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July 1982

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OF  $ZrO_2$ - $Y_2O_3$  THERMAL BARRIER COATINGS

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SUMMARY

E-1255  
A Mach 0.3 burner rig test program was conducted to determine how the fuel-to-air mass ratio affects the durability of  $ZrO_2$ - $Y_2O_3$ /Ni-16Cr-6Al-0.31Y thermal barrier coating systems in combustion products containing 5 ppm Na and 2 ppm V based on Jet A fuel.

Triplicate coated specimens were exposed to Mach 0.3 combustion gases at the fuel-to-air mass ratios of 0.039, 0.044, and 0.049. Exposure cycles consisted of subjecting the specimens to 1 hour at temperature followed by six minutes out of the combustion gases with external forced air cooling on the specimens. Specimens were examined after twenty 1-hour cycles and were removed from test when the ceramic had spalled over approximately one-fourth of the hot zone on the leading edge. Test conditions were: 843° C substrate temperature and 982°, 1010°, and 1038° C ceramic surface temperature for the respective fuel-to-air mass ratios of 0.039, 0.044, and 0.049. Based on these tests, it was found that

- (1) As this fuel-to-air mass ratio is increased from 0.039 to 0.049, the durability of  $ZrO_2$ -6 $Y_2O_3$ ,  $ZrO_2$ -8 $Y_2O_3$ , and  $ZrO_2$ -12 $Y_2O_3$  coatings decreases. This decrease in durability is attributed to the 25 percent increase in fuel impurity flux for the corresponding 25 percent increase in fuel.
- (2)  $ZrO_2$ -8 $Y_2O_3$  coatings were approximately 2X and 1.3X more durable than  $ZrO_2$ -12 $Y_2O_3$  and  $ZrO_2$ -6 $Y_2O_3$  coatings, respectively at the fuel-to-air mass ratio of 0.039.
- (3) The number of cycles endured by  $ZrO_2$ -8 $Y_2O_3$  coated specimen varied from an average of 53 to 200 for the respective fuel-to-air mass ratios of 0.049 and 0.039.
- (4) At a fuel-to-air mass ratio of 0.049, all  $ZrO_2$ - $Y_2O_3$  coated specimens failed in 40 to 60 hours.

INTRODUCTION

With the cost of fuels for electric power generating turbines increasing, numerous alternatives are being explored to improve turbine efficiency. One such alternative is the use of insulating ceramic thermal barrier coatings (TBCs) on cooled hot-section components of gas turbines. These coatings can reduce the metal temperatures of air-cooled components 50 to 200° C which would allow improved component durability. Substantial gains in heat engine efficiency can be realized by using the coatings to maintain current metal



temperatures as turbine inlet temperatures are increased or cooling air requirements are reduced.

Substantial interest was generated in TBCs on the basis of the performance of a NASA-developed two-layer coating system,  $ZrO_2-12Y_2O_3/Ni-16.2Cr-5.6Al-0.61Y$ . This coating system exhibited good durability in furnace, in Mach 0.3 burner rig, and in an aircraft research gas turbine ground tests (Reference 1). Recent studies have concentrated on (1) optimizing the deposition parameters of the ceramic and metallic bond layers, (2) optimizing the Y and Al content of the bond layer, (3) developing strain tolerant ceramic microstructures and reducing ceramic-substrate residual stress, (4) gaining a basic understanding of the effects of phase stability of partially stabilized  $ZrO_2-Y_2O_3$  on coating durability, and (5) determining the effects of thermal cycling on thermal barrier coatings (References 2, 3, 4, 5, 6, 7, 8, 9).

In studies involving coating systems for industrial/utility gas turbines applications, early test results with the  $ZrO_2-12Y_2O_3/Ni-16.2Cr-5.6Al-0.61Y$  system in Na, V-doped combustion gases were not encouraging (Ref. 10). Two coating systems,  $ZrO_2-8Y_2O_3$  and calcium silicate, were identified in the study as having substantially more durability than the  $ZrO_2-12Y_2O_3$  system. Subsequent studies have centered on optimizing bond layer composition, optimizing bond layer deposition parameters, developing new corrosion-resistant ceramic coatings, studying reactions between potential air and fuel impurities, and determining how condensates affect spallation of coatings (References 2, 11, 12, 13, 14, 15).

