

# High Temperature Oxidation Behaviour of Nimonic - 115 Alloy in Presence of Sodium Salts at 850°C

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**ABSTRACT:** *The high temperature oxidation behaviour of Nimonic-115 industrial alloy has been investigated in presence of NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>O<sub>2</sub> at 850°C in flowing air. The oxidation kinetics and effect of salt deposition for the period of 48 h were studied. The scale morphologies were determined on the basis of X-ray diffraction analysis and Scanning electron microscopic techniques. It has been shown that the alloy corrodes at different rate in presence of different sodium salts although each salt contains the same amount of sodium equivalent to Na<sub>2</sub>O.*

**KEY WORDS:** *Oxidation kinetics, Sodium salts, Nimonic-115, SEM studies.*

## INTRODUCTION

The presence of an electrolytic deposit on a metal or alloy surface at high temperatures may bring about accelerated environmental attacks known as hot corrosion. Sodium sulphate and/or other sodium salts are capable of propagating such accelerated attacks. These type of corrosion serious problems in aircraft engines, marine engines, land-based power generating systems, fuel generation or conversion systems, etc.

Nickel-base alloys are used extensively as hot corrosion resistant materials and relatively huge amount of work has been carried out on Na<sub>2</sub>SO<sub>4</sub>-induced hot corrosion studies [1,2]. The influence of NaCl separately or in combination with Na<sub>2</sub>SO<sub>4</sub> has been studied out but not in so much details [ 3, 4 ]. A limited amount of work has been done on the role of NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and other salts in inducing hot corrosion attacks [5-8]. An important aspect of hot corrosion

problem which has hitherto not been seriously attended is the role of sodium in sodium salts during hot corrosion attack. This paper presents the results of a study concerning the high temperature oxidation behaviour of Nickel-115 industrial alloy in presence of some sodium salts e.g. NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>O<sub>2</sub> separately, oxidized at 850°C in flowing air.

## EXPERIMENTAL

Samples of 12 mm diameter and 2 mm thickness were cut from round bar of Nimonic-115 ( N-115 ), having the chemical composition ( wt. % ) 0.12-C, 1.0-Mn, 1.5-Fe, 0.8-Si, 0.2-Cu, 3.5- Ti, 4.0-Mo, 13.0-Co, 16.0-Cr and balance Ni. These samples were ground with 180, 320 and 600 grades of SiC papers with the precaution that scratches produced from a particular

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grade of paper removed by rotating the angles of grinding through  $90^\circ$  on a subsequent grade of paper. The ground samples were washed with water and alcohol, and degreased with trichloroethylene. The alloy samples were uniformly coated with a thin film of sodium-containing salts e.g.  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{O}_2$ , and oxidized at  $850^\circ\text{C}$  for 48 hours.

For a particular set of alloy, the amount of sodium salts deposited were equivalent to the same amount of  $\text{Na}_2\text{O}$ . Saturated solution of the salt was prepared and sprayed on the heated ( $300^\circ\text{C}$ ) alloy and coated alloy was weighed [9]. In most cases, more than one operation were required to get a salt coating of the desired weight. The weighed coated samples were then used for high temperature oxidation studies.

Oxidation studies were carried out in a previously heated Nichrome-wound tubular furnace which had a temperature control sensitivity of  $\pm$  or  $-10^\circ\text{C}$  at  $850^\circ\text{C}$ . For kinetic studies, the coated samples were transferred to a silica bucket and suspended in a vertical tubular furnace attached to a thermal balance with an accuracy of  $\pm 0.01$   $\text{mg}/\text{cm}^2$ . This furnace has a hot temperature zone of  $\pm 5^\circ\text{C}$  at the center. Variation in mass of the sample was recorded at time intervals of 4 h up to 16 h. Then every 8 hours up to 48 h.

For a particular oxidation run, two coated samples were oxidized under nearly identical conditions. Out of the two oxidized samples the first was used for Scanning Electron Microscopic studies while the second was retained for X-ray diffraction analysis and the identification of various constituents present in the scales.

The different constituents present in the scales of the corroded samples as determined by X-ray diffraction studies. X-ray diffractometer was operated at  $\text{KV}/\text{mA} = 40/30$ ; Fe-, Co- or Cu- $\text{K}_\alpha$  targets were used with an appropriate filter. The results of X-ray diffraction analysis are listed in table 1.

