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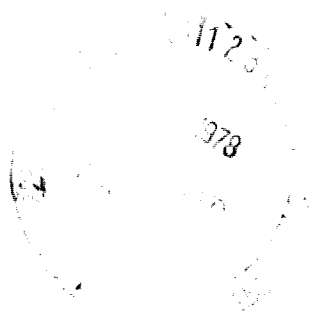
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INHIBITION OF HOT SALT CORROSION BY METALLIC ADDITIVES

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National Aeronautics and Space Administration
Lewis Research Center

July 1978

Prepared for
U.S. DEPARTMENT OF ENERGY
Office of Energy Technology
Division of Fossil Fuel Utilization



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SUMMARY

Hot corrosion testing of several nickel-, cobalt-, and iron-base alloys was performed in a Mach 0.3 burner rig to determine the effectiveness of potential fuel additives for reducing sodium sulfate attack. All tests were carried out at 900^o C for 100, 1 hour cycles. At the conclusion of each test the extent of attack was determined by measuring the maximum metal loss. All corrosion results were compared to cyclic oxidation tests made under the same conditions of time and temperature but in the absence of sodium chloride or additives. While all of the additives tested (salts of Al, Si, Fe, Cr, Zn, Mg, Ca, and Ba) reduced hot corrosion for some alloys, the most effective and consistent additive was barium nitrate. For all alloys this barium additive reduced the corrosion attack to nearly oxidation levels. Although much work is needed to establish cost effectiveness and the extent of a potential fouling problem, this work strongly indicates the desirability of the use of barium to substantially reduce the alkali metal-induced hot corrosion problem.

INTRODUCTION

Hot corrosion has been shown to be a major cause of failure in gas turbines used in marine, ground power, and, to a lesser extent, aircraft applications. Hot corrosion is usually defined as the accelerated metal loss observed at intermediate temperatures (near 900^o C) resulting from sodium sulfate deposition. A review of the literature of hot corrosion has been written by Stringer (ref. 1) and recently expanded by him (ref. 2). Impurities are usually considered to be ingested into the engine with air, especially over water, in the form of sea salt whose major constituent is sodium chloride (NaCl). The salt reacts with sulfur in the fuel during combustion to form sulfates which deposit in the hot section of the turbine. The sulfate deposit is assumed to flux the protective oxide scales normally found on the metals and results in greatly accelerated metal loss by oxidation and sulfida-

tion. Similarly, the use of coal derived fuels, which may contain high concentrations of sodium and potassium (Na and K) impurities, will probably lead to extensive hot corrosion by similar mechanisms.

While the application of surface coatings on hot section airfoils is the usual technique for reducing the effects of hot corrosion, an alternative solution is the use of corrosion inhibitors as a fuel additive. This is especially attractive in ground power and marine turbines where the logistics of fuel additives are much less severe than would be present in using additives for aircraft turbines. Indeed, magnesium (Mg) containing inhibitors for reducing vanadium (V) corrosion have long been commercially available (ref. 3) as has a chromium (Cr) containing additive for reducing sodium sulfate corrosion (ref. 4). This latter additive was tested independently and, as reported in reference 5, it was found to reduce hot corrosion in burner rig tests at 900°C by a factor of approximately two. Other work includes Spengler's identification of barium (Ba) as having excellent potential for the reduction of vanadium attack (ref. 6). The patent literature also offers many examples of work in the area of fuel additives for corrosion control. Zetlmeisl, et al. claimed that calcium (Ca), aluminum (Al) and Ca, Al, silicon (Si) additives were superior to Mg, (ref. 7) while Carlyle (ref. 8) discusses the advantages of Mg, Ca, and Al. Niles (ref. 9), Rocchini (ref. 10), and Young (ref. 11) all claim reduced hot corrosion using alkaline earths as either fuel additives or injecting them into the combustion products. Such inhibitors offer several benefits over other solutions to the hot corrosion problem, e.g., no redesign of airfoils is required to account for possible effects of corrosion resistant coatings on the mechanical properties of the airfoil. On the other hand, an additive injection system must be provided which adds complications to the fuel system and the additive may cause deposit formation with attendant loss in aerodynamic performance.

