

The Role of NaCl in the Hot-Corrosion Behavior of Nimonic Alloy 90

S. Kameswari*

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The influence of sodium chloride on the hot-corrosion behavior of Nimonic alloy 90 has been investigated by employing the half-immersion, crucible test. Nimonic 90 samples were hot corroded in the presence of NaCl between 700–900°C. The results showed that the weight-loss plots with both time and temperature were linear indicating the catastrophic nature of attack. An examination of the corroded samples by XRD, XRF, EPMA, SEM, and chemical analysis indicated that as the corrosion time increased, an increase in the depletion of alloying constituents like Cr, Al, Ti, and Co took place with a resultant enrichment of nickel on the alloy surface. The formation of CoCl_2 and Na_2CrO_4 was observed in all the tests. A few experiments were carried out in the presence of Na_2SO_4 and in a 1% NaCl mixture, in order to see the influence of NaCl on Na_2SO_4 . The results indicated that Na_2SO_4 is innocuous when compared with NaCl. However, the severe attack was observed in the presence of the 1% NaCl mixture between 700–800°C, i.e., above the eutectic temperature and the m.p. of NaCl (800°C). The corrosion was minimum, when the salt mixture existed in the molten state. All the corroded samples were magnetic in nature. The role of NaCl on the hot-corrosion behavior of Nimonic 90 has been discussed in the light of the above crucible-test investigations.

KEY WORDS: hot corrosion; crucible test; Nimonic 90; NaCl; Na_2SO_4 .

INTRODUCTION

Although several investigations have been made on the hot-corrosion behavior of Nimonic alloys in the presence of sulfur and sulfur-bearing atmospheres,^{1–5} the controversial role played by NaCl in hot-corrosion is not very well defined. Some investigators^{6–8} consider that NaCl plays a

*Defence Metallurgical Research Laboratory, Hyderabad 500 258, India.

crucial rôle, while others^{9,10} attribute that hot-corrosion of Nimonic alloys is due mainly to the presence of condensed Na_2SO_4 deposits. It is generally accepted⁶⁻¹¹ that hot corrosion in gas turbines is due to the presence of condensed sulfate deposits. It has been shown¹² that Na_2SO_4 deposits which were observed on cooled blades are the result of a chemical reaction between sulfur from the fuel and NaCl from the marine atmospheres. Though NaCl is not commonly found on cooled engine blades, the presence of NaCl is confirmed from the very fact that Na_2SO_4 is formed from a reaction between NaCl and sulfur. It has been shown by several investigators^{6-8,13-16} that NaCl enhances the corrosion of both land and marine-based turbine hardware, whereas, some other group of workers attribute a major importance to the role played by sulfur in hot corrosion.³⁻⁵ According to Hurst *et al.*,¹¹ NaCl is capable of causing scale disruption even in the vapor phase. Conde⁶ seems to be the first one to propose that NaCl plays a vital role in the mechanism of Na_2SO_4 -induced hot corrosion and also the formation of heavy metal chlorides of chromium and nickel during NaCl attack on turbine components. However, it is proven beyond doubt that the presence of even minor amounts of NaCl will increase the corrosion attack on Nimonic alloys drastically.

In the present investigation a systematic study has been carried out to understand the controversial role played by NaCl during the hot corrosion of Nimonic 90.

EXPERIMENTAL

Cylindrical samples 10 mm in length and 10 mm in diameter of Nimonic 90 were ultrasonically cleaned in acetone prior to subjecting them to hot-corrosion tests. Experiments were carried out by half immersing the samples in salts contained in silica crucibles, and these were introduced into the furnace at the test temperature. After the experiment the crucibles were removed and cooled outside. Tests were conducted over a temperature range 700-900°C, and the test time was between 2 and 20 hrs. Corroded samples were descaled in molten NaOH by cathodic descaling and were cleaned thoroughly by boiling in distilled water and weighed. Corroded samples were examined by XRD, XRF, EPMA, SEM etc.