**Table 1: Constituents identified in scales by X-ray diffraction analysis, oxidized at  $850^\circ\text{C}$  for 48 h in air.**

Salt Coating	Constituents of the Scales
$\text{NaNO}_3$	$\text{NiO}$ , $\text{Cr}_2\text{O}_3$ , $\text{Na}_2\text{NiO}_2$ , $\text{Co}_3\text{O}_4$ , $\text{NaNiO}_2$
$\text{Na}_2\text{CO}_3$	$\text{NiO}$ , $\text{Cr}_2\text{O}_3$ , $\text{Co}_3\text{O}_4$ , $\text{NaNiO}_2$
$\text{Na}_2\text{O}_2$	$\text{Cr}_2\text{O}_3$ , $\text{NiCrO}_4$ , $\text{Co}_3\text{O}_4$ , $\text{Na}_2\text{NiO}_2$

The polished samples were subjected to gold plating in order to make the surface conductive and to fill the pores and were then examined under Joel Scanning Electron Microscope (SEM). The SEM was operated at 30 KV with a tilt angle of  $31^\circ$  and desired regions of the scales were photographed at suitable magnifications.

## RESULTS

Fig.1 representing the oxidation kinetics ( mass change versus time ) curves of N-115 alloy coated with  $\text{NaNO}_3$ ,  $\text{Na}_2\text{CO}_3$  &  $\text{Na}_2\text{O}_2$ , oxidized at  $850^\circ\text{C}$  for 48 h in air. The plots indicate that an alloy oxidized at different rates with different salts although each one containing same amount of  $\text{Na}_2\text{O}$ . The alloy coated with  $\text{NaNO}_3$  showed mass loss with time steadily due to evolution of nitrogenous gases.  $\text{Na}_2\text{CO}_3$  alloy also exhibited mass losses during the exposure time.  $\text{Na}_2\text{O}_2$ -induced alloy exhibiting weight loss during the first 20 h after which there was mass gain with increasing time.

Fig.2 shows the SEM of  $\text{NaNO}_3$ - coated alloy. The inner layer of  $\text{NiO}$  are compact and adhered, however, the outer scales are cracked and this could be attributed to the release of nitrogen or nitrogenous gases during fluxing reactions.

The presence of  $\text{Na}_2\text{CO}_3$ , invariably thick, adherent yet porous scales are obtained (Fig.3). The pores in the scale are produced due to expulsion of  $\text{CO}/\text{CO}_2$ . The relatively thin layer scales of  $\text{NiO}$  are uniform and adherent, however, the outer scales are bulky and porous, and consist of  $\text{NiO}$  and  $\text{Na}_2\text{NiO}_2$  as revealed by X-ray diffraction analysis.

The  $\text{Na}_2\text{O}_2$ - induced corroded alloy shows the presence of inner layers of adhered scales containing  $\text{NiO}$  and  $\text{Na}_2\text{NiO}_2$  (Fig.4).

## DISCUSSION

The high temperature oxidation studies carried out on N-115 alloy in the presence of different sodium-containing salts, e.g.  $\text{NaNO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Na}_2\text{O}_2$  indicate that the oxidation rates are influenced not only by the nature of the salt but on the amount of the salt deposited on the alloy. This has been inferred on the basis of different salts in concentration equivalent to the same amount of  $\text{Na}_2\text{O}$  substrate forming metal halides. While the volatile chloride comes into contact with air, it is converted into oxide:

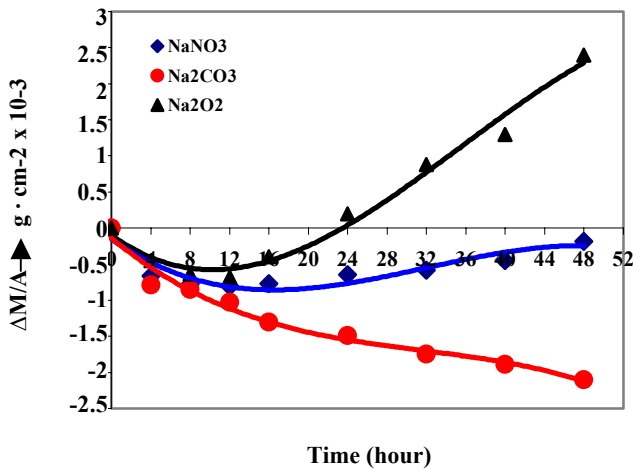
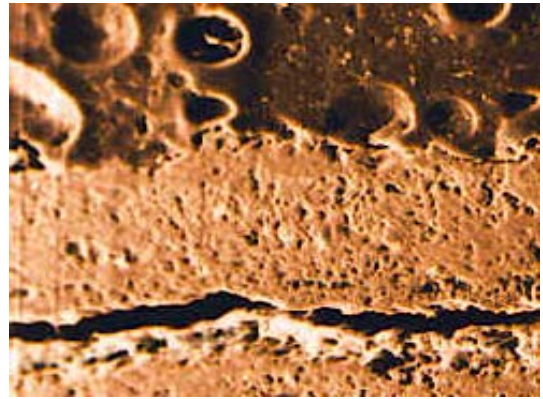
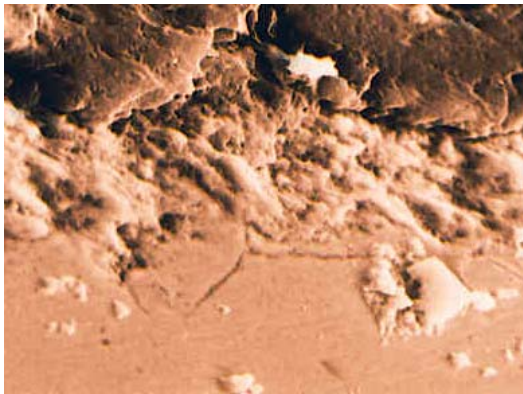


