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National Aeronautics and Space Administration
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SUMMARY REPORT

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SUMMARY

This report summarizes the technical accomplishments attained in the Critical Research and Advanced Technology Project (CRT) sponsored by the Energy Research and Development Administration and the Department of Energy (DOE) and managed by NASA. The objective of the CRT Project was to provide a critical technology data base for application of coal-derived fuels to utility and industrial gas-turbine systems. Two classes of coal-derived fuels, liquids and gases, were investigated. Emphasis was initially given to the development of technology for utilizing coal-derived liquids (CDL's) because of DOE's programmatic interests at the time the work was initiated. Heavy petroleum liquid fuels were also investigated based on their predicted availability and anticipated lower costs as compared with more highly refined fuels. Some difficulties in hardware development for these liquid fuels were anticipated as both CDL's and residual fuels were known to contain relatively high levels of fuel-bound nitrogen (FBN) and trace metallic fuel contaminants which could cause serious corrosion of gas-turbine hot parts or deposition of residual combustion products. The testing of coal-derived gaseous fuels was undertaken in the latter part of the project, and limited catalytic combustor testing was accomplished.

The areas of critical research and technology for this project were (1) the controlled combustion of coal-derived fuels in a manner capable of meeting the operational requirements of utility and industrial gas turbines and the proposed environmental regulations on exhaust emissions, (2) the development of long-lived materials considered necessary for utility and industrial gas-turbine applications, and (3) a system analyses effort to guide the research and technology activities. The work was performed principally at the Lewis Research Center where NASA specialists and facilities provided supporting research and technology in an integrated manner and responded to specific DOE needs.

In the combustion studies, two technology approaches (two-stage combustion and catalytic combustion) were employed. Two-stage, rich-lean combustion in a flametube test rig successfully demonstrated control of the conversion of the FBN contained in CDL's and heavy petroleum fuel oils to oxides of nitrogen (NO_x). Optimum primary and secondary equivalence ratios were identified, which resulted in the minimum generation of NO_x and the attainment of combustion efficiencies greater than 99 percent. The effects of variations of hydrogen and nitrogen in the fuel and their interrelated effects on fuel-bound nitrogen conversion and optimum equivalence ratios were determined. The flametube experiments indicated that very close equivalence ratio control was necessary to obtain minimum NO_x and for stationary gas turbines, which are required to operate over a wide power range, a technique for maintaining both primary and secondary equivalence ratios was necessary. This information was

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used in the design and operation of a variable geometry sector combustor. The sector combustor controlled both the primary and secondary zone equivalence ratios by controlling the airflow into these zones. In addition, steam cooling of the rich-burn primary combustor liner was demonstrated in this test as an effective means of increasing the liner durability.

In support of the above CDL tests, a literature survey of coal-derived synthetic fuel properties was compiled and published, and an analytical modeling program for the combustion of simulated synthetic fuels was developed. For this latter task, a subroutine to perform adiabatic stirred-reactor computations was added to the NASA Lewis General Chemical Kinetics Program. This model was able to predict the performance of the two-stage, rich-lean, flametube experiments.

In the study of catalytic combustors, four classes of fuels were tested at elevated pressures representative of conventional gas-turbine conditions. The fuels included: Number 2 diesel, residual, CDL's, and coal-derived gases. Initially, a 5-atmosphere (atm) endurance test of a catalyst and catalyst support system was performed under contract by Engelhard Industries. Number 2 diesel fuel premixed with air at 590 K (600° F) and 5 atm pressure was used over the test period of 1000 hours. Initial catalyst performance was good but performance degradation, exhibited by increasing carbon monoxide emissions, occurred throughout the test period. Near original performance was regained when the catalyst was inadvertently exposed to heated air for a 48-hour period. The source of the catalyst contaminant has not been ascertained; however, the results demonstrate that available catalysts have the potential for steady-state gas-turbine operation.

The catalytic combustion of residual fuels was investigated both in-house and under contract. Flametube test rigs varying in diameter from 7.6 to 12 cm (3 to 4.75 in.) were used and temperatures in the range of 590 to 960 K (600° to 1200° F) were run. Results of these tests indicate that a catalytic combustor can be successfully operated with residual fuels and meet the proposed NO_x emission standard for fuels with more than 0.25 percent nitrogen. Operational problems including fuel injector plugging and upstream fuel burning at inlet air temperatures less than 800 K (1000° F), make this concept unattractive at the present time.

Catalytic combustion experiments of CDL fuels were conducted at the Lewis Research Center. Three SRC-II fuels were tested in a 12-cm (4.75-in.) diameter flametube test rig at pressures of 3 to 6 atm and inlet air temperatures in the range of 590 to 810 K (600° to 1000° F). These fuels contained 0.58 to 0.95 percent FBN by weight. In general, the combustion of these fuels was stable; however, the NO_x emission levels were well above acceptable stand- ards due to the conversion of FBN to NO_x. A solution to the high NO_x con- version problem must be found before the use of catalytic combustion for CDL fuels can be considered acceptable.

The catalytic combustion of coal-derived gas was performed under contract at Westinghouse and General Electric (GE) where operating coal gasifiers were available. The Westinghouse fluidized bed gasifer was oxygen-blown and produced a medium Btu gas. A simulated low Btu gas was obtained by using an air diluent. The GE air-blown fixed-bed gasifier produced low Btu gas. Testing at both contractor sites was conducted over a wide range of conditions with inlet air temperatures of 500 to 800 K (450° to 1000° F), reactor gas pressures of 5, 10, and 15 atm and inlet air velocities of 10, 20 and 30 m/s (33, 66, and 99 ft/s). The reactors for both contractors were supplied by Lewis and were of same design, small honeycomb channels over the entire length. Gas ignition occurred readily with no igniter required and combustion was gen-

erally stable. With combustion temperatures in the range of 1370 to 1420 K (2000° to 2100° F), almost no unburned hydrocarbon was present and combustion efficiency approached 100 percent for both the low and medium Btu gases.

Catalytic combustors have been shown to operate successfully with a variety of fuels and have the potential for long-term durability. Some operational problems do, however, exist in the combustion of residual and CDL fuels. For the near term catalytic combustion of coal-derived gaseous fuels is considered feasible and practical.

The second major area of investigation, the development of long-lived materials for gas turbines using CDL or residual fuels, involved fuel corrosivity predictions on high-strength superalloys, the deposition and fouling of turbine airfoils, and the development of insulating ceramic thermal barrier coatings for the cooled hot section components of gas turbines. The fuel corrosivity prediction task was supported by testing with doped fuel, actual fuel, and inhibitive fuel additives.

In the doped fuel tests, various potential fuel impurities, impurity combinations, and concentration levels were tested on candidate turbine materials, IN-100, IN-792, U-700 and Mar M-509. The corrosion effects of the various fuel contaminants and concentrations, and the interrelationship of test time, temperature, and corrodent were determined. Results were evaluated and combined in an empirical hot corrosion-life prediction model. The model can be used to predict corrosivity over a broad range of impurity concentrations and for time periods up to 500 hours at various temperatures. The program is unique and includes most fuel impurities common to this class of fuels and a number of typical turbine alloys. The analytical program is available for use by other government agencies and contractors. Actual fuel tests were conducted using two fuels, an SRC-II naptha and a micronized coal-oil mixture. The test time attained with both fuels was limited because of the difficulty of burning the fuels and because of limited fuel supplies. For both fuels, low sodium and potassium levels were present and, as predicted by the hot corrosion-life prediction model, no hot corrosion was noted on the test hardware. Extensive ash deposits were evident, however, from the combustion of the fuels. The resultant deposition and fouling of turbine hot flow passages are potential problems which could restrict their use. In the testing of fuel additives to inhibit hot corrosion, barium was identified as an additive with great potential in reducing hot corrosion of turbine materials caused by the presence of sodium sulfate in the combustion gases. Reduction in corrosion was attained by the deposition of a protective layer of barium sulfate on the turbine materials. Barium sulfate, however, when continuously formed resulted in excessive deposits. This problem was resolved by the intermittent application of the barium additive, which prevented an excessive build-up of the barium sulfate deposit while maintaining a protective barrier.

Deposition and fouling of turbine parts were anticipated from the combustion of impurity-laden, CDL's. The objectives of the deposition and fouling activity were to predict the composition and dewpoints of the deposits formed from the combustion of the coal-derived fuels, to verify these predictions by test, and to determine the potential for plugging the airfoil cooling holes of advanced gas-turbine cooling systems. In the combustion products analyses subtask, four cuts of SRC-II fuels were used in the test series and thermodynamic analyses were used to predict the chemical composition of the deposits. The deposits were mainly metallic oxides. Agreement between the predicted and observed compounds was excellent. In the airfoil cooling hole plugging investigation, tests were conducted using a doped clean fuel with the hot combustion gas directed onto the leading edge of a film-cooled turbine blade.

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Results indicate that at cooling airflow rates necessary to maintain acceptable airfoil temperatures, severe hole plugging was experienced. For this class of fuels, deposition and hole plugging of film-cooled airfoils could be a significant problem.

Thermal barrier coatings (TBC) on gas-turbine cooled hot section components were investigated as a possible solution to hot corrosion because of their good performance in clean fuel combustion gas exposure. The task effort consisted of the following: Evaluation and endurance testing of both existing and advanced TBC systems when exposed to sodium- or vanadium-doped combustion gases; optimization of bond-coat composition; determination of the reaction of TBC materials with potential impurities; and the conduct of technology evaluation studies.

Initial testing of existing TBC systems with candidate low-quality fuels indicated a major problem due to spalling. Therefore, a comprehensive program was initiated to improve spall resistance of the TBC's and to understand the failure mechanisms. Doped fuel tests using various levels of sodium and vanadium dopants in a clean fuel were run and a number of coatings and substrates were investigated. As a result of these tests, an understanding of the failure mechanisms evolved which identified the fuel contaminants and their phase relationship relative to the TBC surface and bond-coat temperatures. Variations in spall behavior for a coating was attributable primarily to the fuel impurity flux. Efforts were concentrated on the identification of ceramic coatings having resistance to these impurities. Various coatings and coating treatments were investigated. The most promising coating system identified was 1.8 $CaO \cdot SiO_2$/Ni-16CR-6Al-0.6Y which survived over 600 1-hour thermal cycles before spalling. Additional tests of this and other coatings with the standard bond coat (Ni-16Cr-6Al-0.6Y) revealed that durability of the coating could be significantly improved by reducing the coating thickness. The thinner coat, however, lessens the temperature drop through the coating and increases the bond-coat temperature and heat losses to the cooled airfoil.

Reaction studies were conducted to determine how powdered zirconia-yttria, calcium silicate, and barium zirconate reacted with potential combustion products of major fuel and air impurities and with bond-coat elements. These reactions have been documented. Bond coat oxidation and corrosion resistance and adherence to the TBC were studied. Oxidation resistance of the bond coat was found to be a function of coating application parameters and thickness. Burner rig test results confirmed the results of the furnace oxidation and endurance tests. Good bond coatings identified in oxidation and endurance tests gave superior results when evaluated in TBC systems exposed to burner rig testing.

In the technology evaluation studies subtask, three studies were conducted in support of the TBC development activity. The thermal barrier coating - liquid-cooling study investigated the performance of steam- and water-cooled turbine airfoils with TBC in gas and steam turbine combined cycle applications. Results of this analysis indicated significant gains in cycle efficiency and specific power as the turbine inlet temperature was increased while maintaining the same airfoil metal temperature. In the thermal barrier coating - low critical alloy study the use of TBC lowered the metal substrate temperatures for equivalent turbine inlet temperatures and permitted decreasing the use of strategic materials such as cobalt, chromium, and tantalum. In the Fuel-Stack Temperature-Performance Study another potential benefit of TBC's was investigated where the coating could serve as a corrosion-protection barrier on the gas-turbine airfoils. This protection resulting from lower substrate temperatures and less corrosion could permit the use of lower cost,

high sulfur content fuels. To realize this gain, a cycle constraint maintaining stack gas temperatures at levels high enough to prevent acid condensation was investigated. Combining this requirement with the results of the liquid cooling study still indicated a positive combined cycle efficiency gain. Thus, if a minimally processed fuel is to be used in the gas turbine, use of a long-lived TBC could be warranted.

INTRODUCTION

The Critical Research and Advanced Technology Support (CRT) Project was performed by NASA for the Energy Research and Development Administration (ERDA) and its successor, the Department of Energy (DOE). This research and technology activity was organized to provide a critical technology base to support the development of gas-turbine systems capable of burning coal-derived fuels in an environmentally acceptable manner. The project was initiated with the signing of Interagency Agreement No. EF-77-A-01-2599 on June 30, 1977 between NASA and ERDA. Upon formation of the DOE, the interagency agreement number was designated DE-AI01-77ET-10350. Project activities were coordinated with the DOE-sponsored, NASA-managed, Advanced Conversion Technology Program (ACT) and with the advanced gas-turbine program of the Electric Power Research Institute (EPRI). All of the planned activities for the CRT project were completed. This report summarizes the major results of the work performed.

Project emphasis was placed on the identification and resolution of the "critical" technologies associated with the utilization of coal-derived fuels in utility and industrial gas-turbine applications. The technologies identified as critical were combustion and hot section materials. Emphasis on the combustion task, which was originally directed to using coal-derived liquids (CDL's) and residual fuels, was reducing both thermal- and fuel-bound oxide of nitrogen (NO_x) emissions. Combustor development effort initially addressed two-stage combustors using these liquid fuels. The task was expanded to include testing of catalytic combustors and coal-derived gases. Emphasis on the materials task was given to the protection of turbine hot section materials from coal-derived fuel contaminants which could lead to unacceptable hot corrosion or fouling. Several approaches were used to investigate the hot corrosion problem: Developing the capability to predict fuel corrosivity as a function of fuel contaminants and turbine operating parameters; investigation of fuel additives to inhibit hot corrosion; and investigation of thermal barrier coatings (TBC's) as protection for the base metal and as a thermal insulator. System studies were conducted to guide the materials effort and be responsive to DOE requirements.

The technical objectives of the CRT project were

(1) To develop combustor concepts that can burn coal-derived fuels in an environmentally acceptable manner.

(2) To develop a hot corrosion data base for materials exposed to combustion products of coal-derived fuels and correlate these data in a hot corrosion life prediction model.

(3) To develop ceramic coatings that provide protection against hot corrosion and have acceptable life in coal-derived fuel combustion products.

(4) To study the trade-offs among various gas-turbine technologies, operating conditions, and component designs.

To attain these objectives, the CRT project development activities were structured as follows:

Combustion Studies
    A. Two-Stage Combustion
        1 Literature Survey
        2 Flametube Experiments
        3 Analytical Modeling
        4 Combustor Sector Tests
    B. Catalytic Combustion
        1 Five-Atmosphere Endurance Test
        2 Catalytic Combustion of Residual Fuels
        3 Catalytic Combustion of Coal-Derived Liquids
        4 Catalytic Combustion of Coal-Derived Gases
Long-Life Materials
    A. Fuel Corrosivity Prediction
        1 Doped Fuel Tests
        2 Actual Fuel Tests
        3 Inhibition
    B. Deposition and Fouling
        1 Combustion Product Analysis
        2 Airfoil Cooling Hole Plugging
    C. Thermal Barrier Coatings
        1 Advanced Coatings
        2 Improved Thermal Barrier Coating Systems
        3 Reaction Studies
        4 Bond-Coat Optimization
        5 Technology Evaluation Studies

    The following sections discuss the above activities, their objectives, the methodology used, and the attained technology development status. References are provided to permit a detailed review of testing procedures and results.

COMBUSTION STUDIES

Two-Stage Combustion

    At the inception of the CRT program in 1977, considerable work was done by other investigators on the burning of heavy petroleum fuels in stationary gas-turbine engines. Engines were in service at that time using numbers 2, 4, and 6 heating oils. These engines were, however, unable to meet the proposed Environmental Protection Agency (EPA) regulations on exhaust emissions for oxides of nitrogen (NO_x). The regulatory NO_x limits for stationary gas turbines varied from 75 ppm for utility gas turbines (larger than 7.5 MW and 25 percent efficient) to 150 ppm for industrial gas turbines (in the range of 0.75 to 30 MW_e and 25 percent efficient), permitting an allowance for fuels containing more than 0.25 fuel-bound nitrogen (FBN) and an upward adjustment for increased thermal efficiencies. Research was completed at that time which indicated that two-stage, rich-lean combustion could possibly control the conversion of FBN, which is present in heavy oils and coal-derived liquids (CDL's), to NO_x. With this advancement it was predicted that stationary gas turbines could be built to meet the proposed EPA regulations. Previous testing showed water injection to be effective in controlling thermal NO_x formation with clean fuels. These tests also demonstrated that water injection was ineffective in controlling the conversion of FBN to NO_x in less refined fuels. Virtually no investigations were conducted to determine the problems of burning CDL synthetic fuels and little was known about the properties of

these fuels, so that estimates of combustor performance could not be reliably made.

A program was needed to determine the composition of the coal-derived synthetic fuels and if two-stage, rich-lean combustion could be used to burn the synthetic fuels and heavy petroleum fuel oils in an environmentally acceptable manner. A task was initiated to accomplish these goals.

The effort was organized into four subtasks. The activities were ordered to provide a steady acquisition and transition of knowledge beginning with a literature survey of coal-derived fuels and culminating in the successful testing of preprototype combustor hardware. The two intermediate tasks consisted of a NO_x modeling effort and a flametube experiment.

Literature survey. - The literature survey was undertaken to document the range of fuel properties characteristic of coal-derived synthetic fuels. Of particular interest were the percentages of nitrogen (N), carbon (C), and hydrogen (H) contained in the fuels and the viscosity and distillation curves of each potential fuel. Determination of the N content was required to ascertain the potential for FBN conversion to NO_x and to estimate the thermal stability of the fuel. A lower FBN implies a more thermally stable fuel and minimizes the potential for the formation of gums and subsequent choking in the engine fuel system. Minimizing this problem increases the likelihood that a premixed system can be used in the combustor. A high percentage of H implies a high "quality" fuel, that is, one that has a high heating value, a low flame radiation potential (due to its implied lower carbon content), and a low freezing point. The H content in coal synfuels varied from about 5 to 13.5 percent while the FBN varied from zero to 2.0 percent with the highest FBN fuels having the lowest percentage of H (refs. 1 and 2). Also, the lower heating value of the coal synfuels varied from 15 500 to 19 500 Btu with the lesser values found in fuels containing the lowest percentage of H. These trends are also characteristic of petroleum fuels.

Using these data, the H range studied was set at 9 to 18 percent and the N range at zero to 1.5 percent for both the computer modeling effort and the flametube testing.

Flametube experiments. - In the flametube tests conducted at the Lewis Research Center, the H content of the fuel was varied by blending various quantities of propane and toluene, and the percentage of N was varied by the addition of pyridine, an organic solvent. In actual fuels tests SRC-II middle-to-heavy distillate and SRC-II naphtha were tested and the results compared favorably with the simulated blended fuels. During the conduct of the tests, inlet airflow was held constant at 0.26 kg/sec (0.57 lb/sec) as was the inlet air temperature at 670 K (750° F) and the inlet air pressure at 0.48 MPa (70 psia). A two-stage, partially premixed, rich-lean parametric combustion study was conducted in which the primary equivalence ratio was varied from 0.5 to 2.0 while the secondary equivalence ratio was varied from 0.5 to 0.7. The equivalence ratio is defined as the ratio of the actual fuel-air ratio over the stoichiometric fuel-air ratio. Thus, an equivalence ratio of 1.0 means operating at stoichiometric conditions.

Figure 1 is a typical plot of the combustion generated NO_x in ppm V corrected to 15 percent oxygen (O) versus primary equivalence ratio. A family of curves with constant percentage of FBN is shown. This plot generated from test data in which a fuel blend containing 9 percent H was burned. The burner had a primary volume of 6030 cm^3 (370 in.^{3}), a secondary residence time of 2 msec, and a secondary equivalence ratio of 0.5. The correction to 15 per-

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cent O_2 normalized the data as required by EPA regulations. The formula for this correction is

$$C_{adj} = C_{meas} \times \frac{5.9}{20.9 - \% \, O_2}$$

where:

C_{adj} pollutant concentration adjusted to 15 percent O_2, ppm
C_{meas} pollutant concentration measured, dry basis, ppm
5.9   20.9 percent O_2 - (15 percent O_2), the defined O_2
          correction basis
Percent O_2 percent O_2 measured, dry basis, percent

The figure shows that the generated NO_x reduced to a minimum at a primary equivalence ratio of about 1.7 with no FBN present in the fuel while it attained a minimum at a primary equivalence ratio of about 1.6 for fuel containing 1.5 percent FBN. This trend to a lower optimum primary equivalence ratio with increasing FBN is also shown in figure 2. In addition this figure illustrates that the optimum primary equivalence ratio increased as the percentage of H in the fuel decreased. Thus a fuel with 1.5 percent FBN and 13.8 percent H would produce the least NO_x at a primary equivalence ratio of 1.4, while one with the same 1.5 percent FBN and 9 percent H would require operation at a primary equivalence ratio of 1.6 for minimum NO_x generation.