The purpose of this work was to evaluate the potential of a broad range of additives for reducing hot corrosion under constant condi-

tions on several commercial alloys which represent the extremes of good corrosion resistance to very poor corrosion resistance.

The approach used in this work was to focus on one corrosive compound, sodium sulfate, introduced as sodium chloride into the combustor of a Mach 0.3 burner rig. The sodium chloride reacted with sulfur in the fuel during combustion to form the corrosive sodium sulfate. Each potential inhibitor was also injected into the combustor. A series of cyclic tests were run for 100 hours. The extent of the attack was evaluated by alloy consumption. The effectiveness of the inhibitors was judged by how closely the metal consumption approached that obtained during simple oxidation at the same time and temperature, i. e., the least attack at that temperature.

MATERIALS

The 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 four nickel base alloys cover a range of hot corrosion resistance. IN-792 and IN-738 are similar in composition and moderately good in hot corrosion, while U-700 has somewhat poorer hot corrosion resistance and IN-100 has the least resistance to such attack. An iron base alloy, 304 stainless steel, was also included.

All of the alloys except the 304 stainless steel were cast by a commercial vendor into the shape shown in figure 1(a). The 304 stainless steel was used as a 1.27 cm diameter wrought rod 7.62 cm long. 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 (fig. 1(a)) with a bench micrometer to a precision of ± 2 micrometers (μm) and weighed to ± 0.2 milligrams (mg).

PROCEDURE

The burner rig used for these tests is shown in figure 1(b) and has been described in reference 12. Briefly the rig is a nominal Mach 0.3 type fired with A-1 jet fuel whose sulfur content ranges from 0.02 to 0.05 weight percent. The fuel to air ratio was varied from about 0.044 to 0.046. Sodium chloride was injected into the combustion chamber as an aqueous solution. Eight samples were rotated rapidly in front of the exhaust nozzle and reached the desired temperature (900°C) in a few minutes. After each 1 hour exposure the burner pivoted away and a forced air cooling nozzle was directed on the specimens for 3 minutes. This cycle was repeated. Approximately every 15 cycles the samples were removed, weighed, and replaced. After 100 cycles 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 and where all temperature measurements were made during the run. The cut sections were mounted metallographically, polished, and etched. Thickness measurements were made to determine the final thickness at maximum penetration t_f and to calculate metal loss Δt . While both the initial and final thickness were measured to a precision of $\pm 2\ \mu\text{m}$, experience has shown (ref. 5) that the resultant Δt is only accurate to $\pm 20\ \mu\text{m}$ because of the irregularity of attack, etc.

Two initial tests were run before the introduction of inhibitors: an oxidation test in which no solutions were added to the combustor and a hot corrosion test where only 3 parts per million sodium was introduced as sodium chloride into the combustor. The tests in which inhibitors were used were run with this same sodium level. All the inhibitors, except silicon, were injected into the combustor as water soluble salts. The inhibitors, their concentrations, and the compound used are shown in table II. Since no water soluble

compound of Si could be found, a colloidal suspension was injected into the combustor. However, because of the limitations of such a procedure the maximum Si level used was only 1.8 ppm.

RESULTS AND DISCUSSION

Aluminum and Silicon

The aluminum additive had little, if any, effect on the hot corrosion attack of sodium on the nickel base alloys tested; U-700 was not tested in this series (fig. 2). On the other hand, the corrosion of Mar M-509 and 304 stainless steel was substantially reduced, although in the case of Mar M-509 considerable hot corrosion still took place in spite of the Al. Si, which has been tested as a corrosion inhibitor in earlier work (ref. 3), markedly reduced the effects of hot corrosion in all but the most corrosion prone alloy, IN-100. However, the effect of going from 0.5 to 1.8 ppm Si was not large except for the 304 stainless.

Neither the Si or Al could be said to "stop" hot corrosion in the cobalt- or nickel-base alloys. Substantially greater attack occurred with the additives than during oxidation. Evaluation of the 304 stainless steel results is hampered by the fact that in oxidation only, the chromia forming steel loses excessive weight due to volatilization of its protective oxide. Any deposit, either a normally aggressive Na_2SO_4 or an inert oxide, reduces this volatilization and, as a result, its metal consumption rate. Therefore, one can compare the effectiveness of the inhibitors to each other in reducing Na attack but not directly to oxidation of 304 stainless steel.

