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FOULING AND THE INHIBITION OF SALT CORROSION

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NOTICE

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SUMMARY

In an attempt to reduce fouling while retaining the beneficial effects of alkaline earth inhibitors on the hot corrosion of superalloys, the use of both additives and the intermittant application of the inhibitors were evaluated. Additions of alkaline earth compounds to combustion gases containing sodium sulfate were shown to inhibit hot corrosion. However, sulfate deposits can lead to turbine fouling in service. For that reason, dual additives and intermittant inhibitor applications were evaluated to reduce such deposit formation. Silicon in conjunction with barium showed some promise. Total deposition was apparently reduced while the inhibition of hot corrosion by barium was unimpaired. The intermittant application of the inhibitor was found to be more effective and controllable.

INTRODUCTION

If future utility gas turbines are to burn either minimally processed liquids or gases derived from coal (or petroleum residual fuels), they may be subject to accelerated hot section corrosion due to the combustion products of residual impurities in these fuels. One of the methods now being used to reduce or prevent hot corrosion is the use of inhibitors that are added to the fuel or injected into the combustor. This method is particularly attractive in treating a hot corrosion problem in existing turbines because it requires no redesign to accommodate either new alloys or coatings systems. Previous work at NASA-Lewis has shown that barium additions hold great promise in inhibiting hot corrosion; a few parts per million of barium can reduce hot corrosion (ref. 1) by several orders of magnitude. The mechanism by which barium reduces hot corrosion has not been fully clarified, but it is apparent that the formation of a deposit of barium sulfate is an important step in the process. The barium sulfate deposits, however, if excessive, could lead to turbine fouling which would lower efficiency and could lead to premature shutdown. The objective of the work described in this report is to explore ways to retain the hot corrosion resistance offered by the use of barium or similar hot corrosion inhibitors while decreasing the amount of sulfate deposits, i.e. fouling. Two approaches were studied. The first was the use of a second additive element in conjunction with the barium inhibitor in an attempt to produce a deposit which either formed at a lower rate or was more easily removed during thermal cycling. The second approach was to use the inhibitor in a non-continuous application, that is, pretreatment or intermittent treatment with the inhibitor. This work was performed at Lewis Research Center using burner rig test facilities. The extent of hot corrosion and its reduction was judged by the degree of metal recession. The hot corrosion attack was induced by adding NaCl to the combustor. The Na then

combined with the S in the fuel to form Na_2SO_4. The deposition of this compound causes the accelerated attack called hot corrosion (ref. 1).

MATERIALS

The nominal compositions of the alloys used in this program are listed in table I. The cobalt-base alloy, Mar M-509, is a typical cast vane material which is generally considered to have good hot corrosion resistance due to its high chromium content. The three nickel-base alloys cover a range of hot corrosion resistance. IN-792 has moderately good hot corrosion resistance while IN-100 has minimal resistance to such attack. U-700 is intermediate in resistance between IN-792 and IN-100. The alloys were cast by a commercial vendor into the shape shown in figure 1(a). All samples were grit-blasted and cleaned with alcohol. Prior to test, each sample was measured along a diameter in the center of the expected hot zone (see fig. 1(a)) with a bench micrometer to a precision of ± 2 μm and weighed to ± 0.2 m gm.

