

SULFIDATION AND ITS INHIBITION IN TURBOMACHINERY

by

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cleaning is often recommended to remove accumulated salt deposits. Reducing the turbine's operating temperature can lower corrosion rates, but at the expense of reduced power and efficiency.

BACKGROUND

Hot corrosion is the term generally used to describe the accelerated rate of oxidation of gas turbine components. Sulfidation attack refers to the enhanced rates of oxidation associated with the presence of condensed alkali sulfate salts. One of the first mechanisms proposed to explain sulfidation was by Simons, Browning and Liebhafsky [1] who proposed that a reducing agent, "R", reacted with the sodium sulfate to reduce sulfur. Microstructural changes ensue as sulfides are formed to lower the oxidation resistance of the normally oxidation resistant alloy. Dean [2] hypothesized that carbon was the reducing agent, while Gambino [3] suggested that the sulfate reacted with the substrate to form sulfides and soda (Na_2O). The SO_3 formed during the subsequent oxidation of the sulfides recombined with the soda to reform sulfate. Seybolt and Beltran [4], and then Seybolt [5] later proposed that the accelerated rates of oxidation were due to a loss of oxidation inhibition by chromium-depletion through formation of chromium-rich sulfide precipitates.

However, the role of sulfur in sulfidation corrosion is quite complex. Studies have been made by many investigators [6,7,8,9,10,11] and it is currently agreed that, as proposed by DeCrescente, Bornstein, et. al., [12] in order for sulfidation attack to occur, a fused salt must be present in the condensed state. Whereas condensed (liquid or solid) Na_2SO_4 caused accelerated oxidation of a nickel base superalloy, gaseous mixtures of Na_2SO_4 and air are quite harmless. Moreover, based upon a study of the microstructural changes that occur as a function of the oxidation rate of a nickel-base superalloy [13,14,15,16], the most rapid rates of oxidation occur shortly after the fused salt reacts with the substrate. The microstructural changes associated with sulfidation attack are related to the subsequent oxidation and movement of sulfur into the alloy.

Another form of hot corrosion is associated with the presence of liquid metal oxides. When the molten deposit which accumulates on the component surface is rich in vanadium pentoxide, the phenomena is often called "vanadium-induced corrosion". In studies at United Technologies Research Center (UTRC) [14], superalloys were readily attacked by V_2O_5 . Vanadium pentoxide melts at approximately 690°C (1275°F). It wets, reacts, and dissolves with the oxide scales that normally form on protective coatings and superalloys. The incorporation of alumina and titania into the corrosion (following oxidation) produces a glass-like phase, thereby extending the corrosivity of V_2O_5 . An even more severe form of hot corrosion occurs at temperatures as low as 650°C (1200°F) when turbine deposits contain both alkali sulfates and vanadium oxides.

ABSTRACT

United Technologies Research Center has carefully investigated the detailed mechanisms of gas turbine sulfidation and its inhibitions. Sulfidation, the salt accelerated oxidation of superalloys, is addressed in terms of the relationships between fuel and combustion air contamination, turbine deposit composition, alloy composition, and metal temperature. Superalloy oxidation kinetics and deposit electrochemical data is presented to substantiate that oxide ion-initiated and sustained attack to the normally protective oxide scale is responsible for hot corrosion. Application of this mechanism to field experience is made to explain corrosion performance.

INTRODUCTION

The durability and availability of gas turbine engines used in electric utility service is being increased and the maintenance costs reduced by controlling the losses due to hot corrosion. Hot corrosion, called sulfidation by many, is the accelerated rate of metal wastage caused by the reaction of alkali metal salts and liquid metal oxides which exist as contaminants in the fuel and air and which deposit and react with the turbine components. This situation may exist in utility engines which now operate primarily with distilled fuels and can worsen as the utilization of lower quality residual and certain coal-derived fuels becomes common.