These and other significant flametube results are summarized as follows (additional detail can be found in ref. 3): (1) Two-stage, rich-lean combustion reduced the conversion of FBN to NO_x. Conversion rates of less than 10 percent (with a minimum of 6 percent) were achieved at the optimum primary conditions for 0.5 to 1.5 percent fuel N content. (2) the optimum primary equivalence ratios for the fuel blends tested ranged between 1.4 and 1.7, and the optimum secondary equivalence ratio for these tests was about 0.5. These values resulted in minimum NO_x production at acceptable combustion efficiencies of 99 percent or more; (3) hydrogen content of the fuel affected the optimum primary equivalence ratio. Decreased hydrogen content shifted the optimum primary operating conditions to higher primary equivalence ratios; (4) increased fuel N levels reduced the percentage of fuel nitrogen to NO_x conversion. Exhaust NO_x levels, however, always increased with additional fuel N. Increased fuel N content also tended to shift the optimum primary equivalence ratio to a lower value; and (5) emissions of NO_x from SRC-II naphtha and mid-heavy distillate liquid-synfuels combustion matched very closely those from the fuel blends used to simulate the synfuels. Thus, the fuel blend data should be useful in selecting optimum operating conditions for two-stage synfuel combustion when the SRC-II fuels are burned. The fuel blend data may not, however, simulate other synfuels because of molecular dissimilarities in fuel nitrogen bonding.

Analytical modeling. - Results of the NO_x modeling effort supported the flametube results. This model used a simple two-stage, well-stirred reactor which did not consider effects of mixing and heat transfer losses. Figure 3 illustrates the agreement between the computed and experimental percentage of FBN conversion as a function of primary equivalence ratios. The simple model predicted the observed shift of the optimum primary equivalence ratio to richer values as the H content of the fuel decreased. The model also suggested an explanation for this effect: It may be caused by the direct reaction of the pyrolysis fragments of aromatic fuels with nitric oxide. It is the increased amount of aromatics that lowered the H content of the fuel. Most of the computations were performed for a pressure of 5 atm to obtain a direct

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comparison with the flametube results. However, a series of computations were performed at a pressure of 12 atm, which is considered to be a more realistic ground-based gas-turbine combustor pressure. Results showed that the high pressure increased NO_x generation only moderately, between 3 and 30 percent at the rich equivalence ratios required for minimum NO_x formation. The increase was due to the formation of thermal NO_x. The percent conversion of FBN to NO_x computed at 12 atm pressure was slightly less than at 5 atm. In addition, both the theoretical model and the experimental flametube results show that carbon monoxide (CO) emissions increased significantly with decreasing fuel H content. The CO emissions were also calculated to be highest at the rich primary equivalence ratios that produce minimum NO_x. For high-pressure combustion, calculations show that the CO which was generated decreases significantly as the pressure is increased. Both the theoretical and experimental work indicated that trade-offs will be necessary between the conditions that minimize NO_x and those that control CO emissions. Additional modeling details and results can be found in references 4 and 5.

Combustor sector tests. - The sector rig experimental task was undertaken to advance the state of the art for two-stage combustion. Rich-burn primary combustor liner durability and staged combustion equivalence ratio control were addressed, as these appeared to be the major developmental problems for two-stage combustion.

The rich-burn primary combustor-liner durability problems arose because in a rich-burn system film-cooling air cannot be used to internally cool the liner as is done in a conventional lean-burn system. If film cooling were used, the local fuel-air mixture would be less rich (nearer stoichiometric) and could burn at a higher temperature then that of the bulk gas flow. This lack of film cooling means that there is a hot side convective heat load present that doesn't exist in a lean-burn system where the film-cooling air insulates and cools the wall on the hot gas side. In addition, flame radiation in a rich-burn system is also higher due to the higher flame emissivities of unburnt C which results from the fuel-rich condition. To minimize potential combustor-liner temperature problems, a liner which was externally steam-cooled was used to maintain low liner temperature, on the order of 920 K (1200° F). In applying this cooling concept to production hardware, these relatively low temperatures permitted the use of less costly liner materials such as A-286 stainless steel instead of the conventional Hastelloy materials. In addition, the generated steam from the combustor could be used for additional power generation in a combined cycle application, for steam input to a coal gasifier, or for other plant uses.

The flametube experiments indicated that very close control of the equivalence ratio was necessary to obtain minimum NO_x emissions. Since a stationary power gas turbine is required to operate over a wide power range from idle to full power and meet EPA emission standards at all operating points, a technique for maintaining primary and secondary zone equivalence ratio control and a means of insuring primary zone liner durability were required. A variable vane angle air swirler was used to control the primary airflow while a rotating collar was used to modulate the secondary airflow. To maintain overall pressure drop and provide for variations in the dilution airflow rate as the secondary equivalence ratio is varied, a third variable geometry element and a second rotating collar was used in the tertiary or dilution zone. Figure 4 illustrates both the variable geometry and the steam-cooled features of this hardware. The variable geometry hardware performed flawlessly throughout the testing program.

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Results of the three-stage, variable geometry, rich-burn combustor are (1) Variable geometry provides a satisfactory means of maintaining equivalence ratio control in multizone combustors, and (2) steam cooling of the rich primary zone provides a satisfactory technique to increase liner durability. Thus, steam-cooled primary zone combustors provide the potential for using less strategic materials for combustor liners due to their lower operating temperatures, and variable geometry combustion can be effectively used to control NO_x generation. Additional details of the combustor sector test program are contained in reference 6.

Two patent disclosures have resulted from the development efforts in the combustor sector test program. One is NASA Case No. 13609-1 "Steam Cooled Rich-Burn Combustor Liner" and the other NASA Case No. 13696-1 "Ignitor Seal for Rich-Burn Combustor Liner."

Catalytic Combustion

The CRT catalytic combustion development effort was divided into four subtasks: (1) 5-Atm endurance tests, (2) tests with residual fuels, (3) tests with CDL fuels, and (4) tests with coal-derived gaseous fuels.

Catalytic combustion was under study for several years by a number of investigators (refs. 7 and 8). Most of these studies were made using propane, methane (CH_4), or liquid distillate fuels and involved only short periods of testing. Before the CRT catalytic combustion effort, the only evaluation of long term catalyst durability was made by Engelhard Minerals and Chemicals Corporation at a 1 atm combustion pressure (ref. 9). Because the effect of pressure on catalyst durability was of concern for stationary power applications, a contract was awarded to the Engelhard Industries Division in fiscal year 1978 under CRT project sponsorship to further demonstrate catalyst durability at a combustion pressure of 5 atm.

Additional investigations under the CRT project were added in fiscal years 1979 to 1981 to fill gaps in the existing knowledge for the behavior of alternate fuels in catalytic combustion. The fuels involved were residual, CDL's, and coal-derived gases. Although catalytic combustion was previously been demonstrated with each of these fuels, it was generally done at low pressures, typically 1 atm. Clearly, data at higher pressures were required for all three fuel groups. In addition, it was necessary to establish the effects of various degrees of vaporization for residual fuels, which are difficult to vaporize, and to test several CDL's not previously tested with catalytic combustors. Also, previous catalytic tests with coal-derived gases used blends of CO, carbon dioxide (CO_2), CH_4, and H_2 to simulate a coal-gas (refs. 10, 11, and 12), and most of the testing was limited to small combustor duct diameters of 2.5 to 6 cm (1 to 2.5 in.). Under CRT sponsorship catalytic combustion tests were made using the actual products of coal gasifiers with pressures and duct sizes more representative of true engine conditions of 5 to 15 atm in ducts of 12 cm (4.75 in.) diameter. The objectives of the CRT catalytic combustion studies with alternate fuels were (1) to demonstrate the feasibility of catalytic combustion with each fuel and (2) to identify potential problem areas which might require further study.

A description of the activities and results in each of the subproject elements is given in the following sections.

5-atm endurance tests. - Tests were performed at Engelhard in a 2.5-cm-(1-in.) diameter test rig at a combustion pressure of 5 atm for 1000 hours to demonstrate the durability of current catalysts and substrates. Number 2 diesel fuel was premixed with the 590 K (600° F) airstream for these tests and

the combustor exit temperature was maintained in the range of 1420 to 1530 K (2100° to 2300° F). The temperature at various stations and the concentrations of CO, CO_2, unburned hydrocarbons, and NO_x were recorded during the test. Parametric tests were initially performed with a fresh catalyst and repeated at the conclusion of the 1000 hours of combustor aging. Details of the tests and the results are discussed in reference 13.

The results are summarized with the plot of CO emissions as a function of test time in figure 5. Carbon monoxide emissions increased throughout the combustion period of about 1000 hours. Clearly, the performance of the catalyst degraded throughout the test period. At just over 1000 hours and after catalyst exposure to air at high temperature, the trend reversed and CO emissions decreased with further increases in combustor operational time. These results suggest that the catalyst was exposed to a contaminant which was continuously deposited throughout the 1000 hour test period. After 1000 hours the contaminant apparently dissipated, possibly due to a change in fuel composition, and further operation resulted in the cleansing of the material from the catalyst surface. By 1062 hours, performance returned to the initial CO emission level, indicating that no permanent loss of catalyst activity occurred. These results demonstrated that currently available catalysts have the potential for acceptable steady-state operation at stationary gas-turbine conditions. What remains to be shown is catalyst durability for longer periods of steady-state operation and for a number of thermal cycles representing actual field-use conditions.

Catalytic combustion of residual fuels. - The catalytic combustion of residual fuels was studied at the Lewis Research Center and under contract. The objectives of these studies were to (1) characterize catalyst performance at inlet temperatures high enough to insure complete vaporization of the residual fuel, (2) determine if fuel remaining in the form of liquid droplets at the catalyst inlet might affect catalyst performance, and (3) identify potential problem areas involved in the catalytic combustion of residual fuels.

The experiments at Lewis were performed in fiscal year 1980. A flametube test rig with a 12-cm (4.75-in.) inside diameter was used. Residual fuels with a N concentration of about 0.5 percent were tested at pressures of 3 and 6 atm with inlet air temperatures of 590 to 960 K (600° to 1270° F). At the lower inlet air temperatures the catalyst was preheated by operating with No. 2 diesel fuel before introducing the residual fuel; however, preheating was not necessary at higher inlet air temperatures. For inlet air temperatures below 800 K (1000° F), the residual fuel tended to collect on the duct walls upstream of the catalyst, and periodically this fuel would ignite and burn. For inlet air temperatures above 800 K (1000° F), the duct wall was apparently hot enough to prevent fuel from accumulating and no upstream burning was experienced. The high air temperatures did, however, cause plugging of the fuel tubes. This condition was overcome by cooling the fuel tubes with air. For additional test details see reference 14.

Contracts to demonstrate catalytic combustion with residual fuel were awarded to the United Technology Research Center (UTRC) in fiscal year 1979 and to the General Electric Company (GE) in fiscal year 1980. Subcontractors for catalytic reactor design, supply, and instrumentation were the Acurex Corporation and Engelhard Industries Division, respectively. Both of the experimental programs were completed in fiscal year 1981. The UTRC tests (ref. 15) were performed in a 7.6-cm (3-in.) inside diameter test rig with a multiple-source fuel injector and a graded-cell reactor (having a low density of honeycomb channels at the reactor inlet and a higher density at the exit). The residual fuel used in these test series contained 0.15 percent N. Tests

were made with reactor pressures in the range of 3 to 6 atm. General Electric (ref. 16) used a 11.4-cm (4.5-in.) inside diameter test duct with a single air-assist fuel injector and three different catalytic reactor geometries. Included were three different substrate channel densities at the reactor inlet. The residual fuel used by GE contained 0.22 percent N and the tests were conducted at a reactor pressure of 4 atm.

Results of the residual fuel testing performed in-house and at the GE are summarized in figures 6(a) and (b). Combustion efficiency for three residual fuels is given in figure 6(a). Although the performance varied for the three fuels, an operating condition could always be found for which combustion efficiency approached 100 percent. For an inlet air temperature lower than 800 K (1000° F), upstream burning such as that which occurred in in-house testing was experienced in the GE contract studies. The GE tests also showed that (1) catalytic reactors operating on residual fuel tend to plug with fuel deposits if the inlet channels of the reactor are smaller than about 0.6 cm (0.25 in.) diameter, (2) catalyst performance improves with a graded-cell reactor as compared with one having small uniform channels throughout the reactor length, and (3) the catalyst does not deactivate.

Emissions of NO_x resulting from the catalytic combustion of residual fuel is summarized in figure 6(b). Data for all three of the fuels shown tend to fall near the same curve in spite of differences in fuel N percentages. For combustion temperatures below 1460 K (2170° F), NO_x emissions were below 120 ppm and met the 125-ppm EPA-proposed standard for fuels with more than 0.25 percent FBN.

UTRC test results are not shown because they were unable to operate at the required inlet air temperatures. The UTRC tests did, however, demonstrate that with No. 2 diesel fuel the degree of vaporization of the fuel had a strong effect on the performance of the catalytic reactor (fig. 7).

Both in-house and contract studies demonstrated clearly that catalysts can operate successfully with residual fuels. They also identified several problems associated with the fuel. In particular, the tendency to ignite and burn in the premixing duct except at fairly high inlet air temperatures greater than 800 K (1000° F) and the plugging of fuel injectors at the required high inlet air temperatures makes the use of residual fuel with catalytic combustors unattractive at the present time.

Catalytic combustion of coal-derived liquids. - Experiments with CDL fuels were carried out in-house at Lewis during fiscal year 1980. The objectives of this study were to (1) demonstrate catalytic combustion with three SRC-II fuels: Naphtha, mid-distillate, and a midheavy blend, (2) compare the combustion performance with that obtained with No. 2 distillate fuel, and (3) identify potential problem areas. Tests were conducted in a 12-cm (4.75-in.) inside diameter flametube test rig with inlet air temperatures of 590 to 810 K (600° to 1000° F) and combustion pressures of 3 and 6 atm. (ref. 17).

Initial tests with the naphtha fuel using a small-cell catalytic reactor resulted in rapid plugging of the honeycomb channels at the inlet. A graded-cell catalytic reactor (with large cells at the inlet) was substituted for subsequent tests. For inlet air temperatures below 640 K (700° F) no plugging was experienced with the lighter fuels. The graded-cell reactor did, however, tend to plug when operated on the middle-to-heavy blend. No problem was experienced with the midheavy blend at higher inlet air temperatures. Apparently, the catalytic reactor surface had to be maintained above a minimum temperature to avoid deposition of unburnt fuel constituents which would eventually close off the reactor channels.

Figure 8(a) presents the combustion efficiencies attained for the three SRC-II fuels and the No. 2 diesel. The naphtha gave slightly higher efficiency than the No. 2 diesel, the mid-distillate about the same efficiency, and the midheavy blend slightly worse. In general, the combustion of these fuels was stable with no upstream burning problems as was encountered with the residual fuels. In figure 8(b), NO_x emissions are shown to be well above the proposed 125-ppm EPA standard for fuels with greater than 0.25 percent FBN. The FBN ranged from 0.58 percent in the naphtha to 0.95 percent in the middle-to-heavy blend, and NO_x conversion approached 75 percent for all three coal-derived fuels.

Although catalytic combustion of the SRC-II fuels was relatively successful, the development of a practical catalytic combustor to operate on these fuels will depend on finding a solution to the high NO_x conversion problem.

Catalytic combustion of coal-derived gases. - In fiscal year 1981 contracts were awarded to Westinghouse and GE for the purposes of (1) demonstrating catalytic combustion with the products from operating coal gasifiers and (2) identifying potential problems with the catalytic combustion of the coal gases.

The Westinghouse Waltz Mill fluid-bed gasifier was oxygen-blown to produce a medium Btu gas which was introduced into the catalytic reactor after cleanup in a water scrubber. In addition, some tests were made using an air diluent to simulate a low Btu gas. The GE tests used a low Btu gas obtained from their fixed-bed reactor, which was airblown, in Schenectady. The GE gasifier had a water wash (which was reinjected to conserve cycle energy), a Benfield sulfur removal system, and a condensing system for the removal of heavy oils and tars. The Westinghouse scrubber effectively removed all but traces of the ammonia (NH_3) from the coal-gas stream. The GE coal-gas, however, contained typically about 1500 ppm NH_3, which resulted from the reinjection of the wash water.

Tests were made with inlet air temperatures of 500 to 800 K (450° to 1000° F), combustion pressures of 5, 10, and 15 atm, and inlet air velocities of 10, 20, and 30 m/s (33, 66, and 99 ft/s). The test hardware used by both contractors was supplied by NASA and were of the same design. The test duct had uniform small honeycomb channels throughout the entire length. Gas ignition occurred readily with no igniter, and combustion was generally stable. Although occasional upstream burning did occur, it was probably caused by fuel property variations. It was easily extinguished by momentarily interrupting the fuel flow. Methane in the coal-gas was the most difficult constituent to burn, but with combustion temperatures in the range of 1370 to 1420 K (2000° to 2100° F), there was almost no unburned hydrocarbon, and combustion efficiency approached 100 percent for both the low and medium Btu gases. Typical results from the Westinghouse tests are shown in figure 9. These results indicate that high combustion efficiencies can be attained with coal-derived gases. Some catalyst deactivation was observed during the Westinghouse tests. Inspection of the combustor hardware revealed a coating of fine iron (Fe) and nickel (NiO) oxide powders on the surface of the fuel injector and catalyst, and some passages of the multiple-source fuel injector were blocked with deposits. The powders apparently came from facility ducting.

The NO_x emissions levels observed were dependent on the concentrations of NH_3 in the feed gas. For the Westinghouse tests NO_x was typically 10 to 20 ppm, which is well below the allowable level of 75 ppm for fuels with no FBN. In the GE tests, because of the high NH_3 concentration in the feed gas which resulted from the recycling of the wash water, NO_x values of several

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hundred ppm were measured during the experiments. Details of the Westinghouse and GE tests are presented in references 18 and 19, respectively.

Catalytic combustion appears to be well-suited to applications involving the use of coal-derived gases. Clearly, NH_3 must be removed from the coal-gas to insure low NO_x emissions, and the removal of trace impurities and tars is probably necessary to insure long term catalyst durability.

The effort under the catalytic combustion subtask showed that catalytic reactors have the potential for long-term durability and have the capability to operate with a variety of alternate fuels. The problem areas encountered included upstream burning during operation with residual fuel and high NO_x emissions with CDL fuels. Due to these problems with petroleum residual and coal-derived liquid fuels, it appears that, at least for the near term, catalytic combustion can best be applied to coal-derived gaseous fuel combustion.

LONG-LIFE MATERIALS

Fuel Corrosivity Prediction

At the inception of the CRT program little was known about the interaction of a wide variety of potential impurities that might be found in CDL's. The objective of the fuel corrosivity prediction subtask was to predict and evaluate the resistance of high-strength superalloys to these potential fuel impurities as well as to predict and evaluate techniques for the reduction of the corrosive effect of such liquid fuel impurities.

Doped-fuel tests. - These tests attempted to simulate CDL's by adding selected contaminants to a clean fuel to (1) isolate the corrosion effects of a given contaminant and its concentration and (2) determine the interrelationships of time and temperature and corrodent on the hot corrosion of high-strength superalloys. The tests were carried out in a Mach 0.3 burner rig (ref. 20) and the data accumulated from these tests are presented in detail in reference 21. The parameters, which were varied in accordance with the statistical design (ref. 20), were the dopant concentrations and temperatures. The dopants were sodium (Na), potassium (K), magnesium (Mg), calcium (Ca), and chlorine (Cl). The concentrations varied from approximately 0.01 to 10 wppm. The ranges are shown schematically in figure 10. The metal temperature was varied between 1070 and 1370 K (1470° and 2000° F).

There were 322 data points per alloy. The metal recession data from these experiments were fit to a polynomial equation using multilinear regression. The final model was chosen by a backward elimination type of regression. Scaling was required for each variable to achieve a reasonable degree of orthogonality among the terms of the model. An example of the type of predictions that can be made from such a model is shown in figure 11. For additional detail see reference 21.