PROCEDURE

The burner used in these tests is shown in figure 1(b) and has been described extensively elsewhere (for example, ref. 2). Briefly, the rig is a nominal Mach 0.3 type fired with Jet A-1 fuel whose sulfur content ranges from about 0.02 to 0.05 weight percent. The fuel-to-air ratio was varied from about 0.044 to 0.046 which resulted in measured flame temperatures of 1320° to 1360° C. Sodium chloride was injected into the combustor chamber as an aqueous solution and the barium inhibitor as well as other additives (B, Ca, Mg, Al, Si, Ni, Zn, P, Pb, and Sr) were injected similarly as aqueous solutions of nitrate salts either separately or together. Eight samples, two of each alloy, were rotated rapidly in front of the exhaust nozzle of the burner rig and reached the desired temperature, 900° C, in a few minutes. After each 1-hour exposure the burner pivoted away and compressed air at ambient temperature was directed onto the specimens for 3 minutes. This severe thermal cycle was then repeated. Approximately every fifteen cycles, the samples were removed, weighed and replaced. After the completion of the test, the samples were removed, weighed, washed and reweighed. Washing consisted of immersion of each blade in 300 cc of water at 80° C, followed by soft brushing in running water, an alcohol rinse, and air drying. The samples were then sectioned along the plane shown in figure 1(a) which is the center of the hot zone where all metal temperatures were monitored during the test. The cut sections were mounted metallographically, polished and etched. Thickness measurements were made to determine the final thickness at maximum penetration and to calculate metal loss. While both the initial and final thicknesses were measured to a precision of ± 2 μm, experience has shown (ref. 3) that surface recession is only accurate to ± 20 μm or less because of the irregularity of attack.

An initial 100-hour hot corrosion run was made with only NaCl added (3 ppm by weight of Na with respect to the combustion products), to provide baseline data for maximum hot corrosion rates. To test the effectiveness of barium (Ba) and a second additive, a series of tests was run in which sodium was injected by

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means of one solution and a second solution, was simultaneously injected containing Ba and a third element. The results of these runs are shown in table II, along with the concentrations used during the tests. A second set of tests was run to determine the effectiveness of intermittent application of the inhibitor. The results of these tests are shown in table III. Here the inhibitor alone or the inhibitor plus Na was injected into the burner for an initial 40 hour exposure. Then no more inhibitor was injected with the 3 ppm sodium while the exposure was continued for an additional 100 hours. A final set of runs was used to evaluate the approximate rate of deposition. In these tests the inhibitor plus Na were added for times up to 140 hours and the weight of the samples was measured periodically.

RESULTS AND DISCUSSION

Additions for Fouling Reduction

Deposition test results are shown in table II and figures 2(a) and (b). Figure 2, shows the metal recession rates and total deposition under all of the conditions for IN-100 and IN-792. This figure indicates that especially in the case of IN-100 (the alloy in this study most susceptible to hot corrosion), most of the secondary additions to the Ba inhibited combustion gases cause an increase in hot corrosion attack, and would therefore not be considered to be good candidates for fouling reduction. In addition, as hot corrosion becomes more and more extensive and metal recession increases, the weight change numbers become progressively more meaningless because they are the net result of both deposition which contributes to a weight gain and metal recession which tends to give a weight loss. Of the elements added, only Sr and Si gave metal recession values equivalent to Ba alone for IN-100. With IN-792 and the other alloys, the situation is not quite so bad, but these alloys, not being as sensitive to hot corrosion, are not as good an indicator of the effectiveness of the third element. Of the most effective of the elements added, Sr and Si, Sr tended to increase the amount of deposition while Si tended to decrease the amount of deposition. In general one can summarize these tests as demonstrating that, of the elements tested, Si is the only one that has much promise for reducing the degree of deposition while retaining hot corrosion resistance. Thus, it would appear that an inhibitor consisting of a combination of Ba and Si offers some potential for providing a high degree of hot corrosion resistance with only a moderate amount of deposition. In addition, Sr appears to be an acceptable alternative to Ba. As a result of this observation, it was decided to include Sr in the intermittent additive tests discussed below.

Intermittent Application and Deposition Rates

As described previously, these tests consisted of a 40-hour pretreatment in combustion gas also containing either the inhibitor alone, or the inhibitor in conjunction with Na. This pretreatment was followed by 100 hours of testing in only Na containing combustion gases (i.e. hot corrosion producing gases). The results of this work are summarized in table III. It can be seen from the amount of deposit during these tests that the direct addition of Na salts to the

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inhibitor solution in the pretreatment portion of the test (in contrast to the tests with no sodium injection) leads to a much increased deposition. Here deposition was greater by nearly a factor of 10 than in the runs made with Ba alone or Sr alone, and was more than a factor of 2 greater than in the run made with Ba + Sr.

