

## Investigations on the Effect of Sodium Chloride in Low Temperature Hot Corrosion of Mar-M 509 AT 750°C

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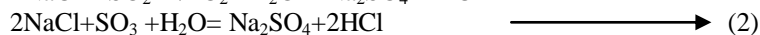
**Abstract:** Hot corrosion is the degradation of materials caused by the presence of a deposit or ash, predominantly sodium sulfate. Hot corrosion is observed in marine and aircraft engines. It is very well established that sodium sulfate alone causes accelerated oxidation of super alloys and coatings at high temperatures, where  $\text{Na}_2\text{SO}_4$  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  $\text{Na}_2\text{SO}_4$ , 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 salt. The mixture of  $\text{Na}_2\text{SO}_4$  and NaCl salt is applied to alloy samples to investigate mechanism of Low temperature hot corrosion. Hot corroded samples of Mar-M 509 have been analyzed using SEM, EDS, X-ray mapping, XRD, correlated with corrosion kinetics. The results indicated that  $\text{Na}_2\text{SO}_4 + 25\%\text{NaCl}$  were very aggressive compared to that of either pure  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4 + 1\%\text{NaCl}$ . Sulfidation-Oxidation mechanism has been proposed for low temperature hot corrosion of Mar-M 509.

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

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### 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  $\text{Na}_2\text{SO}_4$ . 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 equation (1) or (2) 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 [4] 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. Conde[5] showed that  $\text{Na}_2\text{SO}_4 + 25\%\text{NaCl}$  is very aggressive than 1% NaCl enriched salt for Cr<sub>2</sub>O<sub>3</sub> formers and attributed the cracking of surface scales to the formation of volatile oxychlorides. Berkolow and Petit[6] tried to explain the LTHC of CoCrAlY coatings in sulfate/chloride mixtures and attributed the attack to the preferential removal of Al and the formation of internal network of pores in Al-depleted region. Hancock [7] opposed considering of oxide scales in type II hot corrosion because the NaCl is constantly replenished in marine turbines which may re-initiate a localized form of attack.

Based on this,  $\text{Na}_2\text{SO}_4+\text{NaCl}$  coated samples are selected for studying the low temperature hot corrosion behavior of alloy samples because a low melting eutectic (m.p.  $625^\circ\text{C}$ ) forms on the specimen surface which is liquid at the test temperature. This eutectic may decompose at the test temperature under thermal cyclic conditions and act as a source for release of  $\text{SO}_3$ . The present study concerns the understanding of the effects of  $\text{NaCl}$  on low temperature hot corrosion behavior of Mar-M 509 under thermal cyclic conditions.

## 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  $\text{Na}_2\text{SO}_4+1\%\text{NaCl}$  and  $\text{Na}_2\text{SO}_4+25\%\text{NaCl}$  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 kinetic results of thermally cycled Mar-M 509 specimen exposed under different hot corrosion conditions. The sample corroded in  $75\%\text{Na}_2\text{SO}_4+25\%\text{NaCl}$  mixture exhibited high corrosion rate than the specimen subjected to either pure  $\text{Na}_2\text{SO}_4$  or  $99\% \text{Na}_2\text{SO}_4 + 1\%\text{NaCl}$ . The initiation of hot corrosion is faster for  $25\%\text{NaCl}$  enriched salt because of faster growth rate of  $\text{CoO}$ . The oxidation of Co-base alloys continues after the breakdown of  $\text{NaCl}$  in  $\text{Na}_2\text{SO}_4$ . Fig[3] shows the corrosion morphology of  $75\% \text{Na}_2\text{SO}_4+25\% \text{NaCl}$ -coated specimen of Mar-M 509 after exposure for 1 cycles(1 hr) at  $750^\circ\text{C}$ . The scale formed on the alloy surface is a thin, adherent and protective layer of cobalt oxide with little amount of  $\text{Cr}_2\text{O}_3$  (spot A). EDS analysis at spot B shows few embedded particles that are enriched in W indicating the presence of WC particles.

After exposure for 20 cycles, Fig[4], the outer scale formed on the alloy surface appearing light at the salt-gas interface is fairly porous and enriched mainly in Co,Cr and S indicating that it may consists of sulfides of Co and Cr (spot F). The intermediate grey layer is primarily enriched in Cr, indicating the presence of  $\text{Cr}_2\text{O}_3$  (spot D). A dark phase in the matrix of grey oxide layer is enriched in Co and Cr, probably as  $\text{CoCr}_2\text{O}_4$  (spot E). Below the alloy/oxide interface, the subscale consists of numerous particles of sulfides rich in Cr indicating the presence of  $\text{CrS}$ (spotB). This micrograph shows the presence of a lot internal sulfides. Fig[5] shows the cross-sectioned morphology of the Mar-M 509 specimen, coated with the  $75\% \text{Na}_2\text{SO}_4 + 25\%\text{NaCl}$  after extended cyclic exposure upto 150 cycles at  $750^\circ\text{C}$ . X-ray micrograph indicates that a thin enriched zone of sulfur at the pit/metal interface may consists of  $\text{CrS}$ . Below the pit/metal interface, there is no layer of alloy depleted in Cr. However, Co is depleted in the pit and probably reprecipitated as  $\text{Co}_3\text{O}_4$  at the salt-gas interface. The presence of  $\text{Co}_3\text{O}_4$  has been confirmed by XRD [fig 6].