In general, the model thus derived can be used to predict corrosivity over a broad range of impurity concentrations (0.01 to 10 ppm) and for exposure times from 40 to 500 hours at temperatures in the range of 1070 to 1370 K (1470° to 2010° F). Extrapolation, however, from such a model is not likely to be successful. The range of impurities tested covers the concentration levels expected in CDL's.

In addition to the statistical model, a broad range of impurities were studied in combination with Na. These elements included vanadium (V), molybdenum (Mo), tungsten (W), phosphorus (P), and lead (Pb). Again these tests were run in the Mach 0.3 burner rig and the results were compared with samples

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run with only Na added. An example of the data obtained from these tests is shown in figure 12 and the work is described in detail in reference 22.

In general, it was determined that all of the elements caused corrosion greater than Na alone under some operating conditions. The increased corrosion was indicated by the lowering of the temperature for the onset of hot corrosion. The resultant lowering of the hot corrosion threshold was determined to be due, at least in part, to the formation of low melting point deposits which can flux the protective oxide scales thus causing accelerated attack of the alloy. As serious as Na attack is in causing accelerated corrosion, there is a broad spectrum of conditions under which attack can be further accelerated by the presence of second impurities.

Actual fuel tests. - These experiments were also conducted in Mach 0.3 burner rigs as an attempt to demonstrate the validity of the corrosion predictions derived from the attack model in the previous section. Two types of fuels were burned in these tests: The SRC-II naptha fuel and a micronized coal-oil mixture. For both of these fuel types, extensive modifications were made to the burner rig to get them to burn consistently (refs. 23 and 24). Because of the difficulty of burning the fuels even after rig modifications, the total test time using SRC-II naptha fuel was limited to approximately 190 hours, while that using the micronized coal-oil mixture was limited to about 45 hours. In both cases, because of the low Na and K levels in the fuels, no hot corrosion attack was anticipated, which was found to be true (fig. 13). Microstructures confirmed that the corrosion attack is the same as that found in oxidation tests where no corrodent was added. They did, however, show extensive deposits, iron oxides, silicon oxides, and aluminum silicate formed on the surface of the sample. Thus, the conclusions drawn from this work are that accurate predictions of fuel corrosivity can be made and, while no potential for hot corrosion is likely to exist for this class of fuels, deposition and fouling are anticipated to be a problem.

Inhibition. - In this series of tests, a number of additives were used in an attempt to find an effective inhibitor for hot corrosion of superalloys (refs. 25 and 26). The elements considered were aluminum (Al), silicon (Si), iron (Fe), chromium (Cr), zinc (Zn), magnesium (Mg), Ca, strontium (Sr), and barium (Ba). While all of these additives reduced hot corrosion for some alloys, the most effective and consistent additives were Ba and Sr. For all alloys, the addition of Ba or Sr reduced the corrosion attack to nearly oxidative attack levels (fig. 14). As can be seen in figure 15, the microstructure of alloys protected by Ba inhibition shows an extensive barium sulfate ($BaSO_4$) coating on the outer surface of the alloy. This coating is quite dense and accounts for a major part of the inhibiting effect of both Ba and Sr. However, the deposit can lead to fouling.

In an attempt to reduce fouling while retaining the beneficial effects of such alkaline earth inhibitors on hot corrosion of superalloys, both Ba and Sr additives and pretreatments (inhibitor introduced by firing with clean fuel) with Ba or Sr were evaluated. In general it was found that other additives, especially Si, could show a reduction of deposition, but always at the expense of some loss of corrosive resistance. Pretreatment using the inhibitor was found to be much more effective and controllable.

From a comparison of additives and pretreatment some conclusions were drawn. None of the secondary additives such as Si, Al, and Fe produced dramatic decreases in fouling, and indeed there is some evidence that even under ideal situations some loss in inhibition was apparent. The pretreatment with Ba and Sr inhibitors, however, was shown to have definite potential. Such a technique can be used to keep fouling under close control. The specific

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parameters for the intermittent application and effectiveness of this approach will be related to such factors as specific turbine operating conditions and impurities in the fuel. The technique does, however, offer a flexible way to meet changing Na and K levels found in the combustion gases of turbines burning coal-derived or heavy distillate petroleum fuels, or from ingested airborne salt.

Deposition and Fouling

When these tests began there was very little predictive ability for determining the composition of deposits that might be formed on turbine parts following the combustion of such complex fuels as impurity-laden CDL's. The objectives of this part of the program were (1) to make thermodynamic predictions of the composition and dewpoints of the deposits formed from the combustion of coal-derived fuels and (2) to determine the potential for plugging of advanced cooling systems on the airfoils of turbines operating on such fuels.

Combustion product analysis. - Four cuts of SRC-II fuels were used in this test: (1) A naptha, (2) a light oil, (3) a wash solvent, and (4) a mid-heavy distillate blend. These fuels were analyzed before running in a modified burner rig where the deposits were carefully collected and analyzed. The major metallic impurities which contributed to the deposits were copper (Cu), Fe, Cr, Ca, Al, nickel (Ni), Si, titanium (Ti), Zn, and Na. The deposits (ref. 23) were mainly metal oxides. Thermodynamic analysis was used to predict the chemical composition of the deposits. Agreement between the predicted and observed compounds was excellent (table I). As a result, considerable confidence in determining deposit compositions from the thermodynamic analysis was gained. This enables evaluation of the severity of deposition resulting from the use of CDL's when impurities are known.

Airfoil cooling hole plugging. - In these tests (ref. 27), airfoils with advanced cooling hole schemes were exposed to the combustion gases of a Mach 0.3 burner rig. A clean fuel (Jet A) was burned and deposits that were formed resulted from impurities that were added in the combustor of the burner rig. In general, the amount of cooling hole plugging caused by the various dopants was a function of the composition of the dopant. In these particular tests, the two dopant combinations used were the same except that P (phosphorous) was added to the second dopant (dopant B, table II). The deposit became stickier with the addition of the P. This confirmed the earlier conclusions of work done (ref. 28) which demonstrated that P in combination with Fe and Ca greatly accelerated the tendency for cooling hole plugging.

Generally with little or no cooling airflow any deposit will eventually plug the airholes. As the cooling airflow rate increases, the tendency for plugging is reduced markedly, and above a certain value no plugging is observed. The amount of flow required to keep the holes open is a strong function of the impurity content of the fuel. It appears probable that any composition could be prevented from depositing by providing sufficient cooling air mass flow. Whether an engine designer could afford to divert sufficient airflow to keep the holes clear and still retain sufficient cycle efficiency would depend strongly on the nature of the deposit, the cycle, and the penalty associated with the increased cooling air requirement. It does appear that the combustion of CDL's could cause plugging problems.

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Thermal Barrier Coatings

The current interest in the use of insulating ceramic TBC's on cooled hot section components of gas turbines was brought about by the good performance of such coatings in clean fuel combustion gas exposures (refs. 29 to 31). Use of such coatings could permit turbine inlet temperature increases, cooling airflow rate reductions, or the simplification of cooling schemes. Alternatively, existing gas temperatures and cooling schemes could be maintained and the components operated at lower metal temperatures. In this latter instance, increased component durability and reliability would result. These benefits were examined analytically for utility gas turbines, and important fuel and capital cost savings were identified (refs. 32 to 34).

The purpose of this task was to examine the sensitivity of yttria-stabilized zirconia coatings to the contaminated combustion products of coal-derived fuels and to identify alternate coatings and coating systems that demonstrated improved resistance to these contaminants. Under CRT, initial results with the ZrO_2-12 wt % Y_2O_3/NiCrAlY baseline system in the presence of the usual heavy fuel impurities (such as Na and V) were less than encouraging (ref. 35). As a consequence of these early test results, a comprehensive program within the CRT project was undertaken to improve the spall resistance of TBC's exposed to the combustion products of potential coal-derived fuels, and to understand the mechanisms which induce TBC's to degrade in this environment. The program consisted of separate studies involving (1) the evaluation and endurance testing of both existing and advanced TBC systems when exposed to Na and/or V-doped combustion gases, (2) the optimization of bond-coat composition, thickness, and deposition parameters, (3) a determination of the reaction of TBC materials with potential air, fuel, and bond-coat impurities, and (4) the conduct of technology evaluation studies.

Advanced coatings. - The behavior of the baseline yttria NiCrAlY system and the advanced TBC's in corrosive environments was investigated. The response of single ZrO_2-12 wt % Y_2O_3/Ni-15Cr-6Al-0.6Y coated air-cooled hollow erosion bar specimens to Mach 0.3 burner rig exposure with various levels of Na and V fuel contaminants is summarized in figure 16. This baseline coating was developed for clean fuel, aircraft gas-turbine applications (ref. 29).

As shown in figure 17, at the 0.5-ppm Na fuel equivalent level the coating survived 1300 1-hour cycles without spallation. Appreciable erosion, presumably due to carbon (C) particles, was noted. At the 5 ppm Na fuel equivalent level the coating failed after 92 1-hour cycles at a location outside the hot zone. With 0.2 and 2.0 ppm V in the combustion gases, the coating failed in the hot zone at 200 and 25 1-hour cycles, respectively (fig. 18). When a fuel equivalent dopant level of 5 ppm Na plus 2 ppm V was used the coating failed in 43 1-hour cycles.

The microstructure of the coating on this latter specimen after exposure is shown in figure 19 along with the microstructure of the as-deposited coating. Here, as well as in the other tests, no bond-coat corrosion was detected. The coating failure in these tests occurred within the ceramic near the bond-coat oxide interface. This mode of failure is similar to tensile failures (reported by Levine in ref. 36) and the furnace and burner rig oxidation failures observed by Stecura (refs. 29 and 30).

The locations of coating spallation corresponded to areas where combustion products were predicted to condense based on the calculated dewpoints of the condensates and the temperature profile of the specimens (ref. 37). A summary

of the calculated dewpoints and melting points for the various fuel impurity conditions is given in table III.

The most severe conditions for a porous plasma spray deposited ceramic coating such as ZrO_2-12 wt % Y_2O_3 occur when a corrosive liquid such as vanadium oxide (V_2O_5) or sodium vanadate ($Na_2V_2O_6$) can condense at the surface and completely permeate the coating. That is the dewpoint, T_{dp}, is above the surface temperature, T_s, of the ceramic, and the melting point, T_{mp}, is below the bond-coat temperature, T_{bc}. This was the case with V_2O_5 formed in the 0.2- and 2-ppm V tests and with $Na_2V_2O_6$ formed in the 5-ppm Na plus 2-ppm V test.

The problem with fuel or air impurities should not be as severe if the condensed combustion product does not react with the ceramic coating. If the melting point of the condensate is above the dewpoint (i.e., the condensate is a solid) or if the dewpoint is below the bond coat temperature, the fuel contaminant may be harmless. The fuel contaminant may also be harmless if the dewpoint is less than the surface temperature.

With 5 ppm Na in the fuel, the dewpoint of the nonreactive sodium sulfate (Na_2SO_4) condensate was below the surface temperature in the hot zone. Failure occurred out of the hot zone where the dewpoint was above the surface temperature (fig. 20). With 0.5 ppm Na in the fuel, the dewpoint was below the bond-coat temperature in the hot zone and below the surface temperature, but above the bond-coat temperature elsewhere. Experimentally, under these conditions there was little penetration of the coating even though the coating was permeable. Thus, this test was no more severe than an oxidation test.

In a second series of Mach 0.3 burner rig tests, three yttria-stabilized zirconias were tested at three fuel-to-air mass ratios and at a fuel equivalent impurity level of 5 ppm Na plus 2 ppm V. The conditions were similar to the conditions of previous tests except that eight specimens were tested simultaneously and the substrates were 1.27-cm (0.5-in.) O.D. Waspaloy cylinders. Results of this test are summarized graphically in figure 21. Data indicated that the spall behavior of yttria-stabilized zirconia TBC's was sensitive to changes in the fuel-to-air mass ratio and that the 8 percent yttria coatings were more spall resistant in this type of combustion environment.

As the fuel-to-air mass ratio was increased from 0.039 to 0.049 the following occurred: The amount of impurities increased 25 percent; the surface temperature of the ceramic increased; the temperature gradient through the coating increased. However, based on the responses of single-coated ZrO_2-12 wt % Y_2O_3 specimens to changes in the fuel impurity concentration, the difference in spall behavior as a consequence of increasing the fuel-to-air mass ratio was attributed primarily to an increase in fuel impurity flux.

Improved thermal barrier coating systems. - Results of early tests on TBC's developed for clean fuel aircraft gas-turbine service indicated a need to identify ceramic coatings having improved resistance to fuel and air impurities (refs. 38 and 39). An initial step toward this goal was taken when a series of coating systems were tested in a Mach 0.3 burner rig with the flame doped to the fuel equivalent impurity level of 5 ppm Na plus 2 ppm V (ref. 35). Ceramic coating thickness was maintained at 0.04 cm (0.016 in.) and bond-coat thickness was maintained at 0.013 cm (0.005 in.). Results of these tests are summarized in figure 22. Various thermal and chemical treatments (such as infiltration with colloidal silica followed by 1370 K (2000° F) exposure) of the baseline ZrO_2-12 wt % Y_2O_3/Ni-16Cr-6Al-0.6Y system resulted in little or no improvement. A more oxidation-hot corrosion-resistant bond coat (Ni-21Co-19Cr-13Al-0.6Y) and a dense Y_2O_3 top-coat with the baseline coating offered some improvement. The ZrO_2-8 wt %

Y_2O_3/Ni-16Cr-5Al-0.15Y coating offered an even greater improvement. The most promising coating was $1.8CaO.SiO_2$/Ni-16Cr-6Al-0.6Y which survived over 600 1-hour cycles before spalling compared with about 60 cycles for ZrO_2-12 wt % Y_2O_3/Ni-16Cr-6Al-0.6Y. A higher thermal conductivity cermet coating consisting of over 50 vol % MgO (50 vol % Ni-20Cr-17Al-1.0Y over the baseline bond coating) survived 1000 1-hour cycles without spalling. Coating thickness, however, was reduced about 50 percent by erosion or microspalling.

In a second series of Mach 0.3 burner rig tests, the lives of $1.8CaO.SiO_2$ and ZrO_2-8 wt % Y_2O_3 TBC's baseline bond coat exposed to Mach 0.3 Na plus V-doped combustion gases were about four times longer when the ceramic thickness was reduced from 0.038 to 0.013 cm (0.015 to 0.005 in.)(ref. 40). High Cr + Al, Ni-31Cr-11Al-0.5Y, and Ni-16Cr-13Al-0.4Y bond coatings improved the durability of calcium silicate (Ca_2SiO_4) and ZrO_2-8 wt % Y_2O_3 TBC's by approximately two to three times. Similarly, Co-22Cr-13Al-0.3Y and Co-20Cr-9Al-0.6Y bond coatings improved the durability of Ca_2SiO_4 TBC's by factors of approximately three times and two times, respectively. Results of these tests are summarized in figure 23.

Chemical and electron microprobe analyses supported the predictions of condensate compositions and their roles in inducing spalling of ZrO_2-8 wt % Y_2O_3 (fig. 24). Failure in the Ca_2SiO_4 coating involved condensation and penetration of Na, V, and cobalt (Co) containing condensates, calcium sulfate ($CaSO_4$) formation as a result of a gas-phase reaction with sulfur dioxide (SO_2), and the phase change from larnite (Ca_2SiO_4) to wollastonite ($CaSiO_3$).

Reaction studies. - In support of the burner rig tests, basic studies were conducted to determine how powdered zirconia-yttria, Ca_2SiO_4 (actual composition was $1.8CaO.SiO_2$) and the candidate coating material barium zirconate ($BaZrO_3$) react with powders of the potential combustion product compounds of major fuel and air impurities and with bond-coating elements (refs. 41 and 42). Equivalent amounts of each compound and thermal barrier powder were mixed and reacted in crimped platinum tubes; the reactions were monitored as a function of time by X-ray diffraction.

Based on the reactions at 1200° and 1400° C (2200° and 2550° F), the chemical compounds which were used to react with zirconia-yttria were divided into four distinct groups:

(1)   Compounds that did not react with zirconia-yttria: Na_2SO_4, K_2SO_4, Cr_2O_3, Al_2O_3 and NiO.

(2)   Compounds that reacted completely with zirconia-yttria: $CaCO_3$ (CaO), $BaCO_3$ (BaO), and $BaSO_4$.

(3)   Compounds that reacted preferentially with the monoclinic phase: Na_2CO_3 (Na_2O), K_2CO_3 (K_2O), $CoCO_3$ (CoO), Fe_2O_3, MgO, SiO_2, and ZnO.

(4)   Compounds that reacted preferentially with the cubic phase: V_2O_5, $(NH_4)_2HPO_4$ (P_2O_5).

The results of reactions of Ca_2SiO_4 and $BaZrO_3$ with essentially the same set of compounds are summarized as follows:

(1)   The impurities that reacted with $2CaO.SiO_2$ were Na_2O, BaO, MgO, CoO, Al_2O_3, Cr_2O_3, P_2O_5, and V_2O_5.

(2)   The impurities that did not react with $2CaO.SiO_2$ were Na_2SO_4, K_2O, K_2SO_4, NiO, ZnO, and Fe_2O_3.

(3)   The impurities that reacted with $BaZrO_3$ were Al_2O_3, Fe_2O_3, Cr_2O_3, SiO_2, P_2O_5, and V_2O_5.

(4)   The impurities that did not react with $BaZrO_3$ were Na_2O, Na_2SO_4, K_2O, K_2SO_4, MgO, CaO, CoO, and ZnO.

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no monovalent or divalent oxides and sulfates reacted with $BaZrO_3$. Similarly Ca_2SiO_4 was not affected by sulfates in these high-temperature reactions; however, it was attacked by Na, Ba, and Co oxides. Vanadium and P are impurities generally contained in industrial fuels, and their pentoxides reacted readily with zirconia-yttria, $BaZrO_3$, and Ca_2SiO_4.

Bond-coat optimization. - The work in this study was aimed at improving the oxidation and corrosion resistance of the bond coatings and the adherence of the TBC's (ref. 43). Three testing methods were used to evaluate bond coatings. Cyclic furnace tests were used to determine the durability of bond coatings alone (oxidation) and their performance as bond coatings in a TBC system (endurance). The third method of evaluation tested TBC systems on solid superalloy pin specimens in a Mach 0.3 burner rig.

In cyclic oxidation tests at 1100° C (2000° F), 14 bond coats were evaluated. Based on specific weight change data and post-test metallography results, the most oxidation resistant bond coatings for B-1900+Hf were Ni-14.0Cr-13.4Al-0.10Zr, Ni-14.3Cr-14.4Al-0.16Y, and Ni-15.8Cr-12.8Al-0.36Y. A typical set of oxidation curves is given in figure 25 for cyclic oxidation of bond coats on B1900+Hf at 1280 and 1370 K (1850° and 2000° F). For Mar M-509 the most oxidation resistant bond coating was Ni-30.9Cr-11.1Al-0.48Y.

In endurance testing at 1280 K (1850° F), 22 bond coats were evaluated on B1900+Hf and eight bond coats were evaluated on Mar M-509. The main criterion for evaluating TBC system performance (life) in endurance testing was the time to crack initiation in the TBC.

On B-1900+Hf the 0.010-cm(0.004-in.) thick Ni-15.8Cr-12.8Al-0.36Y and Ni-14.1Cr-13.4Al-0.10Zr bond coatings (plasma deposited at 11 kw with argon) appeared to significantly improve the life of the TBC relative to the reference Ni-16.2Cr-5.6Al-0.61Y bond coating. Although Ni-30.9Cr-11.1Al-0.48Y was characterized as a good oxidation resistant bond coating on Mar M-509, TBC life was shorter with this bond coating than life of a coating system with the reference bond coating.

In addition to the effect observed for compositional changes of the bond coatings, it became apparent that coating deposition parameters have a significant effect on the oxidation behavior of bond coats. It was found that the oxidation resistance of the bond coats was significantly improved by increasing the coating thickness from 0.010 to 0.015 cm (0.004 to 0.006 in.), the arc power from 11 to 20 kW, and the hydrogen concentration in the arc gas from 0 to 3.5 vol %. The effects of plasma arc power and H additions to the arc gas on the 1370 K (2000° F) oxidation behavior of a 0.015-cm(0.006-in.) thick Ni-15.8Cr-12.8Al-0.36Y bond coating on B-1900+Hf are shown in figure 26. Burner rig test results paralleled results of the furnace oxidation and endurance testing. Good bond coatings identified in oxidation and endurance testing gave superior results for TBC systems evaluated on solid superalloy pin specimens in burner rig tests (ref. 44). The effects of improved bond coat composition and processing on Mach 0.3 burner rig life are summarized in figure 27.