Fig.1: Oxidation kinetics (mass change versus time) of Nimonic-115 alloy coated with NaNO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> & Na<sub>2</sub>O<sub>2</sub>, oxidized at 850°C for 48 h.



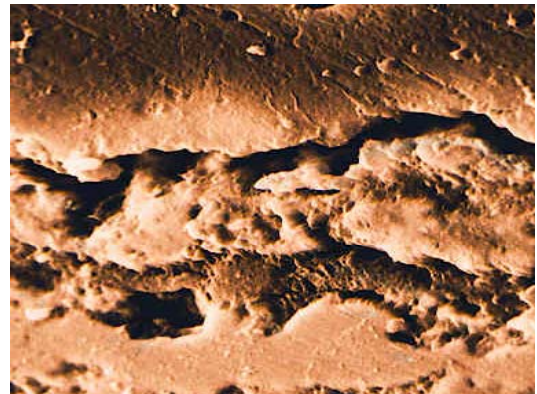
Mag. 500 X.

Fig. 2: Scale morphologies of N-115 alloy coated with NaNO<sub>3</sub>, oxidised at 850°C for 48 h.



Mag. 400 X.

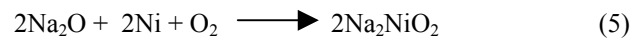
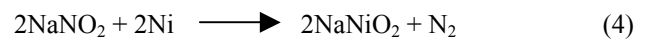
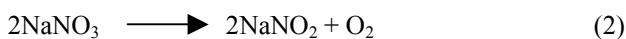
Fig. 3: Scale morphologies of N-115 Alloy coated with Na<sub>2</sub>CO<sub>3</sub>, oxidised at 850°C for 48 h.



Mag. 800 X.

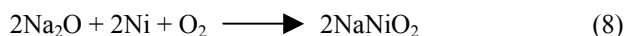
Fig. 4: Scale morphologies of N-115 Alloy coated with Na<sub>2</sub>O<sub>2</sub>, oxidised at 850°C for 48 h.

NaNO<sub>3</sub> seems to be aggressive since being an active oxidizing agents provides additional oxygen during the fluxing reaction. The decomposition of NaNO<sub>3</sub> into NaNO<sub>2</sub> and then involvement of the latter fluxing reaction results in the formation of molten fluxing products and evolution of nitrogenous gases. The consequences of the scale with result that the fused salt would come in contact with the fresh metal resulting in high oxidation rates:

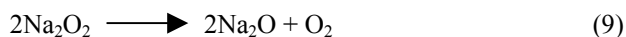


The hot corrosion behaviour of Na<sub>2</sub>CO<sub>3</sub> coated alloy is similar to that of NaNO<sub>3</sub>- coated alloy, however, due to profuse evolution [10,11] of CO/CO<sub>2</sub>, heavy mass losses are observed during corrosion and the scales are more porous than NaNO<sub>3</sub> coated alloy. The following reactions are observed:





The  $\text{Na}_2\text{O}_2$ -coated alloy undergoes fluxing and oxidation reactions. The alloy does not form a volatile product, therefore, mass gains are noted during corrosion. The fluxing reaction resulting in the formation of  $\text{NaNiO}_2$  and/or  $\text{Na}_2\text{NiO}_2$  and oxidation reaction resulting in  $\text{NiO}$  scale are the major reactions occurring during hot corrosion attack:



## CONCLUSIONS

Both the nature of sodium salt and the amount of the deposited salt influence the oxidation rates of N-115 alloy.  $\text{NaNO}_3$  and  $\text{Na}_2\text{CO}_3$  seem to behave similarly although the latter is more aggressive due to heavy mass losses incurred as a result of decarburization and ease in the availability of  $\text{O}^{2-}$  from basic carbonate. Both basically show fluxing reactions but in presence of  $\text{NaNO}_3$  the easy availability of oxygen may produce a positive effect on the fluxing rate of the alloy.  $\text{Na}_2\text{O}_2$  shows fluxing cum oxidation reactions and the morphology of the scale is similar to  $\text{NaNO}_3$ -coated alloy although there is a comparatively slow perturbation in the scales.

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