The cause of the increased deposition rate in the presence of Na is not clear. Perhaps the presence of Na allows a fluxing of the oxide on the metal substrate resulting in better bonding between the inhibitor sulfate and the substrate. Or perhaps the combination of the Na and Ba sulfates gives a low melting point material which in itself is more adherent to the substrate. To study the effect of time on deposition rate for such systems, a series of runs was made using Sr and Na and the amount of deposition was measured as a function of time out to 140 hours. In these tests, which are tabulated in table IV and displayed graphically in figure 3, it is clear that under all conditions the deposition rate is nearly linear indicating no long-term reduction in the rate of deposition. However, at the higher temperature, (e.g., 1000° C) the amount of deposition is drastically reduced, apparently indicating that we are approaching the dew point of the deposit (~1190° C).

All of the pretreatments resulted in a reduction of hot corrosion as compared to no inhibitor use at all. However, the effectiveness of each of these pretreatments is difficult to evaluate quantitatively. Apparently the pretreatment leaves the sample coated with a thick, adherent layer of barium and of strontium sulfate (see fig. 4) which acts as an effective barrier to hot corrosion. When the barium and or strontium is no longer added to the flame the deposit no longer can grow, and with time gradually spalls off as the samples undergo thermal cycling. At some point the inhibitor sulfate layer has been reduced to such an extent that it no longer remains effective and hot corrosion starts once again. Therefore, one can view the effect of the pretreatment as retarding the hot corrosion process, for some period of time. To quantitatively determine how effective the pretreatment is, one would like to know how much time can be "bought". Unfortunately, the only effective measure of the extent of hot corrosion attack requires destruction of the specimen in order to metallographically measure metal recession. Such a technique makes the measurement of hot corrosion kinetics extremely time consuming. In an attempt to evaluate the hot corrosion kinetics, the weight changes for all of the differing pretreatment conditions on IN-100 were plotted in figure 5((a)-(f)). IN-100 is very susceptable to hot corrosion as has been noted above. Once it loses its protective layer, it immediately loses weight very rapidly. The effect of the deposit of Na sulfate and the formation of corrosion products becomes negligible compared to metal loss. Therefore, one can, by looking at the weight gain on IN-100, at least get an estimate as to the length of time over which the precoating has been effective. In general, the Sr pretreatments (5(b) and (e)) (with or without Na) were effective for approximately 80 hours. The Sr + Ba pretreatment (5(c) and 5(f)) seems to have lasted over 100 hours. The least effective pretreatment was Ba alone (5(a)) or Ba with the Na alone (5(a)). In both cases the effect of the pretreatment lasted for less than 40 hours. Since once the pretreatment effect is lost the metal recession proceeds at a catastrophic rate, it is quite obvious that the longer one allows the test to proceed the less will be the percentage difference between the sample which has been pretreated and the sample without pretreatment.

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Therefore, when evaluating metal recession data in table III (which summarizes all the pretreatment metal recession data for all of the alloys), one must keep in mind that ending the test after 100 exposure hours was arbitrary. If the metal recession numbers at the conclusion of the test match closely the continuous application of the inhibitor, then one can conclude that the pretreatment is still being effective even after 100 hours of exposure without the inhibitor. Even with all the uncertainties cited above, it is obvious that the application of 3 ppm Sr plus 3 ppm Na is the most effective pretreatment of any tried. Even at 100 hours the metal recession values are almost the same as those obtained from the continuous application of the inhibitor. This conclusion is consistent with the weight change data shown in Figure 5 ((a)-(f)) for IN-100. It seems almost certain that such intermittent application of the inhibitor can be effectively used to control the amount of deposition adhering to sample airfoils at any given moment. Obviously, as long as the inhibitor is applied, the airfoils will pick up more and more deposit of the inhibitor sulfate. Once the application is discontinued the thickness of the deposit will tend to decrease due to spalling but it can be renewed at will. Note that longer times between turbine shut downs will minimize such spalling and thus will lead to longer pretreatment life. This approach offers a very simple but effective way of controlling both hot corrosion and deposition and seems, of the two techniques tried, to hold the most promise. However, to completely evaluate such an inhibitor system one would require a detailed knowledge of the level of and variation in the sodium content in the fuel to be burned and their effect on the materials in each specific turbine. Operating with such knowledge, an inhibitor injection system could be combined with an apparatus which measures the amount of Na in the fuel as a function of time and could then trigger the appropriate application of Ba or Sr shortly before pretreatment loss occurred.