RESULTS

Gravimetric Data

Hot-corrosion tests were carried out on Nimonic alloy 90 samples in NaCl by varying both time and temperature. Weight loss versus time and temperature plots are shown in Fig. 1. The kinetics of oxidation of Nimonic

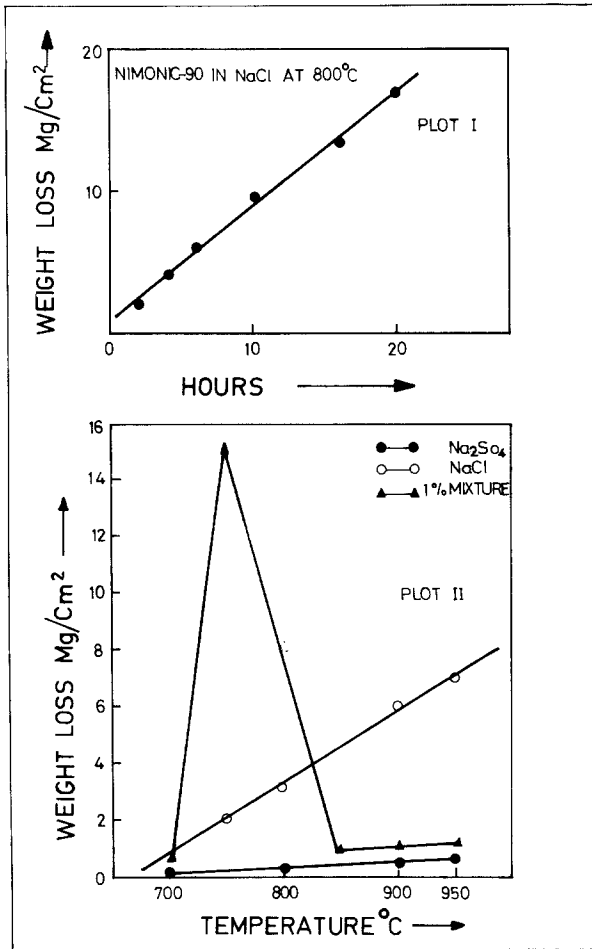


Fig. 1. Weight loss versus time and temperature plots for Nimonic 90.

alloy 90 in NaCl follow a linear rate law, as is seen from plot I (Fig. 1). The scale formed on the corroded samples was loose, porous, and spalled off easily (Fig. 2). The thickness of the scale formed on the corroded samples increased with both time and temperature, and it consisted mainly of Cr₂O₃. Though no chlorides of Cr and Ni were detected in the crucible tests, Na₂CrO₄ and CoCl₂ were detected.

Experimental results obtained in the presence of NaCl, Na₂SO₄, and a mixture containing 1% NaCl in Na₂SO₄ at different temperatures are shown in plot II (Fig. 1). The results indicate that NaCl is much more aggressive than Na₂SO₄ throughout the temperature range studied. On the

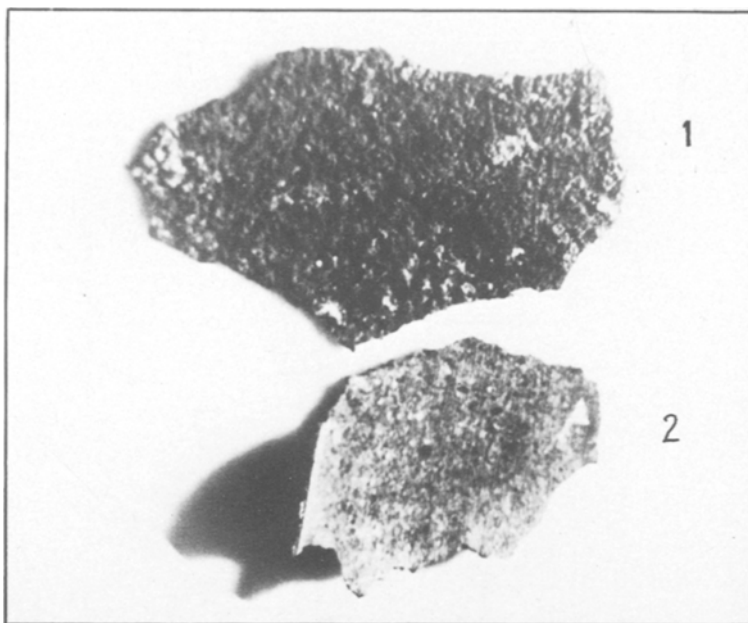


Fig. 2. Stereo photomicrograph of oxide scale formed on the corroded surface of Nimonic 90 in NaCl at 800°C for 20 hrs. (1) Top surface, (2) bottom surface. Magnification 4× (reduced at 90%).

other hand, the 1% NaCl mixture exhibited an anomaly in that, it showed the highest attack between 700–800°C, where the salt mixture exists in solid + liquid phase. The eutectic temperature for the 1% NaCl mixture is around 630 °C. The DTA pattern obtained for the 1% NaCl mixture showed an endotherm in the temperature range 630–650°C, corresponding to the eutectic formation.¹⁷ The corrosion attack is negligible on the alloy before the eutectic formation and also in the presence of molten salt mixture, i.e., above 800°C. The results showed that the solid+liquid region was most detrimental to the alloy and the same trend is shown in Fig. 1.