As a result of the TBC investigations in the CRT project, several coating systems had improved durability in the combustion environment of dirty fuels. Two of the coatings, ZrO_2-8 wt % Y_2O_3 and Ca_2SO_4, were used in the baseline systems specified for the "Advanced Ceramic Coating Development for Utility and Industrial Gas Turbines" development program, which is a part of the DOE-sponsored Advanced Conversion Technology (ACT) project.

While significant progress was made in advancing the state of the art in TBC technology for ground-based gas-turbine applications, results of the CRT investigations indicate that TBC's do not at this time have the potential for

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use in combustion gases containing impurities that can condense as a liquid. Likewise, condensed solids such as V or P compounds have the potential for reaction with current TBC materials and, as such, can degrade the coatings. Thus at their present state of development, TBC's should be considered for clean fuel applications only.

Technology evaluation studies. - In support of the research and technology activities on this project a system analyses effort was conducted at Lewis. Three studies were accomplished and the results are summarized herein.

Thermal-Barrier-Coating - Liquid-Cooling Study: The performance of steam- and water-cooled gas-turbine and steam-turbine combined cycles using TBC's on the gas-turbine airfoils is presented in reference 45. The results are compared with the performance of combined cycles using air-cooled turbines with and without TBC's.

The maximum combined cycle efficiency improvement using TBC's for the steam-cooled cases was 1.9 percentage points as the turbine inlet temperature was increased from 1480 to 1640 K (2200° to 2500° F) while maintaining the same airfoil metal temperatures (fig. 28). The maximum specific power increase was 32.4 percent when the turbine inlet temperature was increased from 1700 to 1950 K (2600° to 3050° F). For the water-cooled cases, the maximum efficiency increase was 2.2 percentage points at a turbine inlet temperature of 1960 K (3062° F), and the maximum specific power improvement was 36.6 percent when the turbine inlet temperature is increased from 1700 to 2000 K (2600° to 3150° F). The combined cycle performance gains were greater for the higher temperature cases since the cooling losses were much higher. The use of thermal barrier at these high temperatures yielded greater reductions in the cooling losses and, thus, greater performance improvements. Large temperature differences over 555 K (1000° F) across the thermal barriers at high temperatures indicate that large thermal stresses may present an obstacle to the implementation of TBC's on high-temperature gas turbines.

Thermal-Barrier-Coating - Low-Critical Alloy Study: The purpose of this study was to identify and quantify the potential cost savings that could result if the use of TBC's on gas-turbine hot section components decreased use of strategic alloys in these components.

As a result of certain geopolitical considerations, the cost of various "critical" materials has risen dramatically in the recent past. Figure 29 illustrates the price of Co, Cr, and tantalum over this time period. For example, it is estimated that the dramatic increase in cost of Co shown would increase the cost of a hypothetical 100-mW gas-turbine engine by about $450,000 (an increase of about 3 percent in the capital cost of the system). The cost of applying TBC to the cooled airfoils and combustor hardware would be somewhat less than this initially (about $150,000 in 1979 dollars), but periodic stripping and reapplication would be required. Over the lifetime of the turbine total costs would probably be about the same for either option. However, it may be advantageous to the nation to achieve invulnerability to the supply of critical materials without a cost penalty.

Fuel-Stack Temperature-Performance Study: The combined cycle performance gains obtained by using TBC's in gas-turbine blades was investigated and previously summarized (ref. 45). In addition to improving performance, another potential benefit of using TBC's is that the coating could serve as a corrosion protection for the airfoils and allow the use of lower cost, higher sulfur (S) content fuels. The use of fuels containing S, however, would require that the cold-end heat exchanger surface and exhaust stack gas temperatures be kept above the sulfuric acid condensation temperatures. Sulfur in the fuel results in acid formation which would then require a higher stack

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inlet temperature as compared with low S fuel. Raising the exhaust stack gas temperature would result in lower combined cycle efficiency compared with a combined cycle system burning a S-free fuel. The performance calculations in reference 45 did not take into account the use of fuel oils containing S and the corresponding efficiency losses previously described.

The effect on combined cycle performance of constraining the stack gas temperatures to levels high enough to avoid acid corrosion when burning high S content fuels was studied and the results are presented in reference 46 and summarized herein. Combined cycle performance calculations were made assuming first a S-free fuel and then a fuel with 0.8 percent S by weight. The maximum difference was less than one percentage point in efficiency. TBC's may, therefore, permit the use of the minimally processed (and hence less expensive) fuels which contain S in gas turbines with an increase in efficiency. Without a TBC, the use of a minimally processed fuel could require a reduction in gas turbine inlet temperature to achieve acceptable corrosion life and, hence, a reduction in efficiency.

SUMMARY OF RESULTS

The Critical Research and Advanced Technology Support Project performed research and technology associated with coal-derived fuel combustors and materials development for utility and industrial gas turbines. Three annual reports for the fiscal periods of 1978, 1979, and 1980 were published which covered the development activities during these time periods. Technical reports documenting results obtained in the various technical areas investigated were also published. This report summarizes the technical accomplishments attained in the overall study. Significant results of this project include the following:

Combustion Studies

(1) A preliminary (issued in 1980) and final (issued in 1982) "Literature Survey of Properties of Synfuels Derived from Coal" have been completed. These documentations of existing data on the physical, chemical, and elemental composition and structural characteristics of the synthetic fuels were accepted by industry as important contributions.

(2) A combustor emissions model was generated by modifying the NASA Lewis General Chemical Kinetics Program to perform two-stage, adiabatic, perfectly stirred model computations. This model closely approximated results obtained in the combustion of synthetic fuels and successfully predicted the effects of two-stage (rich-lean) operating conditions and geometry on the conversion of fuel bound nitrogen to NO_x and on the formation of CO.

(3) Two-stage, rich-lean, flametube tests were successfully conducted to evaluate techniques for minimizing the conversion of fuel-bound nitrogen to nitric oxides in a premixed, homogeneous combustion system. Simulated coal-derived liquid fuels and distillates of a coal syncrude produced by the SRC-II process were tested. Optimum primary equivalence ratios (for minimum NO_x formations) ranged from 1.4 to 1.7. The optimum secondary equivalence ratio was about 0.5. Results of this study were used extensively to guide major contractual combustor development efforts being performed in the DOE-NASA Advanced Conversion Technology Project.

(4) A sector rig (intermediate combustor development between flametube and actual production hardware) experiment was fabricated and tested. The

test section embodied variable air orifices for maintaining primary and secondary zone equivalence ratio control (to accommodate a wide power range) and steam cooling of the primary zone combustor liner. Operation of the test section demonstrated that variable geometry could be used to control the airflow into the primary and secondary combustor zones (and thus the equivalence ratios) over a wide operating range, and that steam cooling of a rich-burn primary combustor liner can increase the durability of the liner at a minimal cost in energy. Two patent disclosures resulted from this test program: A "Steam-Cooled, Rich-Burn Combustor Liner" and an "Igniter Seal for Rich-Burn Combustor Liner."

(5) Catalytic combustion testing of residual fuels were conducted both in-house at Lewis and under contract. Results of the residual fuel tests identified (1) the need to maintain a high degree of fuel vaporization and a high duct-wall temperature upstream of the catalyst above 810 K (1000° F) to prevent the accumulation and periodic ignition of fuel on the duct wall and (2) the beneficial use of graded-cell reactors (low density of honeycomb channels at the reactor inlet and higher density at the exit). Oxides of nitrogen (NO_x) emissions for these tests were within the EPA-proposed standard of 125 ppm for fuels with more than 0.25 percent nitrogen, and combustion efficiencies in excess of 99 percent were attained. Although residual fuels can be burned in a catalytic reactor, operational problems such as the tendency of the fuel to burn in the premixing duct and fuel injector plugging make this concept unattractive at the current state of development.

(6) The catalytic combustion of coal-derived liquids was conducted in-house at Lewis. Three cuts of SRC-II fuels - naptha, mid-distillate, and a midheavy blend - were tested and performance was compared to the Number 2 diesel fuel operation. The tests were relatively successful in that high combustion efficiencies were attained. However, some plugging of the honeycomb reactor inlet was encountered and NO_x emissions exceeded the Environmental Protection Agency gas-turbine standard for fuels containing greater than 0.25 fuel-bound nitrogen. Thus, the development of a practical catalytic combustor operating on coal-derived liquid fuels is dependent on the resolution of the high NO_x emission problem which results from the high fuel-bound nitrogen content of the fuel.

(7) Coal-derived gaseous fuel catalytic combustion investigations were conducted under contract at existing coal-gasifier sites. The test ducts used uniform small honeycomb channels throughout the reactor length. Ignition occurred readily with no igniter, combustion was stable and for combustion temperatures in the range of 1370 to 1420 K (2000° to 2100° F) there was almost no unburnt hydrocarbons, and combustion efficiencies approached 100 percent for both the low and medium Btu gases. Oxides of nitrogen emission levels from combustion of the oxygen-blown gases were typically in the 10- to 20-ppm range, whereas those from the airblown low Btu gas system were above the allowable Environmental Protection Agency level of 75 ppm for fuels with no fuel-bound nitrogen. This latter condition resulted from an operational procedure in the gasifier system which permitted the recirculation of wash water containing ammonia to conserve cycle energy. As a result of these tests it can be concluded that the catalytic combustion of coal-derived gases is a viable concept.

(8) A 1000-hour endurance test of a catalytic combustor reactor was conducted under contract at 5 atm pressure burning Number 2 fuel oil. Some deterioration of performance occurred; however, performance recovered after the catalyst was exposed to air at high temperature and combustor operation continued. Test results indicate that currently available catalysts have the

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potential for acceptable steady-state operation at stationary gas-turbine conditions. Additional endurance testing at design and off-design conditions and thermal cycling are required to better define this system.

Long-Life Materials

(1) A hot corrosion model was developed to predict the corrosion attack of turbine airfoil alloys as a function of coal-derived liquid fuel trace element impurities (Na, K, Ca, Mg and Cl) and of temperature and exposure time. The model is capable of predicting first-order corrosion effects and, as such, should be sufficient for qualitative estimates of the degree of corrosion severity to be expected from the impurities in future synthetic fuels. This model was based on doped fuel materials corrosion testing at Lewis.

(2) Fuel additives were investigated as a means of controlling the hot corrosion of typical turbine airfoil materials. The use of barium (or strontium) salt to react with sulfur in the fuel was identified as an effective inhibitor of hot corrosion. An intermittent application of the salt (added to the fuel or injected into the combustor) was found to effectively reduce the amount of barium sulfate deposition while maintaining an inhibitor effect to hot corrosion.

(3) Actual fuel tests using SRC-II naptha and a diesel fuel oil-micronized coal mixture were conducted at Lewis. Both fuels caused excessive deposition and fouling of turbine airfoils but, as predicted by the hot corrosion model, verified that limited potential for hot corrosion exists for these fuels.

(4) The Lewis Complex Chemical Equilibrium Calculation Program was used to predict the chemical composition and dewpoints of deposits formed from major metallic impurities in SRC-II fuels. Four cuts of the fuel were analyzed and tested, and agreement between the predicted and observed compounds was excellent. Program predictions and burner rig deposition experiments revealed that fouling of turbine parts by deposits composed of trace metal compounds could be a problem when using coal-derived fuels.

(5) The potential for turbine airfoil cooling hole plugging from impurities contained in a typical SRC-light organic liquid was determined by doping a clean fuel and combusting in a Mach 0.3 burner rig at atmospheric pressures. Results of the tests indicate that plugging of the film-cooling holes with deposits from a typical SRC fuel is likely to be a problem and high-cooling airflow rates are required to keep the air passages free.

(6) Advanced Thermal Barrier Coating behavior in a corrosive environment was investigated. Various levels of sodium and vanadium were introduced into the combustor as aqueous salt solutions. Coating durability was affected by inorganic salt deposits which initiated cracks in the ceramic layer parallel to the ceramic bond-coat interface and resulted in spalling of the thermal barrier coating. This reaction to the salt deposits was associated with the dewpoints and melting points of the condensates and the temperature distributions within the coatings. The NASA Lewis Complex Chemical Equilibrium Computer Program was used to identify the anticipated deposition compounds. The dewpoints and melting points were determined and were then related to the observed failure modes of the coated specimens. The most severe conditions to which the coatings could be exposed were expected to be those where a corrosive liquid is condensed on and permeates the coating.

(7) A number of thermal barrier coatings were identified as being more spall resistant. A ZrO_2-8 wt % Y_2O_3/NiCrAlY system lasted more than five times longer than the standard system, ZrO_2-12 wt % Y_2O_3/NiCrAlY.

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Two other coating systems, calcium silicate-1.8CaO-SiO$_2$/NiCrAlY and a cermet 50-vol % MgO-50 vol % NiCrAlY/NiCrAlY, displayed further improvements in life. The cermet coating varied in reaction to the contaminants, and continuous thinning by microspalling was observed. The CaSiO$_4$ coating system was selected for an IR-100 award because of its uniqueness in being an alkali earth silicate, and because of its durability in a hot corrosive environment.

(8)   The durability of duplex thermal barrier coating systems substantially increased when the oxide thickness was decreased. Lifetimes were increased from two to four times. The lessening of coating thickness would, however, diminish the insulating value of the coating and increase the heat loss to the airfoil coolant.

(9)   Basic studies were conducted to determine the reactivity of thermal barrier coating materials with various fuel impurities and candidate bond-coat materials. Potentially benign and harmful reactions were identified and an understanding of the basic material reactions at the planned service conditions was gained.

(10)   Bond-coat optimization studies were undertaken to improve the oxidation and corrosion resistance of the bond coatings and the adherence of the thermal barrier coatings. Several improved bond coatings were identified and evaluated. Improvements in the thermal barrier coating systems resulted from increased bond coating thickness, controlling the yttrium content of the coatings, providing sufficient surface roughness of the bond coat to obtain better adherence of the thermal barrier coating, and modifying the plasma-spraying parameters to include higher power levels and a modified cover gas containing 3.5 percent hydrogen.

(11)   A study was conducted in support of the thermal barrier coating development task to investigate the effect on the performance of advanced steam- and water-cooled gas turbines in combined cycle applications when thermal barrier coatings are used. For the water-cooled cases, the maximum combined cycle efficiency increase was 2.2 percent for a turbine inlet temperature (TIT) of 1960 K (3062° F) and a thermal barrier coating thickness of 0.076 cm (0.030 in.) as compared with no thermal barrier coating at the same TIT. The maximum specific power improvement was calculated as 37 percent when the TIT was increased from 1720 to 2000 K (2639° to 3150° F). Metal substrate temperature was limited to 810 K (1000° F) for this analysis.

(12)   A preliminary study was undertaken to identify and quantify the potential cost savings that could result if thermal barrier coatings on gas-turbine hot section components decreased use of strategic alloys in these components. Results of the study indicate that today's turbine hot section component costs are comparable to costs associated with using thermal barrier coatings on nonstrategic materials and providing for the periodic stripping and reapplication of the coatings. It may be advantageous to the nation to develop this capability and thus decrease vulnerability to outside influences.

CRT PUBLICATIONS AND PRESENTATIONS

Zaplatynsky, Isidor: Reactions of Yttria-Stabilized Zirconia with Oxides and Sulfates of Various Elements.   DOE/NASA/2593-78/1, NASA TM-78942, July 1978.

Deadmore, Daniel L. and Lowell, Carl E.:   Inhibition of Hot Salt Corrosion by Metallic Additives.   DOE/NASA/2593-78/2, NASA TM-78966, July 1978.

Hodge, Philip E., et al.: Thermal Barrier Coatings: Burner Rig Hot Corrosion
Test Results. Journal of Materials for Energy Systems Vol. 1, No. 4, March
1980, pp. 47-58, also DOE/NASA/2593-78/3, NASA TM-79005, 1982.

Nainiger, Joseph J.: Effect of Thermal Barrier Coatings on the Performance of
Steam- and Water-Cooled Gas Turbine/Steam Turbine Combined Cycle Systems.
DOE/NASA/2593-78/4, NASA TM-79057, December 1978.

Deadmore, Daniel L. and Lowell, Carl E.: Airfoil Cooling Hole Plugging by
Combustion Gas Impurities of the Type Found in Coal Derived Fuels.
DOE/NASA/2593-79/1, NASA TM-79076, February 1979.

Lowell, Carl E., Sidik, Steven M. and Deadmore, Daniel L.: Effect of Sodium,
Potassium, Magnesium, Calcium and Chlorine on the High Temperature Corrosion
of IN-100, U-700, IN-792, and MAR M 509. DOE/NASA/2593-79/12, NASA TM-79309.
Prepared for 25th Annual International Gas Turbine Conference Sponsored by the
American Society of Mechanical Engineers, New Orleans, Louisiana, March 9-13,
1980.

Miller, Robert A.: Analysis of the Response of a Thermal Barrier Coating to
Sodium- and Vanadium-Doped Combustion Gases. DOE/NASA/2593-79/7, NASA
TM-79205, June 1979. Presented at 8th Midwest High Temperature Chemistry
Conference, Milwaukee, Wisconsin, June 4-6, 1979.

Clark, John S., Lowell, Carl E., Niedzwiecki, Richard W., and Nainiger,
Joseph J.: Gas-Turbine Critical Research and Advanced Technology Support
Project: FY 1979 Annual Report. DOE/NASA/2593-79/6, NASA TM-79139, June 1979.

Fairbanks, J. W., Levine, S. R. and Cohn, A.: Ceramic Coating Program
Overview. Presented at DOE/EPRI Conference on Advanced Materials for
Alternate Fuel Capable Directly Fired Heat Engines, July 30 - August 3, 1979.

Levine, S. R., Hodge, P. E. and Miller, R. A.: NASA Progress on Ceramic
Coatings for Industrial/Utility Gas Turbines. Presented at DOE/EPRI
Conference on Advanced Materials for Alternate Fuel Capable Directly Fired
Heat Engines, DOE CONF-790749, December 1979, pp. 667-679, July 30 - August 3,
1979, Castine, Maine.

Zaplatynsky, Isidor: Reactions of Calcium Orthosilicate and Barium Zirconate
with Oxides and Sulfates of Various Elements. DOE/NASA/2593-79/9, NASA
TM-79272, October 1979.

Bittker, David A.: An Analytical Study of NO_x and Carbon Monoxide Emissions
in Hydrocarbon Combustion with Added Nitrogen - Preliminary Results. ASME
Paper 80-GT-60, March 1980, also DOE/NASA/2593-79/10, NASA TM-79296, 1979.

Clark, John S., et al.: Gas Turbine Critical Research and Advanced Technology
Support Project: FY 1978 Annual Report. DOE/NASA/2593-79/6, NASA TM-79139,
1979.

Clark, John S.: Status of the DOE/NASA Critical Gas Turbine R and T Project.
ASME 80-GT-104, March 1980; also DOE/NASA/2593-79/11, NASA TM-79307, 1980.

Deadmore, Daniel L. and Lowell, Carl E.: Effects of Impurities in Coal-Derived Liquids on Accelerated Hot Corrosion of Superalloys. DOE/NASA/2593-79/13, NASA TM-81384, March 1980.

Deadmore, D. L. and Lowell, C. E.: Fouling and the Inhibition of Salt Corrosion. DOE/NASA/2593-80/14, NASA TM-81469, April 1980.

Gedwill, Michael A.: Improved Bond Coatings for use with Thermal Barrier Coatings. DOE/NASA/2593-18, NASA TM-81567, September 1980.

Hodge, P. E., Miller, R. A. and Gedwill, M. A.: Evaluation of Hot Corrosion Behavior of Thermal Barrier Coatings. DOE/NASA/2593-16, NASA TM-81520, 1980. Presented at the International Conference on Metallurgical Coatings Sponsored by the American Vacuum Society, San Diego, California, April 21-25, 1980. Thin Solid Films, 73 (1980) pp. 447-453.

Olsen, B. A., et al.: Durability Testing at 5 Atmospheres of Advanced Catalysts and Catalyst Support for Gas Turbine Engine Combustors. DOE/NASA/9416-80/2, NASA CR-159839, April 1980.

Schultz, D. and Wolfbrandt, G.: Flame Tube Parametric Studies for Control of Fuel Bound Nitrogen Using Rich-Lean Two-Stage Combustion. DOE/NASA/2593-80/15, NASA TM-81472, April 1980.

Nainiger, J. J.: Effect on Combined Cycle Efficiency of Stack Gas Temperature Constraints to Avoid Acid Corrosion. DOE/NASA/2593-17, NASA TM-81531, July 1980.

Santoro, G., et al.: Deposition and Material Response from Mach 0.3 Burner Rig Combustion of SRC-II Fuels. DOE/NASA/2593-20, TM-81834, October 1980.

Reynolds, Thaine W., Niedzwiecki, Richard W. and Clark, John S.: Literature Survey of Properties of Synfuels Derived from Coal. DOE/NASA/2593-79/8, NASA TM-79243, 1980.

Osgerby, I. T.: CATCOM Catalyst 5 atm 1000 Hour Aging Study Using #2 Fuel Oil, presented at the 4th Workshop on Catalytic Combustion, sponsored by the U. S. Environmental Protection Agency, Cincinnati, Ohio, May 14-15, 1980.

Rosfjord, T. J.: Catalytic Combustion of Heavy Partially-Vaporized Fuels, presented at the 4th Workshop on Catalytic Combustion, sponsored by the U. S. Environmental Protection Agency, Cincinnati, Ohio, May 14-15, 1980.

Clark, John S., et al.: Gas Turbine Critical Research and Advanced Technology Support Project: FY 1979 Annual Report. DOE/NASA/2593-24, NASA TM-81708, March 1981.

Bittker, D. A. and Wolfbrandt, G.: Effect of Fuel Nitrogen and Hydrogen Content on Emissions in Hydrocarbon Combustion. DOE/NASA/10350-19, NASA TM-81612, March 1982, also ASME Paper 82-GT-63.

Santoro, G. J., Calfo, F. D. and Kohl, F. J.: Material Response from Mach 0.3 Burner Rig Combustion of a Coal-Oil Mixture. DOE/NASA/2593-23, NASA TM-81686, June 1981.

27

Gedwill, Michael A.: Burner Rig Evaluation of Thermal Barrier Coating Systems for Nickel-Base Alloys. DOE/NASA/2593-26, NASA TM-81685, February 1981.

Lowell, C. E., et al.: The Effects of Trace Impurities in Coal-Derived Liquid Fuels of Deposition and Accelerated High Temperature Corrosion of Cast Superalloys. DOE/NASA/2593-22, NASA TM-81678, March 1981.

Rosfjord, Thomas J.: Catalytic Combustion with Incompletely Vaporized Residual Fuel. DOE/NASA/0152-1, NASA CR-165161, UTRC R81-914724-18, March 1981.

Stearns, Carl A. and Kohl, Fred J.: Combustion System Processes Leading to Corrosive Deposits. DOE/NASA/2593-27, NASA TM-81752, March 1981.

Hodge, Phillip E., et al.: Review of NASA Progress in Thermal Barrier Coatings for Stationary Gas Turbines. DOE/NASA/2593-25, NASA TM-81716, March 1981.

Lowell, C. E., Sidik, S. M. and Deadmore, D. L.: High Temperature Alkali Corrosion in High Velocity Gases. DOE/NASA/2593-28, NASA TM-82591, May 1981.

Dodds, W. J. and Ekstedt, E. E.: Demonstration of Catalytic Combustion with Residual Fuel. DOE/NASA/0155-1, NASA CR-165369, August 1981.

Flores, Francisco J.: Summary of a Literature Survey of Properties of Synfuels Derived from Coal, presented at the ASTM Symposium on Alternate Fuels and Future Fuels Specifications for Stationary Gas Turbine Applications in Phoenix, Arizona in December 1981. To be published in ASTM Special Technical Publication "Alternative Fuels and Future Fuel Specifications. ASTM No. to be assigned.

Schwab, John: Low and Medium Btu Coal Gas Catalytic Combustor Characterization. Westinghouse Final Report, DOE/NASA/0277-1, NASA CR-165560, 1981.

Bulzan, D. L., and Tacina, R. R.: Catalytic Combustion of Coal-Derived Liquids. DOE/NASA 10350-21, NASA TM-81594, March 1981. Presented at the 26th Annual ASME International Gas Turbine Conference, Houston, Texas, March 8-12, 1981.

Bulzan, D. L., and Tacina, R. R.: Catalytic Combustion of Residual Fuels. DOE/NASA 10350-29, NASA TM-82731, September 1981. Presented at the 5th Workshop on Catalytic Combustion, sponsored by the U.S. Environmental Protection Agency, San Antonio, Texas, September 15-16, 1981.

Dodds, Willard J.: Demonstration of Catalytic Combustion with Residual Fuel. Presented at the 5th Workshop on Catalytic Combustion, sponsored by the U.S. Environmental Protection Agency, San Antonio, Texas, September 15-16, 1981.

Rosfjord, T. J.: Investigation of Partially-Vaporized Residual Oil Catalytic Combustion. Presented at the 5th Workshop on Catalytic Combustion, sponsored by the U.S. Environmental Protection Agency, San Antonio, Texas, September 15-16, 1981.

Flores, Francisco J.: Literature Survey of Properties of Synfuels Derived from Coal. DOE/NASA/10350-30, NASA TM-82739, 1982.

Schultz, Donald F.: Summary of Synfuel Characterization and Combustor Studies. DOE/NASA/10350-36, NASA TM-83066, 1983.

Schultz, Donald F.: Techniques for Enhancing Durability and Equivalence Ratio Control in a Rich-Lean, Three Stage, Ground Power Gas Turbine Combustor. DOE/NASA/10350-33, NASA TM-82922, 1982. Presented at the IEEE-ASME Joint Power Generation Conference, October 1982

Shisler, Roger, and Blanton, John: Evaluation of Catalytic Combustion of Actual Coal-Derived Gas. General Electric Final Report, DOE/NASA/2818-1, NASA CR-167842, 1982

Hodge, Phillip E.: Effect of Fuel-to-Air Ratio on Mach 0.3 Burner Rig Hot Corrosion of ZrO_2-Y_2O_3 Thermal Barrier Coatings. DOE/NASA/10350-32, NASA TM-82879, 1982.

Furman, Edward R., et al.: Gas Turbine Critical Research and Advanced Technology Support Project: FY 1980 Annual Report. DOE/NASA/10350-31, NASA TM-82872, 1982.

Bulzan, Daniel L.: Catalytic Combustion of Low and Medium Heating Value Gases. Presented at the IEEE-ASME Joint Power Conference in Denver, CO, October 17-21, 1982.

REFERENCES

1. Reynolds, T. W.; Niedzwiecki, R. W.; and Clark, J. S.: Literature Survey of Properties of Synfuels Derived from Coal. DOE/NASA/2593-79-8, NASA TM-79243, Feb. 1980.
2. Flores, F. J.: Literature Survey of Properties of Synfuels Derived from Coal. DOE/NASA 10350-30, NASA TM-82739, Aug. 1982.
3. Schultz, D. F.; and Wolfbrandt, G.: Flame Tube Parametric Studies for Control of Fuel Bound Nitrogen Using Rich-Lean Two-Stage Combustion. DOE/NASA/2593-80/15, NASA TM-81472, Apr. 1980.
4. Bittker, D. A.: An Analytical Study of Nitrogen Oxides and Carbon Monoxide Emissions in Hydrocarbon Combustion with Added Nitrogen - Preliminary Results. DOE/NASA/2593-79/10, NASA TM-79296, 1979.
5. Bittker, D. A.; and Wolfbrandt, G.: Effect of Fuel Nitrogen and Hydrogen Content on Emissions in Hydrocarbon Combustion. DOE/NASA/10350-19, NASA TM-81612, Mar. 1981.
6. Schultz, D. F.: Summary of Synfuel Characterization and Combustor Studies. DOE/NASA/10350-36, NASA TM-83066, 1983.
7. Kesselring, J. P.: Proceedings: Third Workshop on Catalytic Combustion. EPA-600/7-79-038, Feb. 1979.
8. Kesselring, J. P.: Proceedings: Fourth Workshop on Catalytic Combustion. EPA-600/9-80-035, Aug. 1980.
9. Heck, R. M.; et al.: Durability Testing at One Atmosphere of Advanced Catalysts and Catalyst Supports for Automotive Gas Turbine Engine Combustors. (CONS-9416-1, Engelhard Minerals and Chemical Corp.; NASA Contract NAS3-19416.) NASA CR-135132, June 1977.

10. Osgerby, I. T.: Catalytically Supported Thermal Combustion of Coal-Derived Low-Btu Gas. FE-2683-T1-PT-1, Engelhard Minerals and Chemical Corp., 1979.

11. Tong, H.; Chu, E. K.; and Snow, G. C.: Catalytic Combustion of Alternative Fuels. 4th Workshop on Catalytic Combustion, J. P. Kesselring, ed., EPA 600/9-80-035, 1980, pp. 491-515.

12. DeCorso, S. M.; et al.: Catalysts for Gas Turbine Combustors-Experimental Test Results. ASME Paper No. 76-GT-4, Mar. 1976.

13. Olson, B. A.; et al.: Durability Testing at 5 Atmospheres of Advanced Catalysts and Catalyst Supports for Gas Turbine Engine Combustors. DOE/NASA/9416-80/2, NASA CR-159839, Apr. 1980.

14. Bulzan, D. L.; and Tacina, R. R.: Catalytic Combusion of Residual Fuels. NASA TM-82731, Sept. 1981.

15. Rosfjord, T. J.: Catalytic Combustion with Incompletely Vaporized Residual Fuel. (OTRC-R81-914/24-18, United Technologies Research Center; NASA Contract DEN3-152.) NASA CR-165161, Mar. 1981.

16. Dodds, W. J.; and Ekstedt, E. E.: Demonstration of Catalytic Combustion with Residual Fuel. (R81AEG590, General Electric Co.; NASA Contract DEN3-155.) NASA CR-165369, Aug. 1981.

17. Bulzan, D. L.; and Tacina, R. R.: Catalytic Combustion of Coal-Derived Liquids. DOE/NASA/10350-21, NASA TM-81594, March 1981.

18. Schwab, J.: Low- and Medium-Heating Value Coal Gas Catalytic Combustor Characterization. DOE/NASA/0277-1, NASA CR-165560, Nov. 1981.

19. Blanton, J. C.; and Shisler, R. A.: Evaluation of Catalytic Combustion of Actual Coal-Derived Gas. General Electric Final Report, DOE/NASA/2818-1, NASA CR-167842, 1982.

20. Lowell, C. E.; Sidik, S. M.; and Deadmore, D. L.: Effect of Sodium, Potassium, Magnesium, Calcium, and Chlorine on the High Temperature Corrosion of IN-100, U-700, IN-792, and MAR M-509. DOE/NASA/2593-79/12, NASA TM-79309, ASME Paper 80-GT-150, 1980.

21. Lowell, C. E.; Sidik, S. M.; and Deadmore, D. L.: High Temperature Alkali Corrosion in High Velocity Gases. DOE/NASA/2593-26, NASA TM-82591, May 1981.

22. Deadmore, D. L.; and Lowell, C. E.: Effects of Impurities in Coal-Derived Liquids on Accelerated Hot Corrosion of Superalloys. DOE/NASA/2593-79/13, NASA TM-81384, Mar. 1980.

23. Santoro, G. J.; et al: Deposition and Material Response from Mach 0.3 Burner Rig Combustion of SRC-II Fuels. DOE/NASA/2593-20, NASA TM-81634, Oct. 1980.

24. Santoro, G. L.; Calfo, F. D.; and Kohl, F. J.: Material Response from Mach 0.3 Burner Rig Combustion of a Coal-Oil Mixture. DOE/NASA/2593-23, NASA TM-81686, June 1981.

25. Deadmore, D. L.; and Lowell, C. E.: Inhibition of Hot Salt Corrosion by Metallic Additives. DOE/NASA/2593-78/2, NASA TM-78966, July 1978.

26. Deadmore, D. L.; and Lowell, C. E.: Fouling and the Inhibition of Salt Corrosion. DOE/NASA/2593-80/14, NASA TM-81469, Apr. 1980.

27. Deadmore, D. L.; and Lowell, C. E.: Airfoil Cooling Hole Plugging by Combustion Gas Impurities of the Type Found in Coal-Derived Fuels. DOE/NASA/2593-79/1, NASA TM-79076, Feb. 1979.

28. Deadmore, D. L.; and Lowell, C. E.: Plugging of Cooling Holes in Film-Cooled Turbine Vanes. NASA TM-X-73661, Apr. 1977.

29. Stecura, S.: Two-Layer Thermal Barrier Coating for High Temperature Components. Am. Ceramic Soc. Bull., vol. 56, no. 12, 1977, pp. 1082-1089.

30. Stecura, S.: Effects of Compositional Changes on the Performance of a Thermal Barrier Coating System. NASA TM-78976, Aug. 1978.

31. Stecura, S.: Effects of Yttrium, Aluminum and Chromium Concentrations in Bond Coatings on the Performance of Zirconia-Yttria Thermal Barriers. NASA TM-79206, July 1979.

32. Amos, D. J.: Analytical Investigation of Thermal Barrier Coatings on Advanced Power Generation Gas Turbine Engines. (EM-1636, Westinghouse Electric Corp.; NASA Contract NAS3-19407.) NASA CR-135146, Mar. 1977.

33. Clark, J. S.; and Nainiger, J. J.: Potential Benefits of a Ceramic Thermal Barrier Coating on a Large Power Generation Gas Turbine. ERDA/NASA-5022/77/1, NASA TM-73712, 1977.

34. Carlson, N.; and Stoner, B. L.: Thermal Barrier Coating on High Temperature Industrial Gas Turbine Engines. (PSD-R-109, United Technologies Corp.; NASA Contract NAS3-20067.) NASA CR-135147, Feb. 1977.

35. Hodge, P. E., et al.: Thermal Barrier Coatings: Burner Rig Hot Corrosion Test Results. DOE/NASA/2593-78/3, NASA TM-79005, Oct. 1978.

36. Levine, S. R.: Adhesive/Cohesive Strength of ZrO_2-12w/oY_2O_3/NiCrAlY Thermal Barrier Coating. NASA TM-73792, 1978.

37. Miller, R. A.: Analysis of the Response of a Thermal Barrier Coating to Sodium- and Vanadium-Doped Combustion Gases. DOE/NASA/2593-79/7, NASA TM-79205, June 1979.

38. Bratton, R. J.; Singhal, S. C.; and Lee, S. Y.: Ceramic Turbine Components Research and Development, Part II - Evaluation of MCrAlY/ZrO_2 (Y_2O_3) Thermal Barrier Coatings Exposed to Simulated Turbine Environments. EPRI-RP-421-1, 1978.

39. Dapkunas, S. J.; and Clarke, R. L.: Evaluation of the Hot-Corrosion Behavior of Thermal Barrier Coatings. NSRCD-4428, Naval Ship Research and Development Center, Nov. 1974 (AD-A000093).

40. Hodge, P. E.; Miller, R. A.; and Gedwill, M. A.: Evaluation of the Hot Corrosion Behavior of Thermal Barrier Coatings. DOE/NASA/2593-16, NASA TM-81520, Apr. 1980.

41. Zaplatynsky, I.: Reactions of Yttria-Stabilized Zirconia with Oxides and Sulfates of Various Elements. DOE/NASA/2593-78/1, NASA TM-78942, July 1978.

42. Zaplatynsky, I.: Reactions of Calcium Orthosilicate and Barium Zirconate with Oxides and Sulfates of Various Elements. DOE/NASA/2593-79/9, NASA TM-79272, Oct. 1979.

43. Gedwill, M. A.: Improved Bond Coatings for Use with Thermal Barrier Coatings. DOE/NASA/2593-18, NASA TM-81567, Sept. 1980.

44. Gedwill, M. A.: Burner Rig Evaluation of Thermal Barrier Coating Systems for Nickel-Base Alloys. DOE/NASA/2593-26, NASA TM-81684, Feb. 1981.

45. Nainiger, J. J.: Effect of Thermal Barrier Coatings on the Performance of Steam- and Water-Cooled Gas Turbine/Steam Turbine Combined Cycle Systems. DOE/NASA/2593-78/4, NASA TM-79057, Dec. 1978.

46. Nainiger, J. J.: Effect on Combined Cycle Efficiency of Stack Gas Temperature Constraints to Avoid Acid Corrosion. DOE/NASA/2593-17, NASA TM-81531, July 1980.

TABLE I. – DEPOSITION AND MATERIAL RESPONSE FROM MACH 0.3 BURNER RIG

COMBUSTION OF SRC-11 FUELS

[Comparison of predicted and actual deposit compositions.]

	Fuel type			
	Naphtha	Light oil	Wash solvent	Middle-to-heavy distillate blend
Major deposit phases predicted to form (based on trace element chemical analysis of fuel)[b]	$Cu_2O(s)$[a] $CuO(s)$ $NiFe_2O_4(m)$ $Fe_2O_3(m)$	$Fe_2O_3(s)$	$Fe_2O_3(s)$	$Fe_2O_3(s)$ $Cr_2O_3(m)$
Actual deposit collected (identified by X-ray diffraction)[b]	$CuO(s)$ $(Cu,Ni,Zn)Fe_2O_4(s)$ $(Cu_{0.2}Ni_{0.8})O(m)$	$Fe_2O_3(s)$	$Fe_2O_3(s)$ $Fe_3O_4(s)$	$Fe_2O_3(s)$

[a]All solvent-refined coal liquids (SRC-11).
[b]s, strong; m, medium.

TABLE II. — HOLE-PLUGGING CONDITIONS AND RESULTS

(a) Dopant compositions in ppm by weight of combustion products

Element	Dopant A	Dopant B
Fe	2.0	2.0
Pb	.05	.05
Ca	.1	.1
Na	.5	.5
K	.1	.1
P	----	.5

(b) Run Summary

Number	Flame temperature[a]		Dopant	$\dfrac{(\rho V)_C}{(\rho V)_H}$ (b)	Leading edge temperature changes, K	$\dfrac{\text{Total cooling flow}}{\text{Flame temperature}}$
	K	°F				
SH-1	1573	2374	A	1.0	72±10	11×10^{-5}
SH-2	1823	2822	A	2.3	11	27
SH-3	2073	3272	A	3.8	28	40
SH-3A	1373	2012	B	.4	39	4
SH-1A	1493	2228	B	.9	89	9
SH-4	1573	2374	B	1.0	111	11
SH-5	1823	2822	B	2.3	56	24

[a] Measured with a sonic velocity thermocouple probe.
[b] ρ, density; V, velocity; C, cooling air; H, combustion gases.

TABLE III. – RELATION BETWEEN CONDENSATE DEW AND MELTING POINTS

AND $ZrO_2 \cdot 12$ Y_2O_3/NiCrAlY PERFORMANCE

Dopant level (referred to fuel)	Predicted condensate	Dew point, T_{dp}, °C	Melting point, T_{mp}, °C	Condensate location	Cycles to coating failure and failure location
5 ppm Na	$Na_2SO_4(\ell)$	920	884	$T_s > T_{dp} > T_{mp} > T_{bc}$	92, out of hot zone
0.5 ppm Na	$Na_2SO_4(s)$	845	884	$T_s > T_{mp} > T_{bc} > T_{dp}$	1300
2 ppm V	$V_2O_5(\ell)$	1210	670	$T_{dp} > T_s > T_{bc} > T_{mp}$	25, hot zone
0.2 ppm V	$V_2O_5(\ell)$	1125	670	$T_{dp} > T_s > T_{bc} > T_{mp}$	200, hot zone
5 ppm Na + 2 ppm V	$V_2O_5(\ell)$	1210	670	-------------------	
	$Na_2V_2O_6(\ell)$	~1155	627	$T_{dp} > T_s > T_{bc} > T_{mp}$	43, hot and cold zone
	$Na_2SO_4(\ell)$	~910	884	$T_s > T_{dp} > T_{mp} > T_{bc}$	
	$V_2O_5(s)$	575	670	-------------------	

Note: Mach 0.3 burner rig, fuel/air ratio 0.042; specimen temperatures: 980° C surface (T_{surf}), 850° C bond coat/ceramic interface (T_{bc}) in the hot zone; 890° C surface, 760° C bond coat/ceramic interface at tip and root of test specimen.
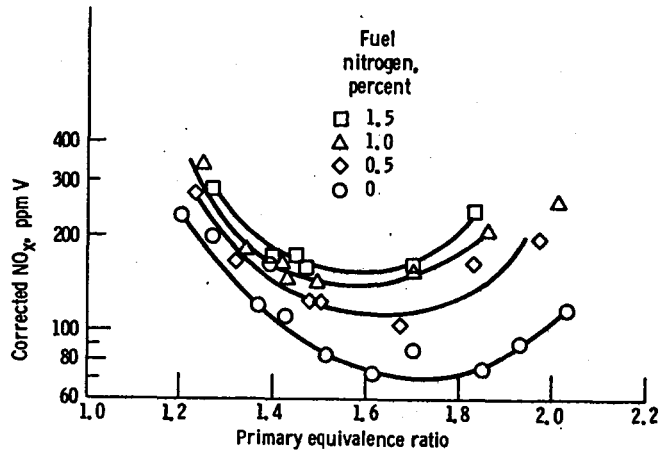
Figure 1. – Corrected oxides of nitrogen as a function of primary equivalence ratio for 9-percent hydrogen fuel blend. Inlet air temperature, 672 K; inlet air pressure, 0.48 MPa; primary volume, 6030 cm³; secondary residence time, 2 m/sec; secondary equivalence ratio, 0.5.
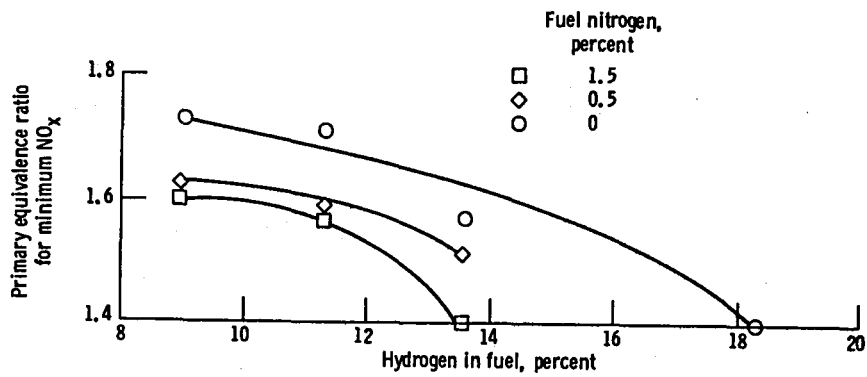
Figure 2. – Optimum primary equivalence ratio versus fuel hydrogen content. Inlet air temperature, 672 K; inlet air pressure, 0.48 MPa; primary volume, 6030 cm³; secondary residence time, 2 m sec; secondary equivalence ratio, 0.5.

