

# INVESTIGATIONS ON Na<sub>2</sub>SO<sub>4</sub>- INDUCED LOW TEMPERATURE HOT CORROSION BEHAVIOR OF Mar-M 509 AT 750°C

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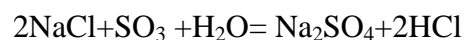
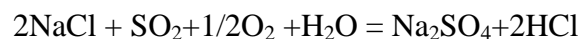
## ABSTRACT

Hot corrosion is the degradation of materials caused by the presence of a deposit or ash, predominantly sodium sulfate. Hot corrosion is observed in marine and aircraft engines. It is very well established that sodium sulfate alone causes accelerated oxidation of super alloys and coatings at high temperatures, where Na<sub>2</sub>SO<sub>4</sub> is in liquid form. In marine environments, because of low power operation the alloys are maintained at lower temperature i.e., below the melting point (m.p) of Na<sub>2</sub>SO<sub>4</sub>, the predominant form of attack is due to Low temperature hot corrosion. To establish a suitable mechanism of low temperature hot corrosion, in this study, the low temperature hot corrosion behavior of Mar-M 509 at 750°C in static air, under thermal cyclic conditions has been studied. Salt-coating technique was employed, in which alloy samples were coated with approximately 2.5 mg/cm<sup>2</sup> of pure Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> +52% CoSO<sub>4</sub> salt. Hot corroded samples of Mar-M 509 have been analyzed using SEM, EDS, X-ray mapping and XRD.. This study investigates the occurrence of LTHC morphology in pure Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>4</sub> +52%CoSO<sub>4</sub> coated samples. The results indicated that Na<sub>2</sub>SO<sub>4</sub> was aggressive and showed extensive unprotected layer of oxides and prolonged internal sulfidation with broad frontal attack. The samples coated with Na<sub>2</sub>SO<sub>4</sub>+52%CoSO<sub>4</sub> showed deep pits resembling LTHC features.

**Key words:** Hot corrosion, Mar-M 509, Low temperature hot corrosion

## I. INTRODUCTION

Hot corrosion is the degradation of a metal and/or an alloy owing to the oxidation processes which are affected by liquid salt deposits, predominantly Na<sub>2</sub>SO<sub>4</sub>. The primary source of sodium sulfate, in marine and aircraft engines, is due to the reaction between NaCl in ingested air and sulfur in fuel according to the following reactions.



It is assumed that the sulfation of sodium chloride may take place in the hot section of a gas turbine and according to above equations and then a thin liquid sulfate film may be deposited on the hot components either by condensation or by direct impingement of liquid droplets from the hot gas stream. The main components that are subjected to severe attack by salt deposit are the turbine blades and vanes.

Depending on the melting point of the salt deposit the hot corrosion phenomena has been divided into two categories. One is high temperature hot corrosion or type I hot corrosion, where the salt is clearly a liquid. The other is low temperature hot corrosion i.e., type II hot corrosion, which occurs below

the m.p of  $\text{Na}_2\text{SO}_4$  and where the salt is solid. It is very well established that sodium sulfate alone causes accelerated oxidation of super alloys and coatings at high temperatures where  $\text{Na}_2\text{SO}_4$  is in liquid form.

In marine environments, where low power operations maintain the alloys at relatively lower temperature (below m.p of  $\text{Na}_2\text{SO}_4$ ), the predominant form of attack of first stage blades and vanes of gas turbines is due to type II hot corrosion which further forms the shallow pits accompanied by a thin layer of sulfide.

Luthra et al [1-3] reports that the characteristic morphology of LTHC is reproduced only when sufficient  $\text{SO}_3$  is employed in oxidizing environment. Jones et al [4-5] showed that catalytic activity of CoO or decomposition reaction of mixed sulfates may increase the pressure of  $\text{SO}_3$  ( $P_{\text{SO}_3}$ ) near the salt-metal interface, which is considered to be important for the occurrence of low temperature hot corrosion. Luthra and shores [6] studied the mechanism of  $\text{Na}_2\text{SO}_4$ -induced hot corrosion of Co-30Cr in  $\text{O}_2+\text{SO}_3$  environments and attributed the initial stage of attack due to sulfation of cobalt oxide and the propagation stage is related to the fluxing of cobalt oxide. A consistent model of hot corrosion for Ni-base alloy has been presented by Misra[7] in  $\text{Na}_2\text{SO}_4\text{-LiSO}_4$  melt system at  $750^\circ\text{C}$  in  $\text{O}_2+1\%\text{SO}_2$  environments. The corrosion attack was attributed to the formation of duplex scale ( $\text{NiO}+\text{Ni}_3\text{S}_2$ ). In this study, alloys were coated with pure  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4+\text{CoSO}_4$  to investigate the type II of LTHC morphology is present or not.