On prolonged exposures to molten NaCl, a loose and porous mass of a thin film of a nickel deposit was observed at the bottom of the crucible in contact with the alloy sample. Figure 3 illustrates the SEM photograph of the film along with energy dispersive X-ray analysis. The film consisted of mostly nickel with a small amount of cobalt, and could be peeled off from the crucible surface for further characterization. The film thickness increased as in the case of oxide scale, with both time and temperature. The corroded sample surface was left with a network of voids as is seen in Fig. 4, which clearly indicates the extent of damage done to the alloy by

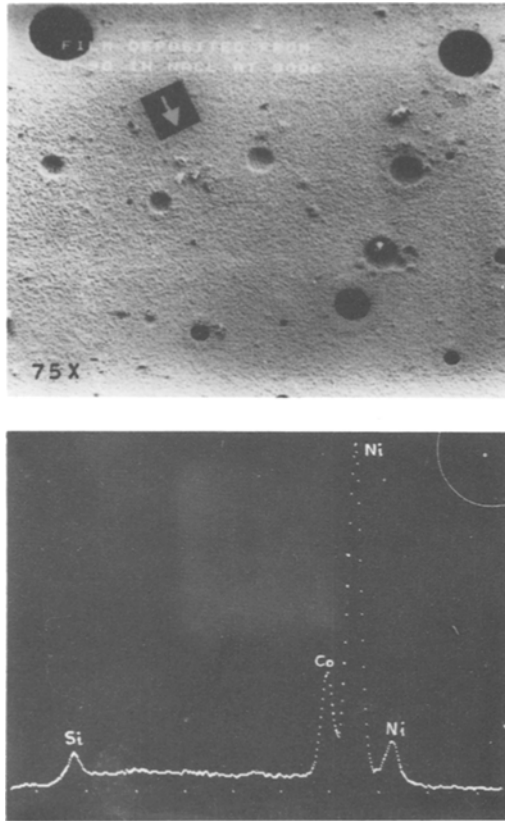


Fig. 3. SEM photograph of alloy film deposited on silica crucible from Nimonic 90 hot corroded in NaCl at 800°C for 20 hrs.

the corrodant. It was also observed that a cobalt-blue ring formed on the sides of the crucible in contact with the molten salt surface. Cobalt from the alloy was removed as cobalt chloride, which was fused on to the crucible surface. It is known that NaCl¹¹ preferentially removes chromium from Nimonic alloys. Our experimental results show that NaCl not only removes Cr but also Co, Ti, and Al. Depletion of these elements from the alloy can be clearly seen from Figs. 3, 4, and 5.

MICROPROBE ANALYSIS

Samples corroded in molten NaCl at 800°C for 20 hrs were examined by the EPMA technique after descaling, in order to assess the extent of

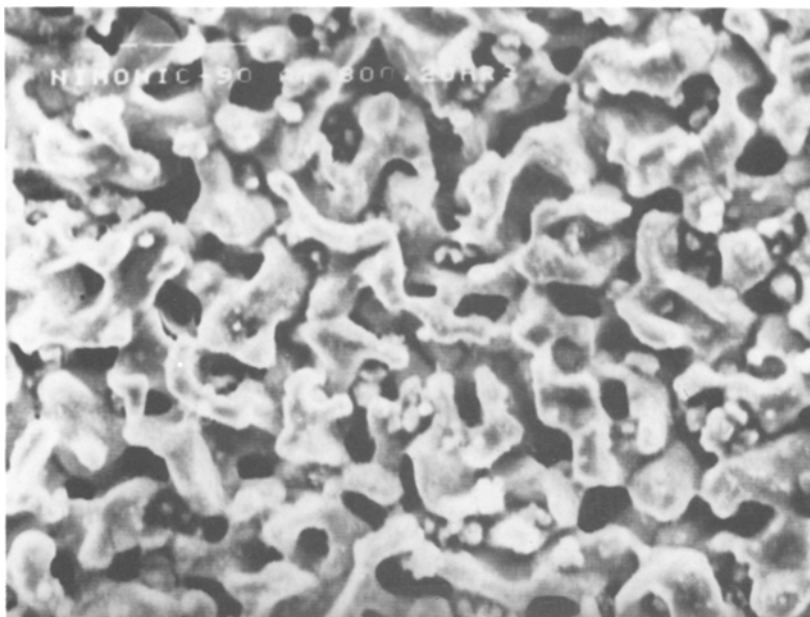


Fig. 4. Surface morphology of Nimonic 90 corroded in NaCl at 800°C for 20 hrs, showing the network of voids. Magnification 1500× (reduced at 90%).