CONCLUDING REMARKS

From an evaluation of the burner rig test of two techniques to inhibit hot corrosion while minimizing fouling there are some generalizations that can be made. Of the secondary additives examined to minimize fouling while retaining hot corrosion inhibitor effectiveness, none produced dramatic decreases in fouling and indeed there was some evidence that even under ideal situations some loss in inhibitor effectiveness was apparent. The intermittent application of inhibitors, however, was shown to have definite potential. It can be used to keep fouling under close control. The specific parameters for intermittant application and the effectiveness of this approach will be related to such factors as the specific turbine operating conditions, the impurities in the fuel etc. However, intermittent application does offer a flexible way to meet changes in the Na and K levels found in the combustion gases of turbines running on coal-derived or heavy distillate petroleum fuels. There are several ways for such intermttient inhibition to be accomplished: for example, by intermittently applying the inhibitor on a predetermined time cycle or by combining injection with a on-line fuel analysis system.

In addition to the utility and industrial turbine applications there are many potential uses for this approach. One interesting possibility is the use of such an inhibitor approach for aircraft turbines. Inhibitors added on a con-

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tinuous basis would present prohibitive logistical problems in order to use the inhibitor while still retaining the flexibility of the aircraft. However, if intermittent application can be shown to have real potential, one could envision injecting the inhibitor directly into the combustion chamber, while the aircraft is on the ground. Then the source of the inhibitor could be removed until the aircraft landed again. Thus, an inhibitor-rich sulfate deposit would be deposited which would not have to last for inordinate times. Certainly one would anticipate, based on the results in the current work, that one application could be made to last for the duration of any expected air flight. Similarly, intermittent application of an inhibitor in a stationary gas turbine could be scheduled daily or weekly, just as water washing has been scheduled in many turbines to combat hot corrosion.

Another, unexplored benefit of these approaches could be the exploration of the inhibitor deposit as a thermal barrier. It is easy to imagine using this type of deposition on convection cooled hardware to control and repair such thermal barrier coatings in situ. The potential of this approach should be explored. In any event, it looks as though intermittent application of inhibitors is a viable approach to the problem of hot corrosion with reduced fouling and should be developed for specific applications.

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2. Deadmore, Daniel L.; and Lowell, Carl E.: Burner Rig Alkalai Salt Corrosion of Several High Temperature Alloys. NASA TM X-73659, 1977.

3. Lowell, Carl E. and Deadmore, Daniel L.: Effect of a Chromium-Containing Fuel Additive on Hot Corrosion. Corros. Sci., vol. 18, no. 8, 1978, pp. 747-763.

TABLE I. – NOMINAL COMPOSITION OF ALLOYS

[All values are in weight percent.]

Element	Mar M-509	IN-792	U-700	IN-100
Cr	23	12.7	14.2	10
Ni	10	Bal.	Bal.	Bal.
Co	Bal.	9.0	15.5	15
Al	----	3.2	4.2	5.5
Ti	.2	4.2	3.3	4.7
Mo	----	2.0	4.4	3.0
W	7	3.9	-----	-----
Ta	3.5	3.9	-----	-----
Nb	----	.9	-----	-----
V	----	-----	-----	1.0
Mn	----	-----	<.01	-----
Fe	----	-----	.1	-----
Si	----	-----	<.1	-----
Zr	.5	.1	<.01	.06
B	----	.02	.02	.014
C	.6	.2	.06	.18

TABLE II. – METAL RECESSION AND DEPOSITION WITH ADDITIONS TO BARIUM
INHIBITED HOT CORROSION

Additives, ppm	τ (μm)				Deposit after washing, grams			
	IN-100	U-700	IN-792	Mar M-509	IN-100	U-700	IN-792	Mar M-509
3-Na+3Ba+3Ca	410	74	61	70	-0.99[a]	0.86	0.88	0.93
3-Na+3Ba+3Mg	1680	62	100	80	-7.19[a]	.52	.61	.58
3-Na+3Ba+3Sr	23	47	10	61	1.00	.78	.92	.97
3-Na+3Ba+3Si	58	29	40	60	.04	.32	.29	.55
3-Na+3Ba+3Al	705	58	43	59	-1.00[a]	.32	.32	.32
3-Na+3Ba+3B	401	70	123	78	-1.60[a]	.38	.57	.64
3-Na+3Ba+3Mn	1587	60	86	44	-6.53[a]	.32	.32	.40
3-Na+3Ba+3Ni	819	52	83	42	-5.08[a]	.51	.63	.60
3-Na+3Ba+3Zn	598	38	36	56	-3.04[a]	.35	.43	.42
3-Na+3Ba+3P	1439	285	244	172	-3.82[a]	-.55[a]	.07	.04
3-Na+3Ba+3Pb	1209	66	66	59	-4.69[a]	.57	.57	.57
3Na	2158	453	760	231	------	-----	----	----
3Na+3Ba	48	54	44	44	.03	.88	.81	.64

[a]Net loss, i.e., corrosion excessive.

TABLE III. - PRETREATMENT EFFECTS ON DEPOSITION AND METAL LOSS

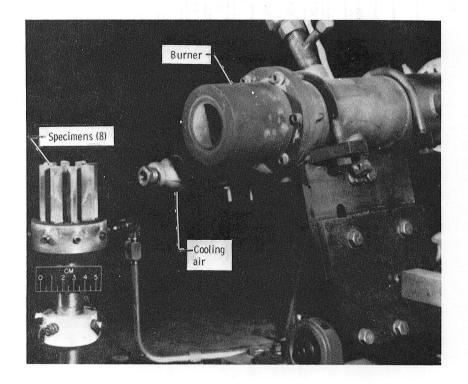| Inhibitor	Alloy	Deposition, grams 40 hr no Na	Deposition, grams 40 hr 3 ppm Na	τ (μm) no pretreatment	τ (μm) 40 hr pretreatment no Na	τ (μm) 40 hr pretreatment 3 ppm Na	τ (μm) continuous inhibitor
3 ppm Ba	IN-100	0.055	0.464	1530	750	1220	50
	U-700	.056	.358	180	20	17	50
	IN-792	.058	.303	490	120	170	40
	Mar M-509	.053	.345	190	40	110	40
3 ppm Sr	IN-100	.052	.449	1600	440	80	60
	U-700	.045	.465	220	2	34	60
	IN-792	.047	.443	610	100	60	30
	Mar M-509	.040	.448	330	110	70	70
3 ppm Ba + 3 ppm Sr	IN-100	.372	.818	1600	820	560	20
	U-700	.358	.830	390	20	20	50
	IN-792	.343	.819	430	30	60	10
	Mar M-509	.351	.866	290	40	30	60

TABLE IV. - DEPOSITION KINETICS OF SULFATES

Time, hr	800° C 3 ppm Sr + 3 ppm Na	900° C 3 ppm Sr + 3 Na	900° C 3 ppm Sr + 1 ppm Na	1000° C[a] 3 ppm Sr + 3 ppm Na
20	0.38	0.39	0.28	0.11
40	.81	.82	.56	.21
60	1.24	1.25	.84	.56
80	1.83	1.89	1.23	.66
100	2.47	2.31	1.53	.76
120	3.18	2.73	1.87	.88
140	3.60	3.63	2.18	1.0

[a]Average of two Mar M-509 bars only.

1.27 cm

30°

Plane of
sectioning

Zone of hot
gas stream
impingement

7.62 cm

1.27 cm diam.