The present study was undertaken to determine how the fuel-to-air mass ratio affects the durability of the  $ZrO_2-Y_2O_3$  thermal barrier coating in Mach 0.3 combustion products containing Na and V. In a previous burner rig hot corrosion study, Deadmore, et al (Reference 16) had shown that hot corrosion attack of Mar M-509 hollow erosion bars was more severe when the fuel-to-air mass ratio was increased while the bars were maintained at constant temperature using cooling air. Similar hot corrosion results were expected for TBC systems, and thus additional understanding of the role of hot corrosion in TBC system failure was anticipated.

#### MATERIALS APPARATUS AND PROCEDURES

The chemical compositions and specifications for the  $ZrO_2-Y_2O_3$  thermal barriers and the  $Ni-16Cr-6Al-.31Y$  bond coating have been reported previously (Refs. 4,5). The burner rig specimens used in this study were 1.27 cm O.D. Waspalloy tubes ( $Ni-20.0Co-19.4Cr-3.9Mo-3.0Ti-1.4Al-0.9Zr$ ) with a wall thickness of 0.127 cm. The procedures outlined by Stecura (Ref. 1) were used for specimen preparation and plasma spray deposition, except that during coating deposition, the tubes were rotated at 2.5Hz. Both the bond and thermal barrier coating were applied manually in air with a subsonic plasma spray gun using argon as the plasma gas. The deposition parameters were 350 amperes and 31 volts for the bond coats and 550 amperes and 31 volts for the  $ZrO_2-Y_2O_3$  coatings. Target thicknesses for the bond coat were 0.013 cm with measured variations from 0.010 to 0.017 cm and 0.038 cm for the  $ZrO_2-Y_2O_3$  coatings with variations from 0.030 to 0.045 cm.



A Mach 0.3 burner rig similar to one shown in Fig. 1 was used in these tests. Air, Jet A fuel, and an aqueous solution of NaOH and  $\text{NH}_4\text{VO}_3$  were injected into the combustors, ignited, and expanded through the nozzle at a velocity of Mach 0.3. The dopant levels of Na and V in the combustion gases corresponds to the fuel equivalent of 5 ppm Na and 2 ppm V. Eight coated specimens were placed in a holder (as shown in Figure 2a) and rotated at 7.5Hz at a distance of 2.54 cm from the front of the burner nozzle. A cooling insert (Figure 2b) was positioned in the holder and specimen to direct cooling air to the inside of the leading edge of the specimen.

Before testing was started, calibration runs were made to determine the cooling air needed to maintain the substrate temperature at  $843^\circ\text{C}$  as the fuel-to-air mass ratio was varied from 0.035 to 0.050. Substrate temperature was measured with a thermocouple embedded in one of the eight Waspalloy specimens. The fuel-to-air mass ratio was changed by varying the fuel at constant combustion air flow and the surface temperature of the ceramic was measured with a disappearing filament optical pyrometer and corrected for emissivity for each fuel-to-air mass ratio.

The test cycle consisted of subjecting the coated specimens to one hour at temperature in the combustion gases followed by six minutes out of the combustion gases with external forced air cooling on the specimens. The internal cooling air remained constant during both the heating and cooling portions of the cycle. The specimens were inspected after each twenty 1-hour cycles and specimens were removed from test when the ceramic had spalled over approximately one-fourth of the hot zone on the leading edge. Coatings were run in triplicate for each test. A representative number of exposed specimens were selected for X-Ray Diffraction (XRD) and Scanning Electron Microscopy/Energy Dispersive (SEM/EDS) analysis to determine phases and identify condensates.

## RESULTS AND DISCUSSION

Typical specimens which had undergone test are shown in Figure 3. Coated specimens spalled at the upper edge of the hot zone as in previous similar tests where the temperature within the ceramic is below the dew points of all of the condensates (Reference 12).

The responses of  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  thermal barrier coated specimens to combustion gases doped with sodium plus vanadium are summarized in Figure 4 and Table I. A regression analysis was performed on the data in Table I and the following equation was developed which expressed coating life as a function of yttria concentration and fuel-to-air mass ratio.

$$1/(\text{coating life}) = Y = 0.0150 + 1.31 (\text{fuel/air value}) - 0.0077 (\text{Y}_2\text{O}_3 \text{ wt. percent}) + 0.0005 (\text{Y}_2\text{O}_3 \text{ wt. percent})^2$$

A t-ratio was calculated in the above expression with the relationship

$$t \text{ ratio} = \frac{\text{coefficient}}{\text{standard deviation of coefficient}}$$



and used to express the level of confidence in the effects of the fuel-to-air mass ratio and yttria content on coating durability (life). Based on these ratios at the 99 percent confidence level, coating life is highly dependent on the fuel-to-air mass ratio and the  $ZrO_2-8Y_2O_3$  coating is more durable in hot corrosion combustion products at lower fuel-to-air mass ratios than  $ZrO_2-6Y_2O_3$  and  $ZrO_2-12Y_2O_3$  coatings.