material degradation due to prolonged exposure to the corrodant. From Fig. 5 it can be seen that the alloy is depleted in Cr, Ti, Al, and Co with resultant nickel enrichment on the alloy surface. The surface of the corroded alloy is highly porous because of depletion of alloying elements by the corrodant. The results clearly indicate that the alloy not only loses Cr but also Al, Ti, and Co which form protective oxides on the alloy surface. NaCl reacts with chromium forming chromium oxide, chromium chloride, and sodium chromate. Both chromium chloride and chromate are volatile at the gas turbine operating temperatures, and the chloride being highly volatile, is not seen on cooling in the corrosion product. The surface of the corroded alloy is found to consist of a loose, porous mesh of nickel, which is highly reactive to sulfur and the reaction is self sustaining. The present investigation also confirms CoCl_2 formation as a blue ring round the crucible rim at the molten salt surface. No blue ring formation was observed in the presence of Na_2SO_4 or Na_2CO_3 . These observations confirm the formation of CoCl_2 in the presence of NaCl.

XRF RESULTS

In order to compare and confirm the data obtained with EPMA, XRF analysis of samples of Nimonic alloy 90 hot corroded in NaCl and Na_2SO_4

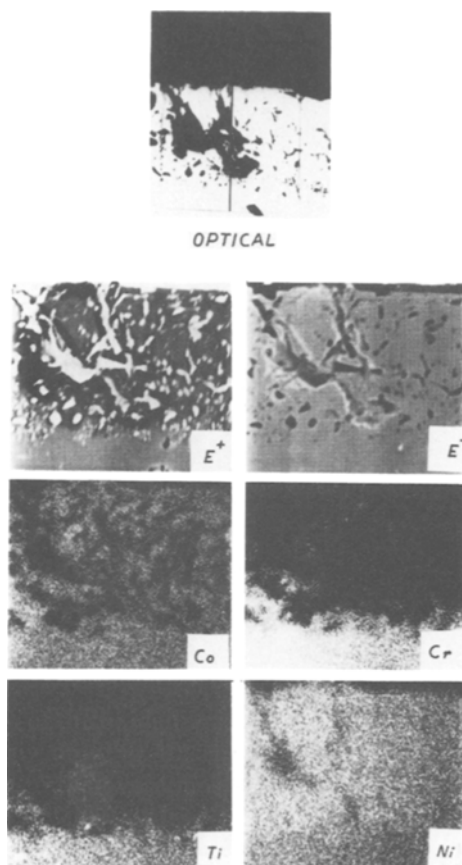


Fig. 5. Electron probe microanalysis of Nimonic 90 corroded in NaCl at 800°C for 20 hrs. Elemental distribution across the corroded surface. Area scanned 200 × 200 microns.

were obtained and are shown in Table I. The results for the sample corroded in NaCl for 20 hrs at 800°C agree with the results obtained with EPMA, in that they show the depletion of Cr, Ti, Al, and Co. On the contrary, the results obtained for the sample corroded in Na₂SO₄ indicate enrichment of Cr, Al, and Ti and depletion of nickel, because sulfur and sulfur compounds have a high affinity for nickel. Similarly Cr, Al, Ti, and cobalt have a high affinity for NaCl.

