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THERMAL BARRIER
COATINGS: BURNER
RIG HOT CORROSION
TEST RESULTS

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SUMMARY

A Mach 0.3 burner rig test program was conducted to examine the sensitivity of yttria-stabilized zirconia coatings to the combustion products of Na- and V-contaminated fuels and to identify alternate coatings with improved resistance to potential utility gas turbine environments. Coatings were evaluated on air-cooled, hollow superalloy erosion bar specimens of nickel-base alloy IN-792 and cobalt-base alloy MM-509. Operating conditions for both single specimen impurity sensitivity and multiple specimen alternate coatings tests were: 1370° C calculated adiabatic flame temperature, 982° C ceramic surface temperature, and 843° C substrate metal temperature.

In the single specimen fuel impurity sensitivity studies of the NASA-developed duplex thermal barrier coating system, - $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3/\text{Ni-}16.2\text{Cr-}5.6\text{Al-}0.6\text{Y}$ - (all in weight percent unless stated otherwise), tests were conducted in combustion gases doped to equivalent fuel impurity levels of 5 ppm Na, 0.5 ppm Na, 2 ppm V, 0.2 ppm V, and 5 ppm Na + 2 ppm V. The numbers of 1-hour cycles to failure (spalling of the coating over approximately one-quarter of the hot zone of the leading edge) were as follows: 5 ppm Na plus 2 ppm V, 43 cycles; 2 ppm V, 25 cycles; 0.2 V, 200 cycles; and 5 ppm Na, 92 cycles. In the 0.5 ppm Na test after 1300 cycles, there was no spalling but the thickness of $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3$ was reduced by 50 percent due to carbon particle erosion.

In the alternate coatings screening tests, two thermal barrier coating systems and one cermet coating system were identified as being significantly more resistant to spalling than the standard $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3/\text{Ni-}16.2\text{Cr-}5.6\text{Al-}0.6\text{Y}$ system which spalled before 80 one-hour cycles. In these tests eight coated specimens were tested simultaneously in a rotating air-cooled fixture and the equivalent fuel impurity level was 5 ppm Na plus 2 ppm V.

The two promising thermal barrier coating systems and the number of 1-hour cycles they endured before spalling are as follows: $\text{Ca}_2\text{SiO}_4/\text{Ni-}16.2\text{Cr-}5.6\text{Al-}0.6\text{Y}$, 675 cycles; and $\text{ZrO}_2\text{-}8\text{Y}_2\text{O}_3/\text{Ni-}16.4\text{Cr-}5.1\text{Al-}0.15\text{Y}$, 384 cycles. The cermet coating system, 50 volume percent MgO - 50 volume percent Ni-19.5Cr-17.1Al-0.97Y/Ni-16.2Cr-5.6Al-0.6Y, which was removed from testing after 1000 1-hour cycles, did not spall but was eroded to approximately 50 percent of its original thickness by carbon particles in the combustion stream.

Cracking and subsequent massive spalling of coatings in both the fuel impurity sensitivity and coatings screening tests occurred within the thermal barrier coating. Generally such cracking occurred from 0.005 to 0.015 cm above the bond coats on specimens exposed in either test.

INTRODUCTION

Thermal barrier coatings based on yttria-stabilized zirconia are in the early stages of development for clean-fueled aircraft gas turbine service. These coatings have been shown by Lewis Research Center investigators to be able to insulate air-cooled vanes, blades, and combustors and thus lower metal temperature several hundred degrees (refs. 1 to 5). The potential applicability of the thermal barrier coatings on utility gas turbines has also been analytically examined and important fuel and capital cost savings have been identified (refs. 6 and 7). However, in a limited EPRI sponsored test program (ref. 8), early coatings developed for aircraft gas turbines were observed to crack and spall in utility fuel combustion gases containing sodium (Na) and vanadium (V) as well as sulfur (S), chlorine (Cl), magnesium (Mg), and lead (Pb).

The purpose of this study was to further examine the sensitivity of yttria-stabilized zirconia coatings to Na and V contaminated fuel, and to identify some alternate compositions with improved resistance to potential coal-derived fuel-fired gas turbine environments. However, this study was limited in scope to thermal barrier coating systems that were being developed by Lewis Research Center investigators and to a few additional coating systems with potential improved corrosion resistance. Since there was no clear definition of impurities in future coal-derived liquid fuels, Na and V were selected. These are potential contaminants of such fuels and in addition they are presently in petroleum-derived heavy fuels. To evaluate these coatings a Mach 0.3 burner rig normally used in oxidation/erosion/hot corrosion programs was modified for single air-cooled and multiple air-cooled specimen operation. The hollow erosion bars chosen for these tests were nickel-base IN-792 and cobalt-base MM-509 cast superalloys.

EXPERIMENTAL PROCEDURE

Materials

Nominal chemical compositions of the NiCrAlY bond coatings, of the fully yttria-stabilized zirconia coatings, and of the alternate thermal barrier coatings evaluated are given in table I. Table I also contains specific additional treatments given to selected coatings. Appropriate references to the Lewis Research Center coating originators as well as to prior characterization and development work (refs. 9 to 11) are also included in table I. Cast hollow

erosion bars of nickel-base alloy IN-792 were used in the alternate coatings screening tests and cobalt-base alloy MM-509 and IN-792 hollow erosion bars were used in the fuel impurity sensitivity study. The nominal compositions of these alloys are given in table II. Both alloys were cast to the shapes and specifications shown in figure 1.

Plasma Spray Coating Deposition

The procedures described by Stecura (ref. 5) were used for specimen preparation and coating deposition of most coating systems in this study. Deviations from these procedures have been recorded in table I, where applicable. All coatings were manually plasma sprayed in air with a target thickness of 0.038 cm for the thermal barrier layer and of 0.010 cm for the bond coatings. The actual thicknesses of these hand-sprayed coatings were measured from metallographic cross sections. On any single hollow erosion bar, coating thicknesses locally varied from 0.030 to 0.050 cm for the thermal barrier coatings and from 0.005 to 0.020 cm for the bond coatings. The nominal thickness values are also presented in table I.

Cyclic Mach 0.3 Burner Rig Tests

The cyclic Mach 0.3 burner rig testing program was divided into two parts. The first part of this study consisted of determining the effects of Na and V contaminated combustion gases on the performance of the ZrO_2 - $12\text{Y}_2\text{O}_3$ /Ni-16.2Cr-5.6Al-0.6Y coating system. Combustion dopant levels of NaOH for Na and NH_4VO_3 for V were based on the amount of Jet A fuel consumed. Dopant levels were set at fuel equivalents of 0.5 ppm Na, 5 ppm Na, 0.2 ppm V, 2 ppm V, and 5 ppm Na + 2 ppm V. These levels were chosen because they encompassed the maximum ASTM fuel specifications for specifying No. 2 gas turbine fuel (ASTM 2880-71). In 1976 ASTM revised these trace metal limits to 0.5 ppm Na + K and 0.5 ppm V. The sulfur content of Jet A and the level used in all testing was approximately 0.05 percent which is one-tenth the amount normally found in No. 2 gas turbine fuels.

The Mach 0.3 burner rig used in the testing of single, air-cooled ZrO_2 - $12\text{Y}_2\text{O}_3$ /Ni-16.2Cr-5.6Al-0.6Y coated specimens has been described previously (ref. 12). Figure 2 shows the test arrangement schematically. Air, fuel, and aqueous solutions of NaOH and NH_4VO_3 were injected into the combustor, ignited, and expanded through a convergent-divergent nozzle with exit

velocities of Mach 0.3. The fuel-to-air mass ratio for all testing in the fuel impurity sensitivity study was 0.040. This fuel-to-air mass ratio corresponded to a calculated adiabatic flame temperature of 1370°C at the coated specimens positioned 5.7 cm back from the exit nozzle. Prior to any Mach 0.3 burner rig testing, the amount of cooling air required to maintain the metal substrate at 843°C was determined from measurements taken on $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3/\text{NiCrAlY}$ coated hollow erosion bars with Chromel-Alumel thermocouples imbedded in the leading edges. Subsequent testing of uninstrumented, coated erosion bars was based on the result of this calibration. A disappearing filament pyrometer was used to measure the surface temperature of the coating in the hot zone (~ 3.4 cm long) on the leading edge with appropriate compensation for the emittance of the coating.

Coated specimens were exposed to thermal cycles consisting of 1 hour at temperature followed by 4 minutes out of the flame with the internal cooling air on. All specimens in this part of the program were examined daily for the first six 1-hour cycles and at the end of the 20th cycle. Testing was stopped when the coating had spalled over approximately one-fourth of the hot zone on the leading edge.

The second part of this program consisted of screening tests of a number of new thermal barrier coating systems along with the baseline NASA thermal barrier system, $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3/\text{Ni-}16.2\text{Cr-}5.6\text{Al-}0.6\text{Y}$. These tests were conducted at the equivalent fuel impurity level of 2 ppm V and 5 ppm Na. The same type of Mach 0.3 burner rig (fig. 2), calibration runs and procedures outlined above were used in this part of the program except that eight thermal barrier coated specimens were tested simultaneously (see fig. 3). A special cooling insert was fitted into each thermal barrier coated hollow erosion bar to provide impingement cooling on the wedge leading edge. Diagrams of the eight-blade, air-cooled specimen holder and the cooling insert are shown in figure 4. Test parameters for the 1000-hour Mach 0.3 burner rig test were: fuel/air mass of 0.040, 1370°C calculated adiabatic flame temperature, holder rotation of 450 rpm, specimen distance 2.5 cm from exit nozzle, and measured metal substrate temperature of 843°C . The amount of cooling air required to maintain the metal substrate temperature of 843°C was again determined from instrumented hollow erosion bars, coated with both $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3/\text{NiCrAlY}$ and $\text{Ca}_2\text{SiO}_4/\text{NiCrAlY}$. This cooling air flow rate was then maintained for all subsequent tests.

Coated specimens were examined at intervals of 20 one-hour cycles. Any

particular coated specimen was removed from testing when the coating had spalled over approximately one-fourth of the hot zone on the leading edge. The number of 1-hour cycles to spall reported for each coating system is the total number of cycles that the coating system had undergone at the end of the inspection interval. Metallographic examination of sections taken from the hot zone and from a cooler region near the base were used to determine the extent of hot corrosion and the mode of spalling. In addition X-ray diffraction analysis (XRDA) was performed on small samples of coating taken from locations near cross-section cuts of the single fuel impurity sensitivity specimens.

RESULTS AND DISCUSSION

Fuel Impurity Sensitivity Tests

The effects of Na- and V-doped combustion gases on coating life of the $\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-16.2Cr-5.6Al-0.6Y}$ thermal barrier coating system on either IN-792 or MM-509 were similar and are summarized in figure 5. Coated specimens were removed from testing when the coating had spalled over approximately one-fourth of the hot zone of the leading edge (fig. 6).

