and amorphous silica, in spite of the apparently substantial reaction with the liquid salt implied by the surface examination and metallography.

A 982°C test at 0.0014 atm SO_3 essentially reproduced the nature and extent of hot corrosion (as judged from SEM examination of post-test surfaces) observed at the same temperature but lower SO_3 pressure. However a 50-hour test of Si_3N_4 and SiO_2 in air clearly showed greater attack (but apparently similar corrosion products) than that characteristic of the same temperature and salt deposit with SO_3 gas in the furnace atmosphere.

The observation of greater attack at the higher test temperature and greater attack in sulfur-free air than in SO_3 -containing atmospheres suggests that hot corrosion of the silicon-containing ceramics was basic in nature; i.e. a reaction between the oxide ion component of the liquid salt deposit and the silica

component of the ceramic of the form

Effect of Vanadium on Na₂SO₄ - SO₃ Hot Corrosion

Crude or residual oils often contain concentrations of vanadium which operating experience has shown to aggravate the hot corrosion of metallic materials and coatings. To evaluate the potential of ceramic coatings to resist this effect, selected materials were tested at 704 and 982°C with deposits of Na₂SO₄ - 10%V₂O₅ (prepared with water-soluble vanadyl sulfate) for comparison with degradation produced by 100% Na₂SO₄.

The results did not establish a significant effect of vanadium at either temperature. At 704°C, x-ray diffraction of the plasma sprayed YSZ coupons suggested slightly greater destabilization due to the presence of 10% V₂O₅ in the salt deposit, although the reproducibility of the data in Table 5 was not evaluated. Si₃N₄, ZrSiO₄, and mullite were very lightly attacked, as in the corresponding test with 100% Na₂SO₄. At 982°C, degradation of YSZ and amounts of corrosion products observed by scanning microscopy of the Si-containing materials were not discernably different from the equivalent experiment without vanadium.

Hot Corrosion Behavior of Segmented YSZ Coatings

The term "segmented" implies a columnar microstructure with high density columns perpendicular to the plane of the coating and free space between the segments to accomodate thermal expansion mismatch strains. To determine the effect of such microstructures on the susceptibility of YSZ coatings to salt-induced degradation, hot corrosion tests were run on 1/2 inch diameter IN 792 bars coated with PVD NiCoCrAlY and 3 mils. of segmented PVD ceramic (20% YSZ).

A longitudinal half of the bar was sprayed with approximately 1 mg/cm² of Na₂SO₄ - 10% V₂O₅ salt mixture, and the sample was exposed 20 hours at 704°C

and 0.0007 atm SO_3 . On removal from the furnace, the salt-covered areas were yellowish in color, but there was no apparent cracking or spallation of the ceramic due to the liquid salt. After washing of the bar for application of fresh salt, however, a long, straight crack was observed (Figure 6). The crack was tangent to several splatter defects, although its point of origin was not apparent.

(a) as removed from furnace

(b) water washed to remove spent salt

Fig. 6. Surface of test bar (arrow marks same area in both photos) after exposure to $\text{Na}_2\text{SO}_4 - \text{V}_2\text{O}_5$ salt for 20 hours at 704°C , 0.0007 atm SO_3 .

The bar was re-salted and exposed for another 20 hours at the same conditions, after which the crack shown in Fig. 6b was slightly longer and the ceramic layer was noticeably bulged out in the immediate vicinity of the crack. On immersion of the bar in water to wash off the residual salt, large sections of the coating spalled, and others were obviously non-adherent (Figure 7).

Fig. 7. Spalling of ceramic layer in center section of test bar.

X-ray diffraction of the outer surface of the remaining ceramic coating material and the inner surface of spalled chips both showed approximately 10 to 15% monoclinic zirconia (versus >98% in the pre-test material). Apparently the exposure to liquid salt resulted in partial destabilization, although it is by no means clear that destabilization was a factor in the salt-induced spalling of the ceramic material.

A second bar was tested in the same manner, and substantial spallation of the ceramic coating was again encountered.

Mixed Sulfate Effects in Hot Corrosion of Ceramic Coatings

Mixtures of Na_2SO_4 and various metallic sulfates can originate from such sources as impurities in the fuel, the metallic content of ingested salt, rust or paint in the ductwork leading to the engine, and bond coat corrosion. To determine if the lower melting point of these mixtures would result in aggravated attack of ceramic coated materials, IN 792 coupons with 5 mils of plasma sprayed YSZ (20%) were exposed at 704 and 982°C with salt deposits of Na_2SO_4 plus 10% PbO , 50% CoSO_4 , 50% FeSO_4 , and 50% ZnSO_4 respectively. Severity of attack, in comparison with that produced by 100% Na_2SO_4 at the same temperature and SO_3 pressure, was evaluated by x-ray diffraction and post-test metallography.