(a) Fuel B: 11 percent hydrogen.

(b) Fuel C: 9 percent hydrogen.
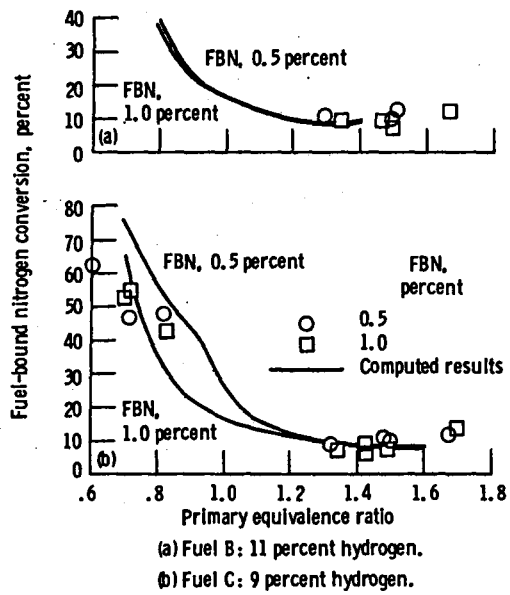
Figure 3. - Comparison of oxides of nitrogen modeling program to flametube rig results. Secondary equivalence ratio; 0.5.
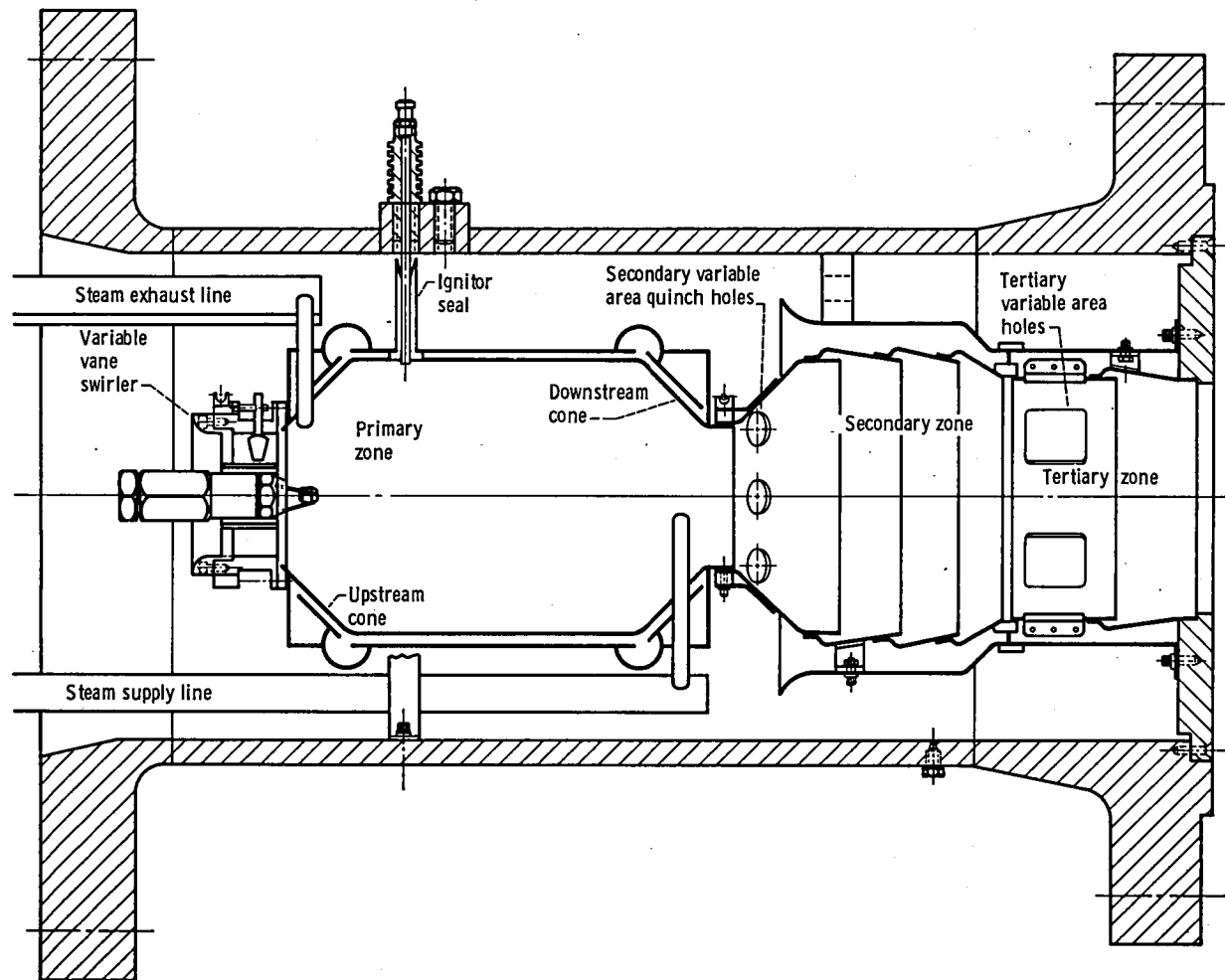
Figure 4. - Cross section of variable geometry combustor.
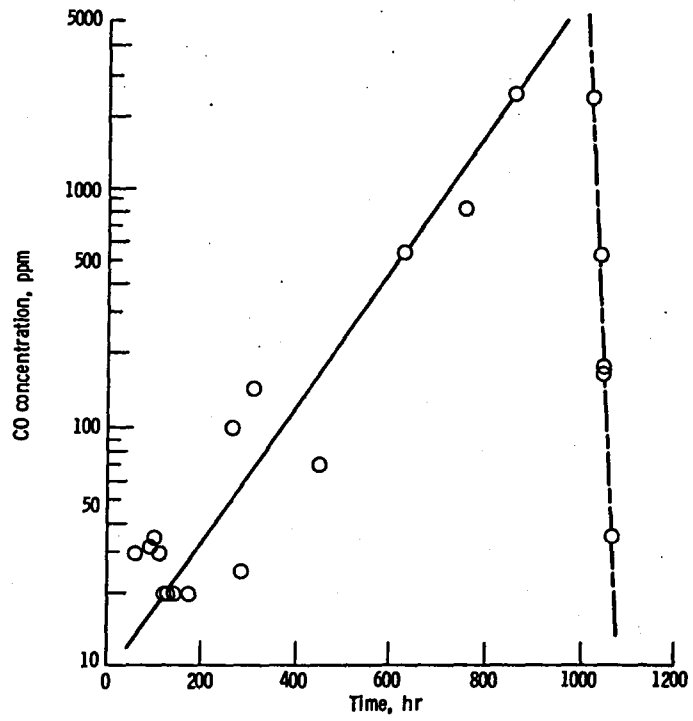
Figure 5. - Endurance test results of catalytic combustor at 5 atm CO emissions as function of testing time.
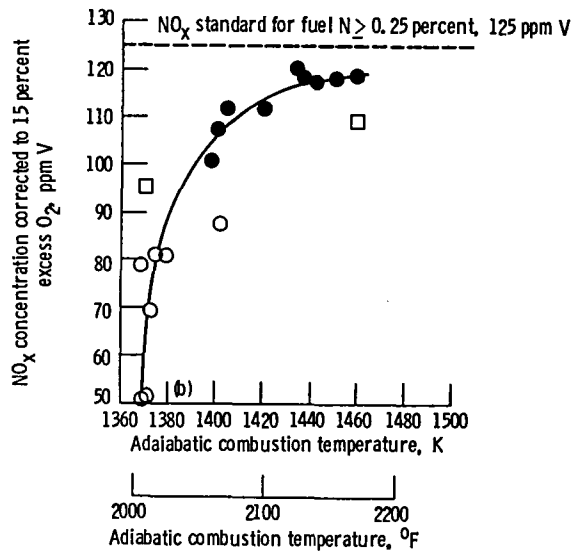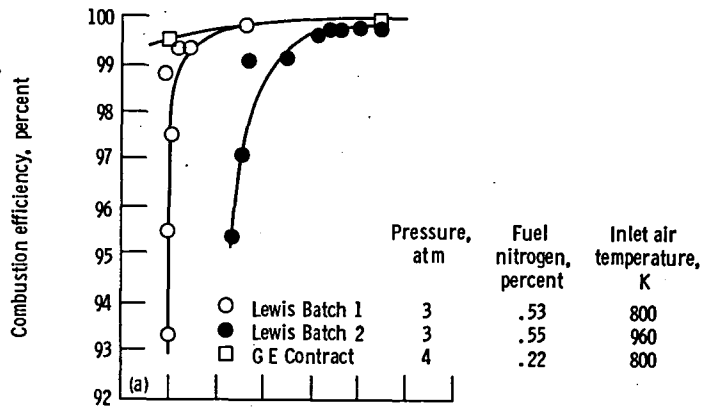
(a) Combustion efficiency.

(b) NO_x emissions.

Figure 6. – Catalytic combustion of residual fuel as function of adiabatic combustion temperature. Reference velocity, 20 m/sec (66 ft/sec).
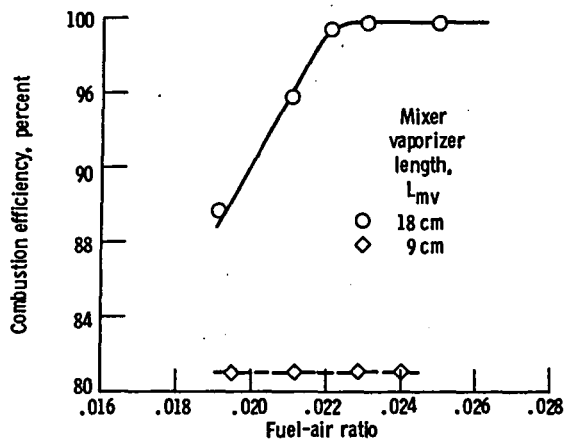
Figure 7. – UTRC catalytic reactor performance dependence on degree of vaporization using No. 2 oil fuel. Inlet air pressure, 0.6 MPa; inlet air temperature, 600 K; reference velocity, 20 m/sec.
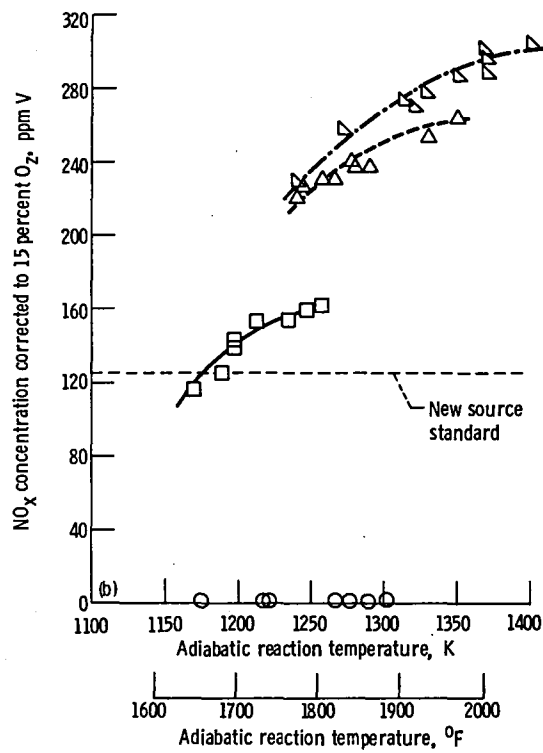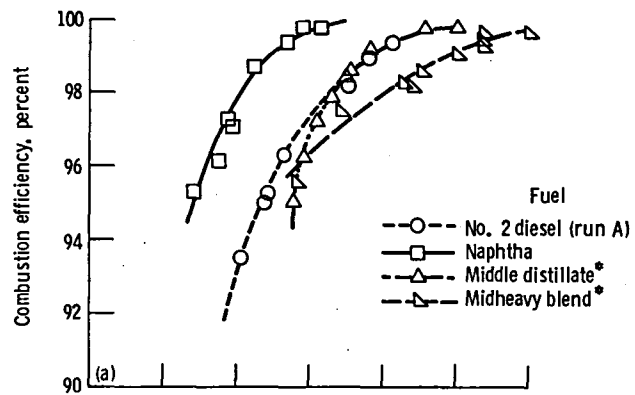
(a) Combustion efficiency.

(b) NO$_x$ emissions.

Figure 8. - Catalytic combustion of coal-derived liquid fuels (SRC-II). Inlet air temperature, 700 K; pressure, 3 atm; reference velocity, 10 m/sec.

*SRC-II fuels.
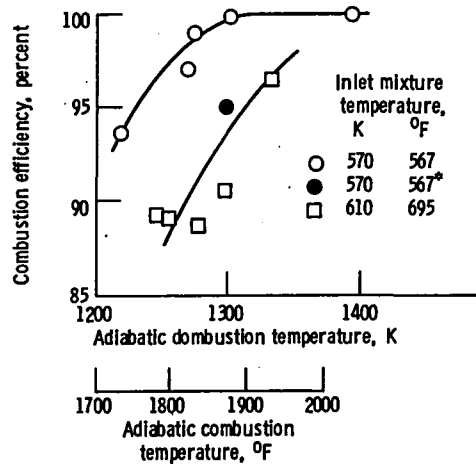
Figure 9. - Westinghouse contract results of
catalytic combustion of low Btu coal-derived
gas. Pressure, 500 kPa (70 psia); reference
velocity, 20 m/sec (66 ft/sec).

*Repeat data.
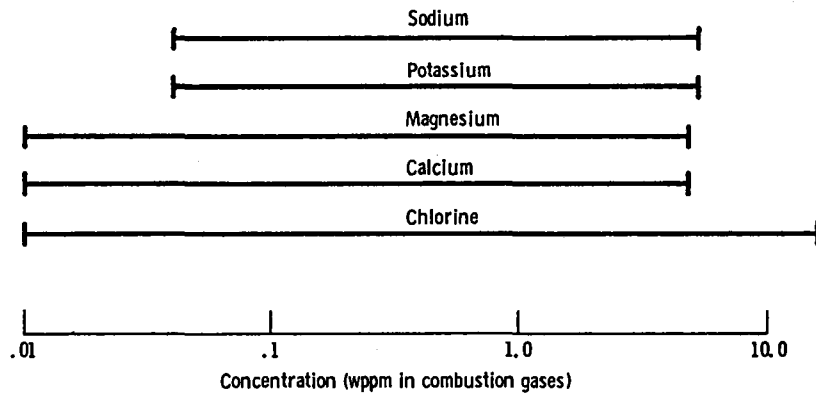
Figure 10. - Impurity ranges in doped fuel experiments.
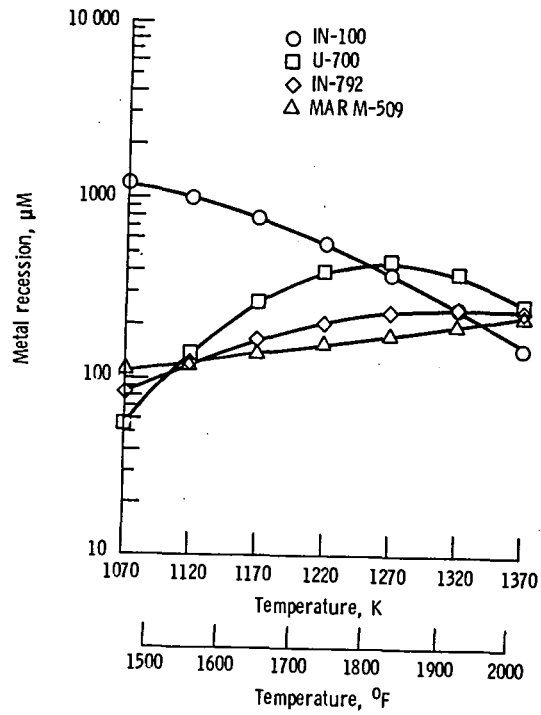
Figure 11. - Predicted hot corrosion attack as function of temperature. Sodium and potassium, 0.9 wppm magnesium and calcium, 0.47 wppm time, 100 hr.