At an equivalent fuel impurity concentration of 5 ppm Na + 2 ppm V, the thermal barrier coating spalled after 43 1-hour cycles. When thermal barrier coated specimens were tested with fuel impurity levels of 5 ppm Na only or with 2 ppm V only, the coated specimens spalled at 92 and 25 1-hour cycles, respectively. From this limited study V appears to be more detrimental to these coatings than Na. At 0.2 ppm V, the coated specimen spalled after 200 1-hour cycles. However, when the Na level was reduced in an equivalent manner, that is, 0.5 ppm Na, there was no apparent distress of the coating after 1300 1-hour cycles. At this Na level useful thermal barrier coating system life appears to be more a function of carbon particle erosion of the ceramic thermal barrier than of slow oxidation or corrosion of the bond coating.

Failure of the thermal barrier coating system occurred usually within the oxide near the bond coat/oxide interface. These failures are similar to the bond tensile failures reported by Levine (ref. 9) and to the furnace and burner rig oxidation failures observed by Stecura (refs. 10 and 13). Typical metallographic cross-sections of the hot zones (figs. 7(a) to (f)) show that 0.005 to 0.015 cm of oxide generally remains over the bond coating and that there was no apparent reaction of fuel impurities with the bond coating. No monoclinic

ZrO_2 or other reaction products were detected in XRDA of as-deposited ZrO_2 - $12\text{Y}_2\text{O}_3$ and of areas where the oxide had spalled. However, the small sample size and the sampling technique used for the burner rig-tested samples could have contributed to this lack of detection. Other phenomena occurring within the ZrO_2 - $12\text{Y}_2\text{O}_3$ coating such as the development of cracks were difficult to assess because of the possible introduction of additional cracks during metallographic specimen preparation.

Recently, at higher temperatures (1200° , 1300° , and 1400° C) then employed here, Zaplatynsky (ref. 14) studied the reactions of a number of potential coal-derived fuel impurities with a partially stabilized zirconia, ZrO_2 - $8\text{Y}_2\text{O}_3$. From XRDA of the reaction products he determined that Na_2CO_3 (Na_2O) reacted preferentially with the monoclinic zirconia present to produce Na_2ZrO_3 and that no monoclinic phase was present in the reaction products. V_2O_5 , however, reacted preferentially with the cubic ZrO_2 present and no cubic ZrO_2 was present in the reaction products. These results when combined with those reported by Bratton, et al. (ref. 8) suggest that destabilization and reaction of ZrO_2 with fuel impurities are probably more important in early coating system failures than corrosion of the bond coating.

Alternate Coatings Screening Study

A wide range of conceptual thermal barrier coating systems was evaluated. Figure 8 is a compilation of the results of Mach 0.3 burner rig testing of these coatings for times to 1000 hours. Thermal barrier coated specimens were removed from test and the number of 1-hour cycles were recorded after the coating had spalled over approximately one-fourth of the hot zone of the leading edge.

ZrO_2 - Y_2O_3 /NiCrAlY thermal barrier systems. - Early fuel impurity tolerance results and hot corrosion burner rig test results of Bratton, et al. (ref. 8) clearly showed a need for improvement in the corrosion resistance of the NASA thermal barrier coating system (ZrO_2 - $12\text{Y}_2\text{O}_3$ /Ni-16.2Cr-5.6Al-0.6Y) which was developed for clean-fueled aircraft gas turbine service. To effect this desired improvement in corrosion resistance, several NASA Lewis Research Center investigators contributed coatings for evaluation which involved the following approaches: (1) modifying the composition of the oxides and bond coats, (2) sealing the oxide with a more dense overcoat oxide, (3) heating the hollow erosion bar before plasma spraying of the oxide to affect

some stress relief of the oxide, (4) impregnating and sealing the oxide with silica, and (5) heat treating the thermal barrier system on hollow erosion bars to selectively establish a crack network to prevent massive spalling.

Several of the modified $\text{ZrO}_2\text{-Y}_2\text{O}_3/\text{NiCrAlY}$ thermal barrier systems were more spall resistant than the standard thermal barrier coating system $\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-16.2Cr-5.6Al-0.6Y}$ (STBC) which spalled before 80 hours of exposure. These included the $\text{ZrO}_2\text{-8Y}_2\text{O}_3/\text{Ni-16.4Cr-5.1Al-0.15Y}$ and $\text{ZrO}_2\text{-4Y}_2\text{O}_3/\text{Ni-16.4Cr-5.1Al-0.15Y}$ coatings (both optimized by Stecura in burner rig, natural gas fired torch, and furnace tests) (ref. 10) which failed after 384- and 145-hour cycles of exposure, respectively. Also, the $\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-31Cr-12Al-0.6Y}$ coating failed after 178-hour cycles. The $\text{Y}_2\text{O}_3/\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-16.2Cr-5.6Al-0.6Y}$ coating was removed from testing after 320 cycles due to continuous hot section surface microspalling that began after 40 cycles. Coating loss, however, was extensive in cooler regions outside the hot zone. The surface appearance of representative $\text{ZrO}_2\text{-Y}_2\text{O}_3/\text{NiCrAlY}$ coated specimens after exposure to Na- and V-containing combustion gases are shown in figure 9. Metallographic crosssections within the spalled areas and in relatively cold areas (0.32 cm from bottom of leading edge) of the $\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-16.2Cr-5.6Al-0.6Y}$ and $\text{ZrO}_2\text{-8Y}_2\text{O}_3/\text{Ni-16.4Cr-5.1Al-0.15Y}$ coated specimens are shown in figures 10(a) to (f). As in the fuel impurity sensitivity study, spalling occurred near the oxide/bond coat interface with approximately 0.005 to 0.015 cm of oxide remaining on the bond coating. Also, no apparent corrosion of the bond coatings was detected from metallographic analysis of spalled areas.

A number of additional coating systems based on the $\text{ZrO}_2\text{-Y}_2\text{O}_3/\text{NiCrAlY}$ system were tested (table I) and their spalling behavior was, for all practical purposes, the same as that of the STBC (coating 1). Based on the results shown in figure 8, it appears that heat treatments of the STBC and the Al_2O_3 overcoat had no beneficial effect on spall resistance. Also, based on the limited amount of data, stress relief of the oxide as a result of heating the substrate during application of the oxide had no effect on spall rate in the Na/V doped combustion gases. Similarly, there is no difference in the rate of spalling of the STBC and that of the $\text{ZrO}_2\text{-18Y}_2\text{O}_3$ coating system. For ZrO_2 thermal barriers with less than 12 weight percent Y_2O_3 , however, the data suggest that an optimum level of Y_2O_3 in ZrO_2 exists below 12 weight percent. This finding is documented by Stecura (ref. 10) in clean-fueled burner rig, natural gas-fired torch, and furnace oxidation tests aimed at determining the optimum levels of Y_2O_3 in ZrO_2 and of Y in the NiCrAlY bond coats. The

existence of an optimum level of Y_2O_3 in ZrO_2 was not clearly established in this hot corrosion burner rig program because different bond coats were used with the ZrO_2 -12 Y_2O_3 and the ZrO_2 -8 Y_2O_3 thermal barriers.

New thermal barrier coating systems and cermets. - Several new duplex coating systems were tried initially in the program in addition to the ZrO_2 -based thermal barrier coatings (table I and fig. 8). Of the coatings that were tested in this category, one based on Ca_2SiO_4 reached 675 1-hour cycles before spalling. Also, a cermet coating of 50 volume percent MgO - 50 volume percent Ni-19.6Cr-17.1Al-0.97Y survived 1000 1-hour cycles without spalling. These two coatings proved to have significantly better hot corrosion resistance than the four STBC specimens which all spalled before 80 cycles. The metal substrate temperature measured during the same calibration run for both Ca_2SiO_4 and ZrO_2 -12 Y_2O_3 coated bars was $843^\circ C$, which indicates that the Ca_2SiO_4 and ZrO_2 -12 Y_2O_3 coatings are equivalent in thermal insulating ability. The thermal conductivity of the cermet coating (No. 16) is much higher than the conductivities of the other coatings. However, it was run at the same hot gas temperature as the other coatings - $T_{gas} = 1370^\circ C$, and the same coolant conditions. Accordingly the cermet surface temperature was less than $982^\circ C$ and the substrate metal temperature was somewhat greater than $843^\circ C$.

Photographs (fig. 11) of tested coated specimens and metallographic cross sections (fig. 12) from hot and cold areas show distinct differences between the mode of degradation of Ca_2SiO_4 and of MgO-NiCrAlY coated specimens. Erosion, corrosion, and possible microspalling appear to be responsible for a 50-percent reduction in thickness of the MgO-NiCrAlY coating. No macrospalling was observed for this coating system. For the Ca_2SiO_4 coated specimen, cracking and subsequent macrospalling within the Ca_2SiO_4 coating near the bond coat/ Ca_2SiO_4 interface occurred in a manner similar to the spalling of the ZrO_2 -based thermal barrier coatings. The spalled area away from the leading edge seen in figure 11 was due to accidental damage on removing this specimen from the test fixture. Also, like other specimens exposed to the same hot corrosion combustion gases, no apparent corrosion of the bond coats was detected.

The CeO_2 and $ZrSiO_4$ coating systems also listed in table I either spalled much sooner than the STBC or had about the same spall rate.

SUMMARY OF RESULTS

A Mach 0.3 burner rig test program was conducted to examine the sensitivity of yttria-stabilized zirconia coatings to Na and V contaminated combustion gases and to identify alternate coatings with improved resistance to potential utility gas turbine environments. Coatings systems were evaluated on cast hollow erosion bars of IN-792, a nickel-base alloy, and MM-509, a cobalt-base alloy. The combustion gases were doped with aqueous solutions of NaOH and NH_4VO_3 to introduce Na and V at appropriate fuel equivalent levels. Operating conditions for both fuel impurity sensitivity tests and for multiple specimen alternate coatings screening tests were (1) 1370°C calculated adiabatic flame temperature, (2) 982°C ceramic surface temperature, and (3) 843°C metal substrate temperature (as measured on the $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3$ and Ca_2SiO_4 coated hollow erosion bars).

Single Specimen Fuel Impurity Sensitivity Tests

1. The number of 1-hour cycles required for approximately one-fourth of the $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3\text{/Ni-}16.2\text{Cr-}5.6\text{Al-}0.6\text{Y}$ coating area in the hot zone to spall varied with dopant concentration as follows: for 5 ppm Na + 2 ppm V, 43 cycles; for 2 ppm V, 25 cycles; for 0.2 ppm V, 200 cycles; and for 5 ppm Na, 92 cycles. For 0.5 ppm Na, no large spalled regions were observed even after 1300 exposure cycles. At the latter dopant fuel impurity equivalent level, carbon particle erosion as a result of the high fuel/air mass ratio was most responsible for coating degradation.

2. In general, cracking and subsequent spalling occurred within the oxide near the bond coat-oxide interface regardless of impurity and impurity level. These coating failures (spalling) were similar to tensile failures reported by Levine (ref. 9) and failures observed by Stecura (ref. 10) in burner rig and cyclic torch or furnace oxidation tests. No apparent corrosion of the bond coating was detected from metallographic analysis of spalled areas.