Chromium, Iron, and Zinc

Chromium was included in these tests to compare this type of additive technique with organometallic additions directly to the fuel (refs. 4 and 5). In the present study addition of chromium roughly halved (fig. 3) the hot corrosion except for 304 stainless steel in

which no effect was noted; this is quite similar to the effects found in reference 5. In contrast the iron (Fe) had little or no effect except on the 304 in which the corrosion was substantially reduced. Surprisingly, the zinc (Zn) was even more effective than Cr in reducing hot corrosion on all the alloys although the results were erratic and in no case was the metal recession reduced to near oxidation levels.

Magnesium, Calcium, and Barium

The alkaline earths were the most interesting group in that all three elements greatly reduced the effects of hot corrosion for all alloys tested (IN 738 was not tested with Ba) as seen in figure 4. Of all of the elements tested, barium stands out as having the most consistently large effect; in most cases the attack was reduced to negligible differences from the minor attack observed in oxidation tests. All of the alloys in the barium inhibitor test had metal recession values of less than $50 \mu\text{m}$; this is especially dramatic for the case of IN-100 which lost over $2000 \mu\text{m}$ in Na alone but less than $50 \mu\text{m}$ with barium added. While the effect of Mg inhibitor additions is comparable for IN-792, IN-738, and U-700, the Mg additions are much inferior to barium in reducing the attack on IN-100 and Mar M-509.

The thickness change data is supported by the outward appearances and the microstructures of the alloys. An example of the effect of alkaline earth additives is shown in figure 5 for IN-792. The extreme conditions are the NaCl additive only on the left and the oxidation only on the right. As anticipated from the Δt values, the samples tested with Mg and Ba inhibitors show only slight attack. The specimens with the Ca inhibitor show less attack than in the presence of NaCl alone, but more than with Ba or Mg inhibitors. Also evident are the nonsoluble deposits on the Ca-inhibited sample. Such deposits, but to a lesser extent, were also observed on the Ba-inhibited sample, and were least observed on

the Mg-inhibited sample. Thus, even though the hot corrosion attack is greatly reduced, the effect of these deposits on fouling and their ease of removal would have to be evaluated before their potential for commercial use could be fully assessed.

These effects are seen more closely at higher magnification on specimen cross sections. Figures 6(a) and 7(a) show the typical hot corrosion microstructures for a nickel- and cobalt-base alloy respectively. The former alloy is characterized by an extensive depletion zone, nickel sulfides, and a heavy oxide scale of predominately NiO. The hot corrosion of the cobalt alloy is characterized by carbide depletion and extensive grain boundary attack. Figures 6(e) and 7(e) are typical of burner rig oxidation microstructures (note decrease in magnification) and are characterized by slight depletion zones and thin oxide scales. Mg and Ba additions yield microstructures which are more characteristic of oxidation than hot salt corrosion. The Ca inhibited samples show more attack but are still closer in appearance to oxidation specimens than to uninhibited hot corrosion specimens.

As pointed out earlier, inert deposits are formed on the alloys when Ba or Ca salts are used to inhibit corrosive attack. In all cases the deposit from the Mg additions was MgO, however, the Ba and Ca deposits were sulfates. In attempting to assess the deleterious effect of such deposits, it should be remembered that the levels of both the corrodent and the inhibitor are a factor of about 50 higher than would be expected in an actual engine. Therefore, to a first approximation the deposit is forming at a rate 50 times faster. All that can be concluded from this is that there might be a problem with deposition when using Ba additives although it is far from certain. This potential fouling problem should be evaluated in follow on efforts. Another factor would be cost. While a detailed cost analysis must be made, it is very unlikely that the cost will be a significant factor as Ba is plentiful. This additive cost would have to be balanced against down time and materials costs, but such a cost analysis is outside the scope of this report.