## II. EXPERIMENTAL SET-UP

A schematic diagram of the high temperature test system used in this study is shown in Figure[1]. The test system consists of Lindberg horizontal tube furnace with a maximum usable 3 inch outer diameter tube

and which can be operated to a maximum temperature of  $1200^\circ\text{C}$ . A one-end closed ceramic tube of 2 inch internal diameter is inserted into the tube furnace supported by tube adapters at both ends of the furnace. Two insulating blankets of alumina sponge were provided at the two-ends of furnace to minimize heat loss and /or temperature gradients within the furnace. The test temperature used in this study is  $750^\circ\text{C}$ . The test temperature in the reaction chamber is continuously checked with a chromel-aluminate thermocouple. In this test system, the samples are corroded for 1 hr and brought to cold zone to cool the specimens during the process of thermal cycling. Test runs were performed for the  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4+\text{CoSO}_4$  salt coating for 20 cycles to study the corrosion morphology during initial stages and 150 cycles to observe the corrosion morphology of corroded samples at the propagation stage. Salt coating method is adopted to coat the samples with salt mixtures after intensive polishing with Sic paper and diamond paste. The corrosion samples were examined using SEM and EDS.

## III. RESULTS AND DISCUSSION

Fig[2] shows the morphology of pure-  $\text{Na}_2\text{SO}_4$  coated Mar-M 509 after exposure for 20 cycles at  $750^\circ\text{C}$ . The scale formed on the alloy surface is primarily enriched in Cr indicating the presence of  $\text{Cr}_2\text{O}_3$  (spot D). At the alloy/oxide interface, Cr-depleted alloy islands were observed (spot A) A dark layer enclosing the metallic islands is rich in Co and Cr, indicating that it may consists of  $\text{Cr}_2\text{O}_3$  and CoO or  $\text{CoCr}_2\text{O}_4$ . It also appears from the EDS analysis at spot D that a few Ni-sulfide particles may be present in the dark layer. XRD results (Figure 3) confirms the presence of  $\text{Cr}_2\text{O}_3$ , CoO and NiS.

After exposure for 150 cycles (figure 4), the outer scale is highly porous and appears to be exfoliated (spot D). EDS analysis at spot D

show that the outer scale (white) is enriched in Cr, Co and S which may consists of either  $\text{Cr}_2\text{O}_3$  or  $\text{Co}_3\text{O}_4$  and few sulfides. Near the alloy/oxide interface an irregular alloy surface containing  $\text{Cr}_2\text{O}_3$  oxide is observed (spot C). A dark layer below the  $\text{Cr}_2\text{O}_3$  is enriched in Cr and Co indicating the formation of mixed oxide layer. Just below the alloy/oxide interface, numerous sulfide particles are formed (spot A). The samples exposed to pure  $\text{Na}_2\text{SO}_4$  for 150 cycles does not show any deep pits resembling LTHC.

Fig[5] shows the cross-sectioned morphology of Mar-M 509 coated with  $\text{Na}_2\text{SO}_4+52\%\text{CoSO}_4$ , when exposed for 150 cycles at  $750^\circ\text{C}$ . The micrograph shows a thin layer of sulfide indicating that it is CrS. At the salt/gas interface, there is an oxide mound rich in Co and O, indicating the presence of cobalt oxide. The features show a deep pit resembling all the features of LTHC morphology

From the above results, it can be inferred that the corrosion attack of  $\text{Na}_2\text{SO}_4+52\%\text{CoSO}_4$  forms deep pits resembling LTHC features where the pure- $\text{Na}_2\text{SO}_4$  coated samples shows the broad frontal attack with extensive internal sulfidation. The formation of pits is attributed to the formation of low melting eutectic of  $\text{Na}_2\text{SO}_4\text{-CoSO}_4$ , (visual examination revealed the presence of liquid at test temperature) further it penetrates and comes in contact with the alloy during thermal cycling. Sulfur ingresses through the liquid melt forms sulfides and further sulfidation-oxidation leads to the formation of these pits.

#### IV. CONCLUSIONS

This study has shown that  $\text{Na}_2\text{SO}_4+52\%\text{CoSO}_4$  mixture is very aggressive compared to that of pure  $\text{Na}_2\text{SO}_4$  for Mar-M 509 alloy. The typical LTHC features, formation of shallow pits with blister cover has been developed in  $\text{Na}_2\text{SO}_4+52\%\text{CoSO}_4$

mixture. These features are attributed to the formation of low melting eutectic of  $\text{Na}_2\text{SO}_4\text{-CoSO}_4$ . No deep pitting morphology was observed in pure  $\text{Na}_2\text{SO}_4$  coated samples.

#### V. REFERENCES

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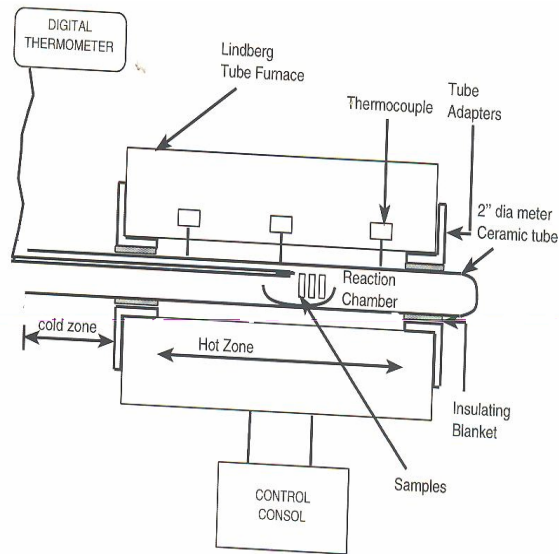


Fig.1 Experimental setup of high temperature Test system

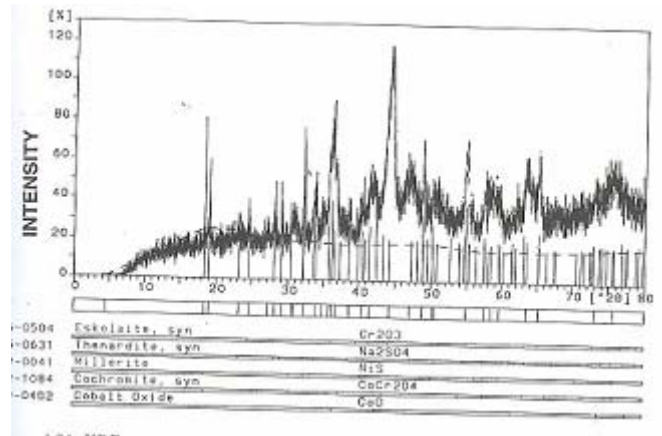


Fig3. XRD of pure  $\text{Na}_2\text{SO}_4$  coated Mar-M 509 for 20 cycles at  $750^\circ\text{C}$

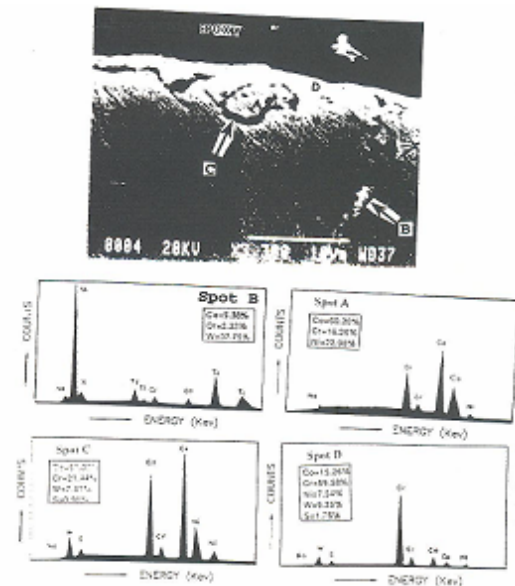


Fig.2 SEM and EDS of pure  $\text{Na}_2\text{SO}_4$  coated Mar-M 509 after 20 cycles  $750^\circ\text{C}$

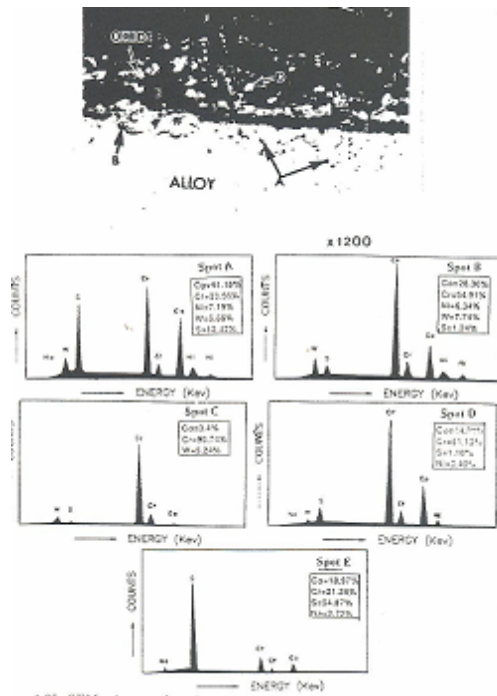


Fig4 . SEM and EDS of pure  $\text{Na}_2\text{SO}_4$  coated Mar-M 509 for 150 cycles at  $750^\circ\text{C}$

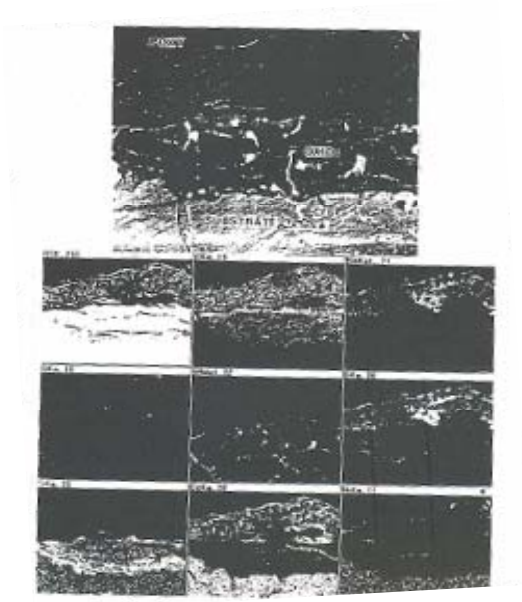


Fig 5. X-ray mapping of  $\text{Na}_2\text{SO}_4 + 52\%\text{CoSO}_4$  coated Mar-M509 after 150 cycles at  $750^\circ\text{C}$