**Advanced Turbine Design for Coal-Fueled Engines
Phase II -- Corrosion of Turbine Hot Gas
Path Blading**

**Final Report
December 1988 - February 1993**

Norman Bornstein

June 1993

Work Performed Under Contract No.: DE-AC21-89MC26052

**For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia**

**By
United Technologies Research Center
East Hartford, Connecticut**

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EXECUTIVE SUMMARY

The U.S. Department of Energy (DOE) Morgantown Energy Technology Center (METC) awarded a 2-phase contract to United Technologies Research Center. The objective of Phase I was to identify turbine airfoil shapes and aerodynamic characteristics which would result in improved turbine blade and vane life for coal-fueled systems. The objective of Phase II is to evaluate the suitability of state-of-the-art hot gas-path turbine materials and coatings for advanced PFBC conditions with regard to oxidation/corrosion aspects. The subject of the present report is the results from Phase II

(1) The Conditions That Favor Sulfidation Corrosion Are Present In PFBC Turbines.

Sulfidation corrosion occurs in industrial, marine and aircraft gas turbine engines and is due to the presence of condensed alkali (sodium) sulfates. The principle source of the alkali in industrial, marine and aircraft gas turbine engines is sea salt crystals. The principle source of the sulfur is not the liquid fuels, but the same ocean born crystals which can travel hundreds of miles inland.. Moreover deposition of the corrosive salt occurs primarily by a non-equilibrium process. Sodium will be present in the cleaned combusted gases that enter the PFBC turbine. Although equilibrium condensation is not favored, deposition via impaction is probable.

(2) Accelerated Oxidation Associated With The Presence Of Chlorine Or Chlorides Is Not Anticipated.

Marine gas turbines operate in sodium chloride rich environments without experiencing the accelerated attack noted in coal fired boilers where condensed chlorides contact metallic surfaces. Gaseous mixtures of sodium chloride and air are reported to mitigate sulfidation corrosion.

(3) Calcium Sulfate Can Be An Aggressive Corrodent

The sulfates of calcium and magnesium are the products of the reactions used to control sulfur. Calcium sulfate, relatively innocuous at 1500°F, becomes an aggressive corrodent as temperatures increase above 1650°F.

(4) The Ternary Sulfates Of Calcium, Magnesium And Sodium Are Very Aggressive Corrodents

The eutectic salt is two-fold more aggressive corrodent than sodium sulfate.

(5) The Alloys Must be Coated

The oxidation and hot corrosion resistance of the polycrystalline and single crystal alloys is insufficient to assure adequate corrosion life of gas turbine components. Surprisingly, the single crystal alloys exhibited superior resistance to the combined calcium-magnesium-sodium sulfate corrosion that the industrial alloys developed to resist sulfidation corrosion.

(6) The Overlay Coatings Exhibit The Longest Life

The superior performance of the overlay coating is related to thickness rather than chemistry. With respect to sodium sulfate corrosion, the life of the overlay coating is 2.7 times longer than that of the platinum aluminide which in turn is 2.2 times longer than that of the simple aluminide. The ranking of the coatings is unchanged with respect to eutectic salt corrosion, however the salt is more aggressive. The life of the overlay coating is 1.4 times longer than that of the platinum aluminide which is 1.9 times longer than that of the simple aluminide.

The environment within the advanced industrial gas turbine is highly oxidizing and contains the compounds, salts and oxides that accelerate the rate of oxidation of structural materials. Protective coatings which differ from each other and the superalloys in composition and phase morphology, enhance the oxidation and corrosion resistance of the superalloys. As temperatures increase, the relative stability and long term effectiveness of the coatings is of concern. The interdiffusion of coating and alloy constituents can affect chemical and mechanical properties. Long term studies are appropriate. Thermal barrier coatings, introduced at the inception of the current program will further improve the thermal efficiency of industrial gas turbine engines. The interaction between state-of-the-art thermal barrier coatings (TBC) and oxidation and corrosion in the coal fired environment is of concern and should be critically examined.

I. LITERATURE SURVEY

A. Introduction

Hot corrosion is defined as the accelerated rate of oxidation of turbine materials associated with the presence of oxidizing agents other than oxygen and nitrogen. Vanadic and sulfidation corrosion are the terms used to describe the accelerated oxidation due to the presence of vanadium oxides and alkali salts, respectively. Alkali salts are present not only in the fuel but are also present in the air. The presence of vanadium rich oxides is not anticipated in second generation PFBC equipment and therefore is not considered in this study.

B. Background

1. Description

Sulfidation corrosion is the rapid oxidation of gas turbine components associated with sodium sulfate. It is characterized by the presence of a non-protective oxide scale separated from the unaffected matrix by a zone containing sulfide precipitates. The corrosion is reproduced in the laboratory by application of sodium sulfate and subsequent exposure at elevated temperatures. The corrosion phenomena is readily monitored from periodic weight changes and can be described in three steps (fig 1). The initial oxidation behavior is similar to that of simple oxidation in which the specimen slowly gains weight as if the salt was not present. This is the "incubation period", (step 1) in which the corrosive salt is separated from the alloy matrix by a protective oxide scale. Once the scale is penetrated, chemical reactions occur which results in the rapid gain in weight as the matrix reacts with oxygen to form oxides. This second step is of short duration and is followed by the third step in which the rate of oxidation of the salt coated material slowly decreases with increasing time.