CONCLUSIONS

Based on burner rig testing of commercial alloys at 900° C for 100 cycles of 1 hour at temperature with 3 ppm Na added as NaCl to the combustion products, as a corrodant and with 3 ppm potential metallic inhibitors added as various salts, the following conclusions may be reached:

1. The most consistent and effective of all additives tested was Ba.
2. Use of Ba almost eliminates the characteristic sulfidation attack found in Na hot salt corrosion under these test conditions.
3. As a class the alkaline earths (Mg, Ca, and Ba) reduced hot corrosion on all alloys tested.
4. The response to the other additives evaluated (Al, Si, Cr, Fe, Zn) varied greatly from alloy to alloy.

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TABLE I. - COMPOSITION OF ALLOYS

[All values are weight percent.]

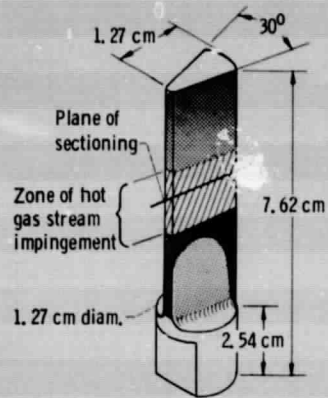
Element	Mar M-509	IN-792	IN-738	U-700	IN-100	304 SS
Cr	23	12.7	16	14.2	10	19
Ni	10	Bal.	Bal.	Bal.	Bal.	10
Co	Bal.	9.0	8.5	15.5	15	-----
Al	-----	3.2	3.4	4.2	5.5	-----
Ti	.2	4.2	3.4	3.3	4.7	-----
Mo	-----	2.0	1.8	4.4	3.0	-----
W	7	3.9	3.9	-----	-----	-----
Ta	3.5	3.9	.9	-----	-----	-----
Nb	-----	.9	-----	-----	-----	-----
V	-----	-----	-----	-----	1.0	-----
Mn	-----	-----	.2	.01	-----	2.0
Fe	-----	-----	.5	.1	-----	Bal.
Si	-----	-----	.3	.1	-----	1.0
Zr	.5	.1	.1	.01	.06	-----
B	-----	.02	.01	.02	.014	-----
C	.6	.2	.17	.06	.18	.08

TABLE II. - ADDITIVES USED

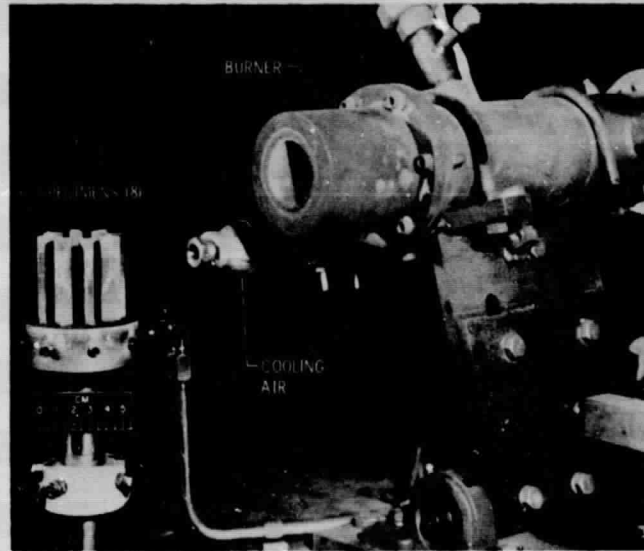
Metal	Concentration, ppm ^a	Metal source compound
Aluminum	3	Al(NO ₃) ₃
Silicon	.5	Colloidal SiO ₂
Silicon	1.8	Colloidal SiO ₂
Chromium	3	(NH ₄) ₂ CrO ₄
Iron	↓	Fe(NO ₃) ₃
Zinc		Zn(NO ₃) ₂
Magnesium		Mg(NO ₃) ₂
Calcium		Ca(NO ₃) ₂
Barium		Ba(NO ₃) ₂

^aParts per million by weight of metal in the combustion products.

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(a) Test bar.



(b) Burner rig.

Figure 1. - Hot corrosion apparatus and test specimen.

