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[54] **PREVENTION OF HOT CORROSION IN GAS TURBINE ENGINES**
8 Claims, 3 Drawing Figs.

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 [50] Field of Search 60/39.01,
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 431/3; 110/1 J, 1 K; 415/212, 213, 214; 44/67, 68
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ABSTRACT: In order to prevent the accelerated sulfidation attack, or hot corrosion, of the nickel-base and cobalt-base alloys in gas turbine engines operating in atmospheres containing sea salt ingredients, the engine is treated with an oxide of chromium, tin, samarium, or columbium whereby the formation of the detrimental alkali metal species and consequent corrosion is forestalled.

VANE CYCLIC OXIDATION-EROSION-SULFIDATION OF UNCOATED B-1900 ALLOY

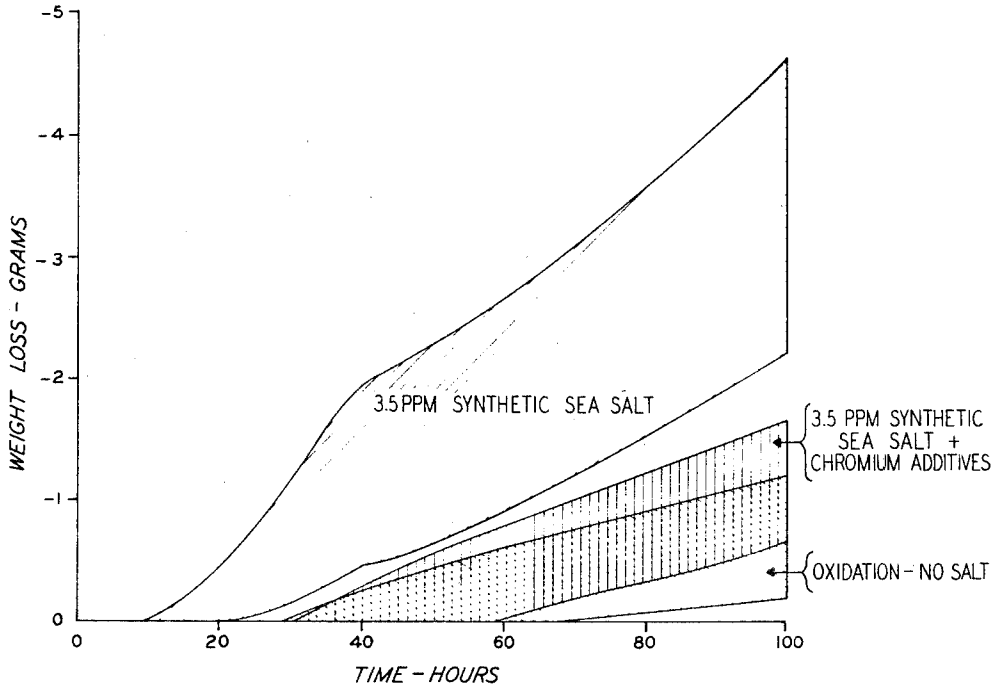


FIG. 1 VANE CYCLIC OXIDATION-EROSION-SULFIDATION OF UNCOATED B-1900 ALLOY

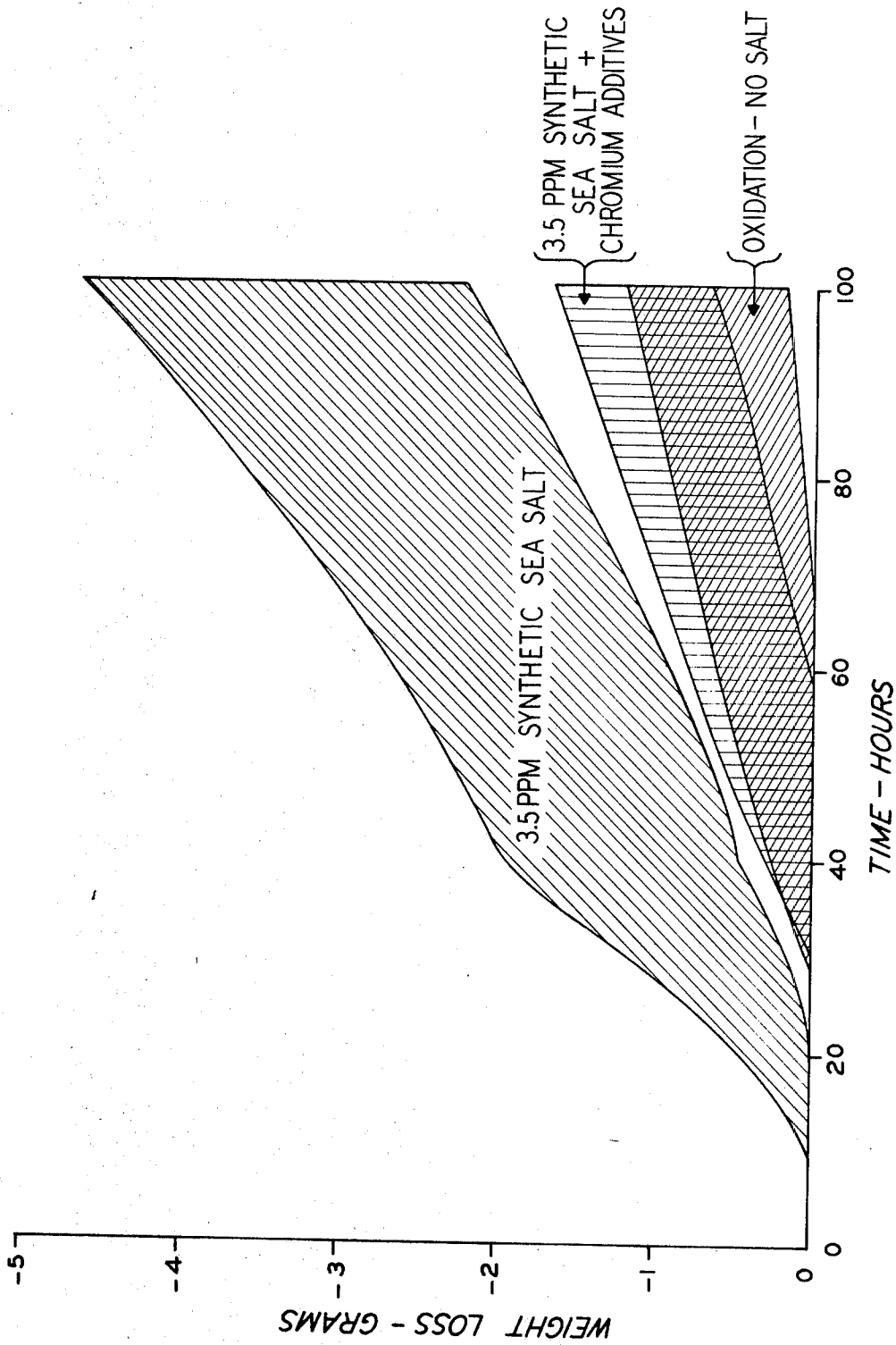


FIG. 1

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FIG. 2

EFFECT OF CHROMIUM BASE FULE ADDITIVES ON THE OXIDATION KINETICS OF A NICKEL BASE ALLOY EXPOSED TO HOT EXHAUST GASES CONTAINING SALT.

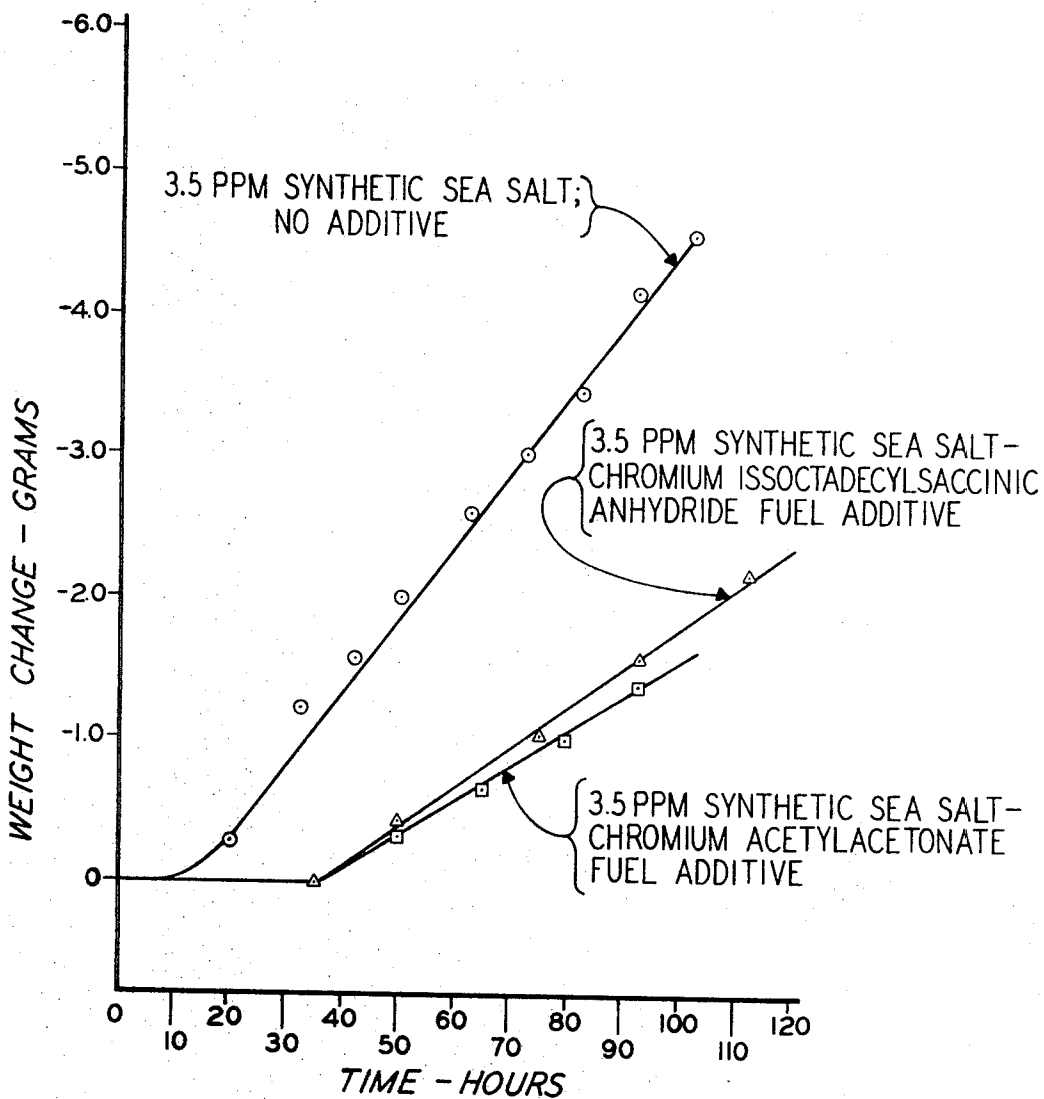
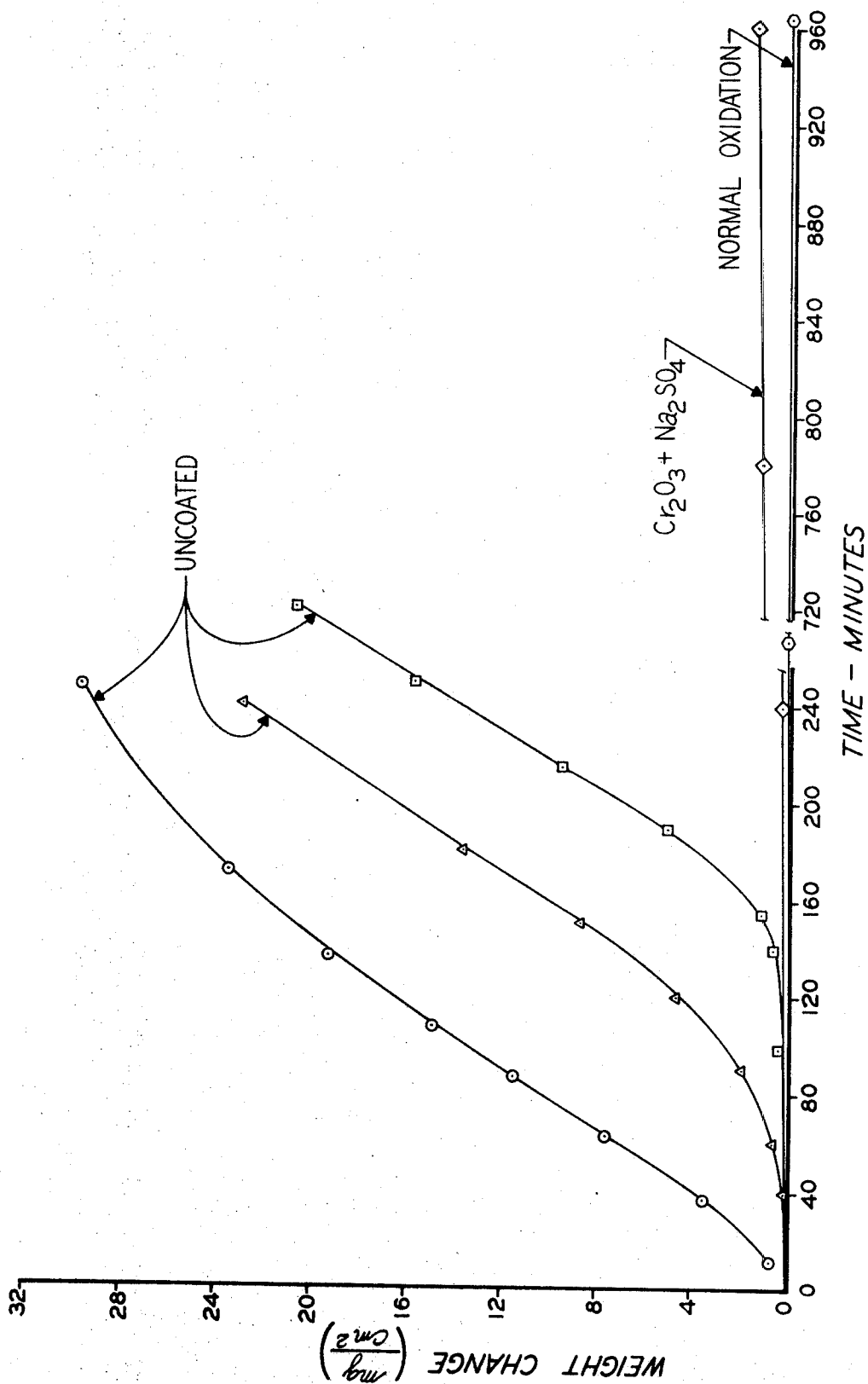


FIG. 3 HOT CORROSION OF ALLOY B-1900, TEMPERATURE 950°C



PREVENTION OF HOT CORROSION IN GAS TURBINE ENGINES

BACKGROUND OF THE INVENTION

The present invention relates in general to the prevention of hot corrosion of the gas turbine engine alloys exposed at high temperature to minor quantities of ingested sea salt.

It is known that various gas turbine engine components, particularly those formed of the nickel-base and cobalt-base superalloys, experience accelerated corrosive attack when run in an environment conducive to the ingestion of sea water compounds. The hot corrosion problem, which affects both the conventionally coated and uncoated alloys, seriously restricts the operating lives of the gas turbines operating on or near the oceans and has even been found to be a problem in certain engines utilizing water injection.

SUMMARY OF THE INVENTION

It is the primary object of the present invention to provide means for preventing hot corrosion in gas turbine engines which have or are apt to suffer mineral salt ingestion.

The above object and other advantages of the invention are achieved by preventing the adverse interaction of the alkali metal salts, principally sodium sulfate formed by a reaction between sea salt and the combustion products of a gas turbine, with the gas turbine engine alloys or coatings. In accordance with the present invention, at least one oxide selected from the oxides of chromium, tin, samarium, or columbium is provided in the hot section of the engine either upstream of or at the alloy surfaces to be protected.

In a preferred embodiment of the invention, a compound mixed with the fuel yields the desired oxide during the combustion process whereby the undesirable species are rendered harmless. In another preferred embodiment the desired oxide is provided at the surface of the alloy in the form of or as a part of a coating thereon.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph depicting the weight change of a nickel-base alloy with time when exposed to various gaseous environments.

FIG. 2 is a graph, illustrating the effect of various fuel additives on the hot corrosion of a nickel-base alloy.

FIG. 3 is a graph demonstrating the hot corrosion of Alloy B-1900 with various protective coatings.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been established that condensed sodium sulfate (Na_2SO_4) formed as a result of the reaction between sea salt ingested by the engine and SO_2 , a product of the combustion of gas turbine engine fuels, is the principal corrosive agent responsible for hot corrosion attack. The alkali metal sulfate attacks the protective oxide present on the alloy surface and exposes the substrate to a sulfidation attack whereby sulfides are formed. The attack is characterized by a loosely adhering oxide scale and sulfide precipitates in an alloy denuded zone which is due primarily to an interaction of condensed salts, liquid or solid, with the alloy, and which can occur with the alloy in either the coated or uncoated condition.

It has now been determined that the corrosive properties of sodium sulfate are significantly attenuated by the presence of certain oxides, specifically those oxides of chromium, tin, samarium and columbium. The common characteristics of these various compounds is that the metallic components can all exist in more than one valency state and that they all, at elevated temperatures form compounds with sodium which are typically more stable than sulfate. Specifically, the various compounds formed are Na_2CrO_4 , Na_2SnO_2 , $\text{Na}_2\text{Sm}_2\text{O}_7$, $\text{Na}_2\text{Cb}_2\text{O}_7$, in the reaction between the combustion products containing sea salts and the oxides of chromium, tin, samarium, and columbium respectively. Although the mechanism by which the particular oxide imparts protection is complex, the

major inhibition process is nevertheless a reduction in the chemical activity of the sodium sulfate.

As may be seen, the key to effective sulfidation inhibition involves the provision of certain oxides which react with the alkali metal salts to form stable alkali metal derivatives. The beneficial effects may be attained in a number of ways including a solid-solid reaction, solid-liquid and gaseous state reaction. Thus the sulfidation-inhibiting medium may be admitted to the engine inlet, at the hot section as, for example, by injection with the fuel, or the oxide may be provided at the alloy surface. Thus, sulfidation attack may be prevented by either preventing the deposition of corrosive salts onto the hot alloy surfaces or by altering the composition and/or chemical activity of the deposited corrosive salts to render them harmless.

Accordingly, in one test, the sulfidation inhibitor, chromium oxide (Cr_2O_3), was injected with the sea salt solution into the air entering the burner section. It was added in the form of the water soluble compound ammonium chromate $(\text{NH}_4)_2\text{CrO}_4$ which readily decomposed in the burner flame to form the desired Cr_2O_3 . The results thereof are graphically illustrated in FIG. 1. It will be observed that, in the presence of the chromate additive, the weight loss of the exposed components after 100 hours of attack approximates that associated with the normal oxidation-erosion associated with salt-free atmosphere, whereas, absent the chromate addition, the corrosive attack is more than 13 times as great.

In another test, two fuel additives, chromium acetyl acetonate and chromium isooctadecylsuccinic anhydride were added to JP-5 fuel. The latter additive is soluble in these fuels while the former additive was dissolved in benzene prior to addition to the fuel. As shown in FIG. 2, these fuel additives were effective in reducing the hot corrosion of the engine alloys, the weight loss of the specimens being substantially less than that observed in tests without the fuel additive.

Both of the above techniques which involve mechanisms whereby the chromium oxide and the alkali metal components can be reacted prior to detrimental deposition of the sodium sulfate on the hot alloy surfaces. The chromium oxide reacts with the gaseous sodium chloride to form sodium chromate which, at these elevated temperatures, is present as a gas and, hence, no deposition occurs or, in the event deposition does occur under some operating conditions, the deposit is a non-corrosive compound.

Alternatively, however, the hot corrosion may be prevented at the component surface itself through the provision of a suitable oxide as or in a coating provided on the component surface. In this case, either a liquid-solid or solid-solid phase reaction may be promoted. While in the case of those techniques whereby deposition of the corrosive species may be prevented by the introduction of other compounds to the air or the fuel which are subsequently converted to the oxide, in the case of coatings on the engine components the sulfidation inhibitor must be present in the form of the oxide or as compounds readily convertible to the oxide. This occurs since the coating must necessarily be oxidation resistant and not prone to oxidation and, hence, the elemental materials are excluded.

Actually, the method by which the protective oxide is provided in the coating is immaterial and a number of alternatives for generating such coatings such as (1) electroplating (2) electrophoresis (3) flame spray (4) plasma spray (5) vapor plating (6) or pack cementation or others. The sulfidation inhibitor may be added prior to or concurrently with an existing coating process.

In one method of achieving the desired coating, a layer of chromium metal applied to the alloy substrate is converted to the oxide by exposure at high temperature to air or by a chemical conversion in an oxidation/reduction reaction. In an alternative technique, the chromium oxide is flame sprayed onto the alloy surface. Usually the chromium oxide addition is an addition to the usual superalloy coatings wherein a stable aluminide is utilized to provide the desired oxidation-erosion resistance. The improvement afforded by the chromium oxide coating is illustrated in FIG. 3.

Further details relative to the present invention are set forth in the following examples.

EXAMPLE 1

Two sets of 8 erosion bars formed of the B-1900 alloy were exposed for 60 hours at 1650° F. to the exhaust of a gas turbine burner fueled with JP-5. One set was exposed to exhaust gases which contained 3.5 p.p.m. sea salt. The second set was exposed in a similar manner except that a chromate modified sea salt solution was used.

The sulfidation inhibitor, Cr_2O_3 , was added to the sea salt solution as water-soluble ammonium chromate, $(\text{NH}_4)_2\text{CrO}_4$. This compound readily decomposes at low temperatures to form Cr_2O_3 . To insure identical distribution of the corrosive salts and the Cr_2O_3 , the inhibitor was added directly to the sea salt solution in the amount of 19.6 grams ammonium chromate for each 3.76 grams sodium chloride, which corresponds to a chromium to sodium molar ratio of about 2/1.

The first set of erosion bars showed distress in less than 20 hours, all specimens exhibiting the loosely adhering green oxide scale typical of sulfidation attack. Metallographic examination of the bars revealed an alloy depleted zone containing sulfide precipitates. The second set of bars exposed under identical condition to the sea salt solution with inhibitor displayed no detrimental sulfidation attack. After 100 hours of test, the specimen weight loss was only very slightly greater than that associated with normal oxidation-erosion.

EXAMPLE 2

Two fuel additives, chromium acetylacetonate and chromium isooctadecylsuccinic anhydride were prepared. The additive, chromium isooctadecylsuccinic anhydride is soluble in JP fuels. The other additive was dissolved in benzene prior to mixing with the fuel.

It was observed that, in the presence of the fuel additives, the weight loss of the specimens was significantly less than those exposed to the combustion products of fuels lacking the additives.

Thus, the role of the chromium base fuel additives in suppressing hot corrosion was established. At turbine metal temperatures of 1,400°—2,000° F. Na_2CrO_4 was proved to be more stable than Na_2SO_4 .

The basic studies have indicated that the principal corrosive agents involved in the accelerated attack on the gas turbine engine alloys are the alkali metal sulfates, specifically sodium and calcium sulfate. After condensation on the alloy surface they promote sulfidation attack through a mechanism which prevents the formation of a protective oxide scale. The deleterious effects of the corrosive agents can be controlled by either rendering them harmless before deposition or by reducing their activity after deposition.

The ingredients effective in abating corrosion in those engines subject to the ingestion of mineral salts are the oxides of those metals which can exist in more than one valency state and which, at elevated temperatures, form more stable compounds with sodium and/or calcium than the sulfates, and which are either less corrosive than the sulfates or do not deposit on the hot component surfaces. Specifically, these metals are chromium, tin, samarium, columbium and mixtures thereof. One or more of the oxides of the above metals, possibly mixed with other oxides such as alumina, will therefore be present in the system.

When incorporated into a coating on the parts to be protected, the sulfidation inhibitor is provided as the oxide. In other systems, the inhibitor may be provided in any form convertible to the oxide at or upstream of the surfaces to be protected. The inhibitor can thus be mixed with the fuel, in appropriate form; utilized in a water injection system; or otherwise be added to the engine gas stream.

There was originally some concern that, once sulfidation at-

tack had commenced in a given system, the reaction would thereafter be self-sustaining. This did not turn out to be the case for it has been established that a continuing source of mineral salt ingestion is necessary for continued sulfidation attack. Furthermore, even those specimens which had previously undergone sulfidation attack exhibited markedly reduced oxidation subsequent to the application of a surface layer of Cr_2O_3 . This is not to imply that any previous damage or detrimental effect is alleviated for once the protective coating or oxide is lost and the substrate is exposed, it is, of course, susceptible to oxidative attack. Probably for this reason gas stream additives in the case of components previously subjected to extensive sulfidation attack were not effective.

It has been clearly established that sulfidation or hot corrosion of the coated and uncoated alloy components in gas turbine engines exposed to atmospheres containing minor quantities of mineral salts, particularly the alkali metal compounds, can be substantially attenuated through adherence to the techniques described herein. While the invention has been described in detail with reference to certain examples and preferred embodiments, these are illustrative only. It will be understood that the invention is not to be limited to the exact details described, for obvious modifications will occur to those skilled in the art.

What we claim is:

1. The method of attenuating sulfidation attack of the nickel-base and cobalt-base alloys in gas turbine engines subject to the ingestion of alkali metal salts in the gas stream traversing the engine which comprises:
 - 30 exposing the gas stream carrying the alkali metal salts at elevated temperatures to at least one oxide selected from the group consisting of the oxides of chromium, tin, samarium, and columbium.
 - 35 2. The method of attenuating sulfidation attack in gas turbine engines subject to the ingestion of alkali metal salts and subject to corrosive attack of nickel-base or cobalt-base alloy turbine section components exposed to hot fuel combustion products containing such salts which comprises:
 - 40 treating the hot combustion products upstream of the turbine section with at least one oxide selected from the group consisting of the oxides of chromium, tin, samarium and columbium to form the stable alkali metal derivatives of these oxides.
 - 45 3. The method of attenuating sulfidation attack in gas turbine engines subject to the ingestion of alkali metal salts in the airstream traversing the engine and subject to corrosive attack of nickel-base or cobalt-base alloy components exposed to hot gases downstream of the fuel combustion zone which comprises:
 - 50 upstream of the fuel combustion zone injecting into the engine airstream a compound of chromium, tin, samarium, columbium, or mixtures thereof which is readily converted to the oxide of such metal or metals at elevated temperatures.
 - 55 4. The method according to claim 3 wherein the compound is water soluble.
 5. The method according to claim 3 wherein the compound is ammonium chromate.
 - 60 6. The method of attenuating sulfidation attack in gas turbine engines incorporating nickel-base and cobalt-base alloys and utilizing fuels containing sulfur and subject to the ingestion of alkali metal salts which comprises:
 - 65 mixing the fuel with a stable, soluble compound of chromium, tin, samarium, columbium or mixtures thereof which is readily convertible to the oxide of such metal or metals at elevated temperatures.
 7. The method according to claim 6 wherein the compound is a chromium compound.
 - 70 8. The method according to claim 7 wherein the compound is chromium isooctadecylsuccinic anhydride.