Alternate Coatings Screening Tests

1. Four standard thermal barrier coated specimens ($\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3\text{/Ni-}16.2\text{Cr-}5.6\text{Al-}0.6\text{Y}$) spalled before 80 1-hour cycles in combustion gases doped with 5 ppm Na + 2 ppm V. Several $\text{ZrO}_2\text{-Y}_2\text{O}_3\text{/NiCrAlY}$ type thermal burner systems were more spall resistant than the standard thermal barrier

system in the same combustion environment. These were $\text{ZrO}_2\text{-8Y}_2\text{O}_3/\text{Ni-16.4Cr-5.1Al-0.15Y}$ which failed after 384 cycles; $\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-31Cr-12Al-0.6Y}$, which failed after 178 cycles; $\text{ZrO}_2\text{-4Y}_2\text{O}_3/\text{Ni-16.4Cr-5.1Al-0.15Y}$ which failed after 145 cycles; and $\text{Y}_2\text{O}_3/\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-16.2Cr-5.6Al-0.6Y}$ which failed in the hot zone after 320 cycles. For the latter, continuous microspalling started after 40 one-hour cycles in areas outside the hot zone.

2. Two new coating systems, $\text{Ca}_2\text{SiO}_4/\text{Ni-16.2Cr-5.6Al-0.6Y}$ and 50 volume percent MgO - 50 volume percent $\text{Ni-19.6Cr-17.1Al-0.97Y}/\text{Ni-16.2Cr-5.6Al-0.6Y}$ were significantly more spall resistant than $\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-16.2Cr-5.6Al-0.6Y}$. The Ca_2SiO_4 coated specimen reached 675 1-hour cycles before spalling and the MgO-NiCrAlY cermet survived 1000 one-hour cycles without spalling. Erosion appeared to be the primary mode of degradation of the MgO-NiCrAlY coating. The metal substrate temperature measured simultaneously during burner rig operation of both Ca_2SiO_4 and $\text{ZrO}_2\text{-12Y}_2\text{O}_3$ coated hollow erosion bars was 843°C which indicated that Ca_2SiO_4 and $\text{ZrO}_2\text{-12Y}_2\text{O}_3$ were equivalent in insulating ability.

3. Cracking and spalling of Ca_2SiO_4 occurred within the Ca_2SiO_4 layer near the bond coating/ Ca_2SiO_4 interface similar to spalling of the ZrO_2 coatings. No apparent corrosion of the bond coatings was observed.

CONCLUDING REMARKS

Coating life of the NASA thermal barrier coating system $\text{ZrO}_2\text{-12Y}_2\text{O}_3/\text{Ni-16.2Cr-5.6Al-0.6Y}$ developed for clean-fueled aircraft gas turbine service is significantly reduced in combustion environments containing high levels of Na and V. Based on observations made on coated specimens which had failed (spalled), it appears that thinner coatings may be more spall resistant.

In this initial test series several coatings - Ca_2SiO_4 and $\text{ZrO}_2\text{-8Y}_2\text{O}_3$ thermal barriers and a 50 weight percent MgO - 50 volume percent NiCrAlY cermet coating - were identified as having much improved corrosion resistance to combustion gases containing Na and V. The state-of-the-art for using ceramic-based coatings to protect utility gas turbine components from corrosive combustion products is in its infancy and continued improvements are required to achieve commercial engine readiness.

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TABLE I. - COATING COMPOSITIONS OF THERMAL BARRIERS AND BOND COATS

Coating number	Thermal barrier ^a	Bond coat ^a	Analysis reference	Thickness, cm		Treatments/comments	Coating originators ^b	Reference
				Thermal barrier	Bond coat			
1	ZrO ₂ -12Y ₂ O ₃	Ni-16.2Cr-5.6Al-0.6Y	9	0.038	0.005-0.013	Only cubic ZrO ₂ phase present	S. Secura	--
2	ZrO ₂ -12Y ₂ O ₃		9	.038		ZrO ₂ deposited on 538° C preheated substrate	S. Levine	--
3	ZrO ₂ -12Y ₂ O ₃		9	.038		1000° C induction heat of final coated specimen	S. Levine	--
4	Al ₂ O ₃ /ZrO ₂ -12Y ₂ O ₃	Ni-16.4Cr-5.1Al-0.15Y	c ₉	0.008/0.038		0.008 cm Plasma spray coating of Al ₂ O ₃ over standard thermal barrier	P. Hodge	--
5	Al ₂ O ₃ /ZrO ₂ -12Y ₂ O ₃		c ₉	0.008/0.038		1000° C induction heat of coated specimen similar to one using coating no. 4	S. Levine	--
6	Y ₂ O ₃ /ZrO ₂ -12Y ₂ O ₃		d ₉	0.008/0.038		0.008 cm Plasma spray coating of over standard thermal barrier coating	P. Hodge	--
7	ZrO ₂ -12Y ₂ O ₃ -SiO ₂	Ni-21.0Co-18.8Cr-12.8Al-0.6Y	e ₉	0.038		Ludox impregnated standard thermal barrier coating, heat treated 1100° C in vacuum for 1 hour	S. Levine	--
8	ZrO ₂ -18Y ₂ O ₃		10	.041			S. Secura	10
9	ZrO ₂ -8Y ₂ O ₃		10	.038		Cubic and monoclinic phases present	S. Secura	10
10	ZrO ₂ -4Y ₂ O ₃	Ni-16.4Cr-5.1Al-0.15Y	10	.041		Cubic and monoclinic phases present	S. Secura	10
11	ZrO ₂ -12Y ₂ O ₃		f ₉	.041			M. Gedwill	--
12	ZrO ₂ -12Y ₂ O ₃		f ₉	.038			M. Gedwill	--
13	Ca ₂ SiO ₄	Ni-16.2Cr-5.6Al-0.6Y	g ₉				S. Levine	--
14	CeO ₂		h ₉				S. Levine	--
15	ZrSiO ₄		i ₉				P. Hodge	--
16	50 vol% MgO-50 vol% Ni-19.6Cr17.1Al-0.97Y		9, 11				I. Zaplatynsky	11

^aWeight percent unless stated otherwise.^bLewis Research Center investigators.^cAluminum oxide -270 mesh.^dYttrium oxide -150 + 400 mesh.^eColloidal silica.^fVendor certified analyses.^gChemical analysis showed that Ca₂SiO₄ was 78 percent Ca₂SiO₄, 22 percent CaSiO₃, -200 + 325 mesh.^h-150 + 325 mesh.ⁱ-325 mesh + 10 microns.

TABLE II. - NOMINAL COMPOSITION

OF IN-792 AND MM-509

[All values in weight percent.]

	IN-792	MM-509
Nickel	Balance	9.9
Cobalt	9.0	Balance
Chromium	12.7	23.4
Tungsten	3.9	7.0
Tantalum	3.9	3.7
Titanium	4.2	.3
Zirconium	.1	.5
Iron	----	.3
Carbon	.2	.6
Boron	.2	<.1
Sulfur	----	<.1
Silicon	----	<.1
Manganese	----	<.1
Aluminum	3.2	----

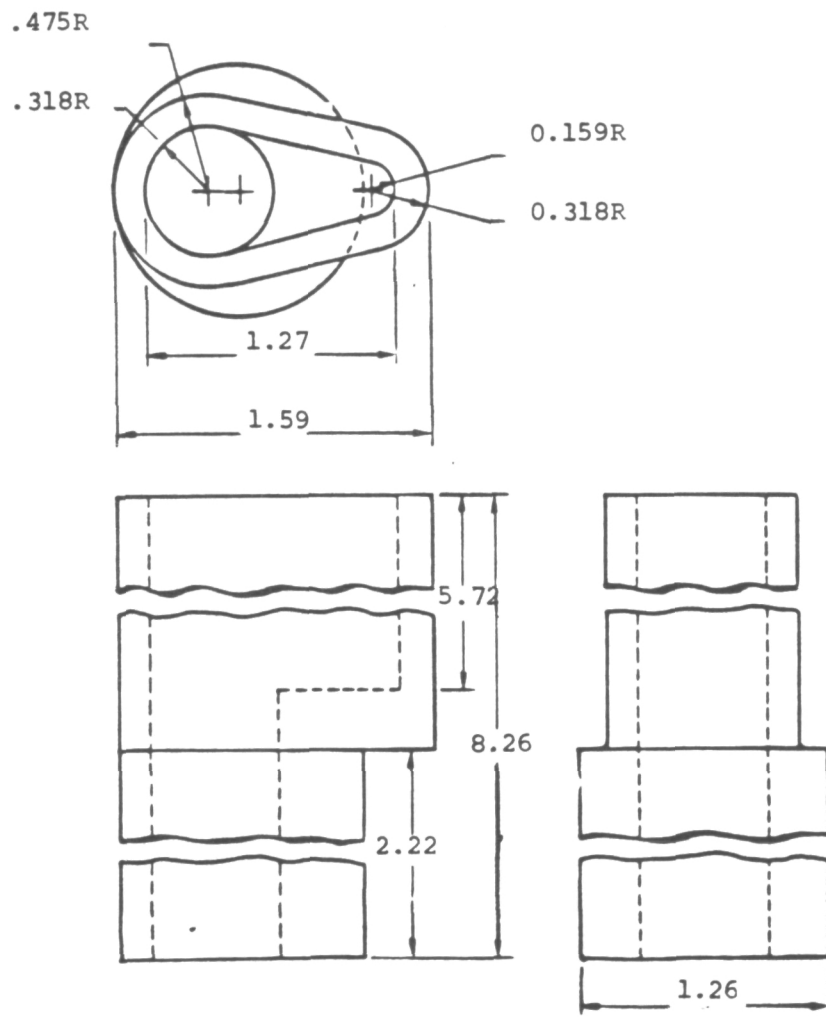


FIGURE 1. Cast superalloy hollow erosion bar
(Dimensions in centimeters)

BURNER RIG

AIR-COOLED WEDGE SPECIMEN

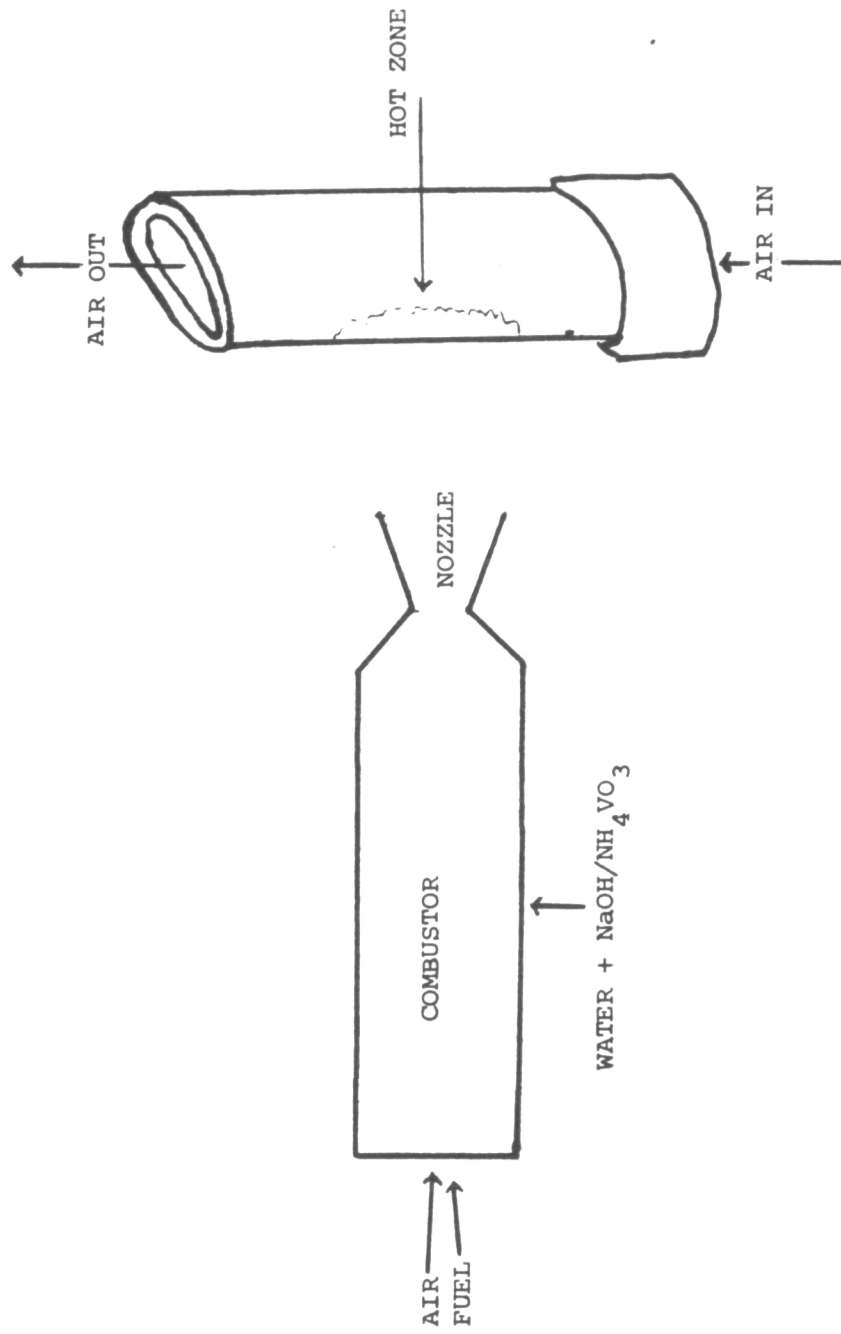


FIGURE 2. Schematic diagram of a Mach 0.3 burner rig test

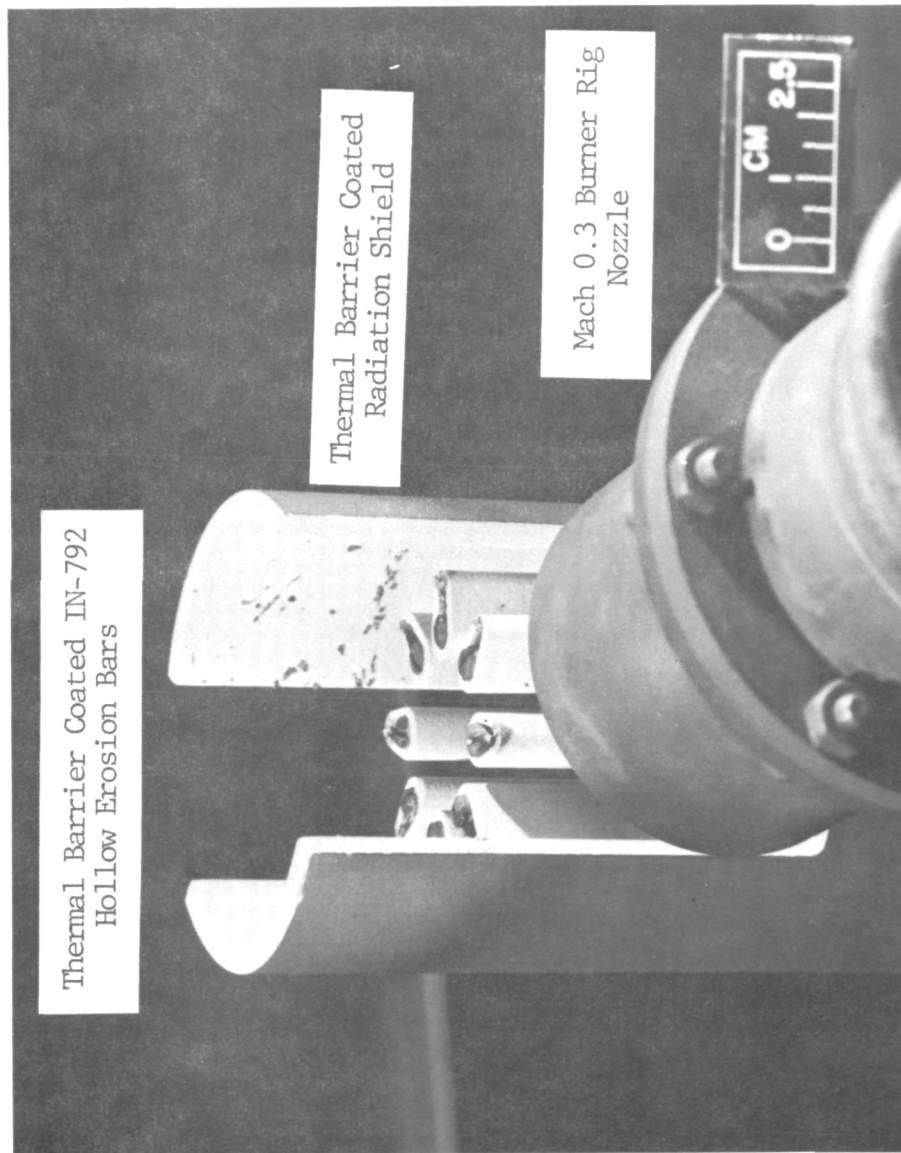
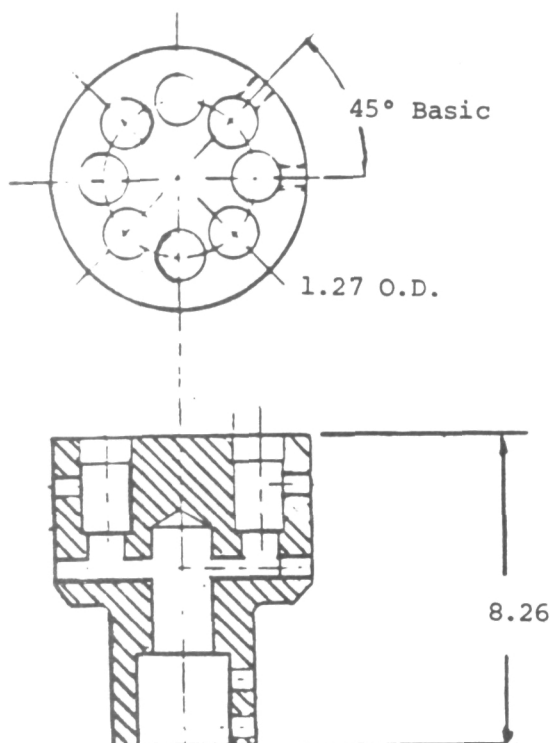


Figure 3. Mach 0.3 burner rig and thermal barrier coated IN-792 hollow-erosion bars

Specimen Holder



Cooling Insert

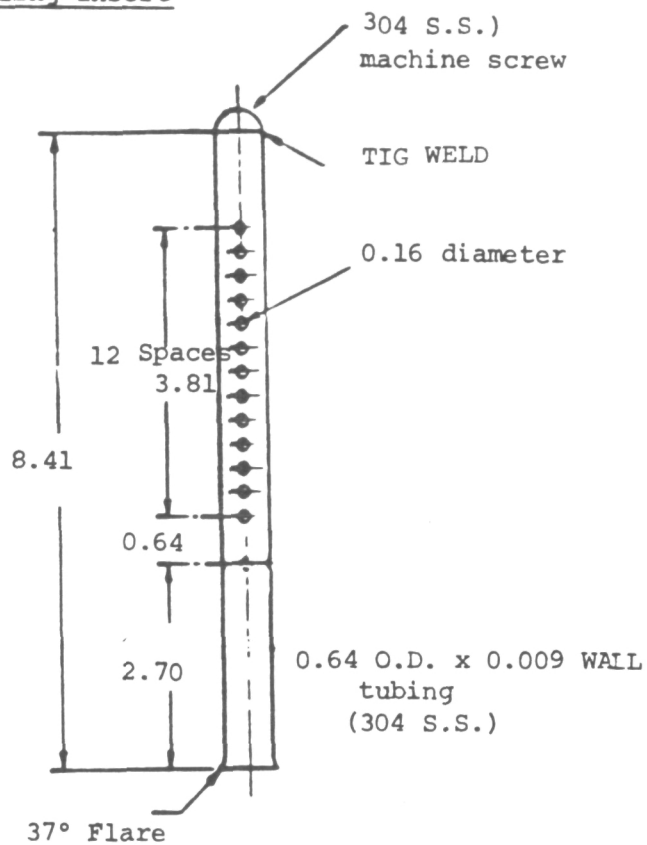


Figure 4. Multiple specimen test fixture and cooling insert for hollow erosion bars.
(All dimensions in centimeters)