In general, the data shows that the durability of all of the  $ZrO_2-Y_2O_3$ -based coating systems decreased as the fuel-to-air mass ratio was increased. This decrease in durability is mainly attributed to the twenty-five percent increase in fuel impurity flux as the fuel-to-air mass ratio is increased from 0.039 to 0.049. This conclusion is based on the results from a series of earlier tests where it was shown that the durability of  $ZrO_2-12Y_2O_3$  coatings was directly proportional to the concentration of Na and V in the combustion products (Ref. 10). One additional factor which was likely to contribute to the decrease in coating system durability observed in these present tests as the fuel-to-air mass ratio was increased is that radial stresses increased accordingly on initial heat-up of the specimens during a given cycle. Hendricks, et al (Ref. 17) used time-temperature data to calculate the radial stresses on thermal barrier coated specimen exposed to Mach 0.3 combustion gases and concluded that the higher the rate of heat input (higher temperature and higher fuel-to-air mass ratio), the higher the resultant stresses. The radial stresses were calculated for a range of fuel-to-air mass ratios of 0.040 to 0.065 and found to be within the boundaries of coating adhesive/cohesive or detachment stresses measured by Levine (Ref. 18).

As the fuel-to-air mass ratio was increased in the present tests, the temperature gradient through the ceramic coating increased because the substrate temperature was held constant and the ceramic surface temperature allowed to rise with increasing combustion gas temperature. Because of the limited scope of this study, however, the effects of this increasing temperature gradient on coating system durability were not investigated.

In the analyses of specimens in previous tests, condensates like  $Na_2SO_4$ ,  $Na_2V_2O_6$ , and  $V_2O_5$  were identified at the edges of the hot zones where the temperatures within the ceramic coatings were below their respective dew points (Ref. 12,15). Condensates in the present study were anticipated to deposit within the ceramic coating further from the hot zone where the temperatures are below the dew points of the condensates. SEM EDS analyses of coated specimens in the present study in areas adjacent to the spalled areas revealed that both Na and V were present. Because the specimen spalled over a large area near the edge of the hot zones, no difference in the spallation morphology for specimens tested at different fuel-to-air mass ratios could be detected.

$ZrO_2-8Y_2O_3$  coatings were found to be more durable in hot corrosion combustion products than  $ZrO_2-6Y_2O_3$  and  $ZrO_2-12Y_2O_3$  at lower fuel-to-air mass ratios. The durability of each  $ZrO_2-Y_2O_3$  coating probably is affected by the overall mechanical and chemical stability of (1) the initial phases, (2) the newly-developed phases, and (3) the reactants (condensates:  $Na_2SO_4$ ,  $Na_2V_2O_6$ , or  $V_2O_5$ , etc.) and products of the reactions as a function of time and temperature. An in-depth determination of these effects was not undertaken because of the limited objectives of these tests.



## SUMMARY OF RESULTS

The present study was conducted to determine how the fuel-to-air mass ratio affects durability of  $ZrO_2-Y_2O_3/Ni-16Cr-6Al-0.3Y$  thermal barrier coating systems in Mach 0.3 combustion products containing 5 ppm Na and 2 ppm V based on the fuel. Tests were conducted at three fuel-to-air mass ratios, 0.039, 0.044, and 0.049 by varying the amount of fuel at constant combustion air flow. The results are as follows:

1. The durability of  $ZrO_2-6Y_2O_3$ ,  $ZrO_2-8Y_2O_3$ , and  $ZrO_2-12Y_2O_3$  coatings decreases as the fuel-to-air mass ratio is increased from 0.039 to 0.049. This decrease in durability is attributed to the 25 percent increase in fuel impurity flux. In some previous Mach 0.3 tests with single specimens,  $ZrO_2-12Y_2O_3$  coating durability was found to be a function of the Na and V concentrations in the combustion products (Ref. 10).
2.  $ZrO_2-8Y_2O_3$  coatings were approximately 2X and 1.3X more durable than  $ZrO_2-12Y_2O_3$  and  $ZrO_2-6Y_2O_3$  coatings, respectively, at the lowest fuel-to-air mass ratio of 0.039. The number of cycles endured by  $ZrO_2-8Y_2O_3$  coated specimen varied from an average of 53 to 200 for the respective fuel-to-air mass ratios of 0.049 and 0.039. At a fuel-to-air mass ratio of 0.049, all  $ZrO_2-Y_2O_3$  coated specimens failed in 40 to 60 hours.

