CHARACTERIZATION OF CORROSION ATTACK OF SUPERALLOYS
IN COMBUSTION TURBINES IN THE TEMPERATURE
RANGE 600-760°C (1110-1400°F)

C. J. Spengler
Westinghouse Research and Development Center
Pittsburgh, Pennsylvania 15235

A form of hot corrosion attack on superalloys in combustion turbines at surface temperatures in the range 600-760°C is characterized by a sulfide-rich inner scale in contact with the alloy that has no depleted region. The attack is confined to component surfaces containing deposits of complex alkali-alkaline earth-transition metal-heavy metal sulfates. It generally occurs at a low rate but, occasionally, produces a rapid pitting mode.

INTRODUCTION

It is the intention of this paper to characterize for the general interest of superalloy users and developers a different form of hot corrosion attack than the familiar type that has been well-described by Stringer (1). This different form of attack occurs in land-based turbines and has a layered scale structure with no depleted alloy region or any subscale sulfide formation. It generally occurs at a low rate but, occasionally, does result in a rapid pitting mode on turbine component surfaces that are below 760°C (1400°F).

A similar type of hot corrosion attack has been identified in naval ship propulsion gas turbines, where it has been variously called "low temperature hot corrosion", "low power corrosion", or "type 2" (2). Current NAVSEA funded research has produced data and theory (3) relating to "low temperature hot corrosion", an aggressive form of hot corrosion at component temperatures of 650 to 760°C (1200-1400°F). At this time it has not been established that the form of corrosion attack in marine gas turbines is the same in structure and genesis as the layered-type of attack found

in land-based turbines; therefore, the latter will be called in this paper "moderate temperature hot corrosion".

CHARACTERISTICS OF SERVICE EXPERIENCE

Land-based turbines with gas inlet temperatures near 800°C (1470°F) have a variety of moderate corrosion attack morphologies (Figure 1). Such differences arise from use of light or heavy distillate oils (0.4 to 1.2 w/o S, respectively), in sites where there can be sea-salt contamination. The corrosion attack is specific to airfoils where the surface temperatures are below 760°C (1400°F). Examples of attack on one nickel-based alloy are on Inconel-700 (Table 1). The scale can contain prominent layers of nickel sulfide (Figure 1-a) or very little sulfide, but with inclusions of Na-Mg sulfate (Figure 1-b) or both nickel sulfide and inclusions of CoSO_4 (Figure 1-c).

FIG. 1 CORROSION MORPHOLOGIES IN TURBINES WITH 790°C GAS INLET TEMPERATURES. A. - AFRICA; B. - CENTRAL AMERICA; C. - SOUTHERN EUROPE. BASE ALLOY IS INCONEL-700.

Table 1. Alloy Compositions

	Wt %							Other
	Ni	Co	Cr	Al	Ti	Mo	W	
Inconel-700	Bal	28.5	15.0	3.0	2.2	3.7	--	
Udimet-500	Bal	18.5	18.5	3.0	3.0	4.0	--	
Udimet-520	Bal	12.0	19.0	2.1	3.0	6.0	1.0	
Udimet-710	Bal	15.0	18.0	2.5	5.0	3.0	1.5	
IN-738	Bal	8.5	16.0	3.4	3.4	1.75	2.6	Ta, Cb
Alloy X-45	10.0	Bal	25.0	--	--	--	7.5	Fe
RA-333	45.0	3.0	25.0	--	--	3.0	3.0	Mn, Si, Fe

All occurrences have the sulfide-rich innerscale in direct contact with the superalloy with no detectable depleted alloy region. Bordering the sulfide-rich inner layer is a prominent Cr_2O_3 -layer with variable amounts of Ti and Al. This layer also can have inclusions of Na-Mg or Co-sulfate. There is a distinct boundary between the Cr_2O_3 -rich layer and a thicker porous outer scale of Ni-Co-based oxides. The deposits on the outer porous oxide scale (Table 2) vary from turbine to turbine and are different Na-Mg sulfates, CoSO_4 and even Co-Ca sulfates. When some vanadium is in the fuel (no additives used) the outer scale is mostly $\text{Ni}(\text{VO}_3)_2$.

The moderate temperature corrosion attack is present in cooler regions of some turbines that operate at gas inlet temperatures to 1000°C (1830°F), with fuels that have < 0.5 w/o S (North America A) or up to 1.0 w/o S (North America B) in environments subject to sea salt contamination. The corrosion attack has been observed on a number of alloys, for example, alloys such as Udimet-710, 520 (Table 2) normally considered resistant to the more familiar type of hot corrosion attack. In such higher-temperature turbines the attack is confined to regions at temperatures below about 760°C (1400°F). It can occur on the suction side of airfoils (Figure 2).