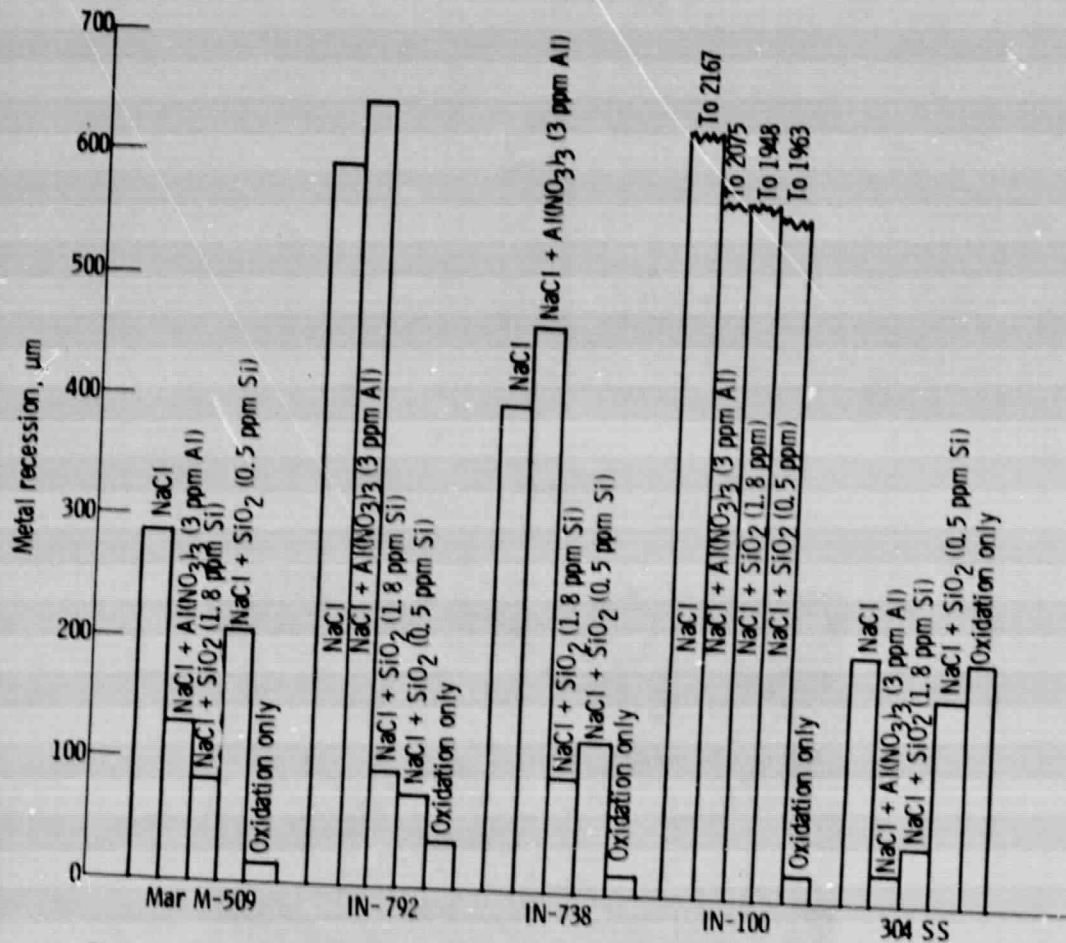


Figure 2. - Effect of Al and Si additions on burner rig hot corrosion after one hundred cycles of one hour at 900^o C, Mach 0.3.