Determinations of volume % cubic zirconia as a function of temperature and salt composition are listed in Table 6. With one exception the data indicate significant destabilization, although there is apparently no interpretable dependence on temperature or salt composition. In comparison with Table 5, the extent of destabilization - even for the samples tested with 100% Na_2SO_4 - is generally greater than expected, especially at the higher temperature.

Table 6

Volume % cubic zirconia determined by surface X-ray diffraction of samples tested 100 hours (5 cycles of 20 hours) with mixed sulfate salt deposits. SO_3 pressure = 0.0007 atm at each temperature.

Temp.	Na_2SO_4	+ 10% PbO	+ 50% CoSO_4	+ 50% FeSO_4	+ 50% ZnSO_4
704°C	85	80	98	75	96
982°C	90	70	80	70	not tested

Visual inspection of the specimens showed no significant damage at 704°C but severe edge attack and ceramic layer spallation at 982°C. Metallographic examination also indicated no discernable microstructural change of the ceramic

and no corrosion of the bond coat. Conversely the 982°C specimens exhibited severe bond coat corrosion (Figure 8), the porous ceramic apparently being highly pervious to the high temperature liquid salt.

Fig. 8. Degradation of YSZ-coated IN 792 after 100 hours at 982°C, 0.0007 atm SO_3 , Na_2SO_4 - 10% PbO salt. Note extensive corrosion and undercutting of NiCo-CrAlY bond coat, in spite of retention of outer ceramic layer in most areas.

Layer Thickness Effects

Although maximum insulating ability of a ceramic thermal barrier coating requires a relatively thick ceramic layer, the concept of ceramics as corrosion resistant materials includes the potential application of much thinner coating intended primarily for corrosion protection. In this respect there have been intriguing observations of unexpectedly slight bond coat corrosion even after spallation of most of the outer ceramic layer on service hardware. Test coupons were therefore prepared with varying thicknesses (<1 to >6 mils) of 20% yttria-stabilized zirconia to investigate the ability of relatively thin ceramic deposits to inhibit salt-induced degradation. Also tested at the same time was plasma sprayed calcium silicate because of recent results of other investigators suggesting favorable performance of this material.

A series of specimens with 0, 1, 3, and 6 mils of 20% YSZ over a plasma-sprayed NiCoCrAlY bond coat was tested at 704°C with Na_2SO_4 - 10% V_2O_5 salt and 0.0007 atm SO_3 in the gaseous environment. Visual inspection indicated severe attack of the NiCoCrAlY exposed without a ceramic overlayer, but the YSZ coatings appeared to be generally protective after 100 hours. XRD, however, indicated substantial transformation of the surface ceramic material to non-stabilized zirconia.

On picking up the samples after the XRD scans, the 6-mil ceramic layer separated from the IN 792 coupon and adhered as a single piece to the double-stick tape being used to hold the specimens in the diffractometer. A scan was then made on the fractured surface, and the material was found to be 98% cubic. This suggests that the salt/gas chemistry was highly destabilizing to the surface material, but the salt apparently did not penetrate to the inner portion of the 6-mil layer.

Post-test metallography confirmed that the as-sprayed NiCoCrAlY bond coat, typically exhibiting the structure and thickness shown in Figure 9a, was almost completely consumed by exposure for 100 hours without a YSZ overlayer (Fig. 9b). Even the 1-mil layer of TSZ, however, apparently prevented corrosion of the bond coat (Fig. 9c), and the specimen with the 3-mil ceramic layer also experienced no metallographically detectable corrosion of the NiCoCrAlY (Fig. 9d).

As expected, metallography of the 6-mil sample showed that the YSZ had broken within the ceramic, leaving a more or less continuous layer of YSZ covering the bond coat. Again, there was no indication of corrosion of the NiCoCrAlY.

Fig. 9. Layer thickness effects in 704°C hot corrosion of NiCoCrAlY/YSZ-coated IN 792: (a) as-sprayed NiCoCrAlY bond coat; (b) corrosion of bond coat tested without YSZ overlayer; (c) post-test microstructure, NiCoCrAlY + 1 mil YSZ; (d) post-test microstructure, NiCoCrAlY + 3 mils YSZ.

These observations show that ceramic coatings are capable of protecting against severe low temperature corrosion which would occur in their absence, although practical applications may require improved resistance (or another type of ceramic material) to the destabilization which YSZ can experience under low temperature acidic conditions.

The plasma sprayed calcium silicate, identified by pre-test XRD as approximately 85% Ca_3SiO_5 and 15% Ca_2SiO_4 , reacted to form a mixture of about 50% SiO_2 (cristobalite) and 40% CaSO_4 in 100 hours at 704°C.

In testing the same materials at 900°C, the more fluid salt was obviously much more penetrating and damaging. Visual inspection again confirmed the expected corrosion of the NiCoCrAlY bond coat in the absence of a ceramic outer layer but also indicated substantial attack under a thin YSZ layer which appeared effective at the lower temperature. Calcium silicate again exhibited substantial transformation to CaSO_4 .

GENERAL DISCUSSION, SUMMARY, AND CONCLUDING REMARKS

Restricted to the case of practical interest with respect to gas turbine engines, hot corrosion is environmentally induced degradation of high temperature materials due to the presence of a liquid salt deposit on the surface of a component. The phenomenon is widespread, universally encountered in utility engines operating on contaminated fuels and frequently observed even in aircraft gas turbines. Consequently the hot corrosion behavior of turbine materials and protective coatings has been extensively studied, and, at least in the case of metallic systems, many aspects are well characterized if not well understood.

Facilitating the study of hot corrosion in metals and metallic coatings are the essentially chemical nature of the degradation mechanisms and the obvious distinction between metal and corrosion products. Since metals are generally ductile and fully dense, physical or mechanical processes such as cracking and spallation of metallic coatings or accelerated penetration of liquid salt along microstructural discontinuities are either not involved or readily discernable in cases where these mechanisms are indeed a factor in coating performance. Microstructure of an alloy or coating, although a major variable, is usually reproducible, such that the hot corrosion behavior of a given material is generally amenable to experimental determination and analytical treatment of its dependence on thermodynamic parameters such as material composition, component temperature, type and amount of salt, and partial pressure of reactive species in the gaseous environment.

Conversely, the characterization of hot corrosion of ceramics and ceramic coatings tends to become formidably complicated by the interaction between chemical and physical processes and the relative difficulty of differentiating between unaffected and degraded material. In comparison with that of multicomponent metallic systems, the fundamental chemistry of reaction of the ceramic compound with the high temperature environment is probably very simple. Ceramic materials, however, are generally brittle and less than fully dense, especially in the case of thermal barrier coatings where a controlled distribution of microstructural discontinuities appears to be necessary to accommodate thermal expansion mismatch strains.

The salt-induced degradation of such coatings, even if chemical decomposition of the ceramic material is clearly involved, is as strong a function of the coating microstructure (i.e. the extent of salt seepage into pores and microcracks) as of the thermodynamics and kinetics of reaction of the ceramic compound with the liquid salt deposit.

Established beyond question, for example, is that yttria-stabilized zirconia ceramics are indeed susceptible to a fundamental chemical reaction between the bulk ceramic material and the high temperature environment of a gas turbine engine. Although the mechanism is not understood, the essential nature of this reaction is removal of the more reactive stabilizing compound and consequent transformation of the material from cubic to monoclinic zirconia. This reaction is favored by acidic conditions such as high SO_3 pressures and vanadium oxide salt deposits and at least for the combination of SO_3 pressures and salt deposits used in these experiments, greater yttrium loss and greater destabilization are observed at relatively low than at relatively high temperatures (Tables 4 and 5). In spite of this tendency, however, very thin YSZ layers were protective against low temperature corrosion which occurred in the absence of the ceramic coating (Fig. 9) but totally ineffective against penetration by liquid salt at 982°C (Fig. 8). This effect must be due to porosity of the microstructure and fluidity of the salt and not to the corrosion chemistry of stabilized zirconia.

Likewise the salt-induced spallation of the segmented YSZ coating in Fig. 7 is apparently related to the segmented microstructure. The obvious implication of this result is that resistance of segmented YSZ coatings to liquid salt deposits may require some type of surface sealing to prevent the seepage of salt down the segments.

Coating adherence remains the most formidable technical challenge in the area of ceramic coatings, and the primary criterion for selection and application of a ceramic coating material will undoubtedly be the microstructural, thermal expansion, and processability characteristics which permit satisfactory and reproducibly attainable coating adherence. In the near term future, these considerations are likely to dictate the use of zirconia-base ceramics as thermal

barrier coatings, in spite of their susceptibility to corrosion in the acidic environments expected in industrial gas turbines. Further developments in processing technology or design concepts utilizing thinner ceramic coatings for corrosion resistance rather than the thermal barrier effect may later permit the selection of ceramic coating materials such as ZrSiO_4 or high purity silica-base or silica-forming ceramics which corrode by basic mechanisms and thus are less likely to experience chemical decomposition under the acidic conditions characteristic of gas turbines.

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