Table 2. Sulfate-Based Deposits on Turbine Parts as Identified by X-ray Diffraction Analysis

<u>Location</u>	<u>Sulfate Phases</u>
Central America	Undifferentiated Na-Mg sulfates
So. Europe	CoSO_4 , Co-Ca sulfate
N. America A	Na_2SO_4 (thenardite), CaSO_4 MSO_4 (M is Co, Mg, Zn)
	CoSO_4 , $\text{Na}_2\text{Co}(\text{SO}_4)_2$
N. America B	$\text{Na}_2\text{Mg}(\text{SO}_4)_2$, CaSO_4 Na_2SO_4 (thenardite), $\text{Na}_6\text{Mg}(\text{SO}_4)_4$

FIG. 2 CORROSION MORPHOLOGY IN TURBINE WITH 1000°C GAS INLET TEMPERATURE (NORTH AMERICAN B). SHOWN IS MODERATE TEMPERATURE CORROSION ATTACK LOCATED ON SUCTION SIDE OF BLADE NEAR TRAILING EDGE.

There is a rather well-defined demarcation between the moderate temperature attack (Figure 3c) and the area showing the more familiar form of intermediate or high temperature attack (Figure 3a). Across these regions there is an uneven zone with a transition-type morphology (Figure 3b) that contains structural features of both types of attack.

The deposits and reaction products collected from turbine components contain double sulfates but are of variable chemistry (Table 2). Many of the Na-Mg and Na-Co sulfate compounds, as well as MgSO_4 and CoSO_4 , are isomorphous when hydrated and are very difficult to distinguish with X-ray diffraction techniques. Chemical analyses are, therefore, necessary for reliable identification. The water-soluble component of the deposit from North American A contains 9.2 w/o Na, 0.6 w/o K, 1.9 w/o Mg, 6.2 w/o Ca, 1.7 w/o Ni, 0.9 w/o Co, 3.4 w/o Zn, 0.5 w/o Cl, 0.1 w/o F and 75.5 w/o SO_4 (normalized), which indicates a possible molten phase at temperatures below 790°C (1450°F). Interestingly, some of the Na-Mg and Na-Co double sulfates and Na_2SO_4 and CoSO_4 are found on surfaces that normally are at temperatures greater than 790°C (1450°F), but the attack is of the intermediate temperature type. Chloride concentrations of 0.02-0.07 w/o have been found in deposits on surfaces both above and below 790°C (1450°F).

FIG. 3 CORROSION MORPHOLOGIES IN TURBINE WITH 1000°C GAS INLET TEMPERATURE (NORTH AMERICAN A). A. - HIGH TEMPERATURE ATTACK; B. - TRANSITIONAL HOT CORROSION ATTACK; C. - MODERATE TEMPERATURE CORROSION ATTACK.

LABORATORY CHARACTERIZATIONS

Direct Simulation

Moderate temperature corrosion has been experimentally investigated using the pressurized test passage (4), where the environment simulated is representative of that associated with the region of earliest corrosion attack. The tests

reported here (Table 3) are with fixed contaminant level except for sulfur. They employed cylindrical test specimens 5.7 cm long by 0.64 cm diameter of superalloys generally resistant to the intermediate temperature form of hot corrosion attack.

At 700°C (1300°F) and 0.5 w/o S the deposit is Na_2SO_4 with some $\text{Na}_6\text{Mg}(\text{SO}_4)_4$ but at 675°C (1250°F) and 2 w/o S the primary phase is $\text{Na}_6\text{Mg}(\text{SO}_4)_4$ with some Na_2SO_4 and, occasionally, $\text{Na}_2\text{Mg}(\text{SO}_4)_2$. The water-soluble fractions of the deposits and reaction products show a higher CoSO_4 content of the solute fraction when the deposit forms on a cobalt-based alloy (5.4 w/o CoSO_4) than on a nickel-based alloy (1.0 w/o CoSO_4). This is consistent with the greater pitting attack observed on the cobalt-based specimens. At 700°C (1300°F) the CoSO_4 -content of the deposit decreased with exposure time (5.4 w/o at 242 hrs to 0.6 w/o at 526 hrs). This reduction occurred because dilution from depositing Na_2SO_4 exceeded the rate of Co-metal ion addition by attack of the alloy protective scale. The corrosion structure in the case of the nickel-based alloy (Figure 4) is similar to that observed in the field in terms of the elemental distributions in the various layers of corrosion products.

Table 3. Turbine Simulation Conditions in Pressurized Test Passage

Fuel Type:	No. 2 distillate
Contaminants:	10 ppm Na, 1.3 ppm Mg, 0.4 ppm K 0.4 ppm Ca, 18 ppm Cl
Fuel Sulfur:	0.5 w/o at 700°C; 2.0 w/o at 675°C
Approach Velocity at Specimens:	150 meters sec^{-1}
Static Pressure:	4.05×10^5 Pa (4 atm)
Air/Fuel Ratio:	60:1

E $(\text{Ni}, \text{Co})\text{O} + (\text{Ni}, \text{Co})\text{Cr}_2\text{O}_3$
 D $\text{Cr}(\text{Ti}, \text{Mo})$ -SULFIDE
 B AL-SULFIDE
 A BASE ALLOY

FIG. 4 CORROSION MORPHOLOGIES FORMED IN PRESSURIZED PASSAGE AT 700°C. DEPOSITS ARE Na_2SO_4 AND $\text{Na}_6\text{Mg}(\text{SO}_4)_2$. ALLOY IS UDIMET-720.

At 675°C (1250°F) and 2.0 w/o S, where the degree of pitting of the cobalt-based alloy is greater than at 700°C (1300°F), the CoSO_4 -content of the solute (0.5 w/o at 110 hrs to 3.1 w/o at 214 hrs) increases with time even though the Na_2SO_4 -flux is comparable to that at 700°C (1300°F). The effect of the higher $\text{pSO}_2(\text{pSO}_3)$ level at 675°C (1250°F) compared to 700°C (1300°F) is to raise the average MgSO_4 -content (from 5.0 w/o to 8.3 w/o) and lower the average K_2SO_4 -content (from 9.0 w/o to 5.5 w/o) of the solute.

The simulations initiated characteristics of moderate temperature attack on the nickel-based alloy quite similar to those found in service exposures of the same materials; however, the Cr_2O_3 portions of the scale did not contain detectable sulfate as has been observed in some of the field exposed alloys. The simulated deposits contain Na-Mg double sulfates, but no detectable chloride.

Additional Morphology Studies

Tabular specimens 1.27 cm wide, 2.54 cm long and 0.16 cm thick of nickel-based superalloys were exposed in air to mixtures of sulfates by partial immersion in a sulfate melt. The alloy IN-738 exposed to 52.4 m/o Na_2SO_4 -47.6 m/o MgSO_4 at 700°C (1300°F) for 66 hours showed pitting attack (Figure 5-a) primarily on the surface of the coupon above the sulfate meniscus. The attack is similar to that of the field and simulator structures. The composition of one of the sulfide-rich zones (Figure 5a at c) indicates 1.8 w/o Al, 19.6 w/o S, 26.2 w/o Cr, 3.8 w/o Mo, 9.1 w/o Ti, 1.2 w/o Co, 3.2 w/o Ni and 35 w/o O (by difference). The sulfur is too low for the layer to be entirely sulfide; therefore, oxides are also present.

The superalloy, IN-738, in contact with a melt of 50 m/o Na_2SO_4 -50 m/o CoSO_4 has a corrosion microstructure (Figure 5b) and sulfide layer chemistry (1.3 w/o Al, 18.2 w/o S, 32.0 w/o Cr, 3.0 w/o Mo, 7.6 w/o Ti, 1.3 w/o Co, 2.2 w/o Ni and 34.4 w/o O, by difference) very similar to the exposure to the Na-Mg sulfate except that the Cr_2O_3 -rich area contains more cobalt.

DISCUSSION AND CONCLUSIONS

It is clear from the evaluation of corrosion attack in some land-based turbines, that there is a form of hot corrosion somewhat different in structure and possibly genesis, from the more familiar form of hot corrosion attack. This

FIG. 5 CORROSION MORPHOLOGIES FORMED BY EXPOSURE OF IN-738 IN AIR TO MOLTEN: A. - 52.4 M/O H_2SO_4 -47.6 M/O MgSO_4 AND B. - 50 M/O Na_2SO_4 -50 M/O CoSO_4 AT 700°C FOR 66 HOURS.

different form of attack is associated with surface temperatures generally lower than 760°C (1400°F) and is characterized by a layered-scale structure with Al, Cr, Ti-sulfide rich zones in immediate contact with the base alloy, which characteristically has no depleted zone. The corrosive deposits associated with this form of corrosion attack are principally Na_2SO_4 -based, but contain sufficient concentrations of Co, Ni, Zn, Mg, K and Ca in solution to indicate the presence of possible molten phases during turbine operation.

Comparable corrosion microstructures to those observed in the field were reproduced both in the pressurized test passage and in a simple laboratory experiment. Other laboratory

experiments with the equipment used to examine hot corrosion reactions at 870°C (1600°F) (5) were performed at 700°C (1300°F) and 790°C (1450°F) in an atmosphere of N_2 -0.2 v/o O_2 -0.2 v/o SO_2 -0.1 v/o SO_3 with deposits of either Na_2SO_4 or 70 m/o Na_2SO_4 -30 m/o $MgSO_4$. These experiments produced severe moderate temperature corrosion attack on IN-738 and Udimet-500 at 700°C (1300°F) with the Na-Mg sulfate, but not with pure Na_2SO_4 at least to 100 hours. At 790°C (1450°F) the IN-738 and Udimet-500 exhibited the more familiar hot corrosion attack. Only at 790°C (1450°F) did Na_2SO_4 alone result in attack of a nickel-based alloy (Udimet-500), but it produced a mixture of moderate temperature and intermediate temperature hot corrosion attack. At 700°C (1300°F) the experiments indicated the rapidity with which a molten Na-Mg sulfate phase initiated the corrosion attack compared to solid Na_2SO_4 in a SO_3 -containing environment.

The postulated mechanisms of corrosion attack in marine gas turbines at surface temperatures between 600 and 760°C are the subject of a review by Jones (3) and study by Luthra and Shores (6). They note that the corrosion attack takes place in the presence of deposited sulfates but that SO_3 is critical to the reactions. Additionally, carbon and NaCl are postulated as having an influence on the initiation of the attack (3).

Very little corrosion data is available on the moderate temperature mode of hot corrosion attack that takes place in land-based turbines. Some data (7) on corrosion penetrations as a function of temperature derived from field observations were extrapolated to 1000 hours by a linear relationship. Penetrations of about 0.025 cm (0.010 in) in normally hot corrosion resistant alloys (RA-333, IN-738) at surface temperatures of $676 \pm 27^\circ C$ ($1250 \pm 50^\circ F$) resulted. Attack of this magnitude necessitates careful choice of alloys and coatings.

Analyses of deposits from land-based turbines with corrosion show deposits, that contain various amounts of Na, K, Mg, Ca, Zn and Pb as sulfate constituents under system pSO_3 derived from fuels with less than 1.0 w/o S. The use of coal-derived fuels is anticipated to introduce the same elements as above, except perhaps in different relative quantities. Experiments based on the contaminants in coal-derived fuels produced Na-K-based sulfates shown (8) to have a greater corrosive effect on superalloys than Na_2SO_4 alone. Assuming, that moderate temperature attack in land-based turbines and low power attack in marine turbines are produced by similar agents, it is likely that coating evaluation and development work in one field is applicable to the other. Whereas, the

CoCrAlY-coatings do not appear to be sufficiently resistant (9) there is evidence that the high Cr-Ni(Co)CrAlY-family provides good resistance to moderate temperature corrosion (9,10). Certain types of diffusion coatings, now state-of-the-art, are proving sufficient for comparable corrosion conditions; however, research is continuing in order to develop optimum compositions.

REFERENCES

1. J. Stringer, "Hot Corrosion in Gas Turbines," Metals and Ceramics Information Center Report 72-08, June 1972.
2. D. J. Wortman, R. E. Fryzell and I. I. Bessen, "A Theory for Accelerated Turbine Corrosion at Intermediate Temperatures," The Third Conference on Gas Turbine Materials in a Marine Environment, Bath, U.K., September 1976, paper 10.
3. R. L. Jones, "A Summary and Review of NAVSEA Funded Low Power Hot Corrosion Studies," NRL Memorandum Report 4072, Washington, DC, September 1979.
4. C. J. Spengler, S. Y. Lee and W. E. Young, "The Pressurized Passage, A Laboratory Rig for Gas Turbine Simulation," Deposition and Corrosion in Gas Turbines, John Wiley & Sons, New York, 1973.
5. R. Viswanathan and C. J. Spengler, "Corrosion of 85 Ni-15 Cr Alloy at 1600°F in Controlled Atmospheres Containing O₂, SO₂, SO₃, H₂S and N₂," Corrosion 26, 1970, p. 29-41.
6. K. L. Luthra and D. A. Shores, "Mechanism of Na₂SO₄-Induced Corrosion at 600-900°C," Submitted for publication, Journal of the Electrochemical Society, 1980.
7. Unpublished data, EPRI Contract RP 234-3, Phase 1A, Task 5.3, 1979.
8. C. J. Sims and H. V. Doering, "Evaluating of Gas Turbine Materials in the Combustion Products of Coal-Derived Fuels," Third Annual Conference on Materials for Coal Conversion and Utilization, Gaithersburg, MD, October 1978.
9. L. F. Aprigliano, "Low and High-Temperature (1300 and 1650°F) Burner Rig Tests of MCrAlY Composition Variations," Report No. DTNSRDC/SME-79/35, D. W. Taylor Naval Ship R&D Center, MD, August 1979.
10. C. J. Spengler, "Hot Corrosion Resistant Fabricable Alloys," U.S. Patent 4,088,479.