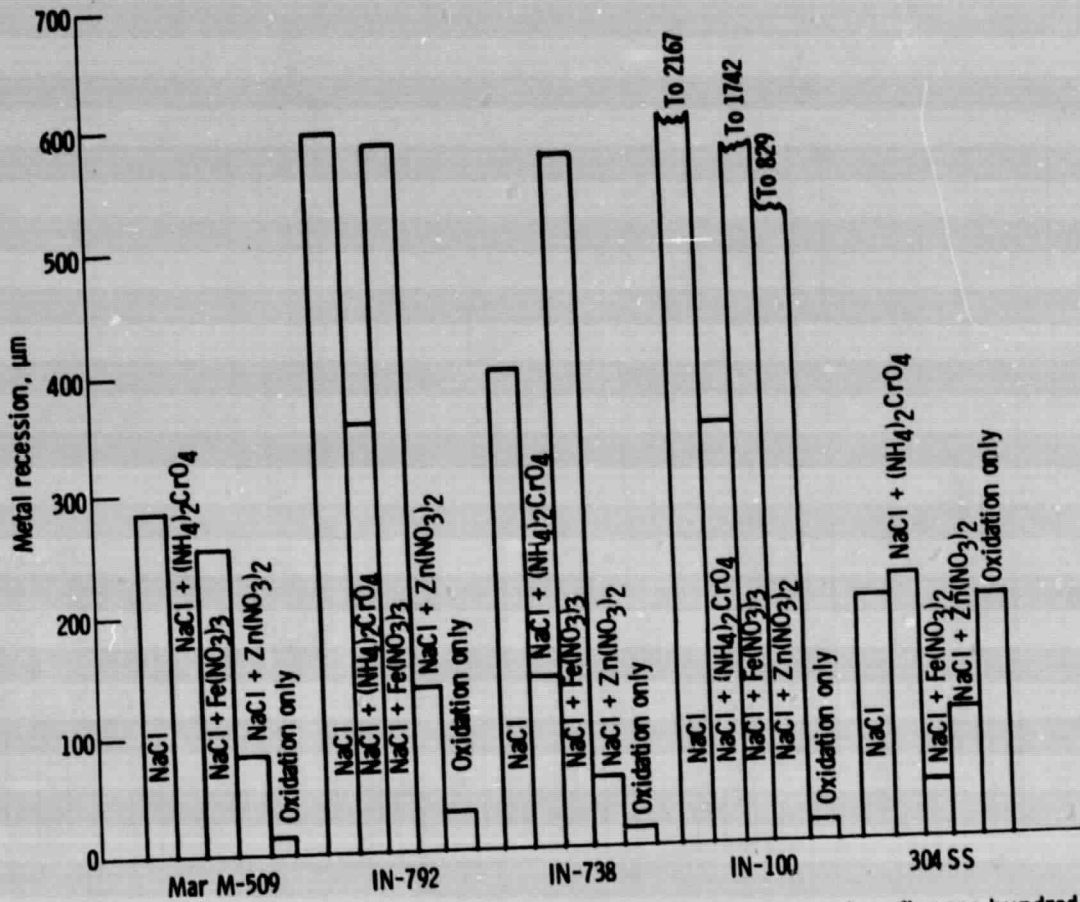


Figure 3. - Effect of Cr, Fe, and Zn additions on burner rig hot corrosion after one hundred cycles of one hour at 900° C, Mach 0.3. All additive concentrations are at 3 ppm of each metal.