2. Mechanism

The corrosion community initially believed that the accelerated rate of oxidation of associated with sulfidation corrosion is related to the preferential oxidation of the sulfur rich phases. Danek (1) reported in a review paper that sulfur acted as the "promotor and propagator" of hot corrosion attack. Hancock (2) related the attack to the transformation of chromium rich sulfides to nickel rich sulfides,

while Seybolt (3,4) related the accelerated rates of oxidation to the preferential oxidation of the intergranular sulfides. Davin et al (5), Spengler and Viswanathan (6) and Erdos (7) examined the kinetics of the gaseous sulfur-metal reactions as a function of temperature and concentration.

Bornstein & DeCrescente (8) were among the early investigators to demonstrate that the rapid rate of oxidation associated with sulfidation corrosion is related to the inability of the substrate to form a protective oxide scale and is not due to the oxidation of the sulfur rich phases. Their work demonstrated that the sulfur rich phase is the signature that sodium sulfate was present, fig. 2.

The oxide ion theory first proposed by Bornstein et al was initially modified by Goebel et al (9). They proposed that the fused alkali salt exhibits both basic (type 1) and acidic (type 2) characteristics which are related to the partial pressure of sulfur oxides in the corrosion environment. Type 1 is generally associated with high temperature corrosion while type 2 is associated with lower temperature corrosion. Type 2 is most prevalent at temperatures between 1200 and 1475°F (650 and 800°C) and requires a significant pressure of SO_3 in the gas phase. Meier (10) reports that there is general agreement that type 1 corrosion propagates via basic fluxing. Although the propagation mode for type 2 is still rather uncertain, Hwang (11) most recently reports that even at 1300°F (700°C) the oxide scale dissolves by basic fluxing. This data further reinforces the original oxide ion mechanism which is shown schematically in figure 3.

In figure 3, the corrosive salt, in equilibrium with oxide ions ("O"), is separated from the matrix by an alumina-rich oxide scale. The oxide ions react with and dissolve alumina. This time dependent reaction corresponds to the incubation period (step 1). Once the oxide is penetrated, another chemical reaction occurs between the salt and the substrate. The products are oxides, sulfides and more oxide ions which prevent the reformation of a protective oxide scale, (step 2). In step 3, the rate of oxidation of the alloy decreases with the dilution of the oxide ion concentration.

3. Chlorides

Although sodium chloride is the principle constituent of sea salt, and sea salt is the precursor for sulfidation corrosion; chloride is rarely found in the deposits associated with sulfidation corrosion. Stringer (12) reports that there is a long

and continuing controversy about the role of chloride in sulfidation corrosion. Most deposits contain no detectable chloride. Small quantities of chloride have been reported in the deposits removed from marine engines, however it is unclear if the source of the chloride is self-contamination. According to Tschinkel (13) sodium chloride is not stable under gas turbine conditions. Not only are the partial pressures of sodium hydroxide and hydrogen chloride much greater than that of sodium chloride, but sulphation, (the chemical formation of sulfur compounds), further decreases the stability of sodium chloride, as shown by the work of Stearns et al (14).

The simultaneous attack of ferrous and nickel base alloys by condensed alkali sulfates and chlorides is well documented (15, 16, 17). However the deleterious effect is almost always associated with reduced or lowered partial pressures of oxygen, a condition never observed in the highly oxidizing environment of the industrial, marine or aircraft gas turbine engine.

Few studies have been made on the effect of gaseous halides with respect to the oxidation of high temperature structural alloys. Smeggil et al (18) found that sodium chloride vapors accelerate the rate of oxidation of a model nickel base superalloy. The same authors also report that sodium chloride vapors affect the growth of chromia and alumina scales, the principle oxides formed on gas turbine components (19). However sodium sulfate attenuates the corrosivity of gaseous sodium chloride. Sodium chloride vapors were found to mitigate the corrosive effect of sodium sulfate and conversely, the attack of chromia forming scales by gaseous sodium chloride was retarded by sodium sulfate. Thus based upon the available data and current engine experience, gaseous sodium chloride in the presence of alkali sulfates is relatively innocuous. The conditions necessary to produce condensed sodium chloride in the turbine section of industrial, marine and aircraft gas turbine engines are not encountered.

4. Life Assessment

a) Alloys and Coatings

The early materials for gas turbine blading were based on the the heater alloy Ni-20 Cr. Chromium imparted both strength and oxidation resistance. It was

soon discovered that the desired mechanical properties of the alloy were significantly increased by the precipitation of an ordered fcc phase formed by the addition of titanium and aluminum. In order to increase the concentration of aluminum and titanium it was necessary to decrease the concentration of chromium in the alloy. In the period from the fifties to late sixties, efforts were concentrated on improving mechanical properties and oxidation and corrosion resistance was achieved through the use of coatings. The introduction of refractory metals and carbides further increased the strength of the alloys. Further improvements in mechanical properties were realized through control of grain boundaries. Weakness associated with grain boundaries were alleviated by the development of directionally solidification and single crystal alloys. A comparison of stress-rupture properties of conventional, directionally solidified and single crystal alloys are shown in figure 4 and the chemical composition of typical alloys is shown graphically in figure 5.

Coatings are used to extend the useful life of gas turbine components. Coatings are composed principally of the elements nickel, (cobalt) chromium and aluminum. Several studies have been made of the oxidation behavior of the Ni-Cr-Al system and an oxide map (21) is reproduced in figure 6. Alumina is the preferred oxide for high temperature performance, because it rapidly forms and slowly thickens. In general chromium in solution decreases the critical concentration of aluminum necessary to form the alumina scale. Chromia scales are not satisfactory at temperatures above 1650°F (900°C) because they tend to volatilize (22). However chromia is the preferred scale for resistance to sulfidation corrosion.

The coatings used to protect the superalloys are generally divided into the groupings of diffusion and overlay. The aluminides are diffusion coatings and are based upon the enrichment of the surface of the alloy with aluminum in order to form the intermetallic compound NiAl. In general the oxidation and hot corrosion resistance of these coatings are dependent upon the chemistry of the underlying alloy. Processes have been developed to modify the intermetallic compound by the addition of precious metals such as platinum, palladium and rhodium. These coatings are more costly than the simple aluminides but often exhibit improved resistance to sulfidation corrosion. The overlay coatings typified by the MCrAlY series (M = Fe, Co, Ni or combinations thereof) offer a wider range of flexibility. Oxidation and hot corrosion can be varied to meet

various requirements. Although few studies have been performed under rigorously controlled conditions, the curve shown in figure 7 is a compilation of available data (23) which shows the relative resistance to sulfidation corrosion as a function of chromium content.

b) Salt Deposition

The concept of an allowable alkali content is probably based upon the assumption that the corrosive sodium sulfate salt is produced from the reaction between sodium salts and the oxides of sulfur. Sulfur is a constituent of petroleum base fuels and its concentration can vary from parts per million to weight percent. Sodium is a principle constituent of the sea-salt crystals born at the ocean-air interface which enter the gas turbine engine with the intake air. Based upon meterological studies, sea salt crystals travel inland more than 200 miles on the prevailing winds (24). Salt water is also a common contaminant of petroleum fuels transported by barge or ship.

DeCrescente and Bornstein (25) were among the first to demonstrate that gaseous mixtures of sodium sulfate and air are relatively innocuous with respect to gas turbine engine materials. However the condensed salt is very corrosive. Numerous studies have been conducted concerning the formation, vapor pressure, and condensation of sodium sulfate in gas turbine engines (26-31).

There is sufficient evidence to conclude that the corrosive sodium sulfate salt is deposited onto gas turbine components by non equilibrium processes (32, 33). In an EPRI supported study (34) it is shown that the thin films of salt adhering to the components of the low compressor are similar in composition to that of sea salt. However the composition of the salts adhering to the latter compressor stages is of the same composition as the salts found on the turbine components that suffer sulfidation corrosion. The principal constituent of the salt is sodium sulfate, Table 1. Moreover the quantity of salt adhering to the latter stages of the high compressor increases with stage number as shown in figure 8. In the same study it is shown that the efficiency of the compressor of an industrial gas turbine engine decreases after the machine is operated during fog. The decrease in efficiency is related to the deposition of salts onto compressor components and the principal constituent of the salt is again sodium sulfate figure 9. Lastly in tests conducted at Long Island Lighting Company it is shown

that the deposition of sodium sulfate onto turbine components is related to the sea breezes that bring the salt laden air into the engine, figure 10.

The fuel is also a source of alkali. Field as well as laboratory experience verify that alkali doped fuels promote sulfidation corrosion. The experimental evidence from UTC studies supports the conclusion that the deposition of sodium sulfate from alkali doped fuel occurs via a non-equilibrium process. The calculated concentration of sodium necessary to promote equilibrium condensation of sodium sulfate at 1650°F (900°C) and 1 atmosphere is 35 ppm. The experimental data is summarized in table 2. The data supports the conclusion that char formation assists in the deposition of the salt.

In summary, the data indicates that an important source of the corrosive sodium sulfate is the periodic release of the salt that accumulates on compressor components. The fuel is also an important source of sodium, however deposition most probably occurs via a non equilibrium process.

5. Oxidation/Corrosion Life-Prediction

Gas turbine manufacturers have developed laboratory tests designed to accelerate the oxidation or corrosion phenomena that eventually contributes to the degradation of a component. Oxidation is the principle degradation mechanism for aircraft gas turbines. High temperature cyclic oxidation tests are used to not only rank but also to measure rates of consumption or material loss. The data is compared to engine performance in order to determine life predictions.

Improvements in material performance is generally achieved through an understanding of the rate controlling process. Coatings are consumed through the loss of aluminum due to the spallation of the oxide scale. Significant improvements in the life of protective coatings is attributed to the discovery that certain reactive elements such as yttrium significantly improve oxide scale adherence.

Sulfidation corrosion is more important in industrial and marine gas turbine engines. The corrosion attack is induced in the laboratory by the application of and subsequent cyclic exposure of salt coated specimens at elevated

temperatures. In general corrosion is induced in the laboratory tests within tens of hours after application of the corrosive salt. The significant improvements in the life of marine and industrial gas turbine components is once again achieved through a better understanding of how the corrosive salt deposits onto turbo machinery, and the process by which the salt defeats the normally protective oxide scale.

The major gas turbine manufacturers limit the concentration of sodium (and potassium) in the fuels. Air filtration is used to limit the quantity of air borne alkalis entering industrial and marine engines. These steps are taken in order to reduce the rate of deposition of salt onto turbomachinery. However the efficiency of the filters is dependent upon many parameters. Moreover filters tend to periodically release captured solids into the air stream. Therefore the limits imposed by manufacturers are based more upon operating experience than calculations.

METC believes that the gases entering the turbine could contain up to 10 ppm alkali, 33 ppm HCl and 144ppm sulfur dioxide. The alkali concentration is significantly higher than the levels established by the major gas turbine producers. However it does not follow that alkali sulfates will form and condense. Deposition is a necessary condition for sulfidation corrosion to occur. Of more concern is the deposition of sulfates associated with the process used to control sulfur. Alkaline earth sulfates which may also contain alkalis will be present on METC turbomachinery. The effect that these compounds can have on turbine materials needs to be determined.