XRD ANALYSIS

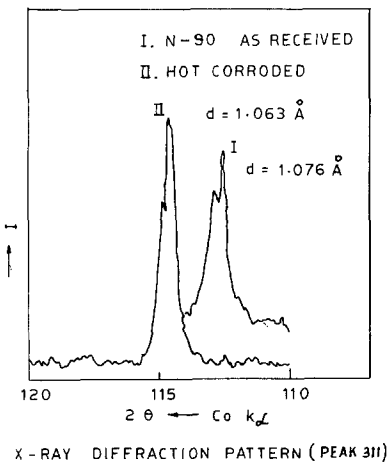
XRD reflections taken for the sample corroded in molten NaCl at 800°C for 20 hrs along with a Nimonic alloy blank sample are presented in

Table I. XRF and chemical analysis of corroded Nimonic alloy 90 corroded in NaCl for 20 hrs at 800°C

Sl. No.	Elements	Nominal composition	XRF analysis				Chemical analysis: corroded in NaCl at 800°C
			Corroded in NaCl at 800°C		Corroded in Na ₂ SO ₄ at 900°C		
			Top	Bottom	Top	Bottom	
1	Ni	58.2	58.98	75.82	36.75	47.31	72.30
2	Co	18.4	15.71	20.53	10.0	18.92	15.70
3	Cr	19.15	3.29	2.84	43.24	25.71	9.70
4	Ti	2.5	0.735	0.193	9.42	6.36	1.05
5	Al	1.65	0.213	0.612	0.567	1.71	0.80

Fig. 6. The shift in the d -spacing from 1.076 Å for the blank sample to 1.063 Å for the corroded one is shown clearly in Fig. 6. The extent of material degradation due to depletion of alloying elements can be seen from the shift in the peak. These results were in turn confirmed by subjecting the corroded sample to chemical analysis. The results are presented in Table I. It can be seen from Table I that half the amount of chromium present in the original alloy is removed as a reaction product. Similar is the case with the other elements Ti and Al. A small amount of Cobalt has also been removed. On prolonged corrosion attack the surface of the alloy consisted of a porous mesh of nickel because of the removal of alloying elements.

In order to study the effect of the presence of oxygen/air on the corrosion behavior of Nimonic alloys, a few samples were corroded by

**Fig. 6.** XRD patterns for (1) Nimonic 90 as received, (2) corroded in NaCl at 800°C for 20 hrs.

completely immersing them in molten NaCl, and the morphology of the corroded sample surface is shown in Fig. 7. Corrosion was negligible in the absence of oxygen/air. However, when the experiment was carried out between 790–795°C, very heavy attack was observed when the salt was partially molten. On repeating the experiments around a few degrees lower than the m.p. of NaCl, reproducible results were obtained with a heavy loss of material, when the salt was in the solid+liquid state. The salt at the bottom of the crucible, which was in direct contact with the crucible bottom, was molten and the rest of the salt on top exposed to the open air was not molten due to a temperature gradient. Air can diffuse through the top layers of salt to the molten region. The moment NaCl comes into contact with air, it attacks the alloy aggressively. This observation suggests that once the molten salt reaches the alloy through cracks in the scale, accelerated oxidation occurs. It also confirms that the initial breakdown of the scale is necessary for catastrophic oxidation. The weight loss obtained for a sample which was completely immersed in molten salt at 800°C for 20 hrs is 3.3 mg/cm², for half-immersed sample it is 18 mg/cm², and sample corroded

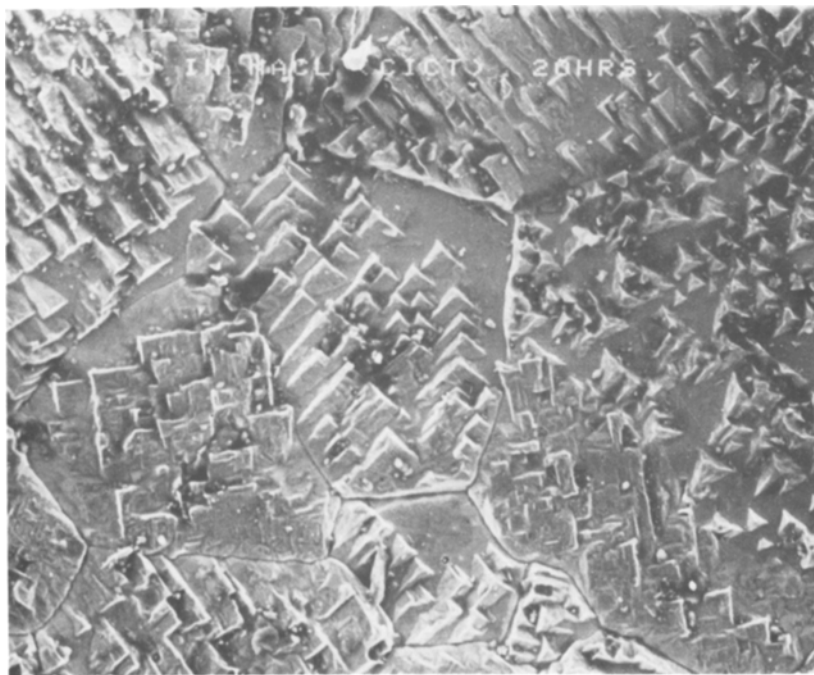


Fig. 7. Surface morphology of Nimonic 90 immersed in molten NaCl at 800°C for 20 hrs. Magnification 300× (reduced at 85%).