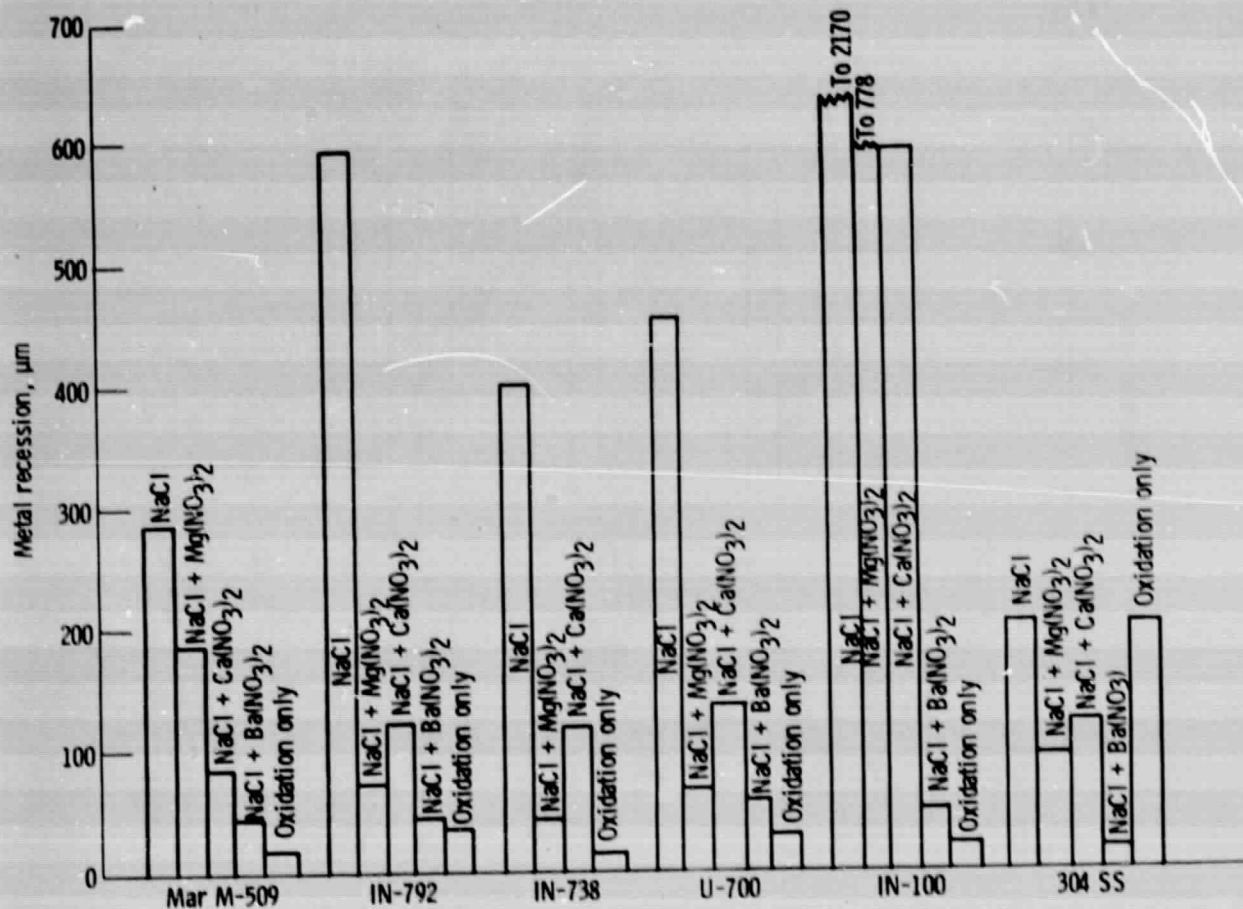


Figure 4. - Effect of alkaline earth additions on burner rig hot corrosion after one hundred cycles of one hour at 900°C. All additive concentrations are at 3 ppm of each metal.

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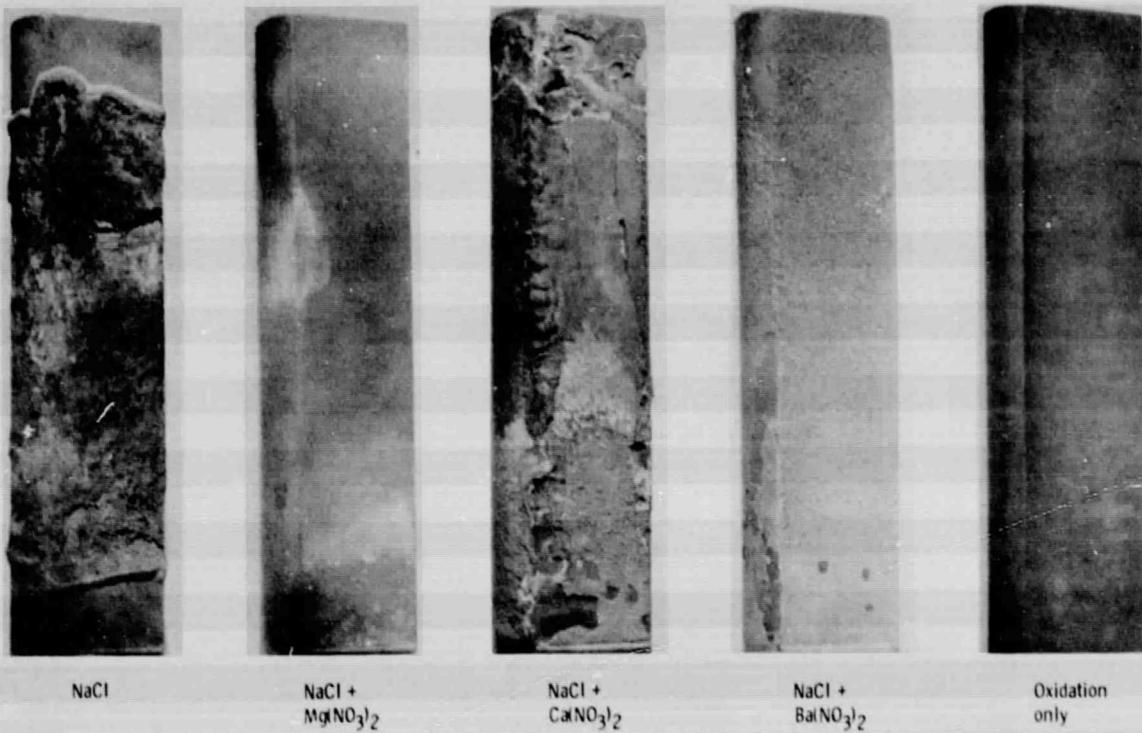