C. Experimental Studies and Results

1. Rationale

The principal corrosive salt associated with sulfidation corrosion is sodium sulfate. The principle oxide which forms on the surface of high temperature components is alumina. The chemical interaction that occurs is reasonably well understood. However the deposits from the DOE fuel are very rich with respect to calcium and magnesium. Calcium oxide and dolomite, (a mixture of the oxides of calcium and magnesium) are used to control sulfur. One micron or finer particles are not anticipated to perform as an errodent, but are expected to deposit onto and adhere as a thin film to turbomachinery. Calcia and magnesia

can react with alumina to form a host of compounds. The stoichiometry of the compounds depends upon concentration as well as temperature. Thus an area of concern is the integrity of the alumina scale.

Calcium sulfate does not suppress the melting temperature of sodium sulfate, fig 11a. Magnesium sulfate will suppress the melting temperature of sodium sulfate fig. 11b, however this salt, unlike the sulfates of calcium and sodium, decomposes in the temperature range of interest to form magnesium oxide. However a stable ternary eutectic is formed in the system.

The alumina scale is the barrier that separates the hostile environment from the metallic surface. The life of turbine components is related to the rate of formation, growth and deterioration of the oxide scale.

2. Experimental Results

In order to assess the corrosivity of calcium sulfate, a series of laboratory experiments were performed in which the surfaces of the nickel base alloy B-1900 were coated with a thin film of calcium sulfate and tested at 1650, 1900 and 2100°F. This nickel base alloy is noted for its high temperature strength, good oxidation resistance and poor resistance to hot corrosion. Uncoated (calcium sulfate free) specimens served as controls.

At 1650°F (900°C), no differences were noted with respect to weight changes, however the calcium sulfate coated specimens appeared discolored consistent with the formation of a chromate compound. Moreover metallographic analyses revealed the presence of sulfide precipitates beneath the oxide scale. At 1900°F (1040°C) and at 2100°F (1150°C) the calcium sulfate coated specimens experienced considerable losses in weight. The weight loss is reported in figure 12 as loss in cross-sectional thickness. The sulfide precipitates observed in the metallographical cross-sections are not consistent with classical sulfidation corrosion. Based upon the results further experiments were performed with the alloys IN-738, IN-792 and PW-1480.

As previously noted, the first two alloys are representative of the alloys currently employed in industrial gas turbines, and the third alloy is representative of the newer family of single crystal alloys used in advanced aircraft gas turbine

engines. Each alloy was coated with, (a) sodium sulfate, (b) calcium sulfate and (c) a mixture of sodium, calcium and magnesium sulfates in the ratios consistent with eutectic formation. The salt coated specimens were exposed at 1900°F and the experimental results are summarized in figure 13.

The sulfidation behavior is consistent with published data. The chromium rich alloy IN-738 is most resistant followed by IN-792 and the least resistant is the alumina forming, chromium poor single crystal alloy PW-1480. Note also that the alumina forming PW-1480 alloy is least affected by the calcium sulfate. The poorer performance of the IN-738 and IN-792 may be related to the formation of chromate salts which were observed to form on the surfaces.

It was anticipated that the eutectic salt would be corrosive. However it was not anticipated to be as aggressive as noted in figure 10. It appears to be at least 5 fold more corrosive than sodium sulfate. Equally surprising is the observation that the single crystal alloy PW-1480, which is more sensitive to sodium sulfate than the equiaxed alloys is, in this test, most resistant to the eutectic salt .

II. LABORATORY CORROSION STUDIES

This section is divided into two phases. The objective of the first phase is to develop an understanding of the the chemistry involved between the corrosive salts and the turbine alloy systems. The objective of phase two is to develop priliminary laboratory burner rig data for life life prediction calculations.

A. Phase I Chemistry and Morphology of Corrosion Process

The objective of this phase is to determine the nature of the chemical attack of the ternary eutectic and correlate the chemistry to the corrosion morphology

1. Experimental Procedure

The response of the alloys IN-738, IN-792 and PW-1480 to the presence of CaSO_4 , Na_2SO_4 and the eutectic mixture of the salts of calcium, sodium and magnesium sulfate is determined from laboratory tests in which each of the alloys are coated with approximately 1 mg/cm^2 of the salt prior to exposure at, 1650°F, and 1900°F. The salt is applied from a saturated solution as a mist

onto the heated (250°F) substrate. Test durations vary from less than one to one hundred hours. Specimens are periodically removed for salt analysis, recoated and finally removed from test when heavy spallation of the oxide scale is observed. The rate of metal consumption is determined from the weight change data. The morphology of the corrosion attack is determined from metallographic examinations of selected specimens. Specimens are periodically removed and immersed into distilled water. The water solution is analyzed to determine the nature of the water soluble salts. PW-73 coated IN-792, a platinum aluminide coated 792 and PW-286 coated 792 are also included in the tests. The coatings represent the families of (a) simple aluminides, precious metal aluminides and overlay coatings.

2. Experimental Results

a) Alloys

The response of the alloys IN-792, IN-738 and PW-1480 to (a) Na_2SO_4 , (b) CaSO_4 and (c) the eutectic of the sulfates of magnesium, calcium and sodium at 1650°F, and 1900°F is shown in figs. 14 & 15, respectively, and the data summarized in Table 3. At 1650°F, the eutectic mixture is very aggressive with respect to IN-792, and similar in behavior to sodium sulfate with respect to the other alloys. Calcium sulfate is relatively innocuous at 1650°F.

At 1900°F, the liquid salts are aggressive corrodents. Neither IN-792 or IN-738 exhibits resistance to sodium sulfate and the eutectic mixture is an order of magnitude more corrosive. The single crystal alloy unlike the polycrystalline alloys is more resistant to the eutectic salt than to sodium sulfate. At the higher temperatures calcium sulfate is no longer innocuous; however the rate of corrosion of the calcium sulfate coated single crystal alloy is not catastrophic.

b) Coatings

The ability of a coating to extend the life of an alloy is related to the formation of an adherent oxide scale that separates the hostile environment from the substrate. The simple aluminides, precious metal aluminides and overlay coatings form an oxide scale consisting primarily of aluminum oxide, alumina. The polycrystalline nickel base superalloys tend to form scales richer in chromia.

The response of the coatings to the liquid salts is shown metallographically in figures 16, 17, and 18. The simple aluminide and platinum aluminide coatings are more resistant to the eutectic mixture than to sodium sulfate. The overlay coating is less resistant to the eutectic mixture than to sodium sulfate.

The sodium sulfate coated simple aluminide failed after 17 hours, fig. 16a. Sulfides are readily visible within the aluminide matrix (fig. 16b). The microstructure of eutectic salt coated aluminide after 17 hours is relatively unchanged (fig. 16c), and consists of bulky beta (NiAl) and precipitates of alpha chromium within the grains and grain boundaries. The eutectic salt coated simple aluminide failed after 60 test hours.

The sodium sulfate coated platinum-aluminide coating failed after 60 hours. The microstructure observed after 41 hours is almost depleted of the beta phase and the sulfides are visible in the gamma zone which separates the non protective scale from the substrate, (fig 17a). The eutectic salt coated platinum aluminide coating after 41 hours is relatively unchanged (fig 17b). The eutectic coated platinum aluminide coated specimen failed after 130 cyclic test hours.

The overlay coating, unlike the aluminides, is more adversely affected by the eutectic salt. A comparison of the microstructures of the overlay coated with sodium sulfate or the eutectic salt is shown in fig 18a and 18b, respectively. At the completion of 60 hours, more than half of the overlay is consumed and the depleted zone that separates the substrate from the corrosive salt is replete with sulfur rich phases. The eutectic coated specimens failed after 140 cyclic test hours.

c) Chemical Analyses

Analysis of the water soluble salts present on sodium sulfate or eutectic coated substrates is a method used to follow corrosion. The composition of the salts is derived from quantitative chemical analyses and verification of electroneutrality. The results for the uncoated alloys exposed at 1650 and 1900°F are summarized in Tables 4-7 and those for the coated alloys in Table 8.

3. Phase 1A-Special Studies

The objective of this phase is to examine the relationship between surface chemistry and morphology. A comparison is made between the metallographical and wet chemical corrosion products for sodium sulfate and eutectic salt coated aluminide coatings tested at 1900°F. The former failed after 21 hours while the later failed after 60 hours. Based upon the wet chemical analyses, the difference may be related to the formation of a calcia rich scale which initially impedes the rate of removal of chromium from the coating. The metallographical supporting evidence for eutectic salt coated aluminides exposed (a) 3 hrs, (b) 21 hrs and (c) 50 hrs is shown in figures 18a-18d.

The aluminide coating in figure 18a consists of the outer layer of nickel aluminide which contains precipitated chromium rich islands within the grain and grain boundaries (white phase). The oxide scale on the surface of the specimen contains, in addition to the oxides of aluminum and nickel, a thin calcium rich zone. The principle ions in the water solution are sodium, calcium, sulfate, and chromate. At the completion of 21 hours, the chromium rich phase is present only at the surface, and no significant changes are observed in the composition of the water soluble salts. After fifty hours, the tungstate ion, in addition to the previously mentioned ions is observed. The presence of the tungstate ion indicates that corrosion of the underlying alloy had occurred. At the end of 60 hours, (figure 18d) the coating is completely consumed and sulfides penetrate deeply into the superalloy.

4 B. Phase II - Life Assessment/Burner Rig Studies

Turbine component life is strongly influenced by oxidation and hot corrosion. The morphology of the oxidation and corrosion attack observed in the field is reproduced from laboratory burner rig tests. Field life is related to laboratory life by a number of factors which include location, environment, as well as engine maintenance procedures. The objective of this phase of the study is to relate the life of aluminides and overlay coatings exposed to the eutectic salts compared to that for sulfidation (sodium sulfate salt).

1. Experimental Procedure

The oxidation/corrosion environment is simulated in the laboratory by exposure of rotating specimens to the exit flame of the laboratory burner, Fig. 19. The specimens rotating at 1725 rpm, are cycled twice an hour. Each cycle consists of 25 minutes at temperature and a five minute cool to black heat. The laboratory burner operates at a 25/1 air/fuel ratio and consumes 13.3# jet fuel per hour. The saline solution is injected directly into the flame within the combustion zone. The exit concentration of salt is 100ppm. Selected specimens are periodically removed for metallographical examination. Initial coating thickness is determined from metallographical examination of the cool end from each specimen and failure is determined from visual observation. The corrosion factor is the parabolic scaling constant ($\text{in}^2/\text{hr.}$).

2. Experimental Results

At 1650°F, sulfidation corrosion of uncoated alloys is generally observed within 2 to 10 hours of exposure. At 1900°F, the time required to initiate and observe severe salt corrosion for uncoated alloys is significantly less than three quarters of an hour (45 minutes), and at higher temperatures, the rate of corrosion of unprotected alloys is catastrophic; exfoliation of the scales occur within minutes of exposure to the hostile environment. The corrosion morphology of the alloys exposed at the higher temperatures to the sodium sulfate or the mixtures of sulfates of sodium, magnesium and calcium differs from that observed at 1650°F in that the former exhibits a liquid phase, Fig. 20. The phase is metallographically identified as the nickel-sulfide eutectic, modified by the elements indigenous to the alloy.

The corrosion data for the (a) simple aluminides, (b) precious metal aluminides and (c) overlays, subjected to the corrosive salts, sodium sulfate or the eutectic mixture of the sulfates of sodium, magnesium and calcium, exposed at 1650°F (900°C) and 1900°F (1038°C), are summarized in Table 9. The representative microstructure associated with corrosion is shown in figures 22, 23, & 24. The kinetic data follows the classical Arrhenius law, figs. 25 & 26.

III. DISCUSSION

A. Chemistry and Morphological Studies

The corrosivity of the eutectic salt with respect to the alloys, is comparable to that of sodium sulfate at 1650°F and more aggressive than sodium sulfate as the temperature is increased. The differences in behavior appears to be related to the enhanced ability of the eutectic salt to extract chromium in the form of another chromate. The exception is the single crystal alloy, PW1480. The single crystal alloy is different not only in microstructure (single crystal versus polycrystalline) but forms an oxide scale that is composed principally of alumina. (Its behavior more closely resembles that of a coating). Based upon the metallographical and wet chemistry studies, the resistance of the PW-1480 to the eutectic salt is related to the formation of a transitory phase possibly calcium aluminate, which separates the salt from the matrix. Corrosion occurs upon the eventual breakdown, either mechanically or chemically, of this phase. Calcium sulfate, unlike sodium sulfate and the eutectic, is a solid rather than a liquid over the temperature range of this study. At 1650°F, calcium sulfate is innocuous. However at the higher temperatures calcium sulfate reacts with the alloys to form sulfides. The presence of a liquid phase is not a prerequisite for hot corrosion.

Lastly there is a paucity of data concerning sulfidation corrosion at 1900°F. The observation of formation of a liquid sulfide on burner rig specimens has not been previously reported. The liquid sulfide is observed when nickel base alloys are immersed into molten sodium sulfate. The formation of the liquid sulfide implies that the sulfur activity at the salt-substrate interface is extremely high.

The composition of the water soluble corrosion products often reflects the degree of corrosion. The corrosion tests performed at 1900°F clearly indicate that, alloying elements from the matrix diffuse into and affect the chemical properties of the overlay coating. The exceptionally high concentration of molybdenum ion in the solutions associated with the eutectic salt are consistent with the metallographical findings that this coating is least resistant to the eutectic salt.

B. Burner Rig Studies

Burner rig tests simulate the hostile corrosion environment and rank the families of alloys and coatings in the same order as obtained from the field. In oxidation tests the overlay coatings usually exhibit at least a three to five-fold improvement when compared to the aluminides. The improvement is related to oxide scale adherence. Yttrium, a very minor constituent of the overlay coatings plays an essential role with respect to oxide scale adherence. The beneficial role of yttrium is long been recognized, but to date there is no commercial process that incorporates yttrium into an aluminide coating.

Sodium sulfate accelerates the rate of removal of the normally protective oxide scale. In general sulfidation tests are performed over the temperature range of 1200 to 1650°F. In prior studies, the activation energy for sulfidation corrosion is reported as 60 Kcal/mole (8). Although thermodynamic data is seldom generated from burner rig tests, the activation energy for sulfidation corrosion for the aluminides and overlay coatings exposed over the temperature range is also 60 Kcal/mole which indicates that the controlling mechanism for the corrosion of overlay and the aluminide coatings is the same. The data implies that the platinum (aluminide) minimizes the deleterious effect attributed to elements present in the substrate and that the significant improvement in life of the overlay coating is thickness not chemistry dependent.

Unexplained is the anomalous behavior of the eutectic salt. Although no significant change in activation energy is noted, it is apparent that at least initially the calcia rich deposit separates the caustic salt from the matrix thereby increasing component life. The eventual breakdown of the deposit, either mechanically or chemically eventually results in classical corrosion. The noted exception is the behavior of the overlay coating. The eutectic salt appears to accelerate the rate of removal of both aluminum and chromium and the life of this coating is decreased.

IV. CONCLUSIONS

Calcium sulfate, relatively innocuous at 1650°F becomes an aggressive corrodent at and above 1900°F.

The eutectic salt is an aggressive corrodent with respect to the polycrystalline

alloys IN-792 and IN-738. The single crystal alloy PW-1480 is ten-fold more resistant. Nevertheless, the rate of corrosion of the uncoated alloys is not acceptable.

The aluminide coatings exhibit longer lives exposed to the eutectic salt as compared to sodium sulfate. The reverse is true for the overlay coating. The difference in behavior appears to be related to the initial formation of a calcia rich scale which forms on the aluminides but is absent on the overlay. Nevertheless the overlay coating exhibits the longest life. From a mechanistic point of view, the increase in life is related to coating thickness rather than chemical composition. In sulfidation corrosion, the overlay coating is six-fold superior to the simple aluminide and almost three-fold superior to the platinum aluminide. With respect to the eutectic salt the overlay is about two and one-half fold superior to the simple aluminide and about two-fold superior to the platinum aluminide.

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TABLE 1
Analysis of Field Data

Turbine stage	Concentration (Mg)		
	Sodium	Chloride	Sulfate
9th	0.056	nil	0.1
10th	0.070	0.02	0.09
11th	0.27	nil	0.12
12th	18.5	0.2	90 +
13th	4.4	0.5	92
14th	9.4	0.7	53
15th	10.6	1.0	42
1st Vane	1.01	nil	5

TABLE 2
Laboratory Evaluation of Sodium in Fuel
(900°C-atmospheric test)

Time hrs		Na in fuel (ppm)	Observation
11	150	Uniform Sulfidation	Attack
11	60	Uniform Sulfidation	Attack
6	65	Uniform Sulfidation	Attack
11	45	Slight attack	
6	45	Slight Attack	
6	35	Oxidation-No	Attack
35	10	Oxidation-No	Attack
52	0	Oxidation	
11	30*	Sulfidation	Attack

* low air/fuel ratio to induce char formation

Table 3
Summary of Laboratory Corrosion Studies
Corrosion Rate mm/hr.

Corrodent	Alloy					
	792		738		1480	
	temp°F		temp°F		temp°F	
	1650	1900	1650	1900	1650	1900
Na ₂ SO ₄	0.004	0.036	0.001	0.010	0.005	0.045
CaSO ₄	-	0.002	-	0.005	-	0.0005
eutectic	0.022	0.174	0.0005	0.140	0.003	0.02

Table 4
Chemical Composition (m/o) of Corrosion Water Soluble Salts
(IN-738-1650°F)

Salt	4 hrs		15 hrs		20 hrs	
	<u>Na₂SO₄</u>	<u>eutectic</u>	<u>Na₂SO₄</u>	<u>eutectic</u>	<u>Na₂SO₄</u>	<u>eutectic</u>
Na ₂ SO ₄	78.4	67.2	75.6	-	82.5	69.5
Na ₂ CrO ₄	20.4	-	24.2	-	17.3	-
Na ₂ (MoW)O ₄	0.1	-	0.2	-	0.2	-
CaSO ₄	-	3.4	-	-	-	4.0
MgSO ₄	-	29.4	-	-	-	26.5

Table 5
Chemical Composition (m/o) of Corrosion Water Soluble Salts
(In-792-1900°F)

Salt	10 min		20 min		30 min	
	<u>Na₂SO₄ eutectic</u>		<u>Na₂SO₄ eutectic</u>		<u>Na₂SO₄ eutectic</u>	
Na ₂ SO ₄	78.2	18.3	71.5	23.4	81.5	2.60
Na ₂ CrO ₄	20.8	14.2	27.2	14.9	12.9	1.73
Na ₂ (MoW)O ₄	1.1	49.8	1.4	55.1	5.6	86.1
CaSO ₄	-	1.1	-	-	-	-
MgSO ₄	-	16.2	-	3.1	-	2.63
NaAlO ₂	-	1.57	-	2.0	-	4.60
CaCrO ₄	-	-	-	1.43	-	2.31

Table 6
Chemical Composition (m/o) of Corrosion Water Soluble Salts
(In-738-1900°F)

Salt	10 min		20 min		30 min	
	<u>Na₂SO₄ eutectic</u>		<u>Na₂SO₄ eutectic</u>		<u>Na₂SO₄ eutectic</u>	
Na ₂ SO ₄	75.9	59.0	58.4	73.2	89.7	87.1
Na ₂ CrO ₄	17.9	25.5	38.2	15.5	8.8	3.8
Na ₂ (MoW)O ₄	7.2	4.8	2.8	4.2	1.5	1.4
CaSO ₄	-	1.6	-	-	-	-
MgSO ₄	-	9.0	-	2.7	-	2.90
CaCrO ₄	-	-	-	4.2	-	4.8

Table 7
Chemical Composition (m/o) of Corrosion Water Soluble Salts
(PW-1480-1900°F)

Salt	10 min.		20 min.		30 min.	
	<u>Na₂SO₄</u>	<u>eutectic</u>	<u>Na₂SO₄</u>	<u>eutectic</u>	<u>Na₂SO₄</u>	<u>eutectic</u>
Na ₂ SO ₄	68.2	58.0	62.6	78.6	77.1	92.2
Na ₂ CrO ₄	31.5	24.2	32.4	5.6	16.9	1.35
Na ₂ (MoW)O ₄	0.2	1.8	4.3	1.0	5.3	-
CaSO ₄	-	1.25	-	-	-	-
MgSO ₄	-	20.8	-	1.8	-	3.3
NaAlO ₂	-	-	0.4	-	0.5	-
CaCrO ₄	-	1.0	-	12.8	-	3.1

Table 8
Chemical Composition (m/o) of Corrosion Water Soluble Salts
(Coatings -1900°F)

Overlay (PW-286)/IN-792**Eutectic**

	<u>2hrs</u>	<u>18 hrs</u>	<u>52 hrs</u>	<u>2hrs</u>	<u>18 hrs</u>	<u>52 hrs</u>
salt						
Na ₂ SO ₄	80.7	64.8	57.3	65.6	19.8	32.6
Na ₂ CrO ₄	19.2	25.9	31.8	32.1	2.1	53.3
Na ₂ MoO ₄	0.2	8.5	10.9	2.3	74	13.2

Na₂SO₄**Simple Aluminide (PW-73)/IN-792**

	<u>3hrs</u>	<u>12 hrs</u>	<u>21 hrs</u>	<u>3 hrs</u>	<u>12 hrs</u>	<u>21 hrs</u>
Na ₂ SO ₄	80.3	14.4	F	71.6	75.1	37
Na ₂ CrO ₄	10.0	76.6	"	17.4	18.0	58.1
Na ₂ MoO ₄	10.0	9.0	"	11.0	5.5	5.9

Precious Metal Aluminide (Pt-Al)/IN-792

	<u>3hrs</u>	<u>61hrs</u>	<u>3hrs</u>	<u>61 hrs</u>
Na ₂ SO ₄	90.0	85.0	90.0	92.1
Na ₂ CrO ₄	10.0	10.6	10.0	7.9
Na ₂ MoO ₄	-	4.4	-	trace

Table 9
Summary of Burner Rig Tests

	<u>Corrodant</u>	<u>Sodium Sulfate (Na₂SO₄)</u>	
	<u>Aluminide</u>	<u>Pt-Aluminide</u>	<u>Overlay</u>
coating thickness mils	2.6	3.0	5.0
Corrosion factor in ² /hr			
at			
1650°F (900°C)	4.17X10-8	2.47X10-8	2.58X10-8
1900°F (1038°C)	3.98X10-7	2.00X10-7	1.92X10-7
2100°F (1149°C)	1.70X10-6	1.00X10-6	8.00X10-7
Life hours at			
1650°F (900°C)	162	365	1000
1900°F (1038°C)	17	45	130
2100°F (1149°C)	5	9	32

	<u>Corrodant</u>	<u>Eutectic Salt (NaMgCa)SO₄</u>	
	<u>Aluminide</u>	<u>Pt-Aluminide</u>	<u>Overlay</u>
coating thickness mils	2.5	3.0	5.0
corrosion factor in ² /hr			
at			
1650°F (900°C)	1.88X10-8	1.45X10-8	2.92X10-8
1900°F (1038°C)	1.79X10-7	1.38X10-7	2.78X10-7
2100°F (1149°C)	6.00X10-7	6.00X10-7	1.3X10-6
Life, hours at			
1650°F (900°C)	330	620	855
1900°F (1038°C)	35	65	90
2100°F (1149°C)	11	15	19

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**SULFIDATION CORROSION
CONSISTS OF THREE DISTINCT STAGES**

SULFIDATION STUDIES

THE SULFIDATION PROCESS

R93-970023-2

HIGH-TEMPERATURE NICKEL-BASED ALLOYS

TEMPERATURE CAPABILITY=MAXIMUM TEMP. FOR 100-HR. RUPTURE LIFE
AT 138 MN/m²

R93-970023-2

**CHEMICAL COMPOSITIONS OF CURRENT ALLOYS
(ATOMIC PERCENT)**

OXIDE MAP FOR THE TERNARY SYSTEM NI-CR-AL AT 1000°C

DEPENDENCE OF RELATIVE RATE OF HOT CORROSION OF MCr-
AlY COATING ALLOYS ON CHROMIUM CONTENT; 1300F BURNER RIG TEST

QUANTITY OF Na_2SO_4 VS COMPRESSOR STAGE

ANALYSIS OF FIELD DATA (Dow)

ANALYSIS OF DEPOSITS ON VANE AFTER DRY CLEANING – mgs

	Na	SO ₄	CL
Vane #1	319	1415	0.67
Vane # 2	295	1250	1.2

R93-970023-2

FIG.9

DISTRIBUTION OF Na_2SO_4 VS TIME (SEASON)

Na₂SO₄ - CaSO₄ HIGH TEMPERATURE CHEMISTRY

Na₂SO₄ - CaSO₄

Na₂SO₄ - CaSO₄ - MgSO₄

FIG 11

91-6-24-7

CaSO₄ ACCELERATES RATE OF OXIDATION OF NICKEL BASE SUPERALLOY (B1900)

Fig. 14 Laboratory Corrosion Studies (1650°F)

EP304-5-1

Fig. 15 Laboratory Corrosion Studies (1900°F)

EP304-5-2

Fig. 16 Laboratory Corrosion Studies (2100°F)

a) Na_2SO_4 SALT

c) EUTECTIC SALT

b)

d)

Fig. 17 Hot Corrosion of Simple Aluminide Coating (21 hrs, 1900°F)

Fig. 18 Hot Corrosion of Platinum Aluminide Coating (41 hrs, 1900°F)

a) Na_2SO_4 SALT

b) EUTECTIC SALT

Fig. 19 Hot Corrosion of Overlay Coating (60 hrs, 1900°F)

EP304-5-6

a) 3 hrs

25μm

b) 21 hrs

25μm

c) 50 hrs

25μm

d) 40 hrs

Sulfides

25μm

Fig. 20 Corrosion Morphology/Chemistry Studies (Eutectic Salt Coated Aluminide, 1900°F)

Fig. 21 Dynamic Laboratory Burner Rig

Fig. 22 Typical Morophology of Uncoated Alloy Exposed 45 min at 1900°F (Burner Rig – 100 ppm Salt)

a) 0 HRS

20μm

b) 10 HRS, SULFIDES VISIBLE BENEATH
OXIDE SCALE

20μm

c) 14 HRS, COATING DEPLETED OF NIAL,
SULFIDES PRESENT IN DIFFUSION ZONE

20μm

d) 17 HRS, SULFIDES PENETRATE INTO ALLOY

20μm

Fig23 Typical Morphology of Sodium Sulfate Coated Simple Aluminide [(1900°F)]

a) 0 HRS

b) 20 HRS

c) 40 HRS

d) 60 HRS

Fig. 24 Typical Morphology of (NaMgCa)SO₄ Coated Precious Metal (1900°F)

Fig. 25 Typical Morphology of $(\text{NaMgCa})\text{SO}_4$ Coated Overlay

Fig. 26 Temperature Dependency for Hot Corrosion [Eutectic Salt, (NaMgCa)SO₄]

EP304-5-13

Fig. 27 Temperature Dependency for Hot Corrosion (Na_2SO_4)

EP304-5-14

This cover stock is 30% post-consumer waste
and 30% pre-consumer waste, and is recyclable.

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Advanced Turbine Design for Coal-Fueled Engines
Phase II -- Corrosion of Turbine Hot Gas Path Blading

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