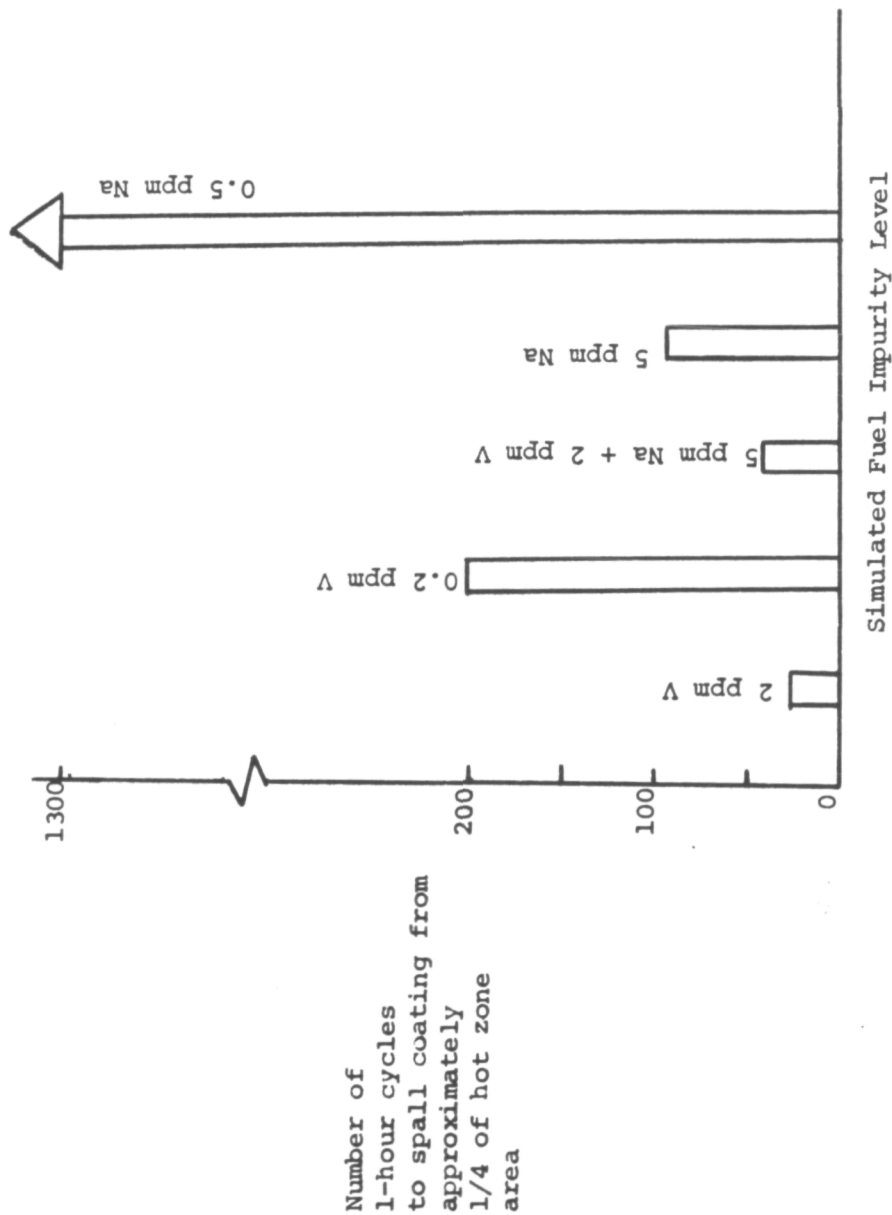
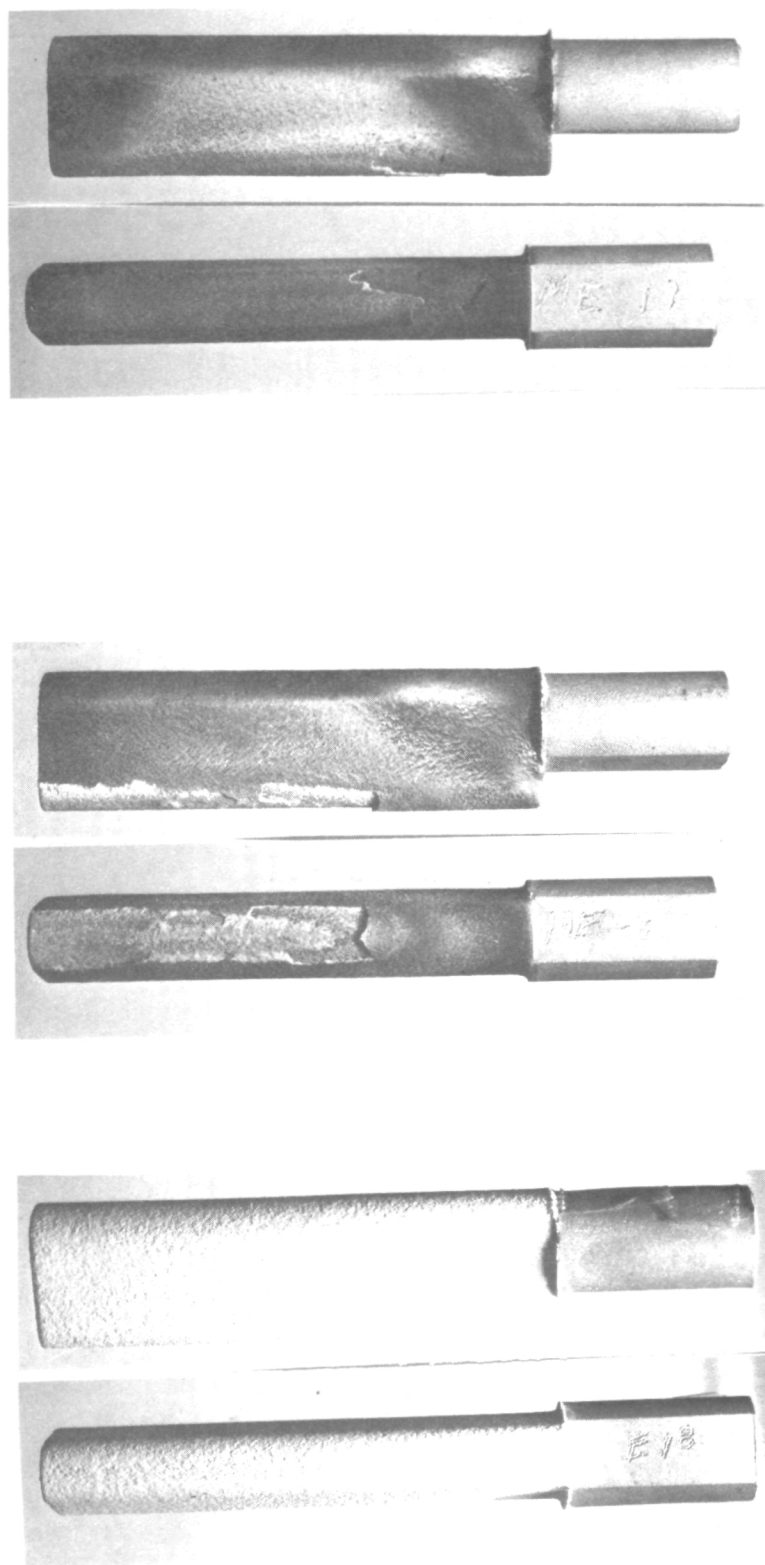


Figure 5. Single specimen Mach 0.3 burner rig fuel impurity sensitivity tests of $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3/\text{NiCrAlY}$ thermal barrier coating system. Operating conditions: flame temperature, 1370°C ; metal substrate temperature, 843°C ; ceramic surface temperature, 982°C .



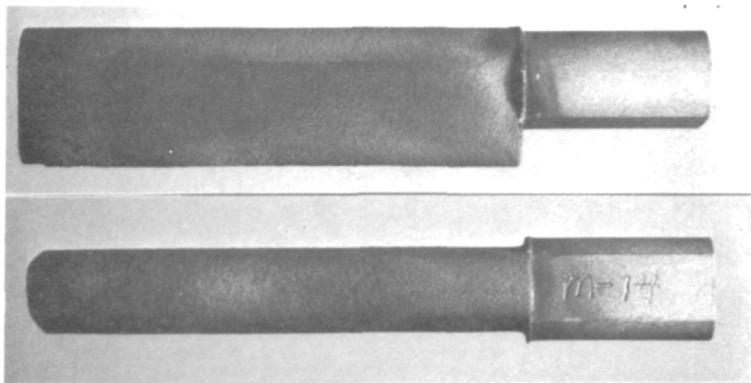
(a) As sprayed

$\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3/\text{Ni-}16.2\text{Cr-}5.6\text{Al-}0.6\text{Y}$

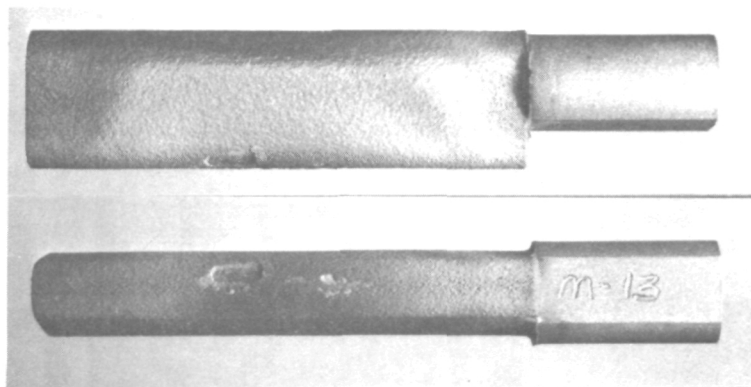
(b) 43 1-hour cycles
5 ppm Na + 2 ppm V

(c) 92 1-hour cycles
5 ppm Na

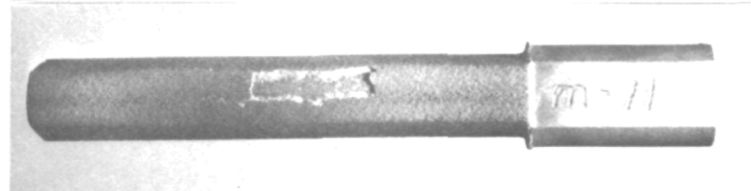
Figure 6. Typical photographs of single specimen thermal barrier coated IN-792 and MM509 hollow erosion bars after exposure to Mach 0.3 combustion gases doped with fuel equivalent amounts of Na and V. Time to spall approximately 1/4 hot zone area is indicated. Operating conditions: 1370°C flame temperature; 982°C ceramic surface temperature; and 843°C substrate metal temperature.



(d) 1300 1-hour cycles
0.5 ppm Na



(e) 200 1-hour cycles
0.2 ppm V



(f) 25 1-hour cycles
2 ppm V

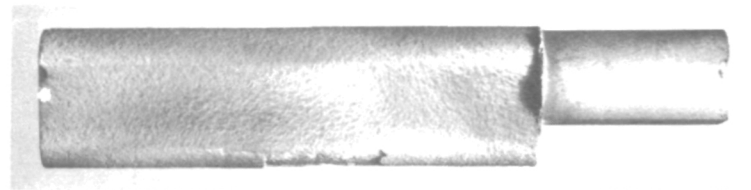
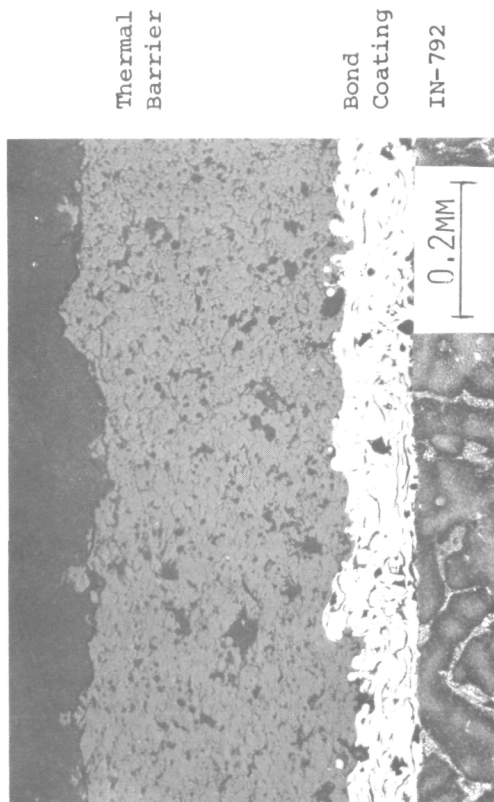
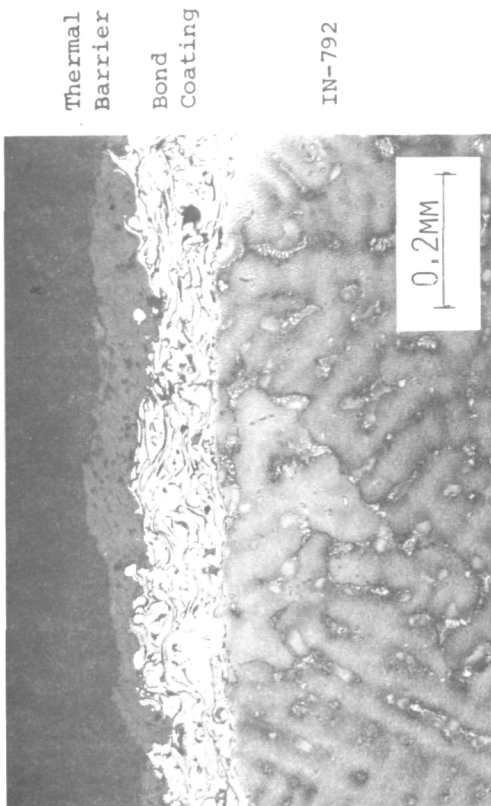


Figure 6. Continued

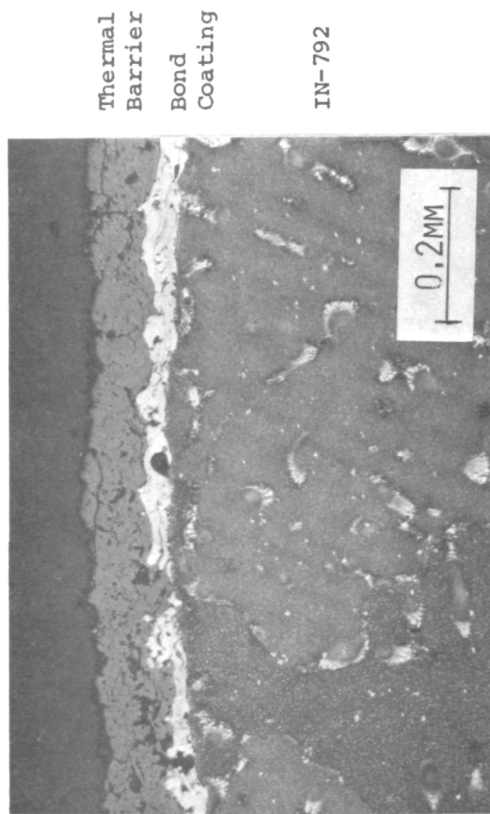


(a) As sprayed
 $\text{ZrO}_2\text{-12Y}_2\text{O}_3$ /
 Ni-16.2Cr-5.6Al-0.6Y

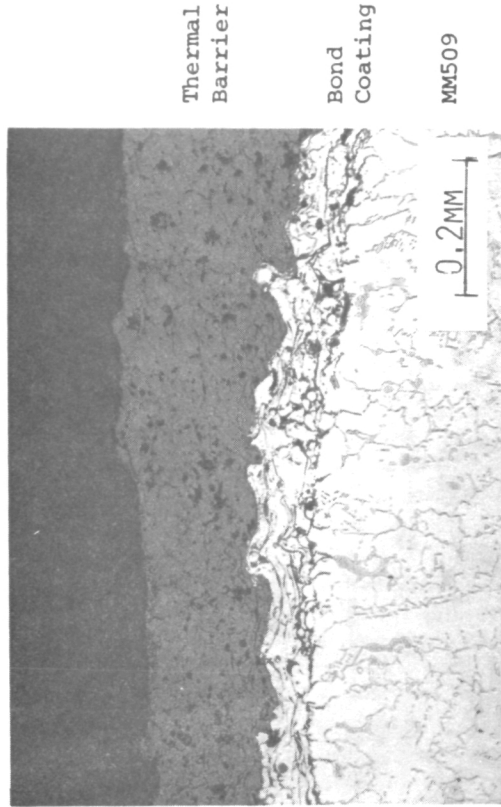


(b) 43 1-hour cycles
 5 ppm Na+ 2 ppm V

Figure 7. Representative microstructures (100X) of hot zones of standard $\text{ZrO}_2/\text{NiCrAlY}$ -coated IN-792 and MM509 hollow erosion bars after exposure to Mach 0.3 combustion gases doped with fuel equivalent amounts of Na and V. Time to spall approximately 1/4 of hot zone area is indicated. Operating conditions: 1370°C flame temperature; 982°C ceramic surface temperature; 843°C metal substrate temperature.

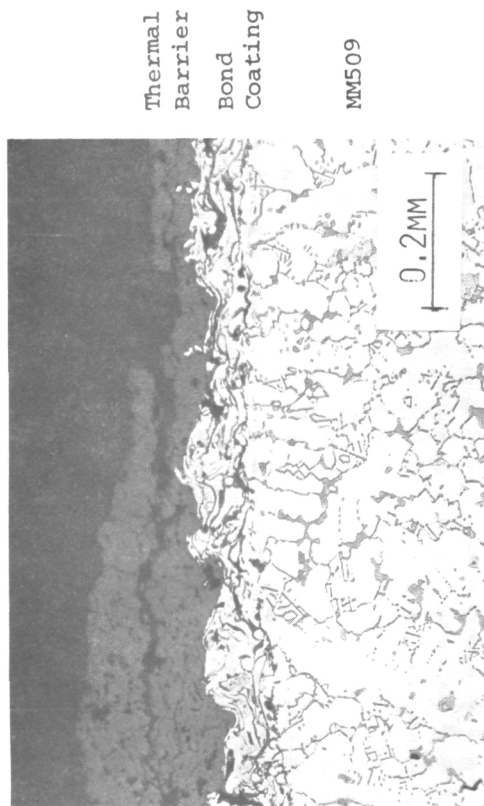


(c) 92 1-hour
cycles
5 ppm Na

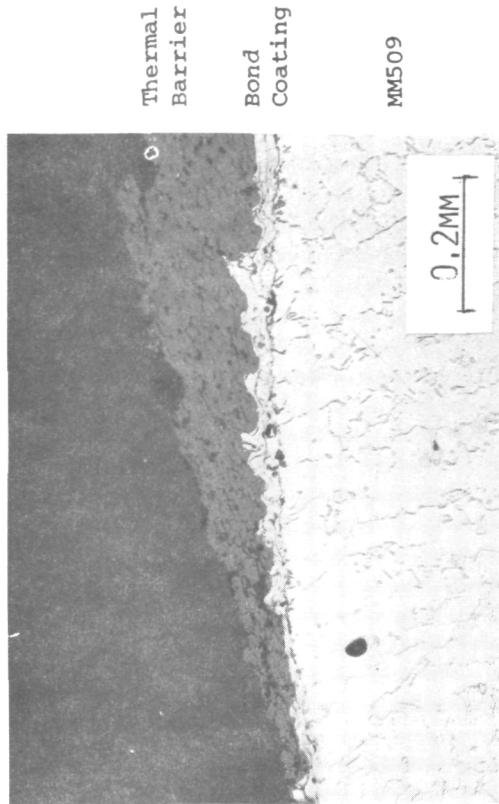


(d) 1300 1-hour
cycles
0.5 ppm Na

Figure 7. Continued



(e) 200 1-hour cycles
0.2 ppm V



(f) 25 1-hour cycles
2 ppm V

Figure 7. Continued

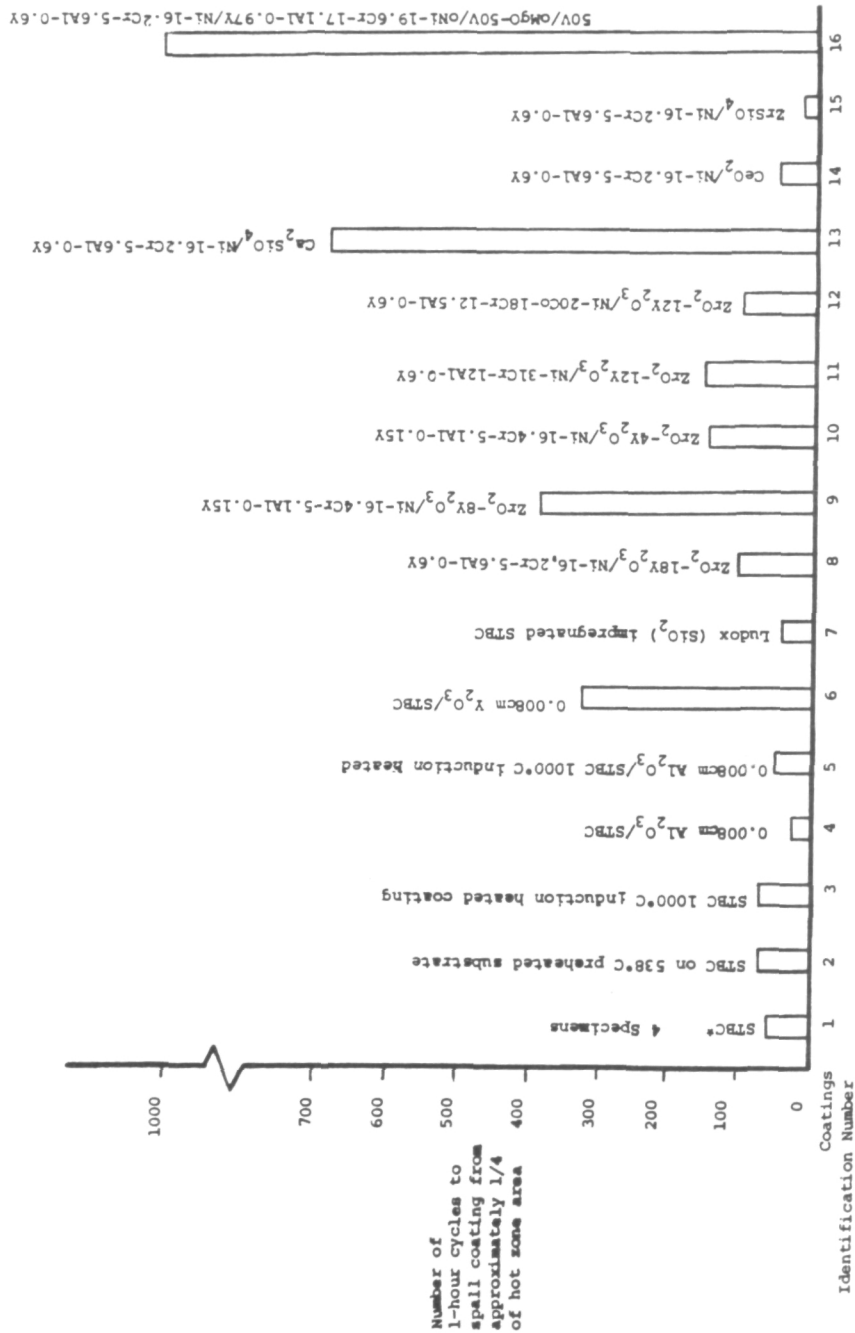


FIGURE 8. Multiple specimen Mach 0.3 burner rig test of thermal barrier coating systems on IN-792 cooled hollow erosion bars. Operating conditions: fuel impurity equivalent of 5 ppm Na+2 ppm V; flame temperature, 1370°C; metal substrate temperature, 843°C; ceramic surface temperature, 982°C.

*STBC - Standard Thermal Barrier Coating - $ZrO_2-12Y_2O_3$ /Ni-16.2Cr-5.6Al-0.6Y

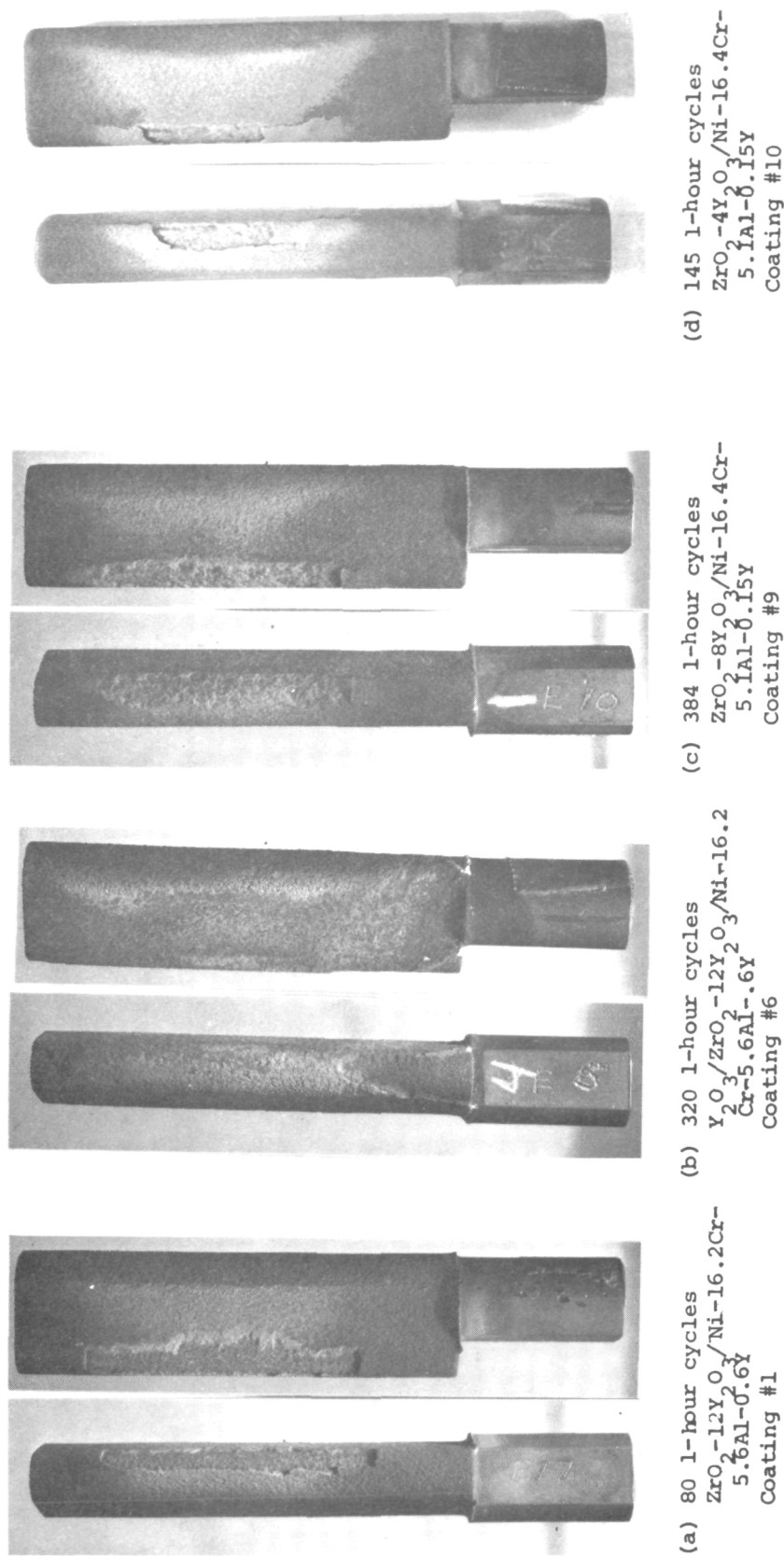
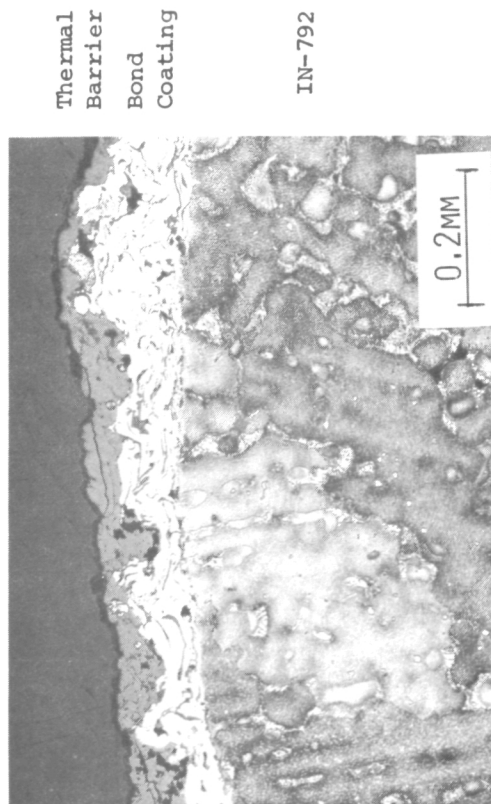
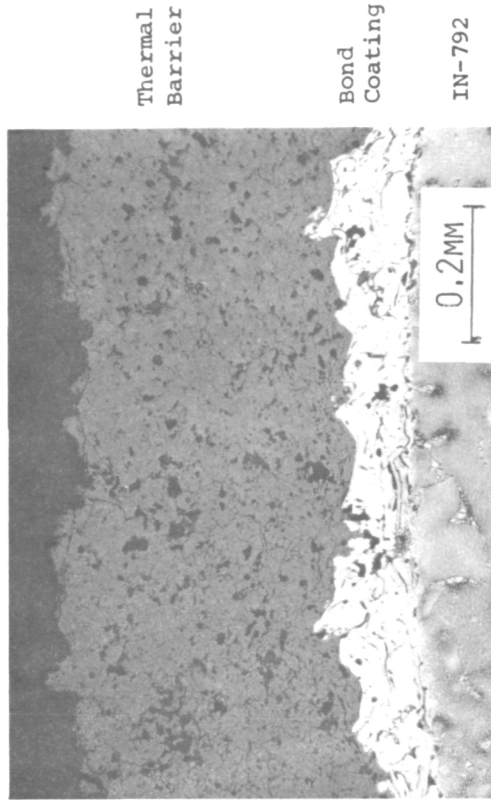


Figure 9. Photographs of $\text{ZrO}_2\text{-Y}_2\text{O}_3/\text{NiCrAlY}$ thermal barrier coating systems on IN-792 hollow erosion bars after exposure to Mach 0.3 burner rig combustion gases loaded with fuel equivalent amount of 5 ppm Na and 2 ppm V. Time to spall 1/4 of the hot zone area indicated. Operating conditions: 1370°C flame temperature; 982°C ceramic surface temperature; and 843°C metal substrate temperature.



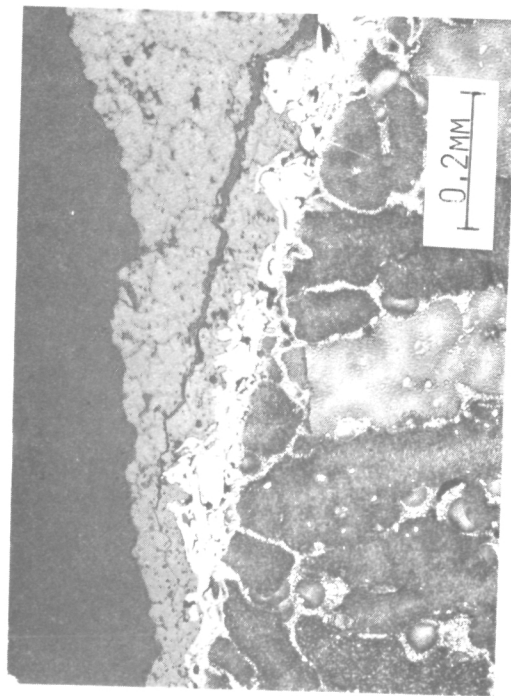
(a) Hot Zone



(b) Cold Zone

80 1-hour cycles NASA
thermal barrier $\text{ZrO}_2\text{-}12\text{Y}_2\text{O}_3/\text{Ni-}16.2\text{Cr-}5.6\text{Al-}0.6\text{Y}$
Coating #1

Figure 10. Typical 100x microstructures of hot and cold zones of $\text{ZrO}_2\text{-Y}_2\text{O}_3/\text{NiCrAlY}$ thermal barriers on IN-792 hollow erosion bars after exposure to Mach 0.3 burner rig combustion gases doped with fuel equivalent amounts of 5 ppm Na and 2 ppm V. Time to spall approximately 1/4 of hot zone area indicated. Operating conditions: 1370°C flame temperature; 982°C ceramic surface temperature; 843°C metal substrate temperature.

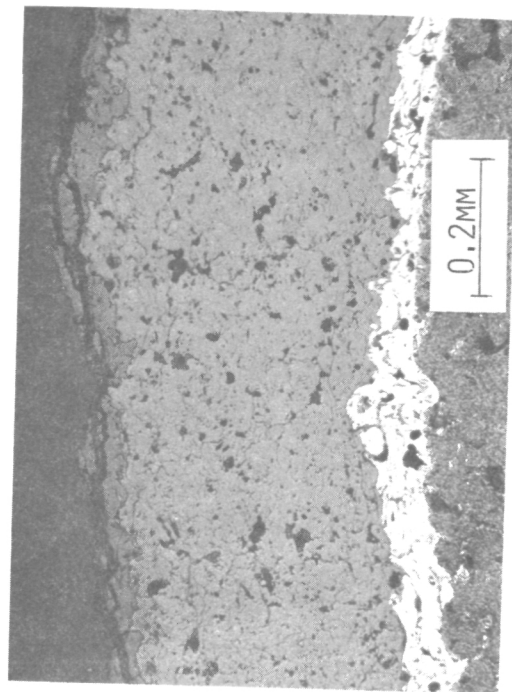


Thermal
Barrier

Bond
Coating

IN-792

(c) Hot Zone



Y_2O_3

Thermal
Barrier

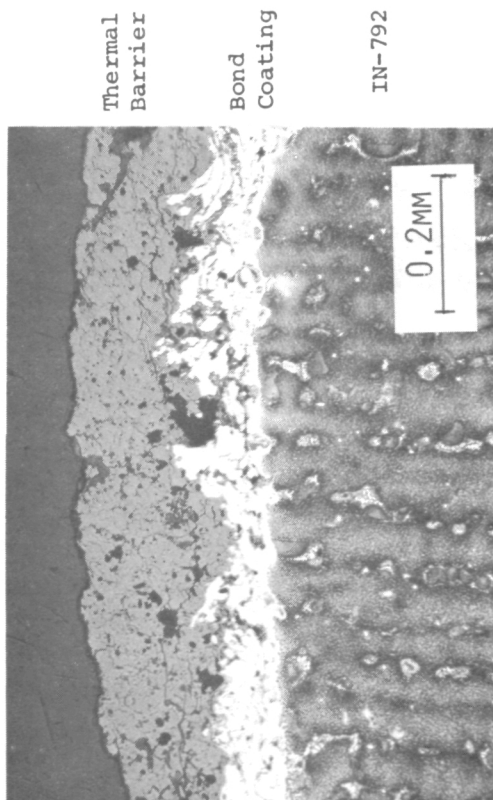
Bond
Coating

IN-792

(d) Cold Zone

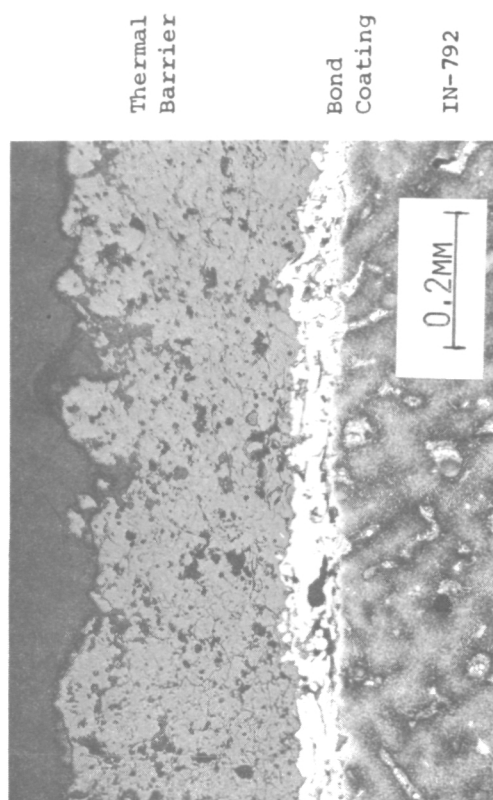
320 1-hour cycles
 $Y_2O_3/ZrO_2-12Y_2O_3/Ni-16.2Cr-5.6Al-0.6Y$
Coating #6

Figure 10. Continued



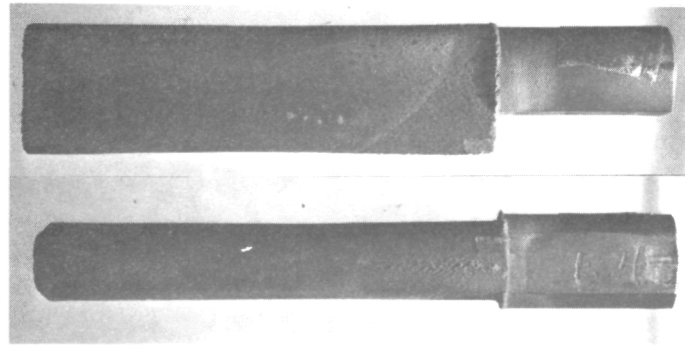
(e) Hot Zone

384 1-hour cycles
 $\text{ZrO}_2\text{-}8\text{Y}_2\text{O}_3/\text{Ni-}16.4\text{Cr-}5.1\text{Al-}0.15\text{Y}$
 Coating #9

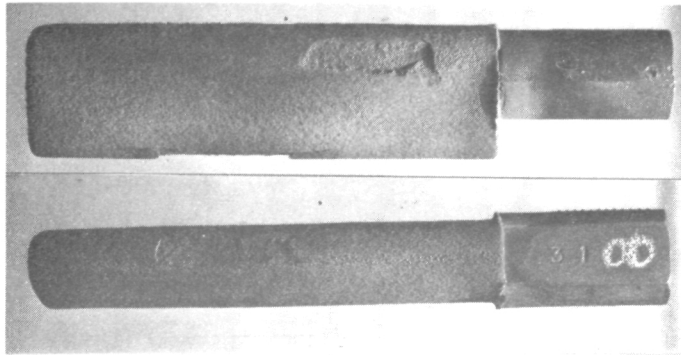


(f) Cold Zone

Figure 10. Continued

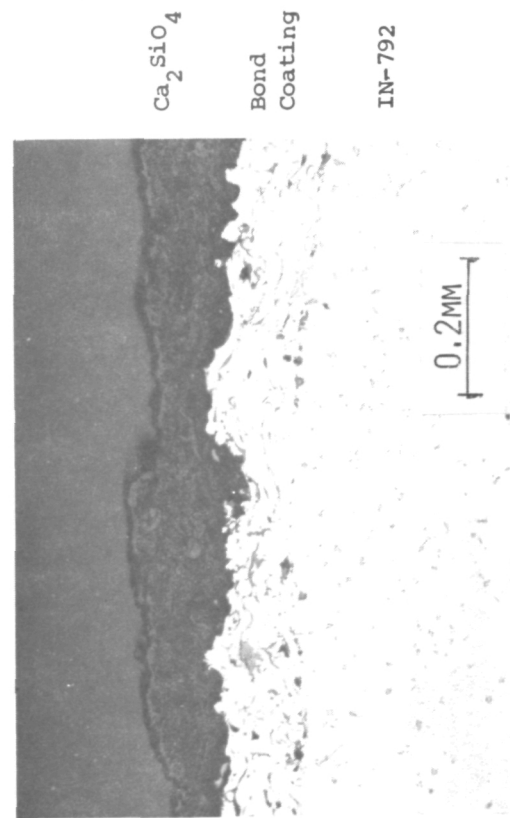


(a) 1000,1-hour cycles
 $50\text{V}, 0\text{MgO}-50\text{V}/\text{O}_2\text{Ni}-19\text{Cr}-17.1\text{Al}-0.97\text{Y}/$
 $\text{Ni}-16.2\text{Cr}-5.6\text{Al}-0.6\text{Y}$
 Coating #16

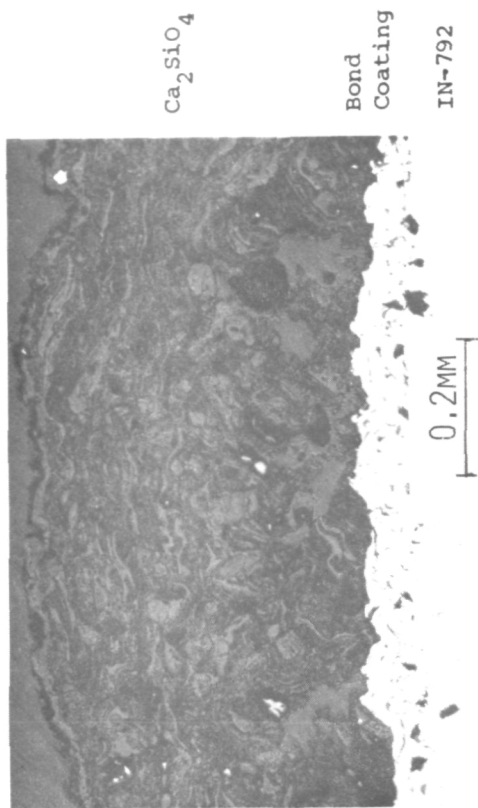


(b) 675,1-hour cycles
 $\text{Ca}_2\text{SiO}_4/\text{Ni}-16,2\text{Cr}-5.6\text{Al}-0.6\text{Y}$
 Coating #13

Figure 11. Photographs of new corrosion resistant coatings on IN-792 hollow erosion bars after exposure to Mach 0.3 burner rig combustion gases doped with fuel equivalent of 5 ppm Na and 2 ppm V. Time to spall of approximately 1/4 hot zone area is indicated. Operating conditions: 1370°C flame temperature; 982°C ceramic surface temperature and 843°C metal substrate temperature.



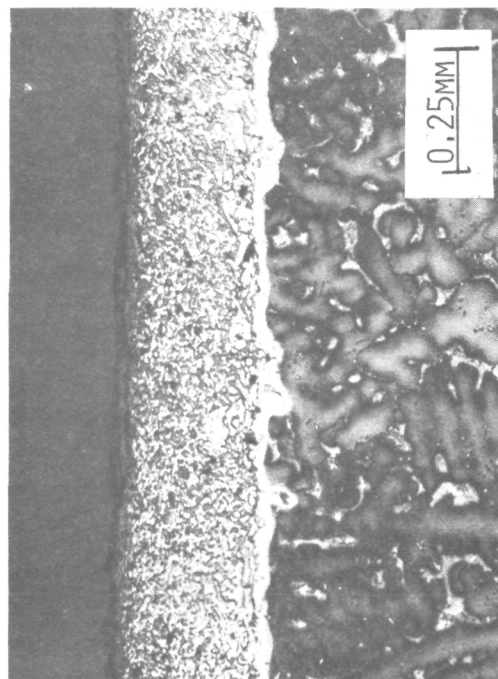
(a) Hot Zone, 100X



(b) Cold Zone, 100X

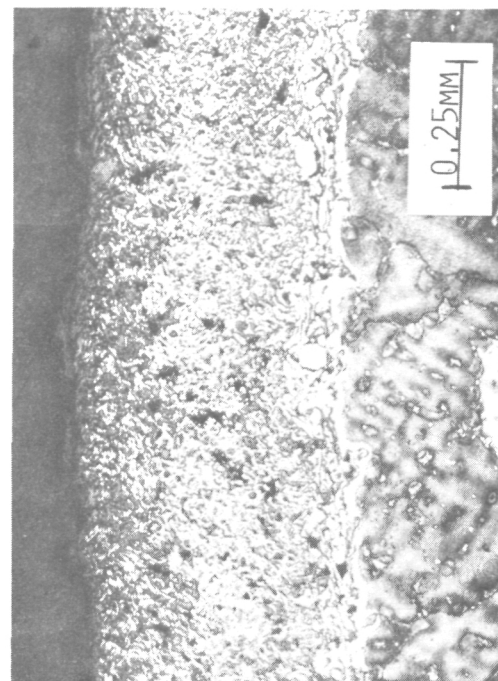
675, 1-hour cycles $\text{Ca}_2\text{SiO}_4/\text{Ni-16.2Cr-5.6Al-0.6Y}$
Coating #13

Figure 12. Microstructures of hot and cold zones of new thermal barrier and corrosion resistant coatings on IN-792 hollow erosion bars after exposure to Mach 0.3 burner rig combustion gases doped with fuel equivalent of 5 ppm Na and 2 ppm V. Time to spall of approximately 1/4 hot zone area is indicated. Operating conditions: 1370°C flame temperature; 982°C ceramic surface temperature; and 843°C metal substrate temperature.



MgO/
NiCrAlY
Bond
Coating
IN-792

(c) Hot Zone, 75x



MgO/
NiCrAlY
Bond
Coating
IN-792

(d) Cold Zone, 75x

1000 1-hour cycles
50 V/0MgO-50 V/0Ni-19Cr-17.1Al-0.97Y/
Ni-16.2Cr-5.6Al-0.6Y

Coating #16

Figure 12. Continued

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16. Abstract A Mach 0.3 burner rig test program was conducted to examine the sensitivity of thermal barrier coatings to Na and V contaminated combustion gases simulating potential utility gas turbine environments. Coating life of the standard $ZrO_2-12Y_2O_3/Ni-16.2Cr-5.6Al-0.6Y$ (composition in weight percent unless stated otherwise) NASA thermal barrier coating system which was developed for aircraft gas turbines was significantly reduced in such environments. Two thermal barrier coating systems, $Ca_2SiO_4/Ni-16.2Cr-5.6Al-0.6Y$ and $ZrO_2-8Y_2O_3/Ni-16.4Cr-5.1Al-0.15Y$ and a less insulative cermet coating system, 50 volume percent MgO-50 volume percent Ni-19.6Cr-17.1Al-0.97Y/Ni-16.2Cr-5.6Al-0.6Y, were identified as having much improved corrosion resistance compared to the standard coating.					
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