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TABLE I. - SUMMARY OF MACH 0.3 BURNER RIG RESULTS  
IN FUEL-TO-AIR MASS RATIO STUDY

Fuel-to-air mass ratio	Number of hours before spallation of 1/4 of coating		
	$ZrO_2-6Y_2O_3$	$ZrO_2-8Y_2O_3$	$ZrO_2-12Y_2O_3$
0.049	60	60	40
	60	40	40
	40	60	40
0.044	80	80	40
	80	100	60
	60	120	60
0.039	100	220	80
	160	180	80
	140	200	100

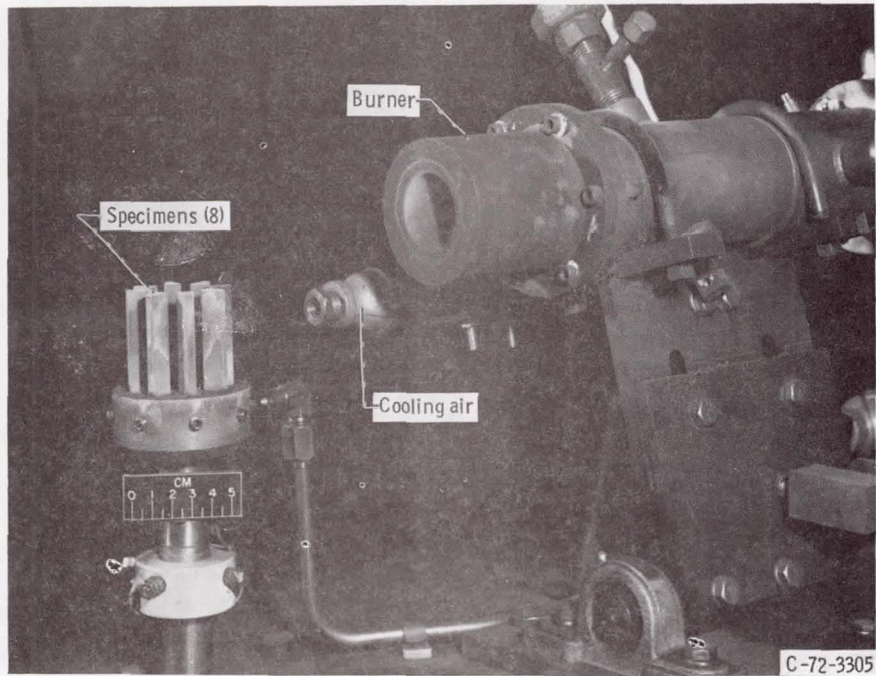
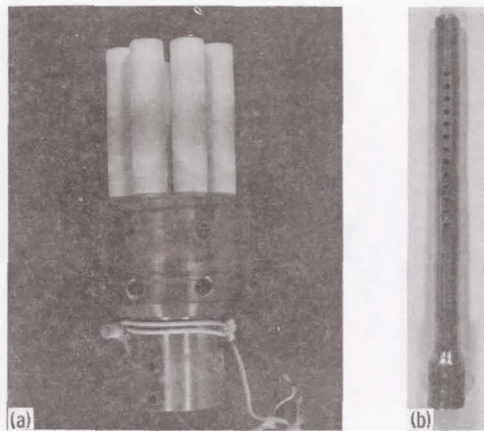


Figure 1. - Mach 0.3 burner rig test configuration.

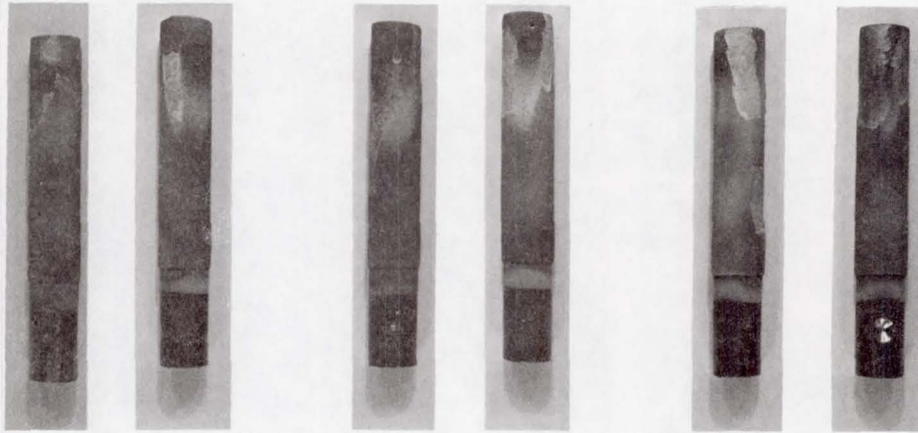


(a) Specimen holder.

(b) Cooling insert.

Figure 2. - Mach 0.3 burner rig specimen holder and cooling insert.





Number of cycles:

80

60

120

80

40

60

ZrO<sub>2</sub>-6Y<sub>2</sub>O<sub>3</sub>

ZrO<sub>2</sub>-8Y<sub>2</sub>O<sub>3</sub>

ZrO<sub>2</sub>-8Y<sub>2</sub>O<sub>3</sub>

Figure 3. - Photographs of ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>-coated specimens after exposure to Mach 0.3 burner rig combustion gases doped with fuel equivalent amount of 5 ppm Na and 2 ppm V. Time of coating spallation is indicated. Operation conditions are 843° C metal temperature, 1010° C ceramic surface temperature, fuel-to-air mass ratio of 0.049, and 1-hour cycles.

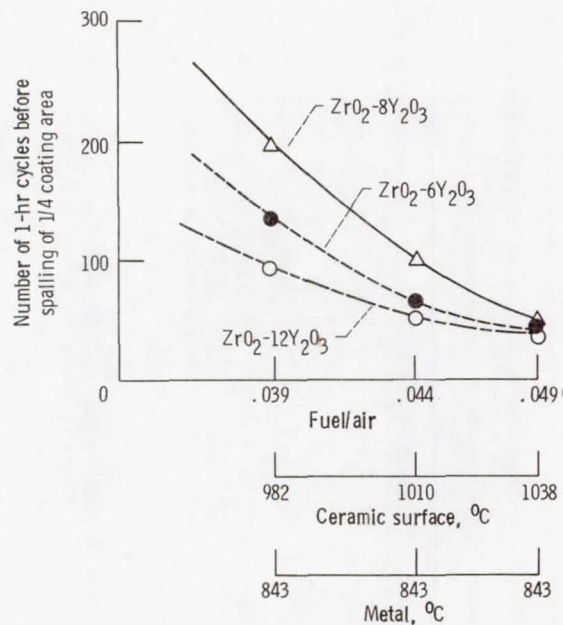


Figure 4. - Fuel-to-air mass ratio burner rig study. Fuel impurity level: 5 ppm Na + 2 ppmV; substrate: 1.27 cm O. D. Waspaloy; bond coat: Ni-16Cr-6Al-0.31Y

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16. Abstract A Mach 0.3 burner rig test program was conducted to determine how the fuel-to-air mass ratio affects the durability of $ZrO_2-Y_2O_3/Ni-16Cr-6Al-0.31Y$ thermal barrier coating systems in combustion products containing 5 ppm Na and 2 ppm V. As the fuel-to-air mass ratio was increased from 0.039 to 0.049, the durability of $ZrO_2-6Y_2O_3$ , $ZrO_2-8Y_2O_3$ and $ZrO_2-12Y_2O_3$ coatings decreased. $ZrO_2-8Y_2O_3$ coatings were approximately 2X and 1.3X more durable than $ZrO_2-12Y_2O_3$ and $ZrO_2-6Y_2O_3$ coatings respectively at the fuel-to-air mass ratio of 0.039. The number of 1-hour cycles endured by $ZrO_2-8Y_2O_3$ coatings varied from averages of 53 to 200 for the fuel-to-air mass ratios of 0.049 and 0.039, respectively. At the fuel-to-air mass ratio of 0.049, all $ZrO_2-Y_2O_3$ coated specimens failed in 40 to 60 1-hour cycles.					
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