The approaches commonly followed to combat hot corrosion in electric utility gas turbines are:

- Protective Coatings — Special corrosion resistant metallic coatings exist which are very effective in protecting base airfoil alloys from attack. Their use can increase turbine maintenance intervals severalfold. However, no one coating is resistant to attack from the many and varied corrosive environments which engines encounter in service at different geographical locations and with different fuels.
- Control of the Turbine Environment — Filtration/cleanup of the air and fuel is used to reduce levels of contaminants which can reach the turbine. Periodic

DEPOSITION STUDIES

It is generally agreed that the presence of a sodium sulfate deposit is a prerequisite for sulfidation attack to occur. However, sodium sulfate is not a naturally occurring impurity in fuels nor a major constituent of the particulate matter often ingested into gas turbine engines. Since sulfidation attack occurs primarily in marine and industrial gas turbine engines, and to a much lesser extent in aviation engines, the principal source of sodium is generally believed to be sea salt crystals. The major constituent of sea salt crystals is sodium chloride.

The fuels used in gas turbine engines contain sulfur as a naturally occurring impurity. Based upon the available thermodynamic data, in the presence of the oxide of sulfur, water vapor, and air, sodium chloride is readily converted to sodium sulfate Na_2SO_4 [1]. Since sulfidation sulfate is a relatively stable salt, it follows that upon introduction of any source of sodium into a gas turbine engine the product will inevitably be converted to sodium sulfate.

Nevertheless, the role of NaCl in sulfidation attack is a controversial one, and although this alkali salt is not commonly found on corroded engine components, it is believed by many investigators [17,18,19] that NaCl is necessary to at least initiate sulfidation attack. It has been argued that the dwell time of NaCl in the gas turbine combustor is insufficient for it to completely react with sulfate. Conversion to sulfate is completed in situ, i.e., on the surface of the turbine component. During the interim, the alkali NaCl has sufficient time to initiate reactions with the substrate. Consequently, the extent to which NaCl participates is related to its rate of reaction with the oxides of sulfur.

In independent studies by Fryxell, et. al., [20] and Bornstein, et. al. [20], the composition of the salts which adhere to compressor components were examined. In their studies both investigators reported that whereas the predominant salts that adhere to the low pressure compressor are essentially sodium chloride-rich sea salt crystals, the salts which adhere to the high pressure compressor consist of the sulfates, primarily sodium sulfate, the sulfidation precursor. The mechanism by which the sulfate salt which is a minor constituent of sea salt accumulates onto the compressor components is not well known; however, the periodic shedding is a mechanism of transferring the corrosive salt from the compressor to the turbine.

Sodium chloride can also enter into the engine with the fuel. The refined gas turbine fuels are essentially sodium-free; however, during shipping contamination with lower fuels or sea water is possible. In a series of tests conducted by the Electric Power Research Institute (EPRI) [21], it was shown that the sodium present in the fuel can be deposited even when the resultant concentration of Na_2SO_4 in the turbine environment is below its "dew point". In a series of burner rig tests, sodium was intentionally added to a distillate fuel until sulfidation attack was observed. Then the sodium content of the fuel was reduced to a few parts per million and the combustion efficiency altered so as to produce a fuel-rich condition. Under these conditions, sulfidation corrosion occurred even though the sodium content of the fuel was only a fraction of that previously needed to cause attack. Based upon the results of these tests, it was concluded that Na_2SO_4 deposited in a nonequilibrium manner is a principle factor in a contaminated fuel induced sulfidation. Deposition of sodium sulfate by equilibrium condensation requires higher salt levels within the fuel than would be normally found during actual practice.

Based upon mechanism studies, it is generally accepted that the initiation step for sulfidation corrosion is the break-

down of the normally protective oxide scale which separates the environment from the alloy substrate. At UTRC it was shown that oxide ions present in the salt react with the oxide scale allowing the fused salt to contact the substrate. The chemical reaction between the salt and the metallic substrate produces oxides and more oxide ions, thereby preventing the reformation of a protective scale.

The vanadium-induced hot corrosion problem involves a mechanism whereby fuel contaminants become concentrated before encountering turbine hot section components. During the combustion of a fuel oil, the oil droplets vaporize and burn in stages. The lighter hydrocarbons distill from the droplets and burn, leaving heavier hydrocarbons, which decompose to form a viscous, tar-like char, and, subsequently, carbon [15]. Fuel-soluble metallic impurities, such as vanadium porphyrins, the major vanadium carrier in fuels, are not very volatile and tend to concentrate and oxidize to V_2O_5 in this portion of the fuel. This vanadium-in-char enrichment mechanism produces a V_2O_5 droplet which can impact airfoils. If the temperature is such that the particles behave as a viscous fluid, the particles adhere to turbine components producing corrosion.

FIELD EXPERIENCE

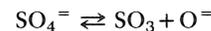
The approaches taken to minimize corrosion include:

- Chemical additions to the fuel to negate the effects of corrosive salts;
- Alloy chemistry modification for improved hot corrosion resistance; and
- Environmental control, including air filtration and turbine washing.

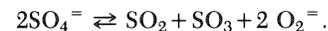
Additives

Based upon the oxide ion theory of sulfidation attack, the corrosive alkali salt is initially separated from the superalloy sulfate by the normally protective oxide scale. If reactions are to occur between the substrate and the salt, the normally protective oxide scale must be rendered ineffectual.

The fused Na_2SO_4 salt is an ionized melt consisting of sodium ions, sulfate ions and to a lesser extent, oxide ions. The concentration of oxide ions is established by the equilibrium



or



Bornstein, Brown, and DeCrescente [22] constructed a high-temperature reversible galvanic cell and demonstrated that sulfidation attack can be attenuated by controlling the oxide ion content of the corrosive salt. It was found that chromia (Cr_2O_3) readily reacts with and reduces the oxide ion content of sodium sulfate.

Consequently, a base fuel additive was produced and evaluated for more than 6000 hours of field testing on gas turbine engines of which more than 5000 hours were completed on marine engines and 1000 hours on electric utility engines. The use of a fuel additive to attenuate sulfidation corrosion was also evaluated in 24,000 hours of testing carried out on engines used to power the CN Turbo Train. Based upon the results of these tests, it was concluded that the chromium base fuel additive increased the life of industrial and marine gas turbine engines operating in the hostile corrosive environments generated by alkali salts.

In the overall picture, the use of the chromium additive ultimately accrues in the economics of operation. In other words, the savings in repair charges obviously must be greater than the total of the additive and injection costs in order for it to be meaningful.

Air Filtration

The size distribution of the sea salt particles in the air is not well known, and the use of air filters to remove all alkali particles from turbine inlet air is not considered realistic. However, the use of air filters can very well reduce the rate at which salt accumulates within the gas turbine engine and therefore prolong engine life.

In engine tests conducted at Long Island Lighting Company [21], it was shown that the amount of sodium salt in turbine airfoil deposits can be reduced substantially by installing inlet air filters (Figure 1). This data was obtained by removing first stage turbine vanes after varying periods of operation and analyzing the amounts of total water soluble deposits. The correlation between the amount of sodium salt found on turbine vanes and the extent of vane corrosion was established by visual observation.

In addition to reducing the incidence of hot corrosion, inlet air filters were also credited with fuel and hardware cost savings. The filtered engine maintained the same fuel con-

sumption over a 2000-hour period, while an unfiltered engine deteriorated with time. Increases in fuel consumption were attributed to erosion of the ninth and tenth stage compressor blade tips. No erosion was observed in the filtered engine. Gas path analysis confirmed compressor degradation in the unfiltered engine.

Alloys and Coatings

The material employed in the hot sections of gas turbine engines are among the strongest and most oxidation resistant engineering materials known. These components maintain their designed load-carrying capabilities up to eighty-five percent of their incipient melting temperature. The mechanical properties and oxidation characteristics of the alloys used in the manufacture of the components are strongly composition dependent; however, alloy developers have been able to maintain an excellent balance between the two properties. In addition, protective coatings are applied which enhance oxidation and corrosion resistance and enable these components to attain additional service life. These coatings (which are based on the elements chromium, silicon, and aluminum) form oxides that have low essential diffusion rates, thus protecting the substrate material from oxidation. Coatings must be diffusionally stable with regard to the substrate, and ductile at elevated temperatures to accommodate thermal stresses.

Programs are currently in progress to further develop coatings for utility gas turbines which will improve the durability of the present generation of industrial gas turbines, thereby increasing on-line availability and subsequently reducing maintenance costs.

The protective coatings that are currently employed can be divided into three groups: (a) simple aluminides, (b) precious metal aluminides, and (c) overlay coatings. In general, the simple aluminides are formed by the reaction and diffusion of aluminum into the alloy and the subsequent conversion of the alloy into the intermetallic compound. Since the substrate alloy is quite complex, the phases present in the coating consist of all the elements present in the substrate, and hence, the behavior of the coating is strongly influenced by the substrate composition.

The precious metal aluminides consist of the application of a layer of either platinum or rhodium or combinations of the two prior to the aluminizing step. It is felt that the presence of the precious metal influences the rates of diffusion of aluminum into the substrate in addition to the formation of precious metal aluminides. Again, since the substrate components enter into the coating composition, the alloy influences the chemical characteristics of the coating.

The overlay coating consists of the application of a coating onto the substrate: all elements necessary for coating formation are simultaneously applied to the substrate. Thus, for the overlay coatings the coating composition is, for all practical purposes, independent of substrate composition. However, at extremely elevated temperatures some interdiffusion will occur, and with time, the composition of the coating will change.

The overlay coatings are the most advanced protection system and studies are currently underway to develop families of coatings exhibiting oxidation resistance for longevity in industrial engines burning high grade distillate fuels as well as the low grade vanadium containing fuels. Burner rigs such as shown schematically in Figure 2 in which both clean number 2 oils and vanadium containing heavier oils are used to rank coating candidates. The results of a recent series of tests used to evaluate modified CoCrAlY compositions are shown in

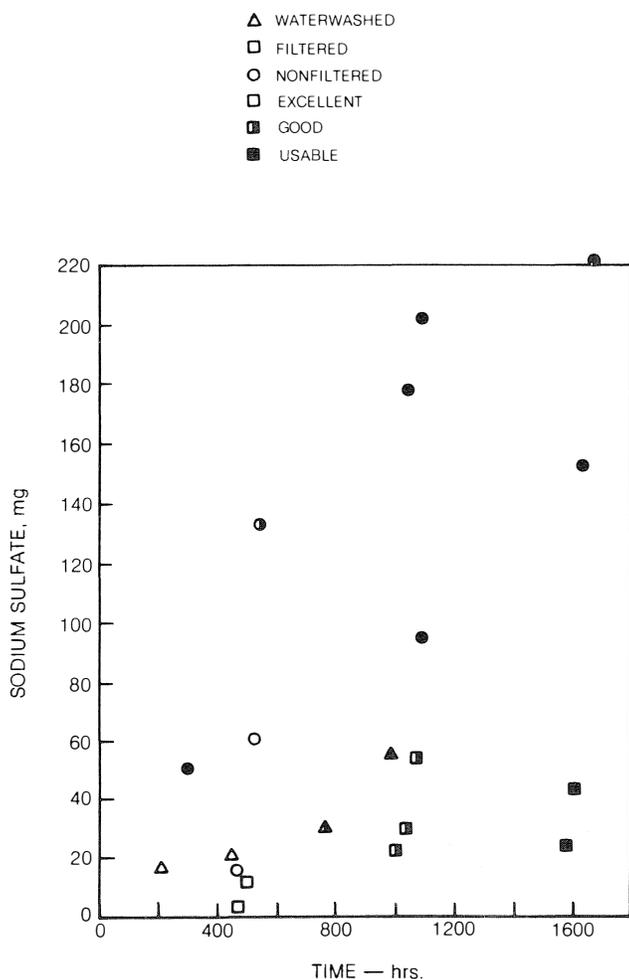


Figure 1. Sulfidation Watch Program.

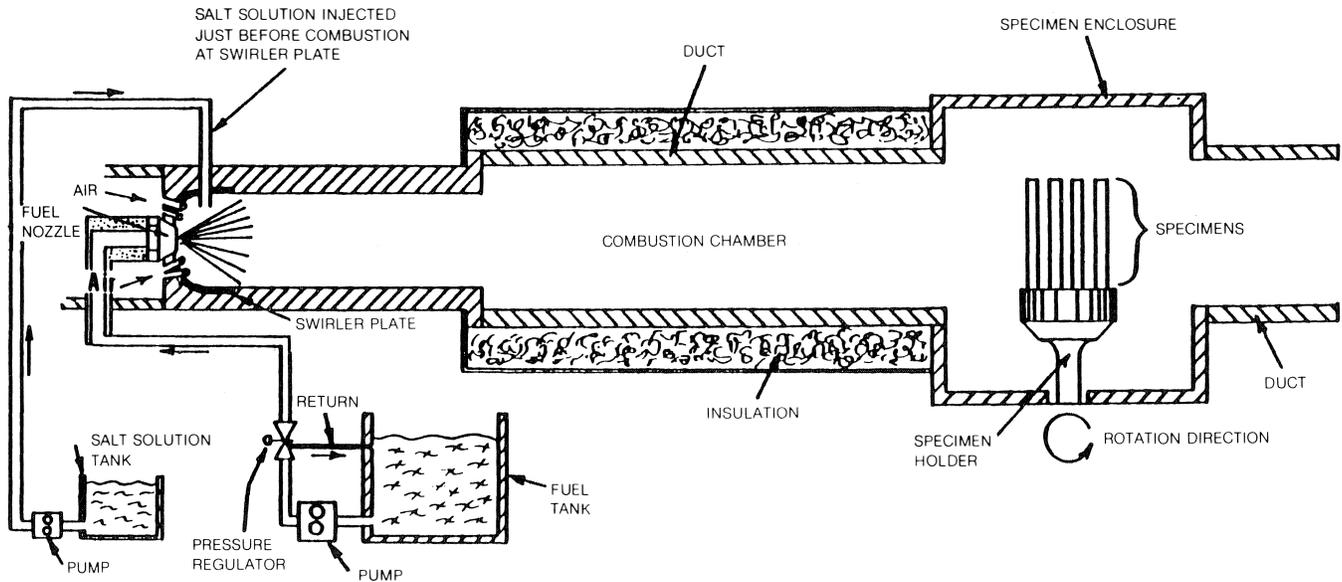


Figure 2. Schematic of Burner Rig.

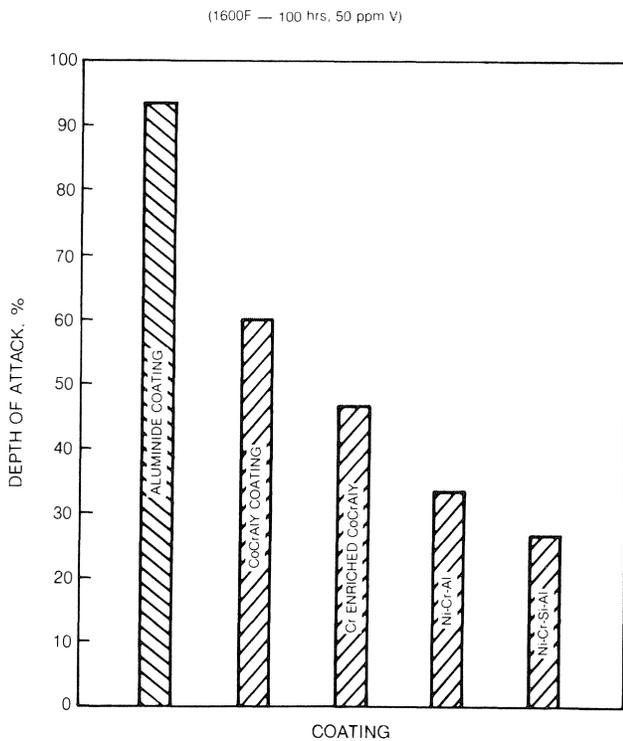


Figure 3. High Temperature Burner Rig Tests.

Figure 3. The next step in the evaluation process are engine tests which are currently in progress.

SUMMARY

Hot corrosion in electric utility gas turbines leads to increased maintenance costs and decreased availability and durability of the gas turbine engine. Based upon laboratory studies combined with field experiences, the corrodent re-

sponsible for the accelerated corrosion has been identified as Na_2SO_4 , the mechanism by which they accumulate determined, and the chemical reactions that occur have been duplicated.

The steps taken to minimize corrosion depend upon needs and economic considerations. The use of air filtration can extend turbine life by decreasing the rate at which the corrosive salts accumulate within the engine. The existence of an incubation period during which the alkali salts are separated from the substrate by an oxide scale and the periodic washing of turbine components can result in increased turbine life provided that the water soluble corrosive salts are removed prior to oxide scale breakdown. The use of fuel additives, which react with the fused salts, further extends the duration of the incubation period, but this practice is expensive and relies on the use of strategic material. Lastly, based upon the result of mechanism studies combined with results of high temperatures metallurgy programs, new coating compositions are being developed which are more resistant to the chemical attack of the deposited salts and metallurgically compatible with superalloy substrates.

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