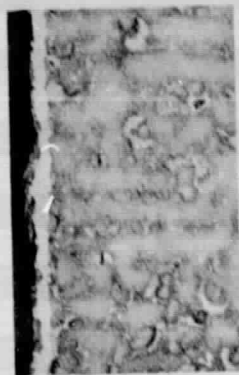
Figure 5. - Effect of alkaline earths on deposition and corrosion on IN-792 after 100 cycles of 1 hour at 900^o C, Mach 0.3. All additions at level of 3 ppm of the metal.



(a) NaCl only.



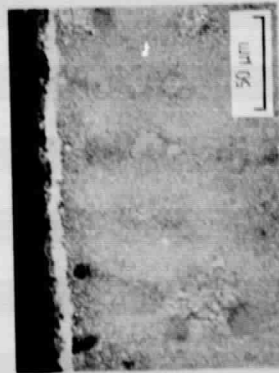
(b) NaCl + Mg(NO₃)₂



(c) NaCl + Ca(NO₃)₂



(d) NaCl + Ba(NO₃)₂

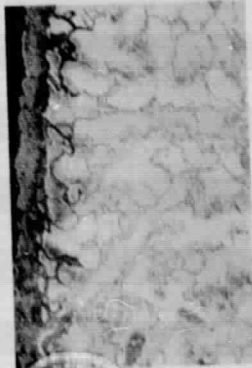


(e) Oxidation only.

Figure 6. - Effect of alkaline earth additions on microstructure of Mar M-509 after burner rig corrosion at 900° C, 100 cycles of 1 hour at temperature, Mach 0.3. All additions at level of 3 ppm of the metal.



(a) NaCl only.



(b) NaCl + Mg(NO₃)₂



(c) NaCl + Ca(NO₃)₂



(d) NaCl + Ba(NO₃)₂



(e) Oxidation only.

Figure 7. - Effect of alkaline earth additions on microstructure of Mar M-509 after burner rig corrosion at 900° C, 100 cycles of 1 hour at temperature, Mach 0.3. All additions at level of 3 ppm of the metal.

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16. Abstract <p>The effectiveness of several potential fuel additives in reducing the effects of sodium sulfate-induced hot corrosion was evaluated in a cyclic Mach 0.3 burner rig. The potential inhibitors examined were salts of Al, Si, Cr, Fe, Zn, Mg, Ca, and Ba. The alloys tested were IN-100, U-700, IN-738, IN-792, Mar M-509, and 304 stainless steel. Each alloy was exposed for 100 cycles of 1 hour each at 900° C in combustion gases doped with the corrodant and inhibitor salts and the extent of attack was determined by measuring maximum metal thickness loss. The most effective and consistent inhibitor additive was Ba (NO₃)₂. Its use reduced the hot corrosion attack to nearly that of simple oxidation.</p>			
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