2.54 cm

(a) Test bar.

Burner

Specimens (8)

Cooling
air

(b) Burner rig.
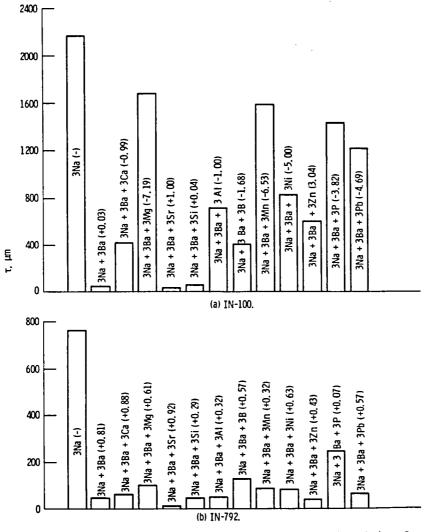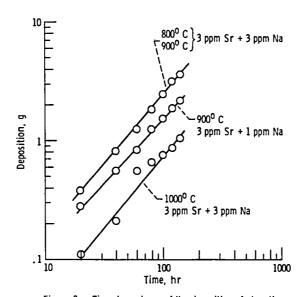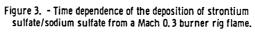
Figure 1. - Hot corrosion apparatus and test specimen.

Figure 2. - Effect of secondary additives on the inhibition of hot corrosion by barium. Deposition in grams in parenthesis. 100 One-hour cycles at 900° C. Dopant levels in parts per million of combustion gases.
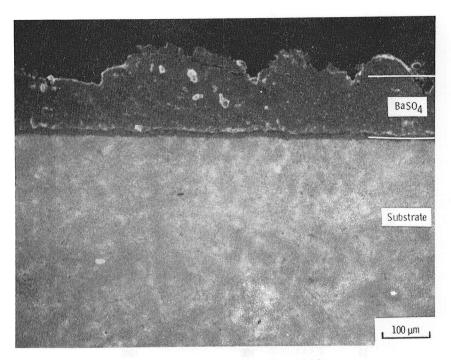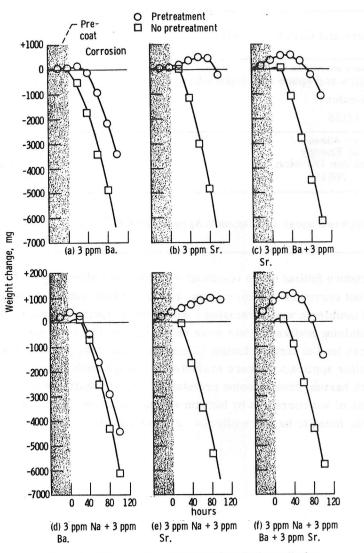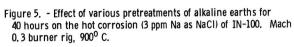
Figure 3. - Time dependence of the deposition of strontium sulfate/sodium sulfate from a Mach 0.3 burner rig flame.

Figure 4. - Deposit of $BaSO_4$ on IN-792 after 100, 1-hour cycles at 900^0 C, Mach 0. 3, 3 ppm Ba + 3 ppm Na as NaCl.

Figure 5. - Effect of various pretreatments of alkaline earths for 40 hours on the hot corrosion (3 ppm Na as NaCl) of IN-100. Mach 0.3 burner rig, 900° C.

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16. Abstract

In an attempt to reduce fouling while retaining the beneficial effects of alkaline earth inhibitors on the hot corrosion of superalloys, the use of both additives and the intermittent application of the inhibitors were evaluated. Additions of alkaline earth compounds to combustion gases containing sodium sulfate were shown to inhibit hot corrosion. However, sulfate deposits can lead to turbine fouling in service. For that reason, dual additives and intermittant inhibitor applications were evaluated to reduce such deposit formation. Silicon in conjunction with barium showed some promise. Total deposition was apparently reduced while the inhibition of hot corrosion by barium was unimpaired. The intermittant application of the inhibitor was found to be more effective and controllable.

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