in a partially molten salt is 85.0 mg/cm^2 . These data clearly show that partially molten salt is detrimental to the alloy.

DISCUSSION

From the results obtained in this investigation and other observations, it is clear that NaCl plays a vital role in hot corrosion. The presence of either pure NaCl or in combination with Na_2SO_4 is detrimental to Nimonic alloys. Its first and foremost action in hot corrosion is to destroy the scale at discrete places by attacking the alloy through cracks and fissures which exist on the alloy surface. Once the molten salt reaches the bare alloy surface, it preferentially reacts and removes the elements which are less noble like Cr, Al, and Ti in preference to nickel. The products of the corrosion reaction are chlorides, chromates, and oxides. The analysis of the final reaction products revealed the presence of Cr_2O_3 , Na_2CrO_4 , and CoCl_2 . Reaction products of Ti and Al or chlorides of Cr and Ni were not observed. Though the formation of metal chlorides takes place during NaCl attack, they immediately get oxidized to their respective oxides.

The products of the corrosion reaction are highly volatile chlorides, chromates, and nonprotective oxides. The volatile material induces scale disruption by cracking and lifting, and thus exposes the fresh surface to further attack. DTA investigations on the hot-corrosion of Nimonic alloys showed evidence of chloride formation, but they subsequently get oxidized at higher temperature to the respective oxides.¹⁷ The DTA results also show that as long as NaCl is not molten, it is not aggressive but once molten, it is highly corrosive. On the other hand, when the salt is in the partially molten condition it triggers catastrophic corrosion. The access of air through the top layers of solid to pockets of molten salt is detrimental either in the presence of pure NaCl or in combination with sodium sulfate. Our earlier results¹⁸ showed that the presence of the salt mixture in the solid plus liquid form is highly corrosive. In this investigation it was observed that partially molten pure NaCl was also highly corrosive (a case where both oxidizing and reducing conditions are prevalent). It has been shown¹² that very high corrosion rates were observed when the corroding media offers both oxidizing and reducing conditions. Molten salt at discrete places favors reducing conditions, and the access of air through the layers of solid salt offers oxidizing conditions in this particular case and causes severe corrosion.

The addition of even small amounts of NaCl to Na_2SO_4 not only causes a drastic increase in corrosion but also lowers the temperature of corrosion attack. The highest attack observed in the presence of NaCl + Na_2SO_4 mixture is between $700\text{--}800^\circ\text{C}$, i.e., above the eutectic temperature (635°C)

and the m.p. of NaCl (800°C). This temperature region is very important for investigation because of the reaction products present such as sulfides, chlorides, and chromate which are either molten or volatile and which can cause severe oxidation in addition to the salt mixture under study. At higher temperatures, i.e., above 800°C, the attack is less, because most of the aggressive and volatile compounds disappear from the corroding media. This is due to volatilization; the sulfides get oxidized to oxides, and the attack is mainly due to Na_2SO_4 which is innocuous. However, sulfidation attack leads to depletion of Ni from the alloy matrix as was observed by the XRF data. When both the salts are present on the alloy surface denudation of alloying elements takes place and the mechanical integrity of the alloy is lost due to material degradation.

The products of corrosion occupy a large volume, and the passage of volatile compounds exert considerable pressure while escaping and thus produce blisters and cracks on the alloy surface during cooling. Corrosion in the presence of several oxidizing agents certainly leads to aggressive oxidation. According to Stringer *et al.*,¹⁹ during heavy corrosion many sulfides and oxides of chromium and nickel are formed along the grain boundaries, and they are preferentially oxidized, releasing sulfur for further attack. Hence, the mechanism of attack is self-sustaining and may produce a severe, localized pitting type of attack. The maximum attack observed around 750°C, corresponds to the heavy attack observed by Stringer *et al.*¹⁹ It is evident from the results reported here that NaCl certainly plays an important role in enhancing the corