UNCLASSIFIED

AD NUMBER
AD870745
LIMITATION CHANGES
TO: **Approved for public release; distribution is unlimited.**
FROM: **Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; MAY 1970. Other requests shall be referred to Office of the of the Director of Defense Research and Engineering, Washington, DC 20301.**
AUTHORITY
ODDRE ltr 19 Oct 1970

THIS PAGE IS UNCLASSIFIED

NMAB-260
MAY 1970

Hot Corrosion in Gas Turbines

. . . Mechanisms

. . . Alloy & Coating Development

. . . Environmental Effects

. . . Evaluation

A Report of the

NMAB NATIONAL MATERIALS ADVISORY BOARD

NATIONAL RESEARCH COUNCIL
NATIONAL ACADEMY OF SCIENCES–NATIONAL ACADEMY OF ENGINEERING

ACCESSION for
CFSTI WHITE SECTION ☐
DDC BUFF SECTION ☑
UNANNOUNCED ☐
JUSTIFICATION .....
BY .....
DISTRIBUTION/AVAILABILITY CODES
DIST. AVAIL. and/or SPECIAL
2

NATIONAL MATERIALS ADVISORY BOARD

DIVISION OF ENGINEERING - NATIONAL RESEARCH COUNCIL

Chairman

Dr. William J. Harris, Jr.
Vice President of Research
and Test
Association of
American Railroads
1920 L Street, N.W.
Washington, D. C. 20036

Past Chairman

Dr. Walter L. Finlay
Director of Research
Copper Range Company
630 Fifth Avenue
New York, New York 10020

Members

Mr. G. Mervin Ault
Associate Chief
Materials & Structure Division
Lewis Research Center, NASA
21000 Brookpark Road
Cleveland, Ohio 44135

Dr. Donald J. Blickwede
Vice President and Director of Research
Bethlehem Steel Company
Homer Research Laboratories
Bethlehem, Pennsylvania 18016

Mr. H. R. Clauser
Consultant
1 Valley Lane
Armonk, New York 10504

Dr. Morris Cohen
Ford Professor of Materials
Science and Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, Massachusetts 02139

Dr. J. H. Crawford, Jr.
Chairman, Physics Department
University of North Carolina
Chapel Hill, North Carolina 27514

Dr. Thomas G Fox
Professor of Chemistry and
Polymer Science
Mellon Institute
Carnegie-Mellon University
and Science Advisor to Governor of Penna.
4400 Fifth Avenue
Pittsburgh, Pennsylvania 15213

Dr. Martin Goland
President
Southwest Research Institute
8500 Culebra Road
San Antonio, Texas 78228

Dr. Jacob E. Goldman
Group Vice President-
Research and Technology
Xerox Corporation
Xerox Square
Rochester, New York 14603

Dr. N. Bruce Hannay
Executive Director
Research-Materials Division
Bell Telephone Laboratories
Murray Hill, New Jersey 07971

Mr. Julius J. Harwood
Assistant Director
Materials Science
Ford Motor Company
P. O. Box 2053
Dearborn, Michigan 48121

Mr. Abraham Hurlich
Manager, Materials & Processes
Department 572-0
General Dynamics/Convair
P. O. Box 1128
San Diego, California 92112

Dr. Harold Liebowitz
Dean of School of Engineering
and Applied Science
The George Washington University
Washington, D. C. 20006

Mr. Louis R. McCreight
Manager, Materials Science Section
Space Sciences Laboratory
General Electric Company
P. O. Box 8555
Philadelphia, Pennsylvania 19101

Dr. E. F. Osborn
Vice President for Research
Pennsylvania State University
207 Old Main Building
University Park, Pennsylvania 16802

Dr. William Rostoker
Professor of Metallurgy
College of Engineering
University of Illinois
P. O. Box 4348
Chicago, Illinois 60680

Mr. Adolph O. Schaefer
Consulting Engineer
R. D. 4
Norristown, Pennsylvania 19401

Dr. Morris Tanenbaum
General Manager-Engineering
Western Electric Company
195 Broadway
New York, New York 10007

Dr. Alan S. Tetelman
Chairman, Materials Department
School of Engineering
6531 Boelter Hall
University of California
Los Angeles, California 90024

Dr. Admiral A. Watts
Director, Advanced Materials
Research
Bell Aerosystems Company
P. O. Box One
Buffalo, New York 14240

N. E. Promisel, Executive Director
A. M. Blamphin, Executive Secretary

(3/70)

HOT CORROSION IN GAS TURBINES

...MECHANISMS

...ALLOY & COATING DEVELOPMENT

...ENVIRONMENTAL EFFECTS

...EVALUATION

REPORT OF

THE COMMITTEE ON
ATMOSPHERIC DETERIORATION OF SUPERALLOYS

NATIONAL MATERIALS ADVISORY BOARD
Division of Engineering - National Research Council

This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Office of the Director of Defense Research and Engineering (Chief, Materials Division, OADCT).

Publication NMAB-260

National Academy of Sciences - National Academy of Engineering

Washington, D. C.

May 1970

This report is one of a series in studies undertaken by the National Materials Advisory Board for the National Academy of Sciences and the National Academy of Engineering in partial execution of work under Contract No. DA-49-083 OSA-3131 with the Department of Defense.

As a part of the National Research Council, the National Materials Advisory Board performs study, evaluation, or advisory functions through groups composed of individuals selected from academic, governmental, and industrial sources for their competence or interest in the subject under consideration. Members of these groups serve as individuals contributing their personal knowledge and judgments and not as representatives of any organization in which they are employed or with which they may be associated.

The quantitative data published in this report are intended only to illustrate the scope and substance of information considered in the study, and should not be used for any other purpose, such as in specifications or in design, unless so stated.

No portion of this report may be republished without prior approval of the National Materials Advisory Board.

Copies of this report are not available from the Clearinghouse for Federal Scientific and Technical Information (CFSTI). Qualified requesters may apply through Defense Documentation Center. Those who do not use the Defense Documentation Center may apply to the National Materials Advisory Board.

NATIONAL MATERIALS ADVISORY BOARD

COMMITTEE ON ATMOSPHERIC DETERIORATION OF SUPERALLOYS

Chairman: Dr. Robert I. Jaffee, Senior Fellow and Associate Manager, Materials Science and Technology, Department of Physics, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201.

Members: Mr. Charles C. Clark, In Charge, Aerospace & Power, The International Nickel Company, Inc., 67 Wall Street, New York, New York 10005.

Dr. Matthew J. Donachie, Jr., Development Metallurgist, MDL-J Building, Pratt & Whitney Aircraft, East Hartford, Conn. 06108.

Dr. William R. Freeman, Jr., Director, Materials Laboratories, AVCO Lycoming Division, 550 S. Main Street, Stratford, Conn. 06497.

Dr. William Hagel, Head, Metallurgy Division, Denver Research Institute, University of Denver, University Park, Denver, Colo. 80210.

Mr. Paul E. Hamilton, Section Chief, Investigations & Development Metallurgy, Aircraft Engine Operations, Allison Division, General Motors Company, P. O. Box 894, Indianapolis, Indiana 46206.

Dr. Robert A. Rapp, Professor, Metallurgical Engineering, College of Engineering, Ohio State University, Columbus, Ohio 43210.

Dr. Alan U. Seybolt, Metallurgy & Ceramics Laboratory, General Electric Company, R&D Center, P.O. Box 8, Schnectady, New York 12301.

Dr. William E. Young, Manager, Combustion, Corrosion & MHD Section, Heat Transfer & Power Generator R&D, Research and Development Center, Westinghouse Electric Corporation, Churchill Borough, Beulah Road, Pittsburgh, Pennsylvania 15235.

Liaison Representatives:

Dr. Hubert B. Probst, Head, Oxidation and Refractory Compounds Section, NASA Lewis Research Center, 21000 Brookpark Road, Cleveland, Ohio 44135.

Mr. Milton Levy, Army Materials & Mechanics Research Center, Watertown, Massachusetts 02172.

Mr. Henry Morrow, U. S. Army Aviation Materiel Laboratories, Fort Eustis, Virginia 23604.

Mr. George J. Danek, Jr., Naval Ship Research and Development Center, Annapolis, Maryland 21402.

Mr. Irving Machlin, Materials Engineering, AIR-52031B, Naval Air Systems Command, Department of the Navy, Washington, D. C. 20360.

Mr. Norman M. Geyer, Air Force Materials Laboratory, (MAMP) 25-53136, Wright-Patterson Air Force Base, Ohio 45433.

Mr. John C. Barrett, ODDR&E, Office of Assistant Director for Chemical Technology, Room 3D117, The Pentagon, Washington, D. C. 20310.

NMAB STAFF:

Dr. Joseph R. Lane, Staff Metallurgist, National Materials Advisory Board, Division of Engineering, National Research Council, NAS-NAE, 2101 Constitution Avenue, N. W., Washington, D. C. 20418.

SUBGROUPS
of the
COMMITTEE ON ATMOSPHERIC DETERIORATION OF SUPERALLOYS

Mechanisms

Dr. Alan U. Seybolt, Chairman
Dr. William Hagel
Dr. Robert A. Rapp

Aided by Contributions From

Mr. Norman Bornstein, United Aircraft Research Center
Mr. M. A. DeCrescente, United Aircraft Research Center

Alloy & Coating Development

Mr. Charles C. Clark, Chairman
Dr. Matthew J. Donachie, Jr.
Mr. Paul E. Hamilton

Mr. Irving Machlin, Naval Air Systems Command
Mr. Warren Rentz, AVCO Lycoming Div.

Environmental Effects

Dr. William E. Young, Chairman
Dr. William R. Freeman

Miss E. J. MacNair, Ministry of Defense, Bath, England
D. R. Carlisle, Rolls Royce Industrial, Ansty, England
Henry L. Morrow, U.S. Army Aviation Materials Laboratory
Jeremy J. Walters, AVCO Lycoming
Irving Machlin, Naval Air Systems Command
R. M. Shirmer, Phillips Petroleum
Alan U. Seybolt, General Electric
G. J. Danek, Naval Ship Research and Development Laboratory
Hubert B. Probst, NASA Lewis Research Center
W. T. Reid, Battelle Memorial Institute
W. E. Somers, Public Service Electric and Gas Company
G. C. Widersum, Philadelphia Electric Company

Evaluation

Dr. William R. Freeman, Chairman
Mr. Paul E. Hamilton

Mr. George J. Danek, Naval Ship Research and Development Laboratory

CONTENTS

		Page
	Abstract	vii
I.	INTRODUCTION	1
II.	MECHANISMS	3
	A. Hot Corrosion Attack	4
	B. High-Temperature Oxidation	11
III.	MATERIAL AND COATING DEVELOPMENT	14
IV.	ENVIRONMENTAL EFFECTS	30
V.	EVALUATION	49
	A. Recommendations	59
VI.	SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS	61

Appendices

I.	Recommendations from Coating Systems for Gas Turbine Engines	64
II.	"Round Robin" Hot Corrosion Testing Program	67

ABSTRACT

Hot corrosion (sulfidation) in gas turbine engines has become a major problem because of the increased use of alloys low in chromium and the operation in environments containing alkali metal salts, especially near sea water.

The mechanism of attack is understood to some extent, but more work is needed. It is clear that sodium and other alkali metal salts are involved. Sodium sulfate is ingested with the combustion air or formed from the sulfur in the fuel, and reacts with the metal oxide scale acting as an Na_2O "sink" to form a complex sodium salt. After scale breakdown, sodium sulfate may attack the underlying metal, forming sulfides. The presence of NaCl in the gas and a liquid salt film seem to be required for accelerated attack. Coatings, alloy modification, and additives to the fuel all help alleviate the immediate problem. Alloy development, dispersion hardened and fiber strengthened alloys, and rare earth additions to superalloys may offer longer-range solutions. Target performance properties are needed to focus the future research and development work.

Sulfur can enter a gas turbine from the fuel, and chloride and sulfate salts from the air. There is little prospect for removal of these contaminants to such a degree as to eliminate the problem. However, from 10 to 75% of sea salt can be removed from the air intake to retard the attack. Data on tolerable levels of contaminants are needed.

Engine testing is still the only reliable evaluation method to check improvements in the hot corrosion resistance of materials. Test rigs are commonly used for a preliminary evaluation of hot corrosion resistance. Reproducibility in test results from test rigs in different laboratories is very poor, and further effort toward test rig standardization, correlation of the data between different tests, and interpolation of tests results and extension to different testing conditions, all are needed.

Specific recommendations for attacking the hot corrosion problem are detailed in the report.

I. INTRODUCTION

The Problem

As temperatures in the turbine section of gas turbine engines have increased, an increasing amount of environmental attack has been encountered in the superalloy parts. Operational personnel generally have ascribed the problem to hot corrosion or sulfidation, whereas the real problem may have been excessive oxidation due to overtemperature. For whatever cause, the results of this attack penalizes engine performance by a severe restriction in operating life.

The major limitation on turbine inlet temperature is the strength of the turbine rotor-blade and stator-vane materials. There have been major improvements in the high-temperature strengths of these materials, primarily through the use of strong casting alloys, hardened by a substantial volume fraction of the coherent γ' precipitate, $(Ni, Co)_3(Al, Ti)$. However, the major means for achieving higher gas temperatures in the turbine is through the use of air cooling, whereby a small percentage of the inlet air is diverted through cooling passages in the hot turbine blading and vanes. Through this means, the temperature of these parts is lowered about 400-500°F (222-288°C) below the gas temperature to the point where their strength capability is sufficient.

Up to the present time, corrosion and oxidation resistance have not been design considerations in aircraft gas turbine material selection other than that the materials resist the environment, which superalloys containing about 20% chromium do adequately up to the temperature at which strength is maintained, about 1650°F (899°C). However, the development of the stronger gas turbine alloys was facilitated by a reduction in chromium content to about 10% chromium, to permit an increased amount of γ' hardening from increased contents of aluminum

and titanium. The high aluminum content maintained the oxidation resistance but not sulfidation resistance equivalent to the higher chromium content.

Hot corrosion is an accelerated oxidation in the presence of NaCl and Na_2SO_4 usually due to operation in marine environments. It also includes attack by lead vanadium and other fuel contaminants. The reduced oxidation and hot corrosion resistance has been combated by coating the hot components with aluminide-type coatings. The coating procedure entails additional expense and a problem with reliability compared with the former situation where uncoated alloys with adequate oxidation and corrosion resistance were operated at lower gas temperatures.

The Committee

The Department of Defense, recognizing the seriousness of the hot corrosion problem, asked the National Research Council to organize a committee to review the problem. The Committee, which was assembled by the National Materials Advisory Board, is shown on page iii. Members of the Committee, acting as individuals and not as representatives of their employers, contributed their services. The Committee reflected varying viewpoints ranging from basic researchers to those of stationary and aircraft gas turbine manufacturers.

Method of Operation

After initially considering their individual positions and viewpoints on the problem, the Committee divided their consideration into four areas: mechanisms, materials development, environmental effects, and testing and evaluation, each of which was assigned to a subgroup. The remainder of this report comprises the findings of the four subgroups, followed by overall conclusions and recommendations.

II. MECHANISMS

Introduction

In this entire report, emphasis has been placed on "hot corrosion" or "sulfidation" of superalloys, as opposed to their oxidation, because this type of reaction is a matter of the most immediate concern and study in current engine service. The subject of hot corrosion is discussed first.

It is generally agreed that the basic corrosion attack occurring in "hot corrosion" or "sulfidation" is oxidation which occurs in a very rapid or near-catastrophic manner because of the disruption caused by the existence of a salt film of the normally protective scale. In addition, sulfides form inside the surface grains and sometimes deep along grain boundaries to cause serious degradation of structural integrity of the alloy.

As has been pointed out in many publications (see, for example, the recent ASTM Symposium [1] on this subject), the immediate agent responsible for hot corrosion in aircraft engines is Na_2SO_4, which forms from chemical reactions taking place between NaCl in sea air and sulfur in the fuel, as well as from the appreciable content of Na_2SO_4 in sea air. There is also evidence that NaCl-Na_2SO_4 mixtures are more corrosive than Na_2SO_4 alone. While the same type of hot corrosion attack has been observed in stainless steels subjected to SO_2 atmospheres [2], attention here is focused on the problem caused by Na_2SO_4 in aircraft jet engines and marine gas turbines.

DeCrescente and Bornstein [2] have shown that Na_2SO_4 must be present on the attacked surface as a condensed phase, ordinarily a liquid, to cause hot corrosion. Na_2SO_4 vapor did not cause hot corrosion. For this reason, most investigations have found that for pressures near atmospheric this accelerated

attack occurs over the temperature range of about 1400-1900°F. In qualitative agreement with the effect of pressure on the dew point of Na_2SO_4, the temperature range of attack is increased with higher total pressures.

There has been comparatively little work aimed at understanding the mechanism of oxidation as altered by the presence of contaminants such as salts like Na_2SO_4, NaCl, or low-melting oxides such as V_2O_5. These materials can form liquid slags and hence cause catastrophic oxidation by virtue of removal of protective scales. This field of high temperature corrosion has recently been reviewed by Hancock.[3] In this review, nearly all the investigations reported were concerned with examination of field-returned samples or with attempts in the laboratory to make high-temperature corrosion tests which essentially duplicated field conditions. Very little work aimed at elucidating mechanisms has been reported, particularly in simple systems amenable to scientific analysis.

A. Hot Corrosion Attack

Characteristics

The alloys of main concern here are used as first- or second-stage blades and vanes in aircraft engines, and are the nickel-base superalloys containing typically 6-22% Cr, 0-26% Co, 1-10% of either Ta, Mo or W, 0-6% Al, 0-5% Ti, and small fractional percentages of carbon and other elements. A sample showing severe hot corrosion attack exhibits a heavy surface layer of oxides, and just below this layer, oxides intermingled with alloy-depleted nickel matrix, and below this level, chromium sulfide particles which may contain appreciable percentages of Ni, Co, Al, Ti, and refractory metals. As corrosion proceeds, the chromium sulfides are converted to oxide with the sulfur atoms thus released diffusing more deeply into the alloy to form more sulfides. The alloy matrix surrounding the chromium sulfides is depleted in chromium to an appreciable extent and would be expected to oxidize more readily than the original

alloy. However, this effect is considered to be of less importance than the rapid oxidation attack proceeding at the oxide/alloy interface because the oxide scale fails to act as a diffusion barrier, as would occur in normal air oxidation. Chromium sulfides both in grains and in grain boundaries cause loss of structural integrity, and in cases where such sulfides are formed deeply along grain boundaries, a severe reduction in mechanical properties results. Such reductions in mechanical properties are particularly severe in blades, which are highly stressed as compared to vanes.

Some recent hot corrosion experiments on a variety of alloys appear to confirm the original suggestion of Simons et al[8], that the catastrophic nature of the corrosion attack involves rapid oxidation of Ni_3S_2/Ni eutectic liquid. This liquid usually is short-lived, and may not be visible in an alloy cooled to room temperature because of the displacement reaction (7) (see below). On the other hand, Bornstein and DeCrescente[9] have found that oxidation attack of several different alloys in the presence of $NaNO_2$ salt closely simulates that for $NaSO_4$ attack. The conclusion reached is that sulfur and "alloy depletion" are not the important aspects of hot corrosion, compared to the presence of sodium compounds.

Hot-corrosion resistance can be achieved by preventing attack by the salt of the initial oxide layer on the alloy. This salt-oxide reaction will be considered first.

Scale - Salt Interaction

Since Na_2SO_4 is a very stable compound there is very little thermal decomposition of Na_2SO_4 according to the following reaction:

$$Na_2SO_4 = Na_2O + SO_2 + \tfrac{1}{2}O_2. \qquad (1)$$

However, if there is available an Na_2O "sink" which effectively retains an Na_2O activity well below unity (which is assumed by equation 1), then Na_2SO_4 can continually decompose. Formation of complex oxides involving Na_2O and oxides normally present in the oxide scale, such as Cr_2O_3, Al_2O_3, SiO_2, or WO_3, can serve as sinks for the Na_2O[4] by such reactions as:

$$2Na_2SO_4 + Cr_2O_3 + \tfrac{1}{2}O_2 \rightarrow 2Na_2CrO_4 + 2SO_2 \qquad (2)$$

Experimental corroboration of Na_2O-oxide interaction has been observed by Bergman and Kaufman[5] who found X-ray diffraction patterns for sodium tungstate, sodium tantalate, and sodium titanate in corrosion products on hot-corroded superalloys. Similarly an NiO scale breakdown by Na_2SO_4 would occur according to the following reaction:

$$Na_2SO_4 + 2NiO = 2Na\,NiO_2 + SO_2 \qquad (3)$$

$NaNiO_2$ has been reported by Bornstein.[6] Alternatively NiO may break down according to the following reaction:

$$Na_2SO_4 + NiO = (Na_2O \text{ in } NiO) + SO_2 + \tfrac{1}{2}O_2 \qquad (4)$$

A combination of both reactions, (3) and (4), may be operative. That NiO can dissolve some Na_2O has been suggested by Danek,[1] and Quets and Dresher.[4] The actual mechanism of scale breakdown is probably more complex than that suggested, but it seems obvious that, for an understanding of the hot corrosion mechanism, the area of salt/oxide interactions should be carefully investigated.

Although they have not as yet developed a detailed theory, DeCrescente and Bornstein[7] indicate from their work on molten salts (EMF measurements and SO_2 evolution) that they have evidence that the presence of oxides such as Cr_2O_3 on an alloy reduces the Na_2O concentration by formation of Na_2CrO_4 and thus lessens hot corrosion attack.

Alloy-Salt Interaction

Once the oxide scale has been penetrated, the next stage of attack is reaction between condensed Na_2SO_4 or Na_2SO_4-NaCl and the alloy itself. Various investigators have suggested reactions based on the early work of Simons[8], who suggested a reaction equivalent to the following:

$$4M + Na_2SO_4 = Na_2O + 3MO + MS. \quad (5)$$

However, Quets and Dresher[4] have shown by the use of Pourbaix-Ellingham diagrams that pure Na_2O, which has been considered as an important product of the hot corrosion attack by Na_2SO_4, cannot exist at unit activity with the products Ni_3S_2, NiS or CrS as would be required by equation (5). For this reason, equation (5) must be modified for both the case of M = Ni or M = Cr. If the Na_2SO_4 reacts with the metal to form a ternary sodium oxide and binary sulfide, a modified reaction becomes possible:

$$xM + Na_2SO_4 = Na_2M_yO_4 + M_{(x-y)}S \quad (6)$$

In support of this mechanism, the stabilities of the ternary sodium oxides extend to much higher values of P_{S_2} than those for pure Na_2O.

This mechanism is very similar to the one proposed for the oxide scale breakdown. However, since the reaction occurs at the metal-scale interface, its oxygen potential is set by that interface. During sulifidization, the oxygen potential at the metal-scale interface should be approximately the same as for a Ni-NiO interface because of the chromium depletion in the alloy. For the formation of a ternary sodium salt, the sulfur potential is high enough to allow the formation of nickel sulfides. However, due to the displacement reaction

$$Cr_{(\text{in alloy})} + NiS = CrS + Ni_{(\text{in alloy})} \quad (7)$$

NiS should be reduced by the matrix chromium to form the more stable chromium sulfide. But if the chromium content in the alloy is rather low, reaction (7) does

not occur rapidly or completely enough to reduce all the NiS. Therefore, in severe cases of hot corrosion, NiS (actually Ni_3S_2 on cooling to room temperature) may be left in the structure.

Effect of Alloy Composition*

As might be expected for a class of alloys with a very complex and widely variable composition, the individual effects of alloy components on resistance to hot corrosion is not unambiguous. Certain generalizations can be made, such as that resistant alloys usually contain fairly high chromium contents, around 15% Cr or higher. There appears to be agreement that molybdenum is harmful, but the behavior of other alloying elements is less consistent, and therefore not clearly established. Better understanding of compositional effects might be obtained after some of the scale-Na_2SO_4 and alloy-Na_2SO_4 interactions are further elucidated.

Research for Defining Mechanisms

The most important areas for additional research are the salt/scale and salt/alloy interactions in the temperature range of hot corrosion, and oxygen/alloy interactions at higher temperatures. Another area which needs attention is the stabilities (thermodynamics) of ternary sodium oxides.

Water vapor, a product of combustion, has not been seriously considered thus far as a corrosion variable, but it seems possible that water vapor in the engine might be significant in view of the ability of water vapor to cause oxidation at engine operation temperatures. Further study is indicated.

The suggestion of DeCrescente and Bornstein[7], that additions of certain oxides affect the Na_2SO_4-alloy reaction should be investigated further, as this obviously would be significant with regard to the type of corrosion mechanism operating.

*A more detailed discussion of the effect of alloy composition of hot corrosion is given in the next section on Material and Coating Development.

Since there is the possibility of using vanadium-containing fuels in gas turbines associated with ship propulsion, V_2O_5 contamination or possibly contamination by other fuel components should be studied. Some work along these lines has already been done, as shown in reference 3, but as in the Na_2SO_4 contamination case, much more work on mechanisms remains to be done.

Closely associated with phenomena already mentioned is the question of sulfur diffusion along grain boundaries and in the grains of nickel-base superalloys. This solid-state diffusion process is of prime importance in the formation of the chromium sulfide inclusions so characteristic of hot corrosion. One aspect that is of considerable practical importance is to ascertain those conditions which lead to excessively deep grain boundary penetration by sulfur. Like sulfur, oxygen tends to concentrate in grain boundaries and to form internal oxides much deeper along the alloy grain boundaries than in the bulk grains.

Research on Reducing Hot Corrosion

There appear to be four main avenues of research aimed at reducing hot corrosion attack.

Alloy Composition

By comparatively minor changes in alloy composition, it has been found that considerable improvement in hot corrosion resistance is possible, usually at a small sacrifice in high-temperature strength. However, as increased demands are made upon the mechanical capabilities of nickel-base superalloys, this road to corrosion resistance appears less feasible.

Coatings

NiAl-type coatings are now standard in military jet engines, where the temperatures are somewhat higher than in commercial engines. Through coating, considerable improvement in both oxidation resistance and hot

corrosion resistance is secured. However, increased demands for higher metal temperatures (approaching 1800°F (982°C)), for longer times between engine overhauls, and for improved coating reliability make current coatings less and less acceptable. Research activity in the coating field should be continued; hopefully some research would be aimed at the fundamental aspects involved, such as measurement of diffusion rates in moderately complex systems.

Rare Earth Additions

Fractional percentages of rare earth metals, such as cerium[10, 11] lanthanum[11], and gadolinium[11], have been found to generally improve hot corrosion resistance in binary Ni-Cr alloys and in superalloys. Much of this work has been carried out in laboratory tests, often of the simple "crucible type," but the few available hot corrosion tests in hot-corrosion rigs, simulating to some degree actual engine tests, have shown marked improvement. One cannot expect that rare earth additions could add more than about 1000 hours of life to jet engine blades and vanes. The principal difficulty with the use of rare earth additions is that a low melting phase associated with the Ni_5M/Ni eutectic (where M is a rare earth) occurs to reduce high-temperature strength properties. Recent laboratory work, however, shows that greater improvements in corrosion resistance are offered by rare earths when added in oxide form. If verified, this fact may imply a change in processing techniques through which rare earths would be present in the alloy as a well-dispersed oxide phase. Most important, theoretical rationalization and understanding of the effect of rare earth additions should be attempted.

Fuel Additives

This is discussed in the section under the heading of Environmental Effects.

B. High-Temperature Oxidation

Improved oxidation resistance for strong superalloys is desirable in blade applications. Higher turbine inlet temperatures could be accommodated, and the requirement for coating constricted air-cooling passages could be avoided. The problem is complicated because a few strong alloys, such as B1900, have excellent oxidation resistance but suffer hot corrosion attack. Therefore, a separation of the two modes of attack is not realistic. In the past, alloy oxidation has been a research area with an emphasis on short-range improvement of existing alloy compositions, with the best theory and experiments in alloy oxidation coming from other countries, namely Germany, England, and France. Suggested alloy oxidation research, with only short bridges to the improvement of commercial superalloys, includes:

a) the use of radiotracers and high resolution techniques to establish the role of rare earth and other additions like Si and Mn on binary and ternary alloy oxidation;

b) a study of the role of carbon in dissolved and combined form in alloy oxidation;

c) the role of the commonly used strengthening components, W and Mo, in alloy oxidation particularly for Co-base alloys;

d) further attempts to study the complex morphology and transport in the metal/scale interface when combined internal oxidation and external scale formation are occurring;

e) further study of the modes of failure of external Cr_2O_3 and Al_2O_3 scales and the "healing" processes;

f) specific studies relating the evaporation rate of Cr_2O_3 to the vapor pressures of the several vapor species for the oxide;

g) further studies of the phases formed and the kinetics of internal oxidation of alloys;

h) studies of the high-temperature mechanical properties of oxides (i.e., creep) and the relation of these properties to scale fracture;

i) preferential grain boundary attack in pure metals and alloys and its prevention;

j) many of the more fundamental aspects of alloy oxidation: nucleation of oxides on clean alloy surfaces, doping effect, solubilities and diffusivities of oxygen in nickel and cobalt, solubilities and diffusivities of aliovalent impurities in simple oxides, particularly CoO, NiO, Cr_2O_3, and Al_2O_3.

REFERENCES

1. "Hot Corrosion Problems Associated with Gas Turbines," ASTM Special Publication No. 421 (1967).

2. DeCrescente, M. A. and Bornstein, N. S., Corrosion, 24, (1968), 127.

3. Hancock, P., "Corrosion of Alloys at High Temperatures in Atmospheres Consisting of Fuel Combustion Products and Associated Impurities," Her Majesty's Stationery Office, London, (1968).

4. Quets, J. M. and Dresher, W. H., Journal of Materials (ASTM), 4, (1969), 583.

5. Bergman, Paul and Kaufman, Murray, Thompson Engineering Laboratory, General Electric River Works, W. Lynn, Massachusetts (personal communication).

6. Bornstein, N. S., United Aircraft Research Laboratories, E. Hartford, Connecticut (personal communication).

7. DeCrescente, M. A. and Bornstein, N.S., United Aircraft Research Laboratories, E. Hartford, Connecticut (To be published).

8. Simons, E. L., Browning, G. V., and Liebhafsky, H. A., Corrosion, 4, (1955), 505.

9. Bornstein, N. S. and DeCrescente, M. A., Trans. Met. Soc. AIME, 245, (1969), 1947.

10. Seybolt, A. U., Trans. Met. Soc. AIME, 242, (1968), 1955.

11. Wasielewski, G. E., Materials and Processes Laboratory, General Electric Company, Schenectady, N.Y., Report no. R68AEG430.

III. MATERIAL AND COATING DEVELOPMENT

Introduction

Although there are many types of hot corrosion which are potentially of interest to industrial gas turbine producers, this portion of the report will only consider those means that might lead to the development of improved sulfidation and oxidation-resistant alloys for turbines operating on diesel quality or better fuels.

This section will discuss the current status of corrosion-resistant cobalt-, nickel-, and iron-base alloy developments, attempt to predict what realistic improvements can be expected in the near and distant future, and suggest areas for potentially fruitful development activity.

A Committee on Coatings of the NMAB has made recommendations[1] regarding coatings for superalloys. We are in agreement with these recommendations. The pertinent recommendations of the Coatings Committee are contained in Appendix I. For this reason, coatings have not been given detailed consideration in this report except as required to place the need for coating development in perspective with the need for alloy development.

Current Status

In the early 1960's, it was apparent that the then-existing advanced alloys did not possess adequate sulfidation resistance to permit long-time operation in environments conducive to this type of attack. Hence, the gas turbine industry devoted considerable attention to coating development. Aluminide coatings were found to provide good corrosion protection. However, as overhaul lives were extended, the existing coatings broke down after several thousand

hours and did not provide adequate protection. This was especially true of those alloys developed for maximum strength capability, which required compositions of lower chromium content.

It soon became apparent that more inherent sulfidation resistance was required of turbine blade and nozzle guide vane alloys. The Naval Ships Systems Command established a program in 1964 with the following objectives:

1) Develop a turbine blade alloy combining the hot corrosion resistance of Udimet 500 in 1% sulfur diesel fuel combustion products with the strength and ductility of alloy 713C at 1600°F (100 hr rupture life at 43,000 psi).

2) Develop a cobalt-base turbine nozzle alloy with the 1900°F strength of WI-52 (100 hr rupture life at 10,000 psi) but with improved hot-corrosion resistance.

These targets were accepted by the metals industry, because, if met, the alloy would offer useful properties for all types of turbines. Soon several alloys appeared, such as MAR-M-421 (Martin Metals), Udimet 710 (Special Metals), IN-738 (The International Nickel Company), and more recently, MAR-M-432 (Martin Metals).* These met or came close to meeting the above targets for blades. They are currently being evaluated by the gas turbine industry and one, MAR-M-421, is being used in production. Several cobalt-base alloys developed in the Navy-General Electric program meet the targets for a cobalt-base nozzle material.

Extensive preliminary studies conducted by several investigators on simple alloy systems suggested that chromium, and, to a lesser extent, titanium and cobalt were the only elements that contributed in a beneficial way to sulfidation

*Compositions of all alloys mentioned in this report are contained in Table 1.

TABLE 1

COMPOSITIONS OF CERTAIN ALLOYS

Alloy Designation	Nominal Chemical Composition, Wt., %										Temperature Capability**-°F	
	C	Cr	Ni	Co	Mo	W	Cb	Ti	Al	Other*	100 hr.	1000 hr.
MAR-M-421		15.5	Bal.	10	1.75	3.5	1.75	1.75	4.25	-	1790	1690
Udimet 710	0.07	18	Bal.	15	3	1.5	-	5.0	2.5	-	1770	1675
IN-738	0.17	16	Bal.	8.5	1.75	2.6	0.9	3.4	3.4	1.75Ta	1810	1710
MAR-M-432	0.15	15.5	Bal.	20	-	3.0	2.0	4.3	2.8	2.0Ta	1810	1710
IN-792	0.21	12.7	Bal.	9	2	3.9	-	4.2	3.2	3.9Ta	1840	1740
Udimet 500	0.08	19	Bal.	19	4.2	-	-	3	3	-	1700	1580
Alloy 713C	0.12	12.5	Bal.	-	4.2	-	2	0.8	6.1	-	1810	1680
René	0.17	14	Bal.	9.5	4.0	4.0	-	5.0	3.0	-	1810	1730

* Most of these alloys contain 0.01-0.02 B and 0.10-0.20 Zr.

**Temperature to produce rupture in indicated time at 20,000 psi

resistance of nickel-base alloys. Some elements, such as tantalum, were beneficial solely with regard to oxidation resistance. Some, such as molybdenum and aluminum, were considered detrimental to sulfidation resistance. Other alloying elements were generally considered neutral or ineffective. These effects are not necessarily true for more complex alloys. Within the last two years it has been found that a proper balance of elements, particularly the refractory metals, can substantially improve sulfidation resistance even at relatively low chromium levels. For example, preliminary tests indicate that a new alloy, IN-792 (12.7 Cr), possesses nearly the corrosion resistance of Udimet 500 (17.5 Cr) but with roughly 50°F increased temperature capability (based on rupture strength) over alloy 713C. It is still under evaluation and has yet to be proven for turbine applications. The rare earths, as will be mentioned later, may also be useful.

While the alloys currently being developed offer improved high-temperature capability, they do not exhibit a corresponding improvement in intermediate temperature (1000 - 1500°F) strength. Similarly, alloys developed for improved sulfidation resistance often lack good high-temperature oxidation resistance, and, hence, may have to be coated. Clearly, therefore, the alloy developer must give more consideration to achieving an optimum balance of properties.

Small evolutionary improvements can be expected to occur in nickel- and cobalt-base alloys, but the lack of clearly defined requirements and markets for future needs tends to limit the support for development work by the alloy industry. An industry-government effort is needed to define requirements in terms of strength, corrosion resistance, and economics. Present generalities such as, "We need an alloy that can be used uncoated in place of the coated alloy XXX which we are now using," is an insufficient base upon which to establish an objective alloy development program. This will be particularly important in the development of fiber composites or dispersion-hardened alloys. These materials

will not have the same balance of properties with which designers are familiar. What will constitute a satisfactory solution to the hot-corrosion problem should be stated in terms commensurate with prudent economics. This can be done only when the different types of gas turbines are considered individually, because an alloy adequate for one type of service may be completely inadequate for another. Some specific requirements of aircraft turbine builders are contained in References 3, 4, and 5.

Alternate Approaches

As indicated, prior efforts to improve the hot-corrosion resistance of turbine blade and nozzle guide vane alloys have been largely in the area of alloying element modifications and/or coating application. Alternate approaches to the development of turbine blade and guide vane materials with better corrosion resistance/temperature capability might be possible if new strengthening mechanisms were evolved, which would permit the use of base systems and/or alloying elements with greater inherent hot-corrosion resistance.

A number of approaches have been considered for use with nickel-cobalt-, or iron-base turbine blades and guide vanes. For the purpose of this report, an improvement was defined as a system having:

- Sulfidation and oxidation resistance $\geq$ Udimet 500
- Temperature-strength capability for blades $\geq$ IN-100
- Temperature-strength capability for vanes $\geq$ WI-52

In order to guide establishment of future development programs so that efforts will be concentrated in the most fruitful areas, an assessment was made of the capability and probability of each approach. "Capability" was considered as an indication of the theoretical possibilities that an approach offers for achieving improvement, whereas "Probability" is a realistic but empirical assessment of the chances for realizing that capability. The

considerations were made in keeping with current technology and a realistic extrapolation of that capability into the near future, i.e., 1975. Results of this estimation are summarized in Tables 2 and 3 and are discussed in the following paragraphs.

Dispersion Hardening

Dispersion hardening is effective in strengthening alloys at high temperature (> 1600°F) but contributes little to low temperature (<1600°F) strength. Therefore, a useful blade material must combine dispersion-hardening with some other strengthening mechanisms such as precipitation-hardening or thermo-mechanical processing. Vanes do not require such great strength as blades. An insoluble dispersion, therefore, may effectively improve the high temperature. corrosion resistance of vane alloys.

1) Cobalt-Base Turbine Blades - There is no known strengthening mechanism which will impart sufficient low temperature strength to cobalt for application in advanced turbine blading, and, hence, this is not considered a worthwhile approach.

2) Cobalt-Base Vanes - Existing cobalt-base alloys possess adequate strength for vanes and, hence, addition of an insoluble dispersant, such as rare earth oxides, could improve temperature capability and/or high temperature corrosion resistance. Techniques for producing a dispersion-hardened complex alloy are not yet known. However, simple Co-Cr-dispersion-hardened alloys may be useful.

3) Nickel-Base Blades - A dispersion-hardened nickel-base alloy would offer improved temperature capability—perhaps as much as 100°F. The use of such an alloy, however, would necessitate the use of wrought blades. Since techniques for imparting dispersion

TABLE 2

ESTIMATED CAPABILITY AND PROBABILITY FOR IMPROVING HOT CORROSION AND/OR STRENGTH IN GAS TURBINE BLADES BY VARIOUS MATERIAL DEVELOPMENT APPROACHES

Base: Sulfidation & Oxidation Resistance ≥ Udimet 500
Temperature-Strength Capability ≥ IN-100

APPROACH	Cobalt-Base		Nickel-Base		Iron-Base	
	Cap.	Prob.	Cap.	Prob.	Cap.	Prob.
Dispersion Hardening	O	-	M	L	O	-
Fiber Strengthening	H	L	H	L	H	L
Mechanistic Study of Rare Earth Effects	M	M	M	M	L	L
New Precipitation Mechanisms	M	L	L	L	O	-
Intermetallic Compounds	L	L	L	L	L	L
Complex Alloy Systems (Extension of Current Efforts)	O	-	L	H	O	-
Coating Developments	O	-	H	M	O	-

O = Nil
L = Low
M = Medium
H = High
- = Not Applicable

TABLE 3

ESTIMATED CAPABILITY AND PROBABILITY FOR IMPROVING HOT CORROSION AND/OR STRENGTH IN GAS TURBINE VANES BY VARIOUS MATERIAL DEVELOPMENT APPROACHES

Base: Sulfidation & Oxidation Resistance ≥ Udimet 500
Temperature-Strength Capability ≥ WI-52

APPROACH	Cobalt-Base		Nickel-Base		Iron-Base	
	Cap.	Prob.	Cap.	Prob.	Cap.	Prob.
Dispersion Hardening	M	M	H	M	M	L
Fiber Strengthening	H	L	H	L	H	L
Mechanistic Study of Rare Earth Effects	H	M	H	M	H	M
New Precipitation Mechanisms	M	L	L	L	O	-
Intermetallic Compounds	H	L	H	L	H	L
Complex Alloy Systems (Extension of Current Efforts)	L	H	L	H	O	-
Coating Developments	H	H	M	M	O	-

O = Nil
L = Low
M = Medium
H = High
- = Not Applicable

strengthening to complex nickel-base super-alloys are not yet known, success will be dependent upon technical development. Addition of small amounts of rare earth oxides may offer improved oxidation and/or sulfidation resistance.

4) Nickel-Base Vanes - The same comments apply as under nickel-base "blades" except that vanes do not require such high strength. Therefore, simple Ni-Cr dispersion-hardened alloys may be useful.

5) Iron-Base Blades - Complex austenitic iron-base alloys have good strength in the lower temperature ranges, but lack good high-temperature strength. Dispersion-hardening could improve high-temperature strength, but it is unlikely that any advantage over a dispersion-hardened nickel-base alloy would be shown. Also, production problems would be the same. Therefore, this possibility warrants little effort, especially since any technology worked out for applying effective dispersion hardening to nickel-base alloys could also be applied to iron-base alloys. Simple Fe-Cr or Fe-Al dispersion-hardened alloys would not have adequate low-temperature strength.

6) Iron-Base Vanes - The comments made under number 5 above about complex austenitic alloys also apply to vanes. However, simpler dispersion strengthened iron-base alloys may develop useful properties for vanes.

Fiber Strengthening

The addition of strong metallic or nonmetallic fibers to a weaker matrix can result in composites with substantially improved strength over polycrystalline metals. Airfoils produced by this technique will probably be expensive and probably difficult to inspect by NDT techniques. Unless three-dimensional reinforcement is used, properties will be highly anistropic.

Fiber strengthening is believed to offer a high potential for increasing the temperature capability of Ni-, Co-, and Fe-base systems for blades and vanes. It will be difficult to produce fiber-strengthened airfoils with complex cooling passages. Hence, the improved temperature capability may be offset by inability to utilize cooling. The higher temperatures that would result would increase compatibility problems between the fibers and matrix. Reinforcement of weak but highly corrosion-resistant matrices should result in airfoils with good corrosion resistance. A problem might arise, however, if the fibers become exposed by foreign object damage.

The anticipated high cost of production would probably make fiber strengthening an unacceptable approach for many types of gas turbines. This combined with fiber-matrix compatibility problems are the main reasons for assigning a low probability for achieving success in all systems.

Fiber strengthening must be considered a long-range possibility.

Mechanistic Studies of Rare Earth Additions

It has been demonstrated that small additions of rare earths and their oxides substantially improve the hot corrosion resistance of cobalt-base and, to a lesser extent, nickel-base superalloys. To date, these studies have been largely empirical in nature. It is thought that if the mechanism (e.g., mechanical oxide keying, increased melting point of the sulfate-scale mixture, grain boundary stabilization, site for vacancy annihilation, etc.) by which rare earths effect this improvement were known, it might be possible to accentuate the effect and gain further improvement. Such information could be particularly useful in future alloy development programs.

It is believed that a study of this type and application of the knowledge gained in alloy development programs will offer a high capability for improving

cobalt-, nickel- and iron-base materials for vanes with a medium probability of achieving success. It is believed to offer a medium capability for improving cobalt- or nickel-base blade materials with a medium probability of achieving success. Iron-base materials are not considered a worthwhile approach because current iron-base alloys lack sufficient high-temperature capability.

This mechanism study might bear fruit in the near future.

New Precipitation Hardening Mechanisms

All commercial cobalt-base alloys rely upon solid solution strengthening or carbide hardening as there is no known precipitation mechanism which imparts high strength combined with high ductility. Nickel-base and austenitic iron-base alloys can be strengthened by a number of precipitation reactions, but only aluminum-titanium has been found effective for very high temperature (>1400°F) service. Other known precipitates ripen or dissolve at temperatures too low to be useful. Conceivably, new precipitation hardening systems, probably by taking advantage of advanced high purity production techniques, could be found to strengthen these alloys more effectively.

New hardening mechanisms must be considered a long-range approach.

1) Cobalt-Base Turbine Blades - Cobalt-base alloys generally possess adequate hot-corrosion resistance for blades but lack strength in all temperature ranges. A precipitation hardenable cobalt-base alloy might overcome this deficiency. This approach is considered to have medium capability potential but a low probability of achieving success.

2) Cobalt-Base Vanes - The above comments also apply to vanes but a much lower degree of strengthening might be realized and be sufficient for vanes.

3) Nickel-Base Blades and Vanes - About the only possibility is to find an element(s) which would increase the solution temperature for precipitates containing Cb, Be, etc. The potential and chance of success, on the basis of past studies, must be considered low.

4) Iron-Base Blades and Vanes - There is little basis for believing that a new precipitation mechanism would make iron-base blades or vanes useful.

Intermetallic Compounds

Intermetallic compounds are substances of high melting point and hardness. Prior developments have indicated inadequate elevated temperature strength and/or ductility. New alloy production techniques, particularly directional solidification, are believed to offer possibilities for obtaining useful properties. Another possibility would involve the use of intermetallic mixtures including insoluble dispersoids. The uses considered in this section are distinct from the well-established applications as a minor second phase in nickel-base alloys, or as a protective coating.

Intermetallic compounds should be considered a long-range approach.

1) Blades - Because intermetallics would not be expected to have good low temperatures ($<$ 1600°F) mechanical properties, this approach is considered to offer low capability for achieving improved characteristics for blade applications. The chances of effecting even a modest improvement are low.

2) Vanes - Since low temperature mechanical properties are not as critical for vanes, intermetallic compounds theoretically offer a high capability for achieving a significant improvement, but the chances for success are low because of ductility limitations.

Complex Alloy Systems

This is an extension of current efforts to develop alloys with improved properties by conventional alloying techniques or by development of eutectic compositions. These efforts will undoubtedly be continued by those skilled who are in the field. Further short-range improvements can be expected. Those who are involved should be given encouragement to make use of new and future production techniques such as directional solidification, dispersion hardening, results of rare earth mechanism studies, etc. If deficiencies in strength, ductility, or hot-corrosion resistance can be overcome thereby, a greater degree of freedom or latitude in compositional possibilities might be provided.

This approach is believed to offer the best short-range chance for improving temperature capability.

1) Cobalt-Base Blades - Lack of a system for imparting high-temperature strength to cobalt-base alloys precludes any fruitful development work being done.

2) Nickel-Base Blades - The temperature capability of nickel-base alloys has been extended to a higher percentage of the homologous melting point than for any other structural base metal. There is little room left for improvement, but the chances of achieving at least some further improvement in strength capability are considered high. As more is learned about factors that influence hot corrosion, higher strength alloys with improved resistance may be possible. New eutectic compositions are believed to offer a significant potential.

3) Cobalt- and Nickel-Base Vanes - It is highly probable that improvements will be made in both base systems, but the increase in capability would be low.

4) Iron-Base Blades and Vanes - Based on past work, there seems little hope for developing iron-base alloys with better temperature capability than cobalt- or nickel-base alloys.

Coating Developments

Improved coatings or coated base-metal systems with improved characteristics are required continually. It is essential that coating-base metal compatibility be evaluated early in the development of alloys. If possible, alloy and coating development should be carried out concurrently in order to maximize compatibility. The reader is referred to Reference 1 for recommended coating development efforts. Such effort is essential, because coatings will continue to be required for many turbine blade and vane applications, unless one of the foregoing material development approaches would result in a complete solution of the hot corrosion problem, an unlikely possibility.

Coated base-metal systems offer the best short-range potential for extending operating temperatures and/or life.

Recommendations

In making the following recommendations, the Subgroup on Alloying and Coating Development has not considered combinations of the various approaches. Some combinations, such as fiber strengthening of improved alloys, lead to synergistic effects which could result in significant improvements.

1) Establish meaningful targets for mechanical and environmental performance of advanced gas turbines. Represented viewpoints should include turbine producers and users as well as materials developers and designers.

2) Encourage a study of the mechanism of the effects of rare earth metal and oxide additions on the mechanical and corrosion-resisting properties of nickel- and cobalt-base alloys.

3) Encourage a study of the mechanism of the effects and interactions of refractory elements on sulfidation/oxidation-resistance of nickel- and cobalt-base alloys.

4) Evaluate the use of dispersion strengthening in conjunction with items (2) and (3) to produce improved vane alloys.

5) Concurrent alloy and coating developments should be carried on with the objective of optimizing the coating to the alloy.

6) Continue development of fiber strengthened composites. After attractive properties are obtained, emphasis should be placed on the development of fabrication techniques which will be economically competitive.

REFERENCES AND SELECTED BIBLIOGRAPHY

1. Myers, J. R., Gadd, J. T., and Talboom, F. P., "Coating Systems for Gas Turbine Engines," NMAB Coatings Committee Report Section V.a, in preparation.

2. Sims, C. T., Bergman, P. A., and Beltran, A. M., "Progress in the Development of Hot Corrosion Resistant Alloys for Marine Applications," Presented at ASME Gas Turbine Conference, March 9, 1969, No. 69-GT-16.

3. Bradley, E., Donachie, M., and Varin, J., "Material Requirements for Cooled Turbine Airfoils," Report to NASA Research & Technology Advisory Panel on Materials for Aircraft Engines (1967).

4. Donachie, M., Varin, J., Berkley, S., and Sprage, R., "Materials for Advanced Airbreathing Aircraft Engines," ASM Report System Paper No. D8-25.2, October 1968.

5. Ross, E. W., Sayer, E. D., Oxx, G. D., and Semmel, J. W., "Advanced Alloy Goals for 1972-76," General Electric Company, January 15, 1969.

6. Lombard, A., "Aircraft Power Plants — Past, Present and Future," Proc. Royal Soc., 298A, March 1967, pp. 1-37.

7. _____: "Business Jets Get Cooled Blades," SAE Journal, 75, December 1967, pp. 78-79.*

*Digest of Three SAE Papers with reference to three pertinent others.

IV. ENVIRONMENTAL EFFECTS

Introduction

The environment of the turbine engine is composed of the combustion products as well as material carried with the fuel and/or air. The latter, for example, could include trace metals and sulfur in the fuel and sea salt in the air. In addition, the operating characteristics of the turbine, namely pressure, temperature, flow velocity, and time of operation, may be considered environmental. These cannot be controlled once the thermodynamic and duty cycles are set. Finally, there are certain modifications of the turbine and its mode of operation that may result in environmental effects. It is assumed that these are subject at least to partial control. They include changes in the combustion system to produce less smoke and flame radiation, the use of fuel additives, and the control of flow paths, reactions, and deposit buildup, all of which can effect corrosion.

As discussed under Mechanisms, contamination of air by sea salt is the primary cause of hot corrosion of both coated and bare superalloys in a marine environment. Increasing sea salt concentration increases the intensity of corrosive attack, sometimes to catastrophic levels. At least in aircraft engines there seems to be no realistic way to remove salt completely from the environment.

Causes of Environmental Effects

This section discusses the individual factors, singly or in combination, that may cause environmental effects leading to high-temperature corrosion of superalloys.

Fuel and Its Contamination

Whereas aviation engines generally burn a highly refined distillate fuel, industrial turbines may burn any fuel, ranging from natural gas to heavy residuals. Natural gas in this country does not have objectionable contaminants, but in some parts of the world it may contain appreciable hydrogen sulfide. Similarly, distillate oils as produced at the refinery are quite free of contaminant, containing a maximum of 0.01% by weight of ash and 0.5% by weight of sulfur. JP5 fuel is limited to 0.4% sulfur. On the other hand, residual oil may contain excessive amounts of several objectionable elements depending upon what part of the world the crude came from and the degree of contamination that may have occurred during shipment. Among the offending elements are vanadium in the fuel as an oil-soluble porphyrin, sodium which may by partly sodium chloride introduced as sea water contaminant during shipment, and sulfur which is a constituent of the fuel. During the combustion process in a turbine many complex reactions take place which may result in the formation of vanadium pentoxide (a corrosive compound in its molten state), sodium sulfate (which is both corrosive and deposit forming), mixtures of alkali sulfates and chlorides, and complex sodium vanadates (which are lower melting and more corrosive than vanadium pentoxide itself).

The specification of fuels for gas turbines is under consideration by the ASTM. The absence of reliable test methods for determining trace metals has posed a problem, but the specification will probably include those elements which can be reliably analyzed. The specification is based on requirements set forth by manufacturers and users of gas turbines. The availability of fuels meeting these specifications has not been established. Four grades of fuel have been designated as shown in Table 4 and the accompanying footnotes. It will be noted that the vanadium content of grade 4-GT can reach 500 ppm. There is no

TABLE 4 - REQUIREMENTS FOR GAS TURBINE FUEL OILS

Designation[a]	Grade of Gas Turbine Fuel Oil	Flash Point, deg F (deg C)	Pour Point, deg F (deg C)	Water and Sediment, percent by Volume	Carbon Residue on 10% Residuum, Percent	Ash, percent by weight	Distillation Temperature, 90 percent point		Saybolt Viscosity, sec[b]		
							Deg F	Deg C	Universal at 100 F (38C)		Furol at 122 F(50C)
		Min	Max	Max	Max	Max	Min	Max	Min	Max	Max
No. 1-GT[c]	A volatile distillate for gas turbines requiring a fuel that burns cleaner than No. 2-GT.	100 (3S) or legal	0 (-18)[d]	0.05	0.15	0.01	-	550 (288)	-	(34.4)	-
No. 2-GT	A distillate fuel of low ash and medium volatility suitable for gas turbines not requiring No. 1-GT.	100 (3S) or legal	20 (-7)[d]	0.05	0.35	0.01	540 (282)	640 (338)	(32.6)	(45.0)	-
No. 3-GT[e]	A low-volatility, low-ash fuel that may contain residual components.	130 (54) or legal	-	1.0	-	0.03	-	-	45	-	300
No. 4-GT	A low-volatility fuel containing residual components and having higher vanadium content than No. 3-GT	150 (66) or legal	-	1.0	-	-	-	-	45	-	300

TABLE 4 (continued)

Designation[a]	Kinematic Viscosity centistokes[b] At 100 F (33C) Min	Kinematic Viscosity centistokes[b] At 100 F (33C) Max	Kinematic Viscosity centistokes[b] At 122 F (50 C) Max	Gravity, Deg API Min	Vanadium (V), ppm by weight Max	Sodium + Potassium (Na + K), ppm by weight Max	Calcium (Ca), ppm by weight Max	Lead (Pb), ppm by weight Max	Magnesium to Vanadium weight Ratio (Mg/V) Min	Magnesium to Vanadium weight Ratio (Mg/V) Max	Sulfur percent by weight Max
No. 1-GT[c]	1.4	2.5	-	35	2	5	5	5	-	-	0.5 or legal
No. 2-GT	2.0	5.8	-	30	2	4.3	10	5	-	-	0.5[h] or legal
No. 3-GT[e]	(5.8)	-	(638)	-	2[e]	5[e]	10[e]	5	-	-	i
No. 4-GT	(5.8)	-	(638)	-	500	10[f]	10[f]	5	3.0[g]	3.5[g]	i

TABLE 4 (continued)

FOOTNOTES

[a] No. 1-GT corresponds in general to Specification D 396 Grade No. 1 fuel and Classification D 975 Grade No. 1-D diesel fuel in physical properties.
No. 2-GT corresponds in general to Specification D 396 Grade No. 2 fuel and Classification D 975 Grade No. 2-D diesel fuel in physical properties.
No. 3-GT and No. 4-GT viscosity range brackets Specification D 396 Grades No. 5, No. 5(light, No. 5(heavy) and No. 6 and Classification D 975 Grade No. 4-D diesel fuel, which may be supplied provided metals composition requirements are met.

[b] Viscosity values in parentheses are for information only and are not limiting.

[c] Recognizing the necessity of additional requirements for certain types of gas turbines, the following may be specified for No. 1-GT fuel:
Luminometer number, min = 40
Thermal stability test for 5 hr. at 250°F (121°C) preheater temperature, 350°F (177°C) filter temperature and at a flow rate of 6 lb. (2.7 kg)/hr:
Filter pressure drop, max = 12 in. (30 cm) of Hg
Preheater deposit code, max = 2

[d] Lower or higher pour points may be specified whenever required by conditions for storage or use. When a pour point less than 0°F (-18°C) is specified for Grade No. 2-GT, the minimum viscosity shall be 1.8 cs (32.0 sec, Saybolt Universal) and the minimum 90 percent points shall be waived.

[e] For gas turbines operating below 1200°F (649°C) maximum gas temperature, the limitations on vanadium, sodium plus potassium, and calcium may be waived, provided that a silicon-base additive, or equivalent, is employed. The special requirements covering the addition of and the type of additive shall be specified only by mutual agreement between purchaser and seller.

[f] Where water washing facilities are available at the point of use, these requirements may be waived by mutual agreement between the purchaser and seller.

[g] Special requirements covering the addition of and the type of magnesium-containing additive, or equivalent, to be used shall be specified only by mutual agreement between the purchaser and the seller.

[h] For products outside the USA, the maximum sulfur limit shall be 1.0 percent by weight.

[i] Legal requirements to be met.

assurance that a turbine can run with this level of contaminant, even with magnesium additions, without producing excessive deposit buildup on the blades. Similarly, it is not certain that turbines will run for extended periods with untreated fuel containing as much as 5 ppm sodium and 2 ppm vanadium.

The U.S. Navy is currently considering the use of a multipurpose distillate fuel for marine gas turbines. This fuel would be used both for boilers and gas turbines. It offers significant improvement in fuel purity for boilers which have been operating on residual oil, but is a less-pure fuel for gas turbines. The permitted vanadium level is 2 ppm corresponding to the ASTM grades of GT-1 and GT-2. However, the sulfur level permitted is much higher, being up to 1.3%. The ash level also corresponds to the light ASTM GT grades. Work will be necessary to determine whether or not the multipurpose fuel will be practical for marine gas turbines.

Contamination of Fuel

Fuel contamination may be a serious problem, because all the foreign material is injected into the high-temperature region of the combustor. Cases have been cited in which sufficient residual oil mixed with the distillate fuel resulted in severe corrosion in about 100 hours. Sea water contamination also is serious. Sea water in diesel fuel may amount to 10 ppm salt expressed as sodium. After settling and coalescing this level may drop to 0.6 ppm. Care in the storage and handling of fuels is therefore indicated, but experience has shown that present standards of fuel cleanliness are unsatisfactory.

Trace Elements in Fuel

Vanadium and sodium are two metals in fuel which are the most critical so far as corrosion is concerned. Vanadium is likely to occur only in

less-refined fuels or from contamination. The field of fuel treatment has been investigated quite thoroughly during the past 15 years. If treatment is not employed, turbines must be operated at lowered firing temperature, with a penalty in performance. Treatments consist of removal of sodium and other water-soluble compounds by washing and centrifuging, or by coalescing and settling. Vanadium being in an oil soluble form is not easily removed and is treated by combination with an additive, such as magnesium or magnesium plus silicon. These additions form high-melting, noncorrosive and nondeposit-forming compounds, which, in theory, can pass harmlessly through the turbine.

Sulfur in Fuel

Sulfur will be found in most fuels, with the possible exception of natural gas, which may occasionally contain some sulfur. Some residuals may contain 4% sulfur although this is rare and 1% is more usual. Sulfur, like vanadium, is inherent in fuel and its economic removal is difficult. Furthermore, it may be present in such large quantities that it would be undesirable to try to tie it up with an additive. Tests have indicated that little or no improvement in turbine blade durability would result from an order of magnitude reduction in the specification limit for JP-5 fuel to 0.04 weight percent of sulfur, approximately the median of present production. Even if all the sulfur in fuel were removed, there still remains approximately 11% sodium sulfate in sea salt, which could be sufficient to initiate sulfate attack.

Air and Its Contamination

Contaminants in the air are more serious than those in fuel because a gas turbine consumes about 50 times as much air as fuel, so that 1 ppm sea salt in air would be equivalent in intake to 50 ppm in fuel. However, much of the air

never reaches a temperature where reactions with fuel sulfur could take place. Some air never reaches the combustor, but is removed from the compressor for blade or disk cooling. Air contaminants may be more serious in industrial and marine turbines than in aircraft turbines, because the exposure is continuous. The aviation turbine is subject to contaminant ingestion mainly when it is near the ground or water, such as in hovering helicopters or in coastal airports.

Although industrial wastes are a source of contamination in land-based turbines, by far the greatest amount of intake results from operation in a marine environment. Sea water has the following approximate salt composition:

$NaCl$	23 grams/liter
$MgCl_2 \cdot 6H_2O$	11 grams/liter
$Na_2SO_4 \cdot 10H_2O$	8 grams/liter
$CaCl_2 \cdot 2H_2O$	1.42 grams/liter
KCl	0.20 grams/liter
KBr	0.90 grams/liter

In this country and in England sea salt measurements have been made, that have led to several findings:

1) The quantity of salt in the air is greatly dependent on wind velocity when measurements are taken at unprotected deck locations. An order of magnitude difference was observed between unprotected and semiprotected locations.

2) Wind velocity also affects the size of particles as shown:

Weather

Fair	0.01 to 0.05 ppm with particle size 5 microns or less
Moderate . . .	up to 0.1 or 0.2 ppm with some particles up to about 20 microns
Rough	up to 1 ppm in gale conditions and higher in severe gales, with some very large particles.

3) For ships, such as fast patrol boats, the data are very dependent upon speed, weather, proximity of other ships, and other factors. Salt levels at engine intake vary from 0.01 to several ppm.

4) Work on particle size analysis has indicated that larger droplets contribute a greater proportion of the salt burden as the seas become rougher. The aerosol concentration is generally considered to include those particles smaller than 4 to 5 microns, and this does not increase as rapidly as the more massive particles as the wind speed rises.

Salt Separation

Experiments have indicated that reducing the amount of sea salt from the air is a reasonable approach to the control of hot corrosion. An extensive program was conducted for the U.S. Navy to determine the suitability of various types of salt separators for use with marine gas turbines. Types considered included knit mesh, electrostatic, cyclonic, moisture and inertial separators. Considering the factors of efficiency, cost, weight and size, ease of cleaning, maintenance, etc., the knitted wire mesh demister was considered to be the

most suitable for use in shipboard applications. It is estimated that at least 75% of the salt can be removed by this means. In England similar tests have demonstrated that the salt burden can be reduced to 0.01 ppm if filtration is efficient. Generally, the greatest efficiency of separation by filtration was found when the relative humidity was high and fell off with decreasing humidity. At low humidity, filtration was only about 10% efficient. However, it is doubtful if filters of this type could be used in aviation turbines.

For typical stationary engines operating under marine conditions with a fuel containing 0.3 ppm sodium and air containing 0.01 ppm sodium, approximately equal quantities of salt will be ingested via fuel and air. For example, a 24,000 bhp engine will ingest 9.11×10^{-3} pounds of sodium chloride per hour with the fuel and 8.28×10^{-3} pounds per hour with the air.

Corrosion by Salts

There is some evidence that sodium sulfate by itself is not particularly aggressive but when combined with other materials such as sodium chloride, other alkali metal salts, alkali earths, or carbon, significant hot corrosion occurs. Sea water contains all the necessary constituents to form an alkali sulfate slag even in the absence of sulfur in the fuel. It has been demonstrated that accelerated hot corrosion occurs only after molten sodium compounds condense on the metal surface; many investigators have reported upper and lower temperature limits for hot corrosion. The lower limit is controlled by the melting point of the compound and the upper limit by its boiling point. This suggests a means of preventing corrosion, namely, the control of engine operating conditions which will be discussed in the next section. If such control is not possible, some improvement may result from the use of blade coatings.

Blades coated with an aluminide layer are effective in aircraft turbine service. In the case of long life industrial turbines, it is doubtful that the coating would have an adequately long life.

Turbine Operation Characteristics

The conditions under which a turbine operates will have a marked effect on corrosion. However, there is very little that can be done to change these conditions without adversely affecting the performance of the turbine. Increasing exhaust gas pressure, temperature, or velocity accelerates hot corrosion although it is not clear whether the effect is all corrosion or partly erosion. Both chemical and physical reactions are pressure dependent. Dewpoints of sodium chloride and sodium sulfate are shown in the following table:

Concentration of NaCl, ppm	Dewpoint of NaCl at six atmospheres	Dewpoint of Na_2SO_4* at six atmospheres
0.01	878°F	1256°F
0.1	1022°F	1382°F
1.0	1157°F	1508°F

*Assuming NaCl has all reacted to form Na_2SO_4

This table indicates that solid sodium chloride is not likely to be deposited on the first rows of blades and only Na_2SO_4 is normally found in the blade deposits. It is also indicated that at 1382°F, for example, no deposition would occur if the concentration equivalent of NaCl before reaction was less than 0.1 ppm. It is not known how far the presence of other salts and surface oxides may change the Na_2SO_4 dewpoint. The current Navy practice of limiting the inlet gas temperature to 1550°F maximum for marine gas turbines circumvents the corrosion problem but seriously reduces the efficiency of the engine. Therefore, this approach cannot be regarded as a long-range solution. Operating a gas turbine

engine at temperature/pressure conditions that preclude condensation in hotter sections is also not a reasonable solution to the hot corrosion problem because there will be succeeding cooler stages where conditions exist for condensation and hot corrosion.

Operating time is another characteristic to be considered. Much more severe conditions can be tolerated in short-life military engines or in "peaking" turbines than in long-life industrial machines.

Controlled Turbine Operating Conditions

There are several conditions associated with the combustion system in existing turbines that might be modified to cause changes in environmental effects. First, considering the combustor itself, it has been shown that design modifications can be made within modest limits which will affect the outlet gas composition. Work has been done with low excess air combustion (mainly in boilers) which tends to prevent the formation of objectionable compounds. Use is made of recirculation to produce a less luminous flame that can result in lower metal surface temperatures. Combustor modifications have also been tried to prevent smoke, mainly for pollution reasons, but the smoke or carbon particles can also cause deterioration of metal surfaces.

Effect of Carbon

Carbon particles are an indication of poor combustion and may result from cracking of fuel at high temperature, poor mixing, or sudden quenching. Once formed, carbon is difficult to eliminate but recirculation is one possibility resulting in less luminous flames. With carbon present and conditions alternately carburizing and oxidizing, a severe growth of scale is noted which involves a selective removal of chromium and which can result in severe embrittlement.

A green appearance results; hence the name "green rot." Lower primary combustor temperatures have resulted in some control of smoke. This is done with more excess air, which may, in turn, result in combustion instability. Another possibility for smoke control lies in the use of fuel additives.

Smoke Suppressing Additives

Several additives containing either barium or manganese are in use as smoke suppressants. One of the more common is methyl cyclopentadienyl manganese tricarbonyl (Ethyl CI-2). As smoke suppressants they are very effective, but it is possible that their use may accelerate corrosion. The Navy feels that smoke additives should not be used on a continuing basis, because of possible harmful side effects. Others have found no increase in corrosion from the use of smoke additives.

Corrosion-inhibiting Additives

Hot corrosion caused by vanadium can be alleviated by the addition of aluminum, alkaline-earth metals (Mg, Ca, or Ba), or chromium to the fuel, air, or combustor exhaust gas. However, this addition can be accompanied by a serious buildup of deposits on turbine blades. These deposits are not molten, and not corrosive, but they could adversely affect the blade performance. Such deposits have been known to coat superheater tubes in boilers, and protect them from corrosion. Another approach might be to tie up the sodium or Na_2O as a low-melting or high-vapor-pressure compound, which would blow away or vaporize. Such a compound would form in preference to the stable sodium sulfate.

Blade Cooling

In the use of cooled components, the engine is operated at gas temperatures that favor the presence of fused salts, but the component surfaces are

maintained at a lower temperature by internal cooling. This appears to be an effective means of controlling hot corrosion, but it is not yet certain which temperature is important, that of the environment or that of the metal surface. There is evidence that cooled surfaces are beneficial in the case of oxidation but not so effective in preventing sulfidation.

Engine Washing

NaCl and Na_2SO_4 are water soluble. Removal of deposits of these salts from turbine surfaces by water washing has been shown to improve life markedly with respect to hot corrosion. The following conditions for washing are necessary:

1) Fresh water (potable at least) must be used.

2) Engine parts must be at final temperature, below ~200°F. This may require a several-hour wait.

3) Turbine should be rotated during washing (may be at relatively low speeds).

4) Sufficient water to remove all detectable salts must be used (exact amount depends on engine size).

5) Use of detergent or other cleaners should be avoided; many contain sulfates and other harmful compounds.

6) After washing, turbine should be rotated long enough to allow all water remaining to evaporate.

7) Engine inlet and exhaust should be covered to prevent subsequent entrance of additional salt.

The unavailability of water aboard Navy ships severely limits the applicability of this technique for both main propulsion and aircraft engines. In any case, the sea spray is immediately available upon takeoff.

Proposed Areas of Investigation

The areas proposed for investigation may be divided into two categories, those most profitable for study and those with less probable return. It will be noted that most of the recommendations for work involve experimental investigation. A very strong recommendation is made to perform any test programs involving fuels, contaminants and superalloys under realistic conditions.

Recommended Research Areas

Contamination levels. A documentation of the practical experience confirming the maximum tolerable level of trace metals (vanadium and sodium) in treated and untreated fuels and permissible salt ingestion levels in marine turbines is needed. Levels from 25 ppb to the ppm range have been reported as detrimental. Salt separation from the intake air would be a profitable area to pursue (if the ppm level is, in fact, detrimental) but futile if only 25 ppb is sufficient to initiate hot corrosion. Decreases from one ppm to lower values might increase blade life, but would not eliminate the problem. The present specifications for maximum sulphur in the fuels seem to be necessary and adequate. However, a further reduction in the specification is not expected to be beneficial.

Fuel modifications. There are a number of fuel additives which may reduce or eliminate hot corrosion resulting from trace metals in the fuel or salt ingestion. Chromium and magnesium salts are examples; further investigation of this approach is warranted.

Engine operating conditions—pressure, temperature, and velocity effects. There have been few systematic investigations of pressure, velocity, and temperature effects to correlate rig test and engine test results. Sufficient definitive studies should be conducted as a guide to establishing realistic rig test conditions.

Reaction and transport effects. This may be one of the prime areas for investigation. The conditions leading to the formation of a deposit from combustion gases passing over a heat-receiving surface have not been studied experimentally to any extent, although theoretical analyses have been made. An experimental study of the formation of deposits would seem to be a worthwhile research area. The role of erosive particles in removing protective oxide layers or detrimental deposits should also be studied.

Effect of metal cooling on corrosion and deposit formation. This area requires further experimental investigation. For instance, is deposit formation more marked in the case of oxidation than sulfidation? Does cooling tend to build up deposits?

Items in the following category are not necessarily less important than topics in category 1, but they are less fundamental, and their effects are apt to vary with designs of machines offered by different manufacturers.

Smoke-reducing additives that may affect corrosion. These may be less desirable than modification to the combustion system to prevent smoke. The problem appears to be one subject to treatment by individual manufacturers and is not considered suitable for a research effort.

Storage and contamination problems. These are problems to be solved by the turbine user.

Combustion environments. Economically, it does not appear attractive to remove noncombustible matter completely from fuel and air. However, combustion systems may conceivably be designed so that the residues will pass through the system instead of being captured. This problem should be attacked by each individual manufacturer, since a solution would most likely be peculiar to his particular machine.

REFERENCES

1. Conde, J. F. G., "The Control of Corrosion in Marinised Gas Turbines," Admiralty Materials Laboratory, Third Inter-Naval Corrosion Conference, London, April 14-18, 1969.

2. Bowers, N. K., Ministry of Defense, "Gas Turbines in the Royal Navy," Journal of Engineering for Power, January 1967, pp. 95-124.

3. MacNair, E. J., Ministry of Defense, "Salt in Air: Data from Meteorological Literature," Report SA/N/100/65, March 3, 1965.

4. Quigg, H. T. and Schirmer, R. M., "Effect of Sulfur in JP-5 Fuel on Hot Corrosion of Coated Superalloys in Marine Environment," Phillips Petroleum Report, 5058-68R, May 1968.

5. Bagnetto, Lucien, "Smoke Abatement in Gas Turbines," Progress Report No. 5, Navy Contract N00156-67-2351, February 1969.

6. Quigg, H. T. and Schirmer, R. M., "Effect of Sulfur in JP-5 Fuel on Hot Corrosion of Coated Superalloys in Marine Environment," Final Summary Report, Phillips Petroleum Report 4792-67R, June 1967.

7. Doering, Harvey von E. and Bergman, Paul A., "Construction and Operation of a Hot Corrosion Test Facility," Naval Ship Research & Development Laboratory Report 2844, March 1969.

8. Quigg, H. T. and Schirmer, R. M., "Effect of JP Fuel Composition on Hot Corrosion," Phillips Petroleum Report 4493-66R, September 20, 1966.

9. Ashbrook, R. L., "A Survey of Salt Deposits in Compressors of Flight Gas Turbine Engines, Lewis Research Center, NASA TN D-4999, January 1969.

10. Danek, Jr., G. J., "Hot Corrosion in Marine Gas Turbines," U.S. Navy Marine Engineering Laboratory, MEL R&D Report 392/66, October 1966.

11. Kaufman, R. E. and Pollini, R. J., "Gas Turbine Combustion Air Salt Aerosol Separation Program," Naval Ship Engineering Center, Project T-454, Task 105005, October 10, 1968.

12. Stringer, John, "Oxidation in the Gas Turbine: A Materials Problem in an Extreme Environment," A Lecture delivered at the University of Manchester Metallurgical Society, March 10, 1969.

13. Carlisle, D. R. and Pilkington, G., "Combustion Aspects of Industrially Applied Aero Gas Turbines," Symposium on Technical Advances in Gas Turbine Design, Warwick, Coventry, England, April 9-11, 1969.

V. EVALUATION

Characterization of Hot Corrosion Rig Tests

Introduction

This section of the report, describing the method for evaluating the hot corrosion resistance of various material systems in the laboratory, is discussed as related to gas turbine applications. Particular attention is paid to corrosive environments germane to engine operation with sea-salt-laden air and sulfur-bearing fuels. No consideration is given here to problems related to the use of lead- or vanadium-bearing fuels; however, the test methods employed are believed to be applicable. Moreover, the test parameters for evaluation of coatings are not covered in detail. Although the test equipment is identical, the severity of the test conditions is necessarily intensified to accelerate failure of coated parts.

The rigs in service today are described, including the test specimens, their method of evaluation, and the numerous applicable variables which control the degree of corrosive attack. In order to equate the performance of the various test rigs, an ASME-ASTM Gas Turbine Panel-sponsored roundrobin was conducted, with specified control of many essential variables. Insofar as they are available, the results are included and evaluated.

Some of the difficulties encountered in simulating and/or reproducing engine conditions are described. Recommendations for further research are given.

Early Testing Methods

Early studies relating to the effect of sulfate attack on superalloys were conducted in "crucible" tests principally by immersion in molten sodium sulfate or by heating a salt precoated specimen in air. Trace additions of NaCl in the Na_2SO_4 were found to greatly accelerate corrosion rates; 5-10% additions subsequently were made as standard practice. Testing normally was conducted near 1700°F, and the test periods ranged up to 100 hours depending upon the material systems being evaluated. A modification of this test, whereby the specimen is partially immersed in the molten salt, is in some use today as a preliminary screening test. Others have employed SO_2 and H_2S environments while maintaining the test specimen at an appropriate elevated temperature. Since these methods largely have been replaced in the U.S. by "dynamic" test rigs, further discussion of crucible tests is considered inappropriate. More details of the early test methods are available[1] elsewhere.

Current Status

The dynamic rig has evolved as a device producing a type of environment representative of that found in a gas turbine engine. Typically, the device consists of a source of combusted fuels into which a sea-salt-corrodent is aspirated prior to impingement on the surface of the test specimen(s). Combustion conditions are maintained on the oxidizing side of stoichiometry, and the specimen may, or may not, be cycled out of the flowing gas stream. The test specimen, which is varied in configuration, generally is evaluated by metallographic examination (i.e., change in cross-section) or weight-loss measurements (i.e., weight after cathodic descaling). In the following paragraphs, a more

1. Rentz, W. A., and Donachie, M. J., Jr., "Oxidation and Sulfidation Corrosion of Nickel Base Superalloys," presented at the 1966 National Metals Congress, 11/66.

detailed review of the rig, test, and evaluation variables employed by various investigators is presented. A summary of these details, identified by source, is presented in Table 5.

Heat Source

From the information available, the combustion of kerosene-type fuels takes place in a simulated turbine engine can-type combustor. One unique variation exists whereby jet fuel is burned to provide the appropriate gaseous environment without regard for temperature, the latter being maintained by passing the combustion products through a resistance heated tube furnace. JP4 and JP5 referee fuels are used predominantly, with some usage of diesel oil and natural gas. Fuel sulfur varies in the range 0.02-0.4% with the former fuels and around 1.0% with the diesel grades. Ditertiary butyl disulfide may be added to the fuel to achieve the desired sulfur level. Fuel - air ratios vary from "oxidizing" (>18:1) to as high as 120:1; however, the most frequented range is between 30-60:1. (Turbines normally operate in the range 50:1.)

Pressure

The pressure, as measured/calculated at the specimen, is nearly at one atmosphere for most rigs. Within the recent past, it has been confirmed that pressure contributes to the amount of salt that condenses on the surface of a test specimen for a given set of test conditions. The unavailability of high pressure systems is not from the lack of appreciation of the importance but rather the high costs associated with the installation of such a facility. Only one known source in the country can test to 15 atmospheres, at a time when engines are being designed to >20:1.

TABLE 5

SUMMARY OF VARIOUS HOT CORROSION TEST RIG PARAMETERS

TEST SOURCE	TEST TYPE	HEAT SOURCE	FUEL	FUEL / AIR RATIO	PRESSURE (ATM)	VELOCITY (FPS)	TEMPERATURE °F	TEMPERATURE ** METHOD	TIME *** CYCLE (MINS)	TIME TOTAL (HOURS)	CORRODENT (SALT) COMPOSITION	CORRODENT (SALT) CONC (PPM)	CORRODENT (SALT) APPLICATION	SPECIMEN TYPE	SPECIMEN Nº / TEST	METHOD OF ANALYSIS
Laboratory A	RIG	2 GAS BURNERS	CITY GAS	OXIDIZING	~1	•	1700 / 2000	TEMPLAC / OPTICAL	1.5 / 0.5	500 CYCLES	1% Na_2SO_4/H_2O		SPRAY-COOL CYCLE	AIRFOIL PADDLE OR BLADES	16	VOLUME LOSS / METALLOGRAPHIC
Laboratory B	RIG	2" CAN COMBUSTOR	MIL T-5621G JP-4R	20-35:1	~1	~700	1400 / 1750	HDN. PIN / OPTICAL	10 / 1	120	FED. SPEC. 66-M 1S1A	6	COMBUSTOR DISCHARGE	AIRFOIL PADDLE	12	VOLUME LOSS / METALLOGRAPHIC
Laboratory C	RIG	2" CAN COMBUSTOR	MIL T-5621G JP-4R	20-35:1	~1	~700	1400 / 1750	HDN. PIN / OPTICAL	10 / 2	•	FED. SPEC. 66-M-151A	•	COMBUSTOR DISCHARGE	WEDGE	•	METALLOGRAPHIC
Laboratory D	RIG	COMBUSTOR	DIESEL	•	~1	•	1900	T.C. (SPEC)	60 / 2	•	•	•	COMBUSTOR DISCHARGE	WEDGE	•	•
Laboratory E	RIG	COMBUSTOR + ELECTRICAL	MIL F-16684 (DIESEL)	>30:1	~1	LOW	1600 / 2050	T.C. (GAS)	VARI-ABLE	100-1000	ASTM D66S	S-200	COMBUSTOR INLET	1/8 D PIN	48	METALLOGRAPHIC
Laboratory F	RIG	1½" COMBUSTOR	DIESEL (1.0S)	54-68:1	~1	70	1600 / 1800	T.C. (GAS)	1440 / 1S	100->1000	ASTM D66S	7-8	FUEL	DISC	21	METALLOGRAPHIC
Laboratory G	RIG	2" COMBUSTOR	JP S	•	~1	MACH 0.S-1	1650 / 2100	T.C. (GAS)	60 / 3	100	ASTM D66S	S	COMBUSTOR DISCHARGE	WEDGE	8	WEIGHT CHANGE / METALLOGRAPHIC
Laboratory H	RIG	2" COMBUSTOR	JP-S (0.04S)	60-120:1	15	160-250	1600 / 2000	T.C. (GAS)	B / 2	VARI-ABLE	ASTM D66S	1	COMBUSTOR DISCHARGE	1/4 D PIN	48	WEIGHT CHANGE / METALLOGRAPHIC
Laboratory I	RIG	COMBUSTOR	JP SR (.05S) DIESEL (1.0S)	OXIDIZING	~1	•	1650 + 1950	OPTICAL	3/2/2	50-500	•	3.S-3S	COMBUSTOR DISCHARGE	WEDGE	9	WEIGHT CHANGE
Laboratory J	CRUCIBLE	ELECTRICAL	–	–	–	•	1700	T.C.	–	16	9S% Na_2SO_4 5% NaCl	–	IMMERSION	–	–	VISUAL / WEIGHT CHANGE
	RIG	2" CAN COMBUSTOR	MIL-J-5624G (JP S)	26:1	~1	>2000	1650 / 2000	T.C. (SPEC) + RADIATION	60 / •	1S0	FED. SPEC. 66-M-151A	3S	COMBUSTOR DISCHARGE	AIRFOIL PADDLE	8	WEIGHT CHANGE / METALLOGRAPHIC
Laboratory K	RIG	COMBUSTOR	JP 4R	•	~1	~700	1650	OPTICAL	600 / •	100	ASTM D66S	S	COMBUSTOR DISCHARGE	WEDGE	8	WEIGHT CHANGE / METALLOGRAPHIC
Laboratory L	RIG	CAN COMBUSTOR	MIL T-5621G (JP 4R)	54:1	~1	200	1650	OPTICAL	1S / 2	100	ASTM D66S	5	COMBUSTOR DISCHARGE	1/4 D PIN	8	METALLOGRAPHIC
Laboratory M	RIG	COMBUSTOR + ELECTRICAL	DIESEL (1.0S)	>30:1	~1	LOW	1600 / 2050	T.C (GAS)	3000 / 5	100-1000	ASTM D66S	S-200	COMBUSTOR INLET	1/8 D PIN	48	METALLOGRAPHIC
Laboratory N	RIG	COMBUSTOR	NAT. GAS / DIESEL (1.0S)	OXIDIZING	~1	25	1800	OPTICAL	60 / 2	1000	ASTM D665 Na + Mg NAPTHANATES	1	FUEL	1/4 D PIN	24	WEIGHT CHANGE / METALLOGRAPHIC
	RIG	6" COMBUSTOR	NAT. GAS / DIESEL	~50:1	1-7	500	1200 / 2100	T.C. (SPEC)	•	1S0	Na + Mg NAPTHANATES	1	FUEL	ID TUBE 1/4 D PIN PADOLE	4	WEIGHT CHANGE / METALLOGRAPHIC

*NOT REPORTED **ANALYTICAL/CONTROL ***HEAT ZONE/COOL ZONE

Velocity

There seems to be less attention focused on this parameter, although in the interest of turbine simulation high velocities appear desirable. Rig operators identify velocities from "moving" to Mach 1; however, most report operation (combustor discharge) in the range 200-700 fps. Velocity has influenced significantly the oxidation rate of TD NiCr (formation of volatile CrO_3); this suggests that further emphasis should be given to this variable.

Temperature

There is little consistency in the temperatures selected or the method of measurement. Many investigators conduct tests at various temperatures, or adjust conditions such that a gradient exists over the specimen test surface. Generally, temperature is controlled/monitored optically after the equipment was calibrated against instrumented (i.e., thermocouple) test specimens. Some workers indicate no means of correlation and apparently assume the specimen metal temperature to be equal to that of the surrounding gas stream as measured by thermocouple.

Time

Cycling between the set temperature and some lower temperature normally is employed; however, the cycle time varies from minutes to days as a function of testing source; most hold at temperature between 10 - 60 minutes, and at least one operator dwells at two temperatures before retracting the specimens from the test environment for cooling. Most frequently, tests are conducted for a period of 100 hours with some reported as high as 1000 hours. the latter being conducted in an effort to stimulate more accurately engine conditions.

Corrodent

Less variation exists with this parameter as most employ synthetic sea salt (ASTM D665) material sometimes diluted with distilled water to facilitate delivery. In order to avoid combustor fouling, the contaminant is introduced downstream of the combustor; this also minimizes salt loss due to deposition on the combustor walls. Concentration (i.e., parts per million of combustor air) is varied to suit the peculiarities of individual rigs so as to produce corrosion in a reasonable time period. (Salt level and temperature frequently are increased when rating coated materials which are more resistant to attack.)

Specimen Configuration

A cylindrical "pin" specimen with diameters varying from 0.125 - 0.25" is employed by a majority of investigators. This configuration is most convenient when metallographic (i.e., depth of attack) evaluation techniques are employed. Its disadvantages are its unsuitability for use in coating evaluation work (lack of small radii tapered section) and its potential effect on gas stream blockage. The airfoil paddle specimen (see Figure 1) is in frequent usage because of its application in thermal fatigue and coating testing. Also, most foundries supplying engine manufacturers have tooling available. Wedge-shaped specimens (modification of pin) also find application, their attractive features relating to ease of manufacture especially when wrought materials are included in a test program.

Evaluation Methods

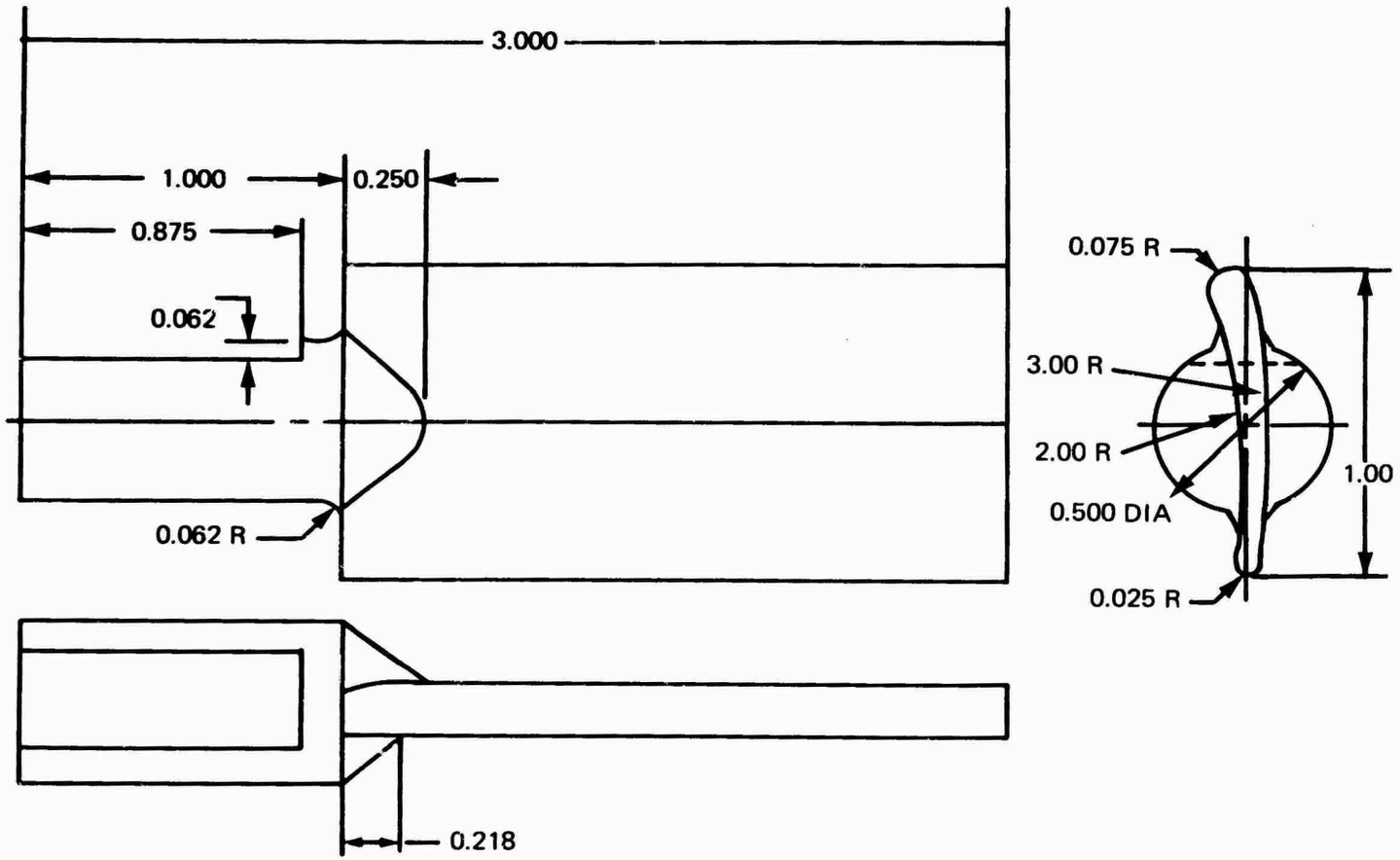
Two methods are employed, namely, weight change (loss) and metallographic (depth of attack). Investigators are divided evenly in their use; some report the use of both techniques in their analysis. The former approach requires the stripping of the oxide scale prior to weighing. This normally is accomplished electrolytically in a molten NaOH bath at approximately 800°F. Its principal

advantage is convenience. A disadvantage is that the partially-oxidized (nonstructural) zone is not stripped, thereby decreasing the accuracy of results. The metallographic approach, as the name implies, requires the sectioning and polishing of predetermined areas based on maximum attack or isotherms. The attractive feature is the ability to measure the loss of "structural" cross section and the availability of the microstructure for other studies. For those rating a material by the sectioning in the area of worst attack (regardless of metal temperature), this method is disadvantageous since proper interpretation is difficult without scale removal.

Selection of Test Parameters

As implied above, there are numerous variables to be selected and controlled in order to achieve satisfactory results. Among the early variables defined were temperature, salt concentration, and test duration. Operation of atmospheric pressure rigs in excess of about 1800°F produce little attack (excluding oxidation) unless special consideration is given to the addition of higher salt concentrations or the specimen is periodically recoated during temperature cycling. Generally, representative attack is produced in the range 1400-1750°F after an appropriate incubation period. This range broadens with test time at the lower (threshold) end of the temperature scale while remaining relatively fixed at the upper (terminal) end, the latter having been influenced by operating pressure. Caution must be taken to avoid too high salt concentrations with the associated short test times because misleading results can be obtained. This condition can be determined metallographically by the absence of the middle depleted metal-oxide zone. (Characteristically, there are three zones: (1) oxide zone, (2) depleted metal-oxide zone, and (3) depleted metal zone.) Test time varies since it is influenced significantly by the choice of the other variables.

Figure 1. Airfoil Paddle Specimen



All dimensions are in inches
unless otherwise specified.

As the test methods evolved, the control of fuel sulfur and the influence of thermal cycling were added. Sulfur has been shown to affect the rate of attack on materials to varying extents depending upon alloy composition. Thermal cycling creates interfacial shear stresses from the thermal expansion mismatch; the result in many cases is an acceleration in rate of attack.

Finally, the influence of pressure has been recognized and included by at least two test rig operators. As previously indicated, this feature is very desirable when conducting tests above 1800°F. Unfortunately, the significant expense associated with its implementation precludes its more extensive use.

The joint ASME-ASTM Gas Turbine Panel has conducted a roundrobin test to compare the performance of the several rigs currently being employed. The test parameters are identified in Appendix II, and the test results displayed in Figure 2. Analysis reveals that most rigs are capable of qualitatively ranking materials where significant differences exist; however, the quantitative results leave something to be desired. This latter variability undoubtedly exists in certain cases from test-to-test in the same rig. It is believed that this can be attributed to lack of precise control of test conditions rather than inherent variability in the hot corrosion process. Metal temperature and salt concentrations are difficult to control throughout an extended test period and may be responsible for the greatest error in results.

Alloy	Lycoming	Caterpillar	TRW	Union Carbide	Allison	Westing	Chromalloy	Phillips	U.S. Navy	P & W	INCO	G.E.	Westing R&D	Average Rank	Order of Alloys by Average Rate
U500	1	2	2	2	1	3	1	1	3	3	3	3	1	2.00	1
IN 738X	2	1	1	3	3	2	3	2	2	2	1	2	3	2.08	2
MAR-M-421	3	3	3	4	4	1	2	4	1	5	2	1	2	2.69	3
U700	4	4	4	1	2	4	4	3	4	1	4	4	4	3.31	4
INCO 713C	5	6	5	5	6	5	6	5	5	6	6	5	5	5.38	5
IN 100	6	5	6	6	5	6	5	6	6	4	5	6	6	5.54	6
No. of Alloys Not ranked according to average	0	4	2	4	5	2	4	2	2	5	5	2	2		
Total number of places removed from average	0	4	2	6	6	4	4	2	4	8	6	4	2		

Figure 2. Ranking of Alloys by Participant

A. Recommendations

1. Promote the standardization of a hot corrosion test to minimize duplication of effort within the turbine engine industry. Although the Committee members agree on those parameters to be controlled, their specification was not readily accepted. The discussion may be summarized as follows:

Parameter	Comment
Heat Source	JP4/JP5 fueled combustor; fuel: air ratio (min.) and sulfur level (range) to be controlled
Pressure	Atmospheric (high pressure desirable but too costly for consideration)
Velocity	200 - 700 fps
Temperature	No agreement but should be between 1500-1800°F; optically monitored (min.) but calibrated against specimen metal temperature
Time	Cycling to be included but no agreed upon duration
Corrodent	ASTM D665; concentration not defined; probably requires two levels (e.g., 1 & 5 ppm); injection point needs study (i.e., reaction time vs. combustor length)
Specimen Configuration	Cylindrical (e.g., 1/4 D)
Evaluation Method	Metallographic (per GTP roundrobin)

2. Investigate causes for lack of repetitive quantitative test results as revealed by roundrobin test effort.

3. Provide industry with an available high pressure testing source (e.g., NASA) to evaluate quantitative importance of this parameter and develop means for proper compensation (e.g., increased salt levels).

4. Collect and analyze, on an industry-wide basis, the degree of correlation between engine and rig experience in rating superalloy materials and coatings.

VI. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

Overall Situation

1. Hot corrosion is a current threat only in the important case of military turbines operating in marine environments. Engine design and operation trends suggest that it will be of more concern to commercial and military cruise engines in the future.

2. Understanding of the mechanism of hot corrosion of turbine alloys is rudimentary and needs additional effort now in view of anticipated future difficulties.

3. The immediate hot corrosion problem is being handled by adjustments in turbine materials and coatings. Attempts to alter the environment for aircraft engine operation appear not worth the considerable effort that would be involved. Such is not true for stationary engine operation, such as in marine turbines.

Mechanisms

1. Hot corrosion resulting from liquid salt deposits is encountered in the temperature range 1400-1900°F, and appears to be the result of a two-step attack: first, a breakdown of the natural scale; second, direct attack on the metallic substrate. Study is needed of the sulphate/scale and sulphate/metal reactions. In this connection, thermodynamic data are needed on the various components involved in the sulphate/scale reaction to substantiate presently proposed mechanisms.

2. Encouraging progress is being made in understanding the kinetics of the oxygen/metal reaction at high temperatures, above the hot corrosion regime. However, much more information is needed, particularly on simple alloy systems amenable to scientific analysis. The microstructure of the scale and that of the substrate and their interdependence have important effects—oxidation and hot corrosion, and are particularly recommended for study, since there is considerable evidence that considerable improvements can be made in oxidation resistance without a trade-off with strength. The use of rare earth oxides as dispersions appears particularly interesting. Information is needed on oxidation kinetics over a range of oxygen pressure, defect structure of doped and mixed oxides, selective oxidation to form sesquioxides and spinels, solubility and diffusion of oxygen in metals and cations in oxides, and mechanical properties of scales.

Alloy and Coating Development

1. There appears to be a reasonable prospect for further enhancement of temperature capability, despite the fact that superalloy-base systems are operating close to their melting points in advanced gas turbines, and further alloy development along traditional lines is encouraged. Of more importance are new approaches, including dispersions via the stable oxide route, dispersed fibers (particularly oxides), intermetallic compounds, and directionally solidified eutectic systems.

2. The practical development of commercial alloys needs guidelines provided by basic research on the effects of individual elements on hot corrosion and oxidation resistance, as recommended above.

3. Practical alloy development for specific applications requires of target properties (principally temperature, stresses, and lives) which reflect the design trends in the next generation of engines and that are realistic in terms of materials capabilities.

4. Since future hot components for advanced gas turbines almost certainly will be coated, it is urged that coating development proceed concurrently with alloy development in a systems approach.

Environmental Effects

1. The data on tolerable contamination limits for impurities like salt, sulphur, and trace metals are avaialble, but need collection, organization, and dissemination.

2. Little can be done to reduce the contamination in aircraft jet engines, since most of it is ingested with the air intake. However, for stationary engines, continued investigations of fuel additives which may reduce hot corrosion are encouraged.

3. The mechanism of deposition of solid particles on turbine parts is not well understood and further experimental work is needed.

Evaluation

1. The lack of correlation among laboratories conducting rig tests is disturbing, although the qualitative agreement on rating of materials appears reasonable. Continued work is needed to standardize rig tests and to establish the correlation of such tests with service conditions.

2. A high-pressure rig which is available to the industry is needed.

APPENDIX I

Recommendations from

COATING SYSTEMS FOR GAS TURBINE ENGINES
(Section Va)

J. R. Meyers, J. D. Gadd, & F. P. Talboom

Prepared for the Coatings Committee of NMAB

It is believed that a number of research and development programs can be outlined that will greatly assist in the development of advanced coating systems for superalloys to be used in future gas-turbine engines:

PRIMARY

1. Conduct studies to thoroughly evaluate the potential (i.e., determine advantages and limitations) of newer coating techniques for depositing advanced coatings on superalloy components used in gas-turbine engines. Processes to be considered should include: (1) cladding, (2) electrodeposition from fused salts, (3) pyrolytic deposition from organometallic vapors or solutions, and (4) physical vapor deposition, especially as applied to alloys. Successful research results in developing new coating processes probably will be necessary in order to permit deposition of advantageous coating alloys.

2. Develop a recoating capability that will minimize (or eliminate) substrate-metal loss.

3. Develop nondestructive testing methods for process control and for predicting the useful-remaining life of coated turbine-engine components. Techniques should measure or identify defects, corrosion damage, coating thickness, extent of coating-substrate interdiffusion, fatigue damage, and wall thicknesses of cooled components.

4. Develop manufacturing techniques for the reliable coating of extremely small diameter internal cooling passages used in convection and transpiration cooling.

5. Develop automated manufacturing processes in order to improve coating reproducibility and reliability.

SECONDARY

1. Conduct research to statistically define the effect of modifier elements (e.g., rare earths) on the oxidation and sulfidation resistance of aluminide coatings.

2. Determine the effect of alloying elements on the compositional range of NiAl (CoAl). If certain elements can be added that will increase the aluminum content of this intermediate phase, the larger reservoir of available aluminum could increase coating life expectancies.

3. Oxidation and sulfidation kinetics (using both kinetic and static tests) should be determined for promising binary, ternary, and quaternary alloys in order to find a replacement coating for the basic, currently-used aluminides. These alloys should have some inherent ductility to be considered for use as future coatings.

4. Attempts should be made to raise the melting point of the nickel (cobalt)-poor, aluminum-rich diffusion zone in currently-used aluminide-coating systems. Modifier elements may prove to be effective in satisfying this necessity for future aluminide coatings.

5. Additional research to develop a coating for dispersion-strengthened alloys that will function for long times at temperatures above 2000°F is recommended.

6. Continue the preliminary studies of adding discrete particles (e.g., Al_2O_3) to the coating in order to improve oxidation and sulfidation resistance of aluminide coatings.

7. Develop a simplified procedure for coating turbine-blade tips to provide for oxidation and sulfidation resistance at this location after minor blade-length modifications have been made to coated blades during engine fit-up.

8. Determine the effect of coating-process variables, coating chemistry, and post-coating heat treatments on (aluminide-type) coating ductility.

9. Establish the effect of long-time service on the mechanical properties of coated components, especially thin sections.

10. Continue research on the use of diffusion barriers (or elements added to the coating to reduce thermodynamic activities of diffusing species) to minimize interdiffusion between the coating and the substrate.

11. Obtain a more comprehensive and fundamental understanding of degradation phenomena for coated components.

12. Continue research on the development of protective coatings for columbium- and chromium-base alloys.

APPENDIX II

"Round Robin" Hot Corrosion Testing Program

The Gas Turbine Panel of the Joint Committee on Effect of Temperature on the Properties of Metals is sponsoring, through its Hot Corrosion Task Force, a roundrobin burner rig testing program.

Hot Corrosion data have been generated in many burner rigs of varying design. Testing procedures from lab to lab differ in operating environment, specimen geometry, time and temperature of testing, and method of assessing corrosion damage. As a result, there is little, if any, common ground on which results can be compared.

It is the purpose of this program to compare the data generated when various rigs are operated to as close a set of target test conditions as peculiarities of individual pieces of equipment will allow. If successful, this program could be extended in directions which, hopefully, would ultimately lead to the definition of a standard procedure. It is recognized by the Task Force that we do not have the necessary background knowledge and understanding of the gas turbine operating environment to specify standard equipment and procedures at this time.

Since this is a committee-sponsored project, those desiring to participate will be expected to conduct exposures in their equipment without charge.

A large number of specimens will be required to conduct this program. It is estimated that about 150 specimens of both U-500 and Inco 713C, and 75 specimens of each of the other four materials listed below, will be required. I have had offers from organizations to furnish some of the specimens needed. It would be desirable to have this burden shared by as many as are willing to contribute. Ideally, if we had six volunteers, each could provide the necessary specimens of one composition.

Participants in the roundrobin should adhere as closely as possible to the target test conditions listed below. Any deviations should be explained when test results are reported. Target test conditions evaluation procedures for the roundrobin are:

1. Specimen - 1/2 inch round, 3 inch long.

2. Materials - all cast, each composition from single heat.

- Inco 713C
- In 100
- U-500
- U-700
- Mar M421
- Inco 738X

3. Fuel - JP-4 referee with 0.15-0.2% S.

4. Time - 100 hours.

5. Temperature - 1650°F metal temperature.

6. Salt composition - Artificial sea water according to ASTM D665, ASTM Standards 1961, Part 7, p. 312, or ASTM Standards 1967, Part 17, p. 253. A similar but simpler-to-make-up specification is ASTM D1141-52, ASTM Standards 1967, Part 23, p.207.

7. Salt concentration - 5 ppm in "high velocity rigs" and 100 ppm in "low velocity rigs." The concentration of corrodent to be used was particularly difficult to deal with because of the wide variation that exists among the different burner rigs in use today. However, there appeared to be one reasonable way to circumvent the problem. Burner rigs seem to fall into two distinct categories, "low velocity" (0 to about 50 ft/sec.) and "high velocity." "High velocity" (50 ft/sec. and above) rigs generally use a few parts per million of corrodent while "low velocity" rigs require hundreds of parts per million. It is suggested that we specify low salt concentrations for the roundrobin instead of one, 5 ppm and 100 ppm. Participants would choose the concentration closest to the one they normally use.

8. Duplication - Duplicate test runs of 8 specimens. Each group of 8 will contain:

U-500	- 2 specimens
Inco 713C	- 2 specimens
IN 100	- 1 specimen
U-700	- 1 specimen
Mar M421	- 1 specimen
Inco 738	- 1 specimen

9. Corrosion Measurement Technique.

Metallographic Measurements. Two cross-sectional areas of each specimen are mounted for examination. One represents a zone of maximum visual attack and the other represents a zone of average visual attack. For a specimen corroded over half or less of its length, the sections are taken in a corroded zone and a noncorroded zone. Each of the cross-sectioned areas is measured for hot-corrosion effects across two diameters approximately 90° apart as shown in the attached figure, thus, each specimen is measured in four places. Two types of hot-corrosion effects are determined; these are gross (massive) attack and maximum attack, illustrated in the attached figure. All values are reported as loss in diameter (mils).

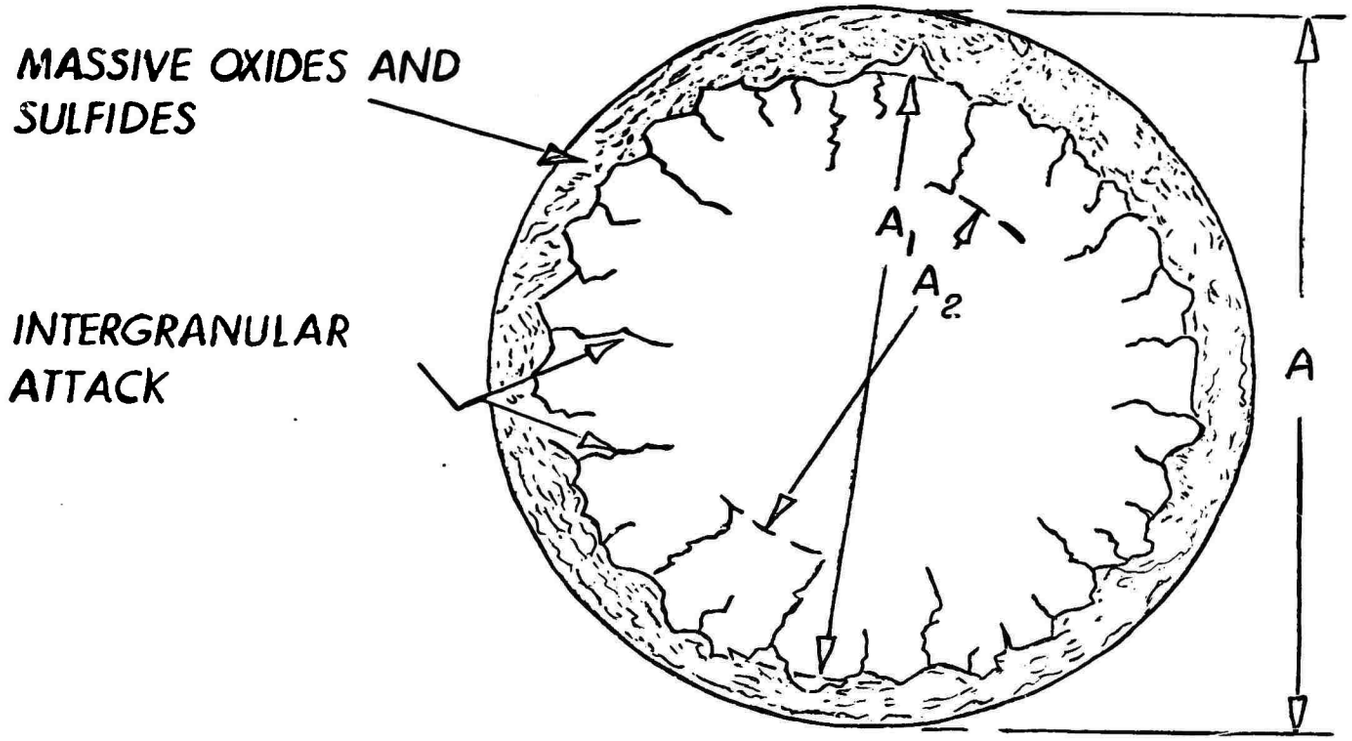
Surface Loss (Gross Attack) is a measurement of all material loss, plus any massive oxidation and sulfidation; it does not factor in other types of subsurface attack,such as intergranular attack. For each specimen, four measurements are reported to show the consistency of attack. The measurements are averaged together, and this new value reported and plotted as the gross attack.

Maximum Attack is a measurement which includes gross attack plus the depth of penetration of all sulfides and oxides, which may be scattered or in local concentrations; e.g., grain boundaries. The depth of subsurface oxides and sulfides may vary from one side of the specimen to the other side; thus, measurements in terms of loss in diameter are qualified as attack on both sides (B), mostly on one side (M), and on one side (O). A measurement for each cross-sectioned area is reported to indicate the consistency of attack, but only the greatest value is considered the maximum attack for the alloy.

10. Thermal Cycling.

No specific thermal cycling schedule has been specified. Rather, each participant should use that, if any, which is customary for his test procedure and report same with his results.

Method of Measuring Hot Corrosion Attack



A = ORIGINAL DIAMETER, MEASURED WITH A MICROMETER.

A_1 = DIAMETER OF STRUCTURALLY USEFUL METAL. MEASURED AT 100X

A_2 = DIAMETER OF METAL UNAFFECTED BY OXIDES AND SULFIDES, MEASURED AT 100X

SURFACE LOSS: $A-A_1$ LOSS IN DIAMETER DUE TO MASSIVE OXIDES AND SULFIDES.

MAXIMUM ATTACK: $A-A_2$ LOSS IN DIAMETER DUE TO ALL FORMS OF OXIDATION AND SULFIDATION.

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* National Materials Advisory Board, Division of Engineering, National Research Council, National Academy of Sciences-National Academy of Engineering	2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b. GROUP

3. REPORT TITLE
HOT CORROSION IN GAS TURBINES: MECHANISMS; ALLOY & COATING DEVELOPMENT; ENVIRONMENTAL EFFECTS; EVALUATION.

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
FINAL REPORT

5. AUTHOR(S) *(First name, middle initial, last name)*
COMMITTEE ON ATMOSPHERIC DETERIORATION OF SUPERALLOYS, National Materials Advisory Board, Division of Engineering, National Research Council, NAS-NAE

6. REPORT DATE May 1970	7a. TOTAL NO. OF PAGES 70	7b. NO. OF REFS 31
8a. CONTRACT OR GRANT NO. DA-49-083 OSA-3131 b. PROJECT NO. c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) NMAB-260 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* None	

10. DISTRIBUTION STATEMENT
This document is subject to special export controls and each transmittal to foreign governments or foreign nationals may be made only with prior approval of the Office of the Director of Defense Research & Engineering (Chief, Materials Division, OADCT).

11. SUPPLEMENTARY NOTES None	12. SPONSORING MILITARY ACTIVITY ODDR&E, Department of Defense The Pentagon, Washington, D. C.

13. ABSTRACT

Hot corrosion (sulfidation) in gas turbine engines has become a major problem because of the increased use of alloys low in chromium and the operation in environments containing alkali metal salts, especially near sea water.

Sulfur can enter a gas turbine from the fuel, and chloride and sulfate salts from the air. There is little prospect for removal of these contaminants to such a degree as to eliminate the problem. However, from 10 to 75% of sea salt can be removed from the air intake to retard the attack. Data on tolerable levels of contaminants are needed.

Engine testing is still the only reliable evaluation method to check improvements in the hot corrosion resistance of materials. Reproducibility in test results from test rigs in different laboratories is very poor, and further effort toward test rig standardization, correlation of the data between different tests, and interpolation of tests results and extension to different testing conditions, all are needed.

Specific recommendations for attacking the hot corrosion problem are detailed in the report.

DD FORM 1 NOV 65 1473 REPLACES DD FORM 1473, 1 JAN 64, WHICH IS OBSOLETE FOR ARMY USE.

UNCLASSIFIED
Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Sulfidation						
Hot Corrosion						
Oxidation						
Alloy Development						
Nickel-Base Alloys						
Coatings						
Test Methods						

UNCLASSIFIED

Security Classification

THE NATIONAL ACADEMY OF SCIENCES is a private, honorary organization of more than 700 scientists and engineers elected on the basis of outstanding contributions to knowledge. Established by a Congressional Act of Incorporation signed by Abraham Lincoln on March 3, 1863, and supported by private and public funds, the Academy works to further science and its use for the general welfare by bringing together the most qualified individuals to deal with scientific and technological problems of broad significance.

Under the terms of its Congressional charter, the Academy is also called upon to act as official—yet independent—advisor to the Federal Government in any matter of science and technology. This provision accounts for the close ties that have always existed between the Academy and the Government, although the Academy is not a governmental agency and its activities are not limited to those on behalf of the Government.

THE NATIONAL ACADEMY OF ENGINEERING was established on December 5, 1964. On that date the Council of the National Academy of Sciences, under the authority of its Act of Incorporation, adopted Articles of Organization bringing the National Academy of Engineering into being, independent and autonomous in its organization and the election of its members, and closely coordinated with the National Academy of Sciences in its advisory activities. The two Academies join in the furtherance of science and engineering and share the responsibility of advising the Federal Government, upon request, on any subject of science or technology.

THE NATIONAL RESEARCH COUNCIL was organized as an agency of the National Academy of Sciences in 1916, at the request of President Wilson, to enable the broad community of U. S. scientists and engineers to associate their efforts with the limited membership of the Academy in service to science and the nation. Its members, who receive their appointments from the President of the National Academy of Sciences, are drawn from academic, industrial and governmental organizations throughout the country. The National Research Council serves both Academies in the discharge of their responsibilities.

Supported by private and public contributions, grants, and contracts, and voluntary contributions of time and effort by several thousand of the nation's leading scientists and engineers, the Academies and their Research Council thus work to serve the national interest, to foster the sound development of science and engineering, and to promote their effective application for the benefit of society.

THE DIVISION OF ENGINEERING is one of the eight major Divisions into which the National Research Council is organized for the conduct of its work. Its membership includes representatives of the nation's leading technical societies as well as a number of members-at-large. Its Chairman is appointed by the Council of the Academy of Sciences upon nomination by the Council of the Academy of Engineering.

THE NATIONAL MATERIALS ADVISORY BOARD is a unit of the Division of Engineering of the National Research Council. Organized in 1951 as the Metallurgical Advisory Board, through a series of changes and expansion of scope, it became the Materials Advisory Board and, in January 1969, the National Materials Advisory Board. In consonance with the scope of the two Academies, the general purpose of the Board is the advancement of materials science and engineering, in the national interest. The Board fulfills its purpose by: providing advice and assistance, on request, to government agencies and to private organizations on matters of materials science and technology affecting the national interest; focusing attention on the materials aspects of national problems and opportunities, both technical and nontechnical in nature, and making appropriate recommendations as to the solution of such problems and the exploitation of these opportunities; performing studies and critical analyses of materials problems of a national scope, recommending approaches to the solution of these problems, and providing continuing guidance in the implementation of resulting activities; identifying problems in the interactions of materials disciplines with other technical functions, and defining approaches for the effective utilization of materials technologies; cooperating in the development of advanced educational concepts and approaches in the materials disciplines; communicating and disseminating information on Board activities and related national concerns; promoting cooperation with and among the materials-related professional societies; maintaining an awareness of trends and significant advances in materials technology, in order to call attention to opportunities and possible roadblocks, and their implications for other fields, and recognizing and promoting the development and application of advanced concepts in materials and materials processes.