During the very early stages of exposure (1 cycle) of Mar-M 509 sample to  $75\%\text{Na}_2\text{SO}_4+\text{NaCl}$  mixture, Co-oxide accompanied by the undergrowth of  $\text{Cr}_2\text{O}_3$  form on the alloy surface. Eventually  $\text{Cr}_2\text{O}_3$  will form a protective oxide layer above scale/metal interface. Simultaneously, a low melting eutectic of  $\text{Na}_2\text{SO}_4-\text{NaCl}$  forms on the top of oxide which is liquid at the test temperature. After 20 cycles the degradation of Mar-M 509 in sulfate/chloride mixture can be primarily attributed to the sulfidation of alloying elements Cr and Co along the boundaries between W-carbide phase and the metal substrate. This is mainly due to the diffusion of sulfur by sodium sulfate decomposition. The sulfur may preferentially attack the underlying alloy along the W-carbide network to form sulfides of Cr/Co in the substrate (see figure 4). Simultaneously, chloride ion from  $\text{NaCl}$  reacts Co and Cr preferentially and forms volatile chlorides. These chlorides migrate outwardly and gets oxidized at salt/gas interface. During the propagation stage, further ingress of oxygen through the outer porous oxide may preferentially oxidize the  $\text{CrS}$  in the alloy. Due to this sulfidation-oxidation mechanism, a thin zone of sulfur at the bottom of pit is observed (figure 5)oxide mount is also observed resembling LTHC features . The sequence of sulfidation-oxidation mechanism is illustrated in schematic diagram as shown in Figure 7.

#### IV. CONCLUSIONS

This study has shown that  $\text{Na}_2\text{SO}_4 + 25\% \text{NaCl}$  mixture is very aggressive compared to that of pure  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{SO}_4 + 1\% \text{NaCl}$  for Mar-M 509 alloy. High corrosion rates were observed in 25%NaCl enriched salt either at initiation stage or at the propagation stage. The typical LTHC features, formation of shallow pits with blister cover has been developed in  $\text{Na}_2\text{SO}_4 + 25\% \text{NaCl}$  mixture. The propagation of LTHC of Mar-M 509 was attributed to the Sulfidation-Oxidation mechanism

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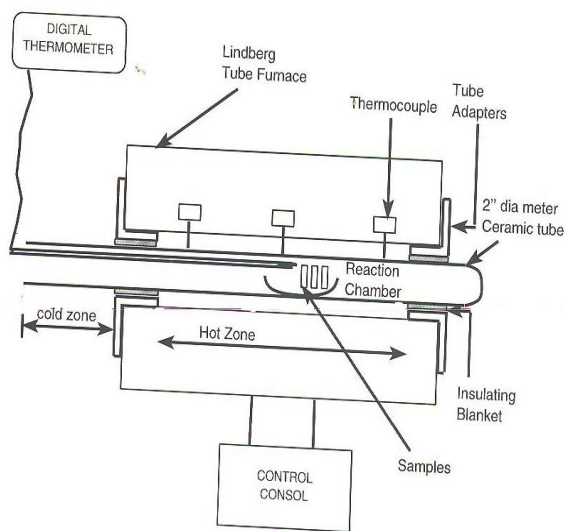


Fig.1 Experimental setup of high temperature

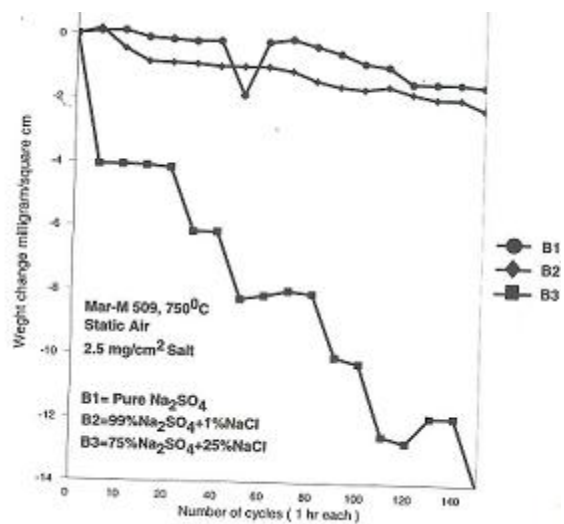


Fig.2 Rate of hot corrosion of Mar-M 509 test system

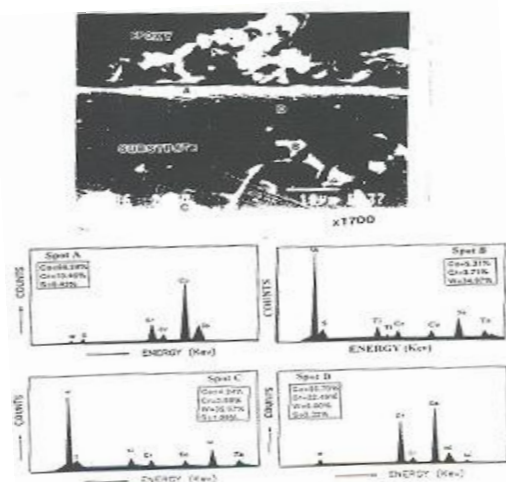


Fig3. SEM and EDS of pure  $\text{Na}_2\text{SO}_4$  coated Mar-M 509 for 1 cycles at 750 °C