Figure 12. – Effect of potential coal-derived liquid fuel impurities on hot corrosion. One hundred 1-hr cycles at temperature in Mach 0.3 burner rig.
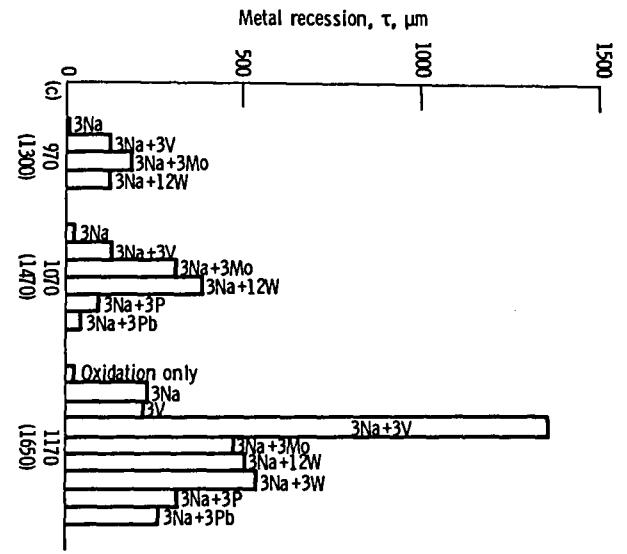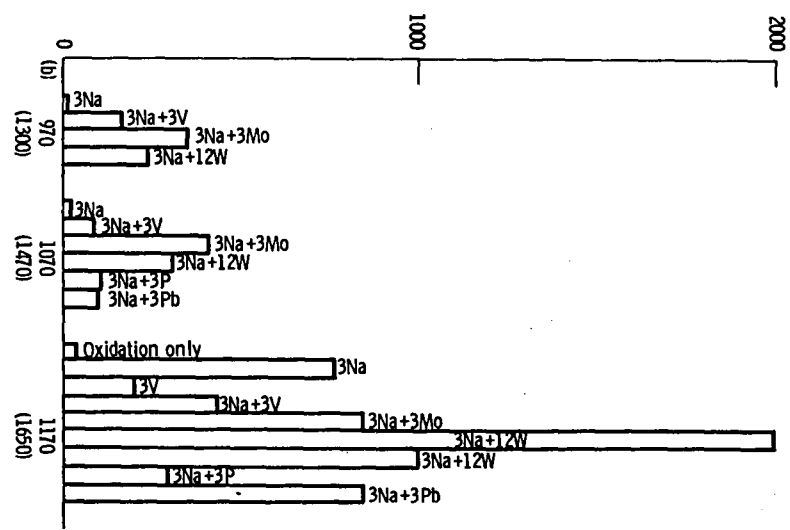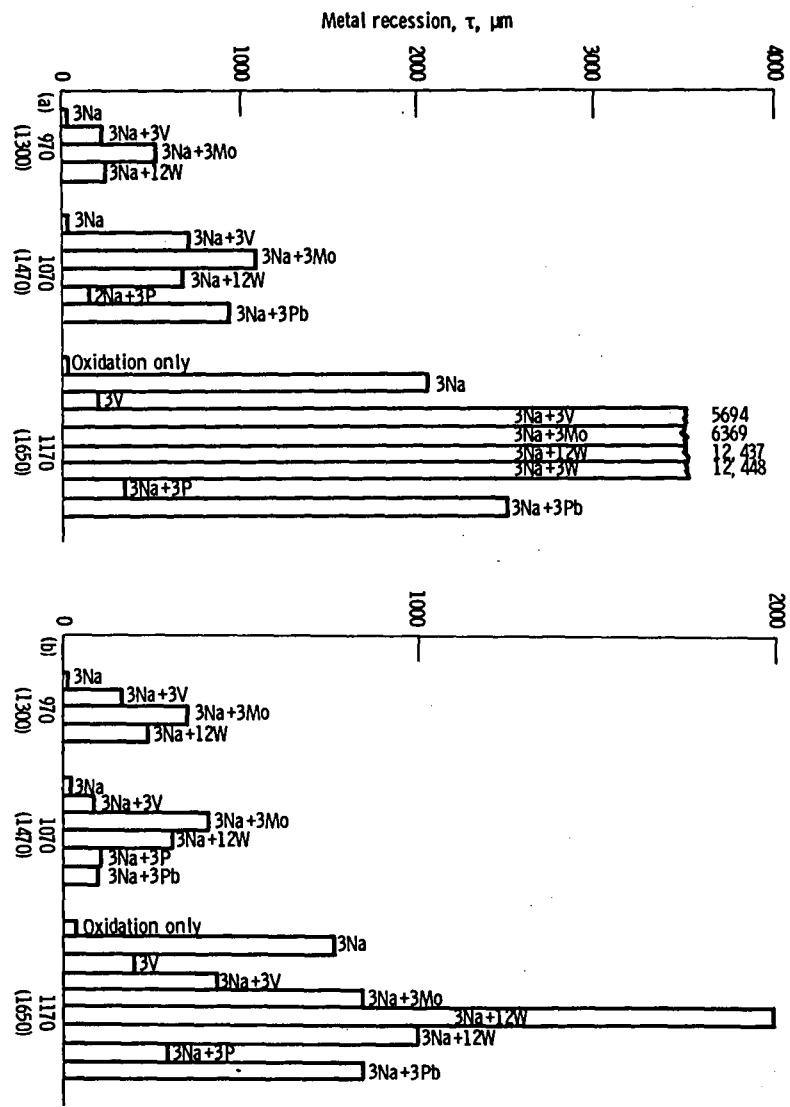
(a) IN-100.
(b) IN-792.
(c) Mar M-509.
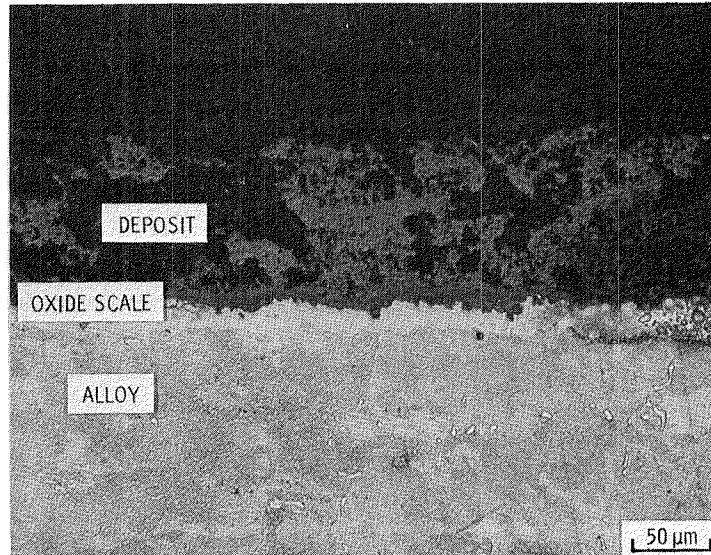
Figure 13. - Deposit morphology on IN-100 exposed in Mach 0.3 burner rig fueled with SRC-II naphtha.
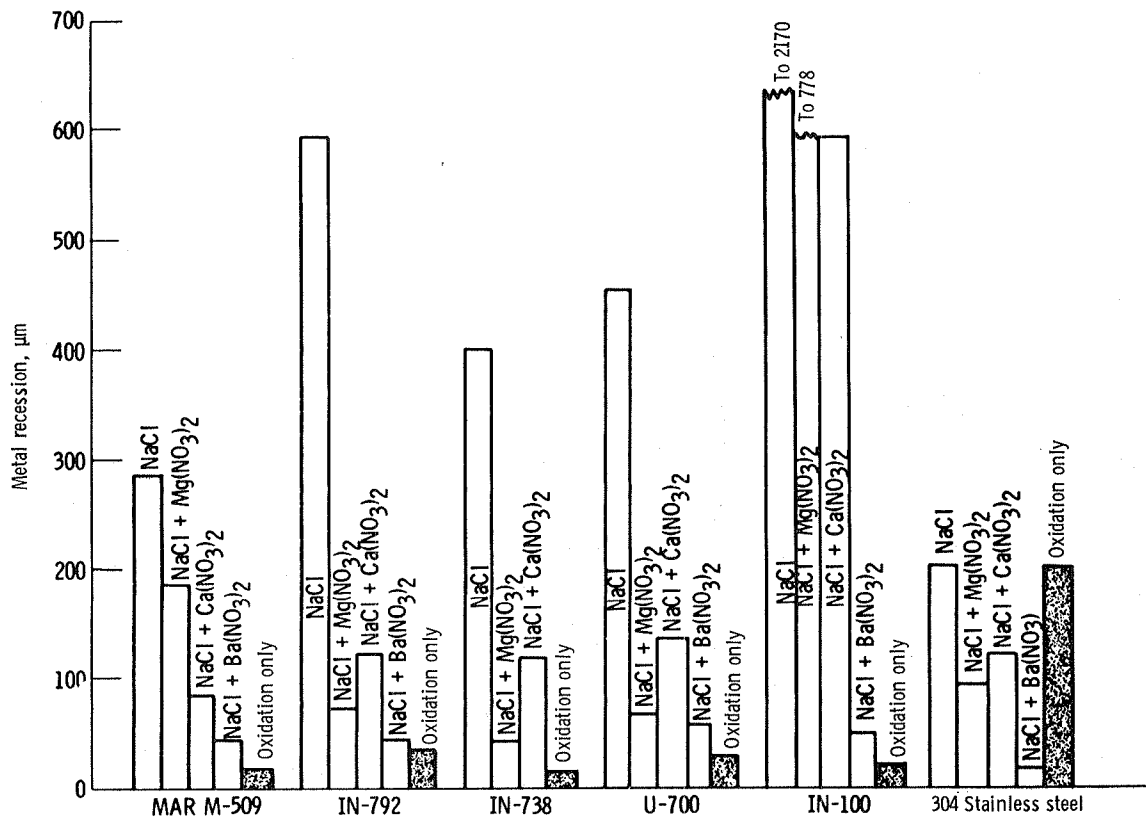
Figure 14. - Effect of alkaline earth additions on burner rig hot corrosion after 100 1-hr cycles at 1170 K (1650° F). All additive concentrations are at 3 ppm of each metal.
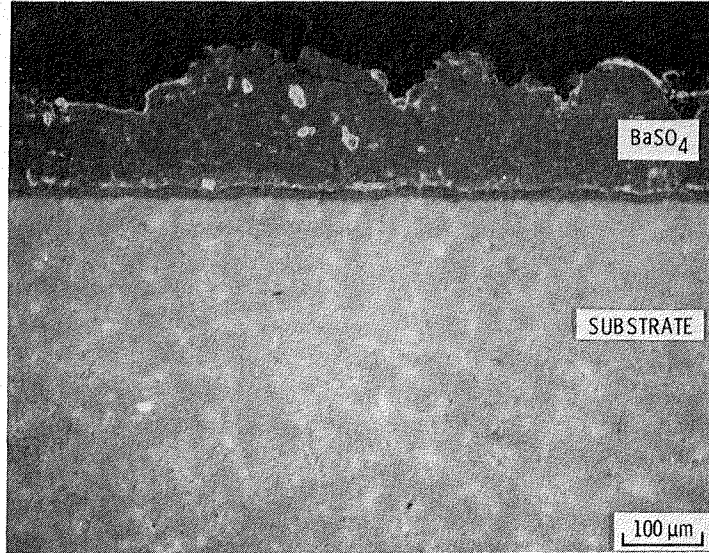
Figure 15. - Deposit of baruim sulfate on IN-792 after 100 1-hour cycles at 1170 K (1650° F) in Mach 0.3 burner rig with 3 ppm Ba + 3 ppm Na as NaCl.
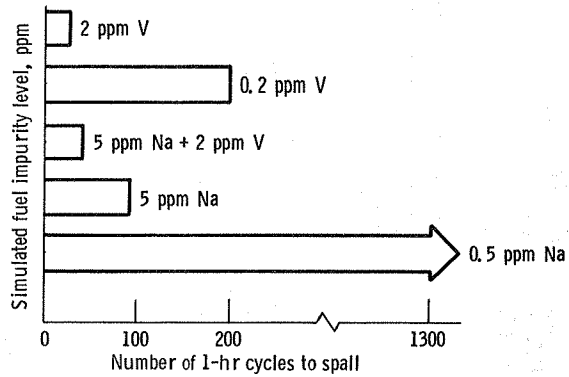
Figure 16. - Results of ZrO_2 12 wt% Y_2O_3 TBC fuel impurity sensitivity tests. Mach 0.3 burner rig, 0.05 wt% sulfur in fuel; surface temperature, 1250 K (1800° F); bond-coat temperature, 1120 K (1560° F).
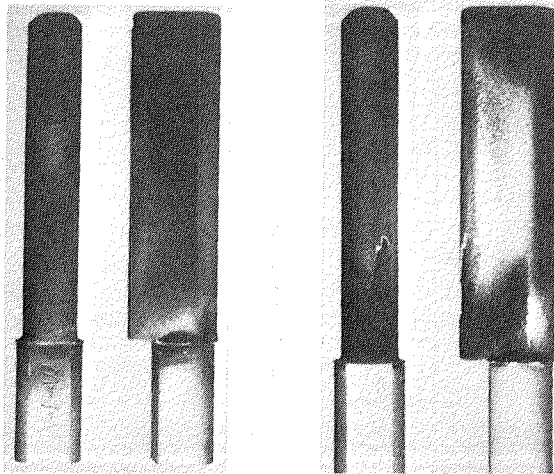
92 1-hr cycles 5 ppm Na   1300 1 -hr cycles 0.5 ppm Na

Figure 17. - Effects of sodium on ZrO_2 · 12 wt % Y_2O_3/Ni-16Cr-6Al-0.6Y. Mach 0.3 burner rig; 0.05 wt % sulphur in fuel; surface temperature, 1250 K (1800° F); bond-coat temperature, 1120 K (1560° F).

CS-79-2817
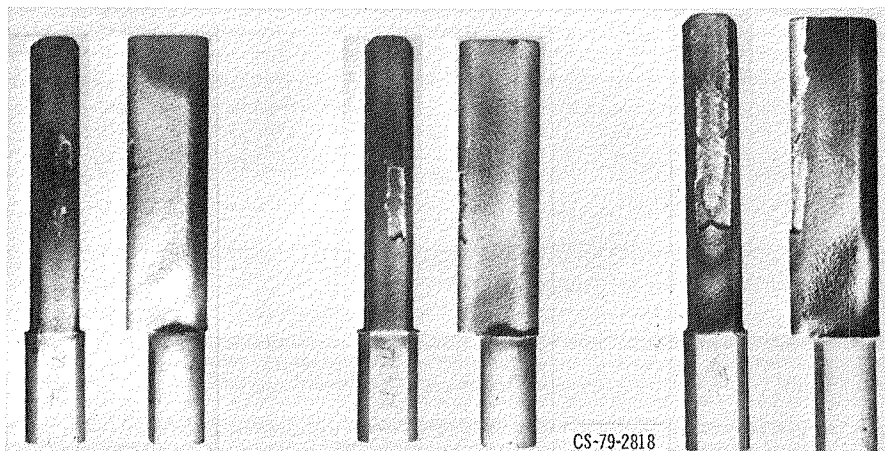
200 1-hr cycles 0.2 ppm V   25 1-hr cycles 2 ppm V   43 1-hr cycles 5 ppm Na + 2 ppm V

Figure 18. - Effect of vanadium and sodium plus vanadium on ZrO_2 · 12 wt % Y_2O_3/Ni-16Cr-6Al-0.6Y. Mach 0.3 burner rig; 0.05 wt % sulphur in fuel; surface temperature, 1250 K (1800° F); bond-coat temperature, 1120 K (1560° F).
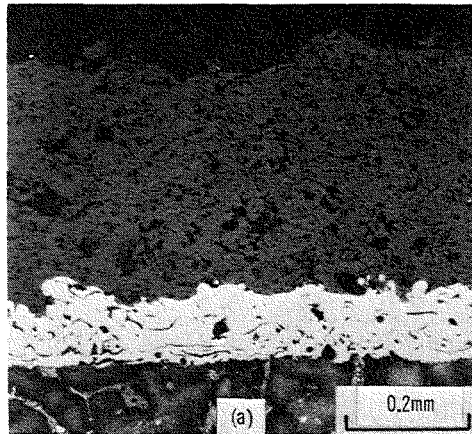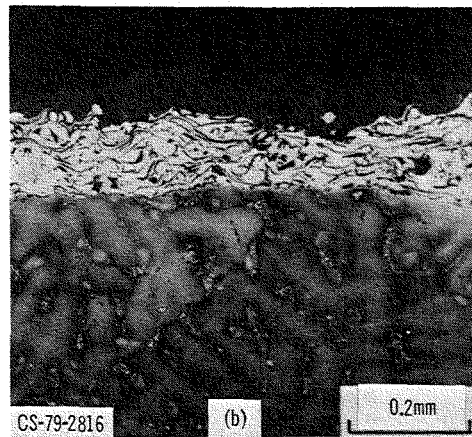
(a) As sprayed ZrO_2-12 wt % Y_2O_3/NiCrAlY.

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

Figure 19. - Microstructures of ZrO_2 . 12 wt % Y_2O_3/Ni-16Cr-6Al-0.6Y on IN-792. Ceramic surface temperature, 1250 K (1800° F); bond-coat temperature, 1120 K (1560° F).
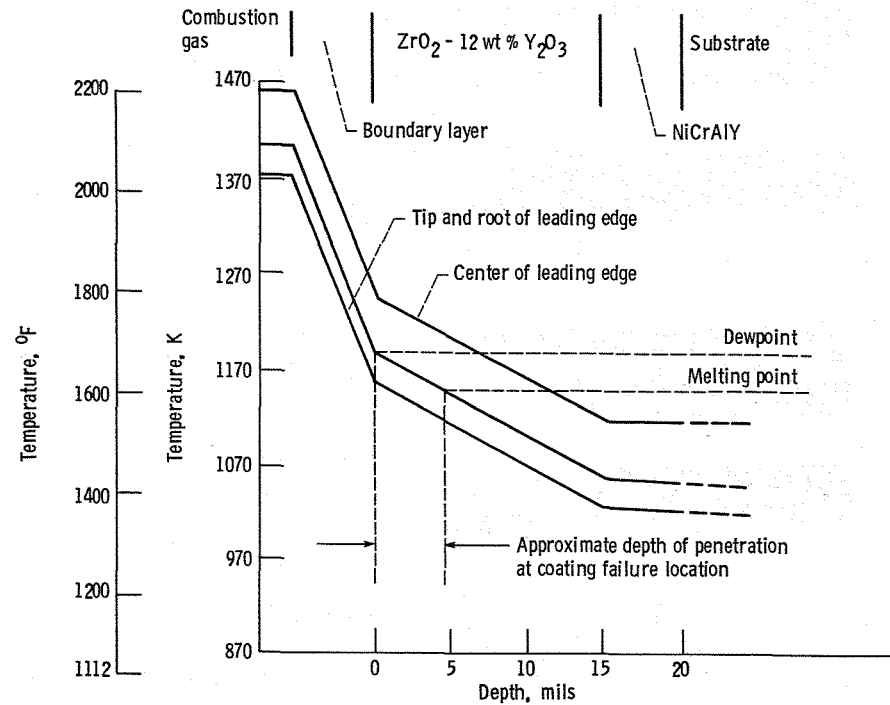

Figure 20. - Penetration of ZrO_2 - 12 wt % Y_2O_3 by sodium sulfate with 5 ppm sodium.
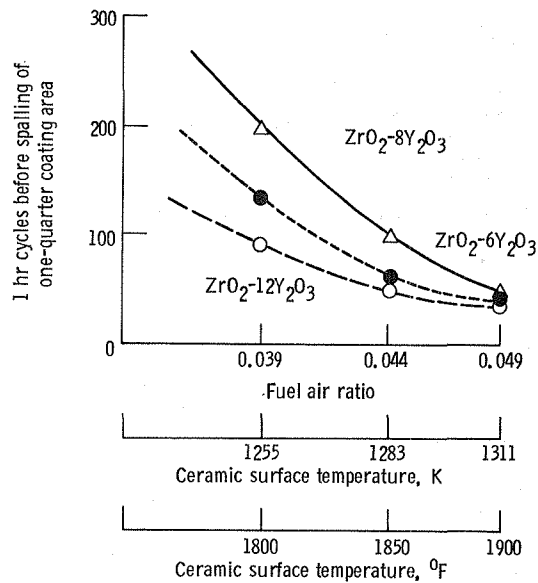
Figure 21. - Fuel-to-air mass ratio burner rig study. Fuel impurity level, 5 ppm Na + 2 ppm V; substrate, 1.27 cm (0.5 in) outside diameter Waspaloy; bond coat, Ni-16Cr-6Al-.31Y; temperature of metal, 1116 K (1550° F).
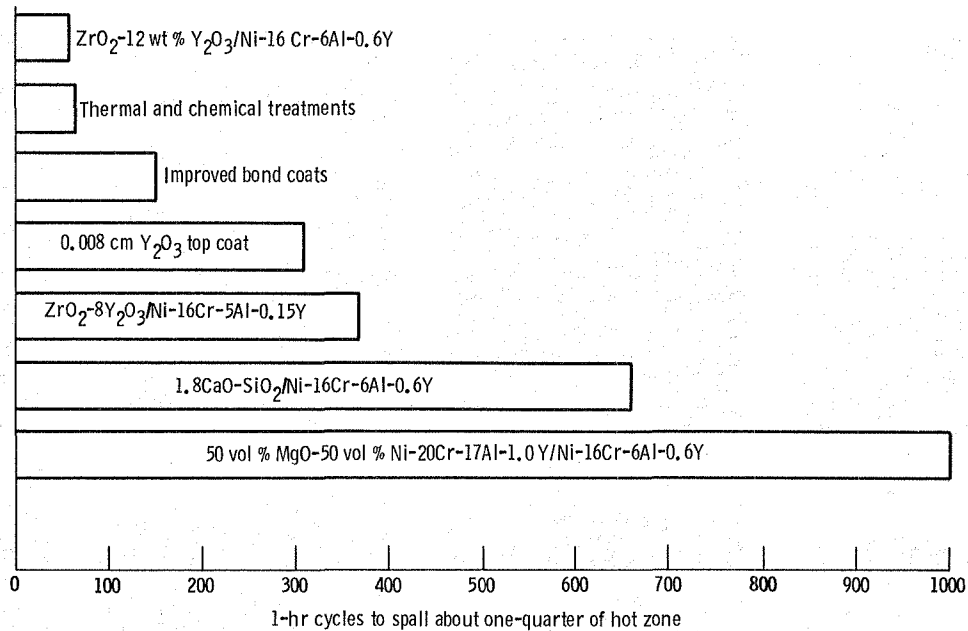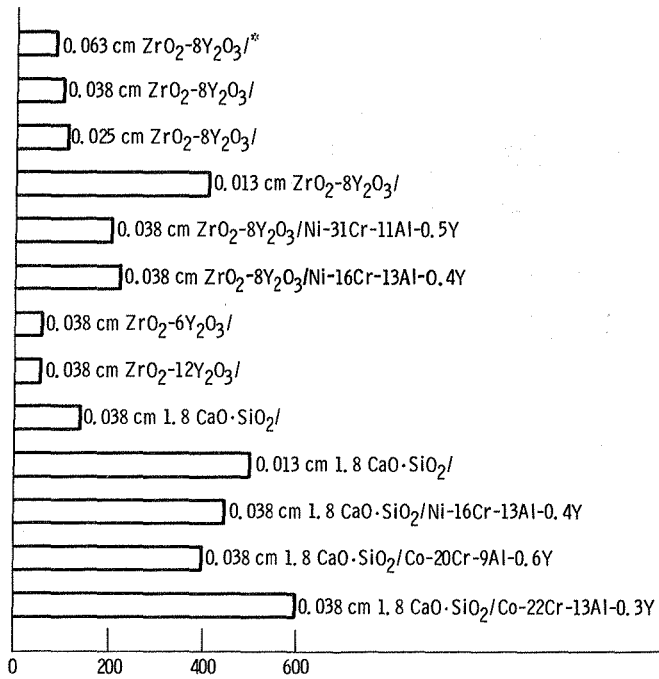

Figure 22. - Improved thermal barrier coatings. Mach 0.3 burner rig; fuel impurities, 5 ppm V, 0.05 percent sulfur; flame temperature, 1650 K (2500° F); ceramic surface temperature, 1250 K (1800° F); bond-coat temperature, 1120 K (1560° F).

0.063 cm ZrO_2-8Y_2O_3/[*]
0.038 cm ZrO_2-8Y_2O_3/
0.025 cm ZrO_2-8Y_2O_3/
0.013 cm ZrO_2-8Y_2O_3/
0.038 cm ZrO_2-8Y_2O_3/Ni-31Cr-11Al-0.5Y
0.038 cm ZrO_2-8Y_2O_3/Ni-16Cr-13Al-0.4Y
0.038 cm ZrO_2-6Y_2O_3/
0.038 cm ZrO_2-12Y_2O_3/
0.038 cm 1.8 $CaO \cdot SiO_2$/
0.013 cm 1.8 $CaO \cdot SiO_2$/
0.038 cm 1.8 $CaO \cdot SiO_2$/Ni-16Cr-13Al-0.4Y
0.038 cm 1.8 $CaO \cdot SiO_2$/Co-20Cr-9Al-0.6Y
0.038 cm 1.8 $CaO \cdot SiO_2$/Co-22Cr-13Al-0.3Y

0   200   400   600

1-Hr cycles before spalling one-
quarter of leading edge area

Figure 23. - Mach 0.3 burner rig corrosion test. Fuel impurity level, 5 ppm
Na + ppm V; fuel-air ratio, 0.046; ceramic surface temperature, 1250 K
(1800° F); temperature, 1120 K (1560° F).

[*]Bond coating is 0.013 cm (0.005 in.) Ni-16Cr-6Al-0.3Y unless
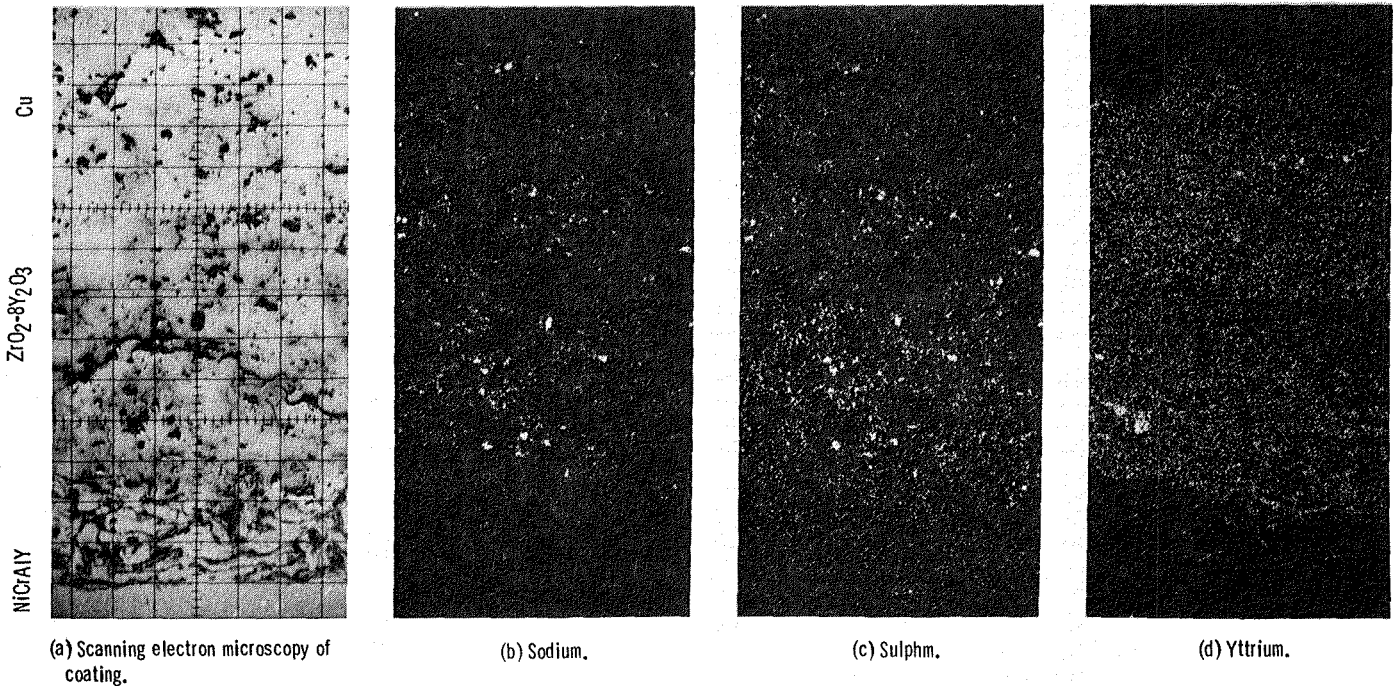otherwise specified.

(a) Scanning electron microscopy of coating.

(b) Sodium.

(c) Sulphm.

(d) Yttrium.

Figure 24. - Electron microprobe maps of ZrO_2-8Y_2O_3/Ni-16Cr-6Al-0.31Y coating system after 120 1-hour cycles. Cross section B leading edge.
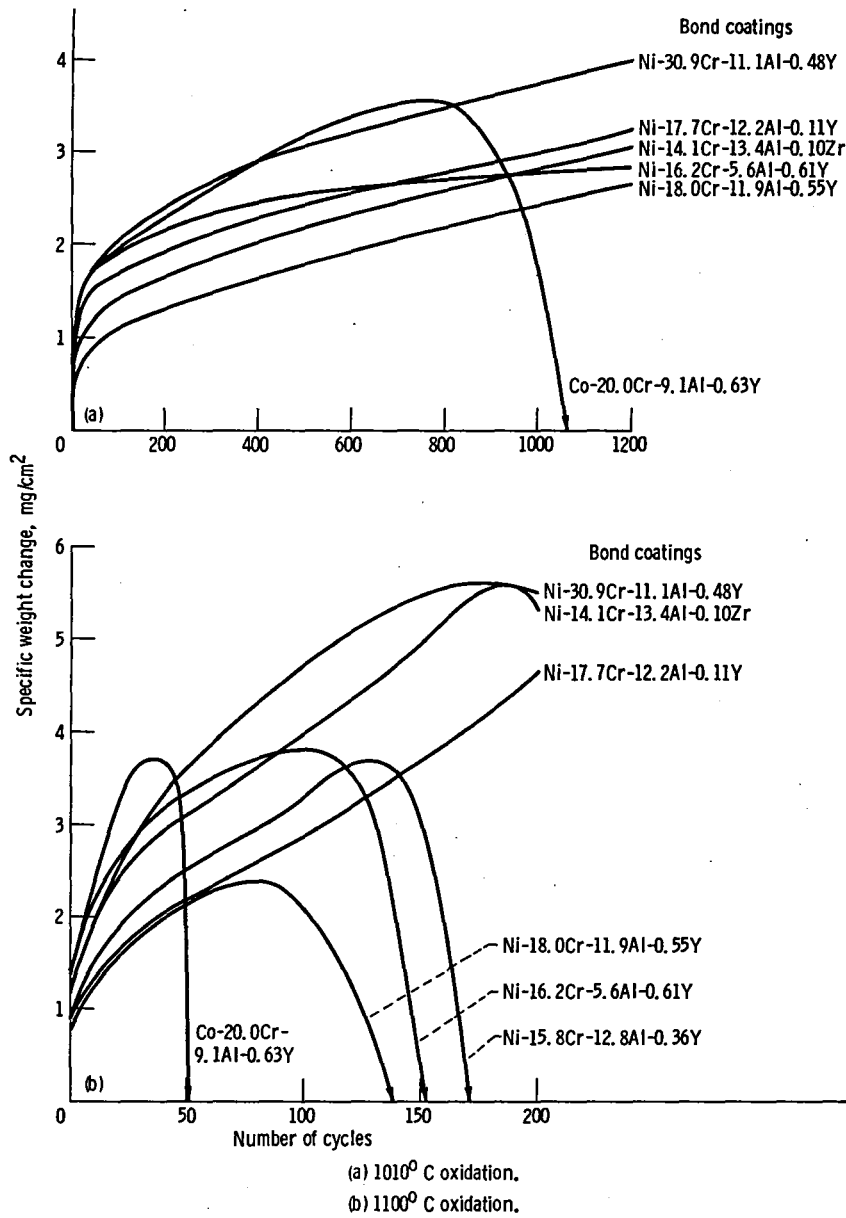
Figure 25. - Effect of oxidation temperature on weight-change behavior of 0. 010-cm-thick plasma-deposited bond coatings on B-1900 + Hf in cyclic furnace oxidation at 12 0 and 1370 K (1830° and 2010° F) in static air. Cycles: 1 hr at test temperature and 20 min or more cooling; coatings applied at 11 kW with argon arc gas.
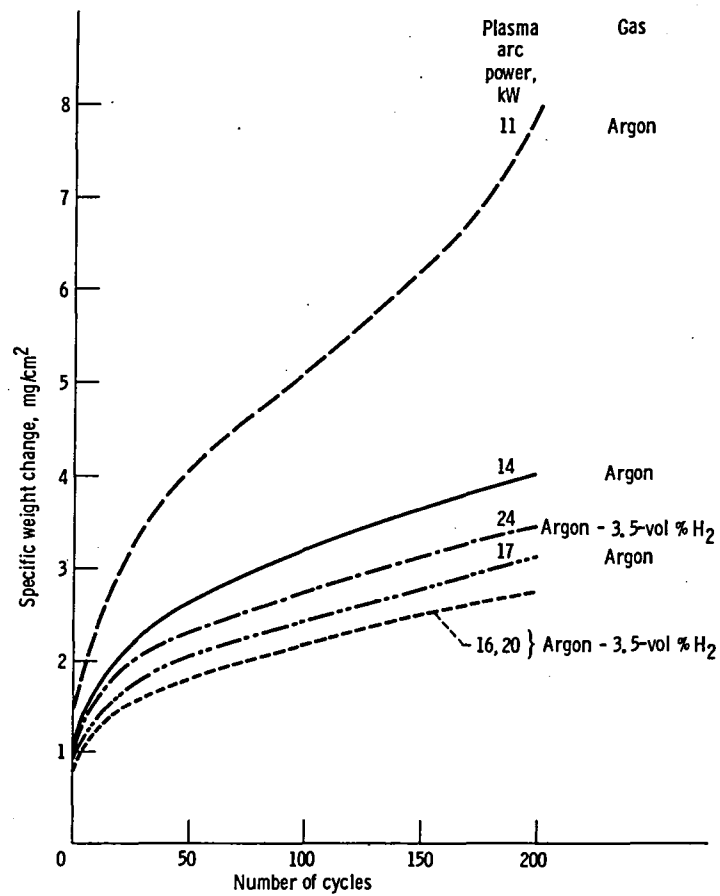
Figure 26. - Effect of plasma-deposition parameters on weight-change behavior of Ni-15.8Cr-12.8Al-0.36 Y bond coating on B-1900 + Hf in cyclic furnace oxidation at 1370 K (2012° F) in static air. Nominal coating thickness, 0.015 cm (0.006 in.)
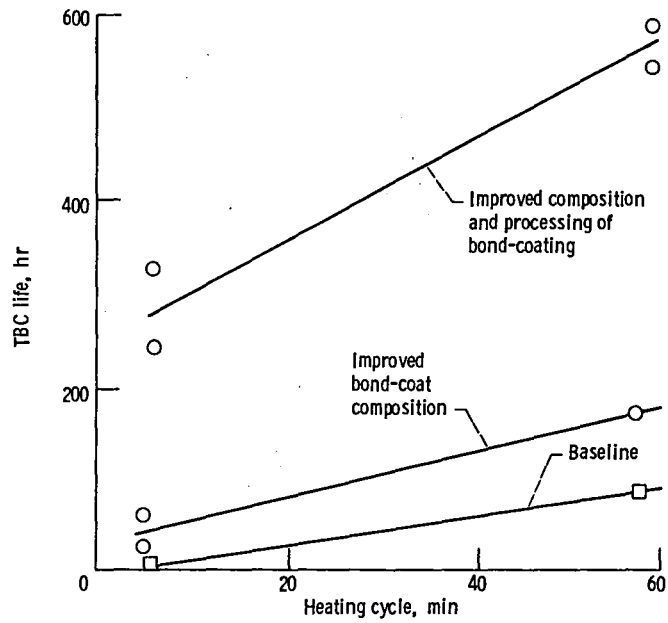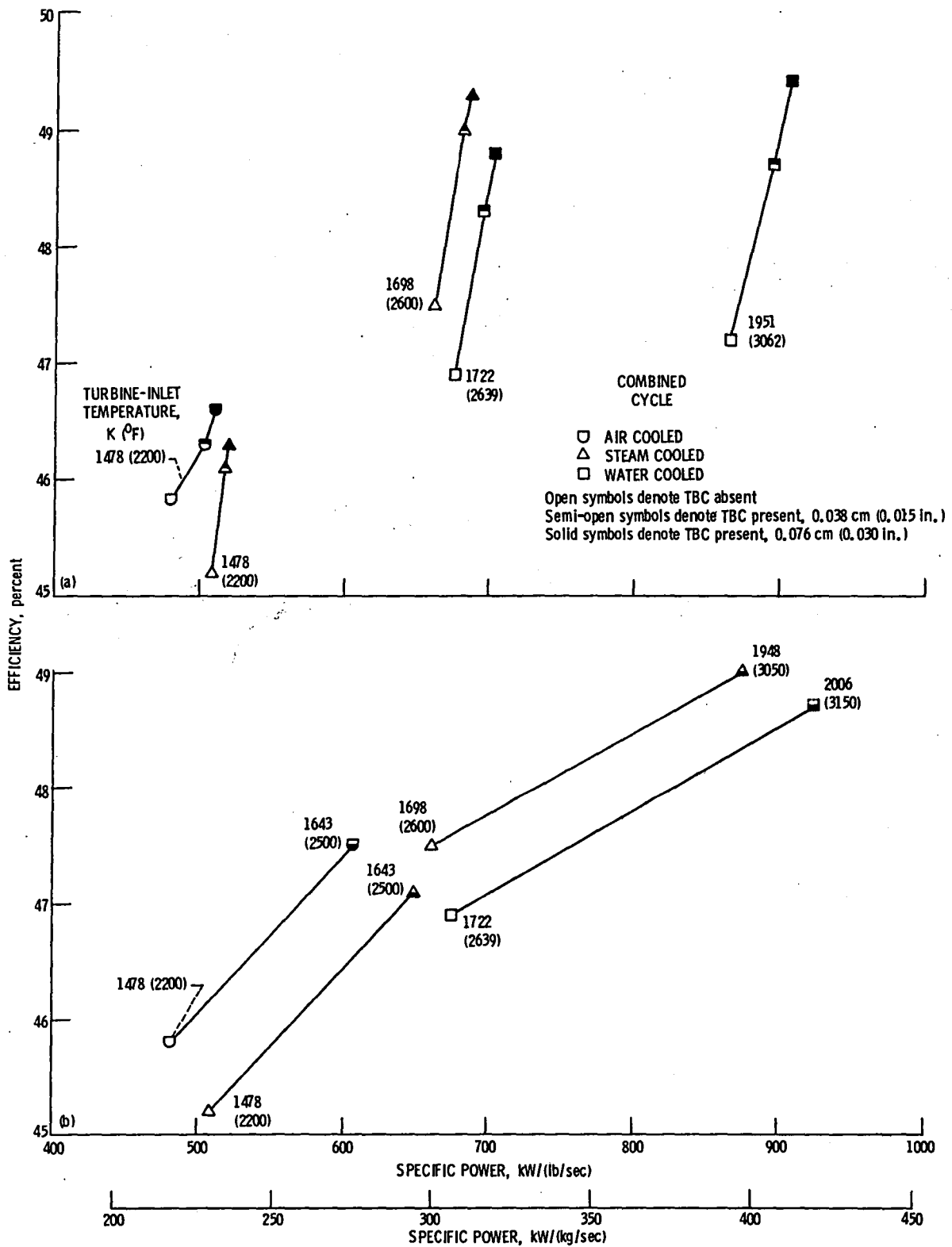
Figure 27. - Improvement of TBC life by going from baseline Ni-16 Cr-
6 Al-0.6 Y bond coat to Ni-16 Cr-6 Al-0.36 Y and improved process-
ing. Thermal barrier coating, ZrO_2-12Y_zO_3; Mach 0.3 burner rig;
temperature, 1422 K (2100° F).

(a) Constant turbine-inlet temperature; reduced cooling flow.

(b) Increased turbine-inlet temperature; constant cooling flow.

Figure 28. - Combined-cycle performance gains with thermal-barrier coatings.
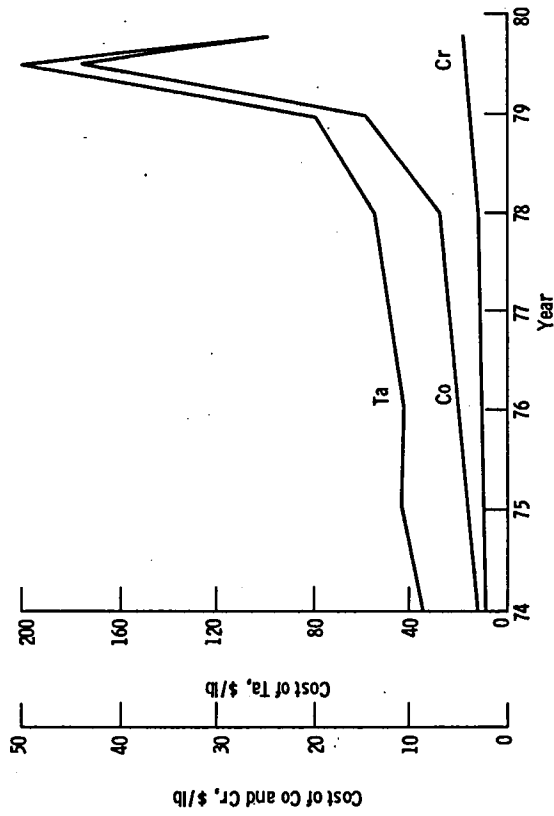
Figure 29. – Price of scarce metals.

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16. Abstract

This report summarizes the technical progress attained during 1977 to 1982 to provide a critical technology base for utility and industrial gas turbines by planning the use of coal-derived fuels. Development tasks were included in the following areas: (1) Combustion - investigate the combustion of coal-derived fuels and methods to minimize the conversion of fuel-bound nitrogen to NO_x; (2) materials - understand and minimize hot corrosion; (3) system studies - integrate and focus the technological efforts. A literature survey of coal-derived fuels was completed and a NO_x emissions model was developed. Flametube tests of a two-stage (rich-lean) combustor defined optimum equivalence ratios for minimizing NO_x emissions. Sector combustor tests demonstrated variable air control to optimize equivalence ratios over a wide load range and steam cooling of the primary zone liner. The catalytic combustion of coal-derived fuels was demonstrated. The combustion of coal-derived gases is very promising. A hot-corrosion life prediction model was formulated and verified with laboratory testing of doped fuels. Fuel additives to control sulfur corrosion were studied. The intermittent application of barium proved effective. Advanced thermal barrier coatings were developed and tested. Coating failure modes were identified and new material formulations and fabrication parameters were specified. System studies in support of the thermal barrier coating development were accomplished.

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