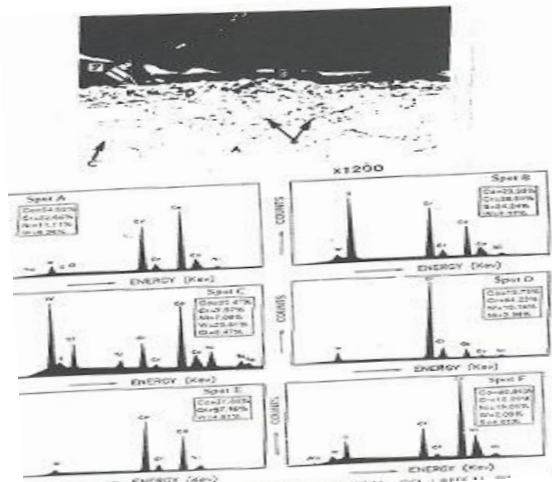


Fig4 . SEM and EDS of 75%  $\text{Na}_2\text{SO}_4 + 25\% \text{NaCl}$  coated Mar-M 509 for 20 cycles at 750 °C

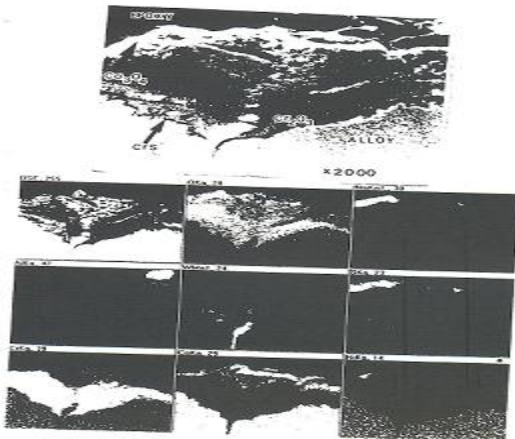


Fig5 . SEM and X-ray mapping of 75% Na<sub>2</sub>SO<sub>4</sub> + 25% NaCl coated Mar-M 509 for 150 cycles at 750 °C

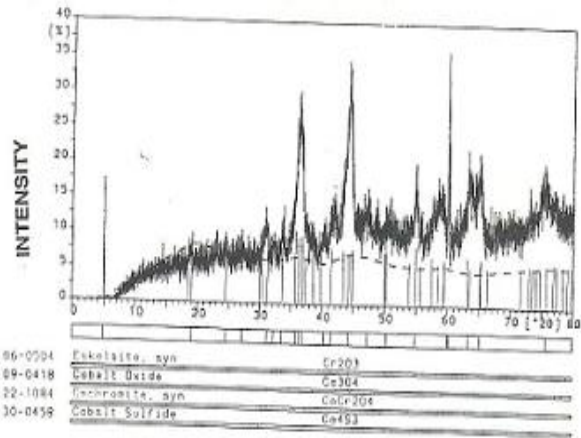


Fig 6. XRD of 75% Na<sub>2</sub>SO<sub>4</sub> + 25% NaCl coated Mar-M 509 for 20 cycles at 750°C

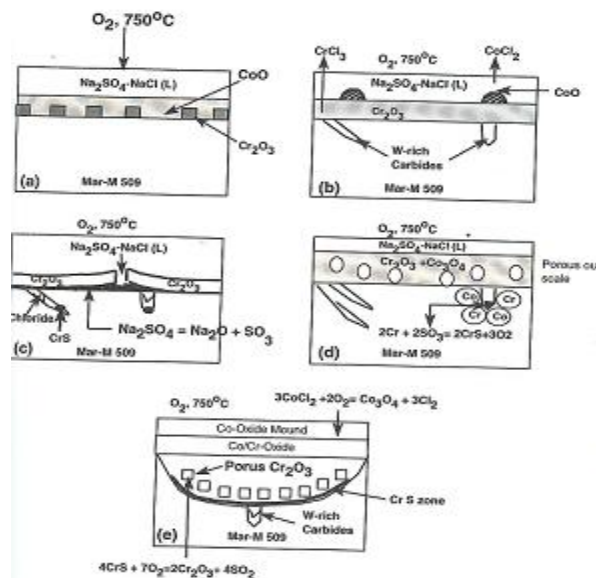


Figure 7: Schematic diagram of proposed mechanism for Mar509 in Na<sub>2</sub>SO<sub>4</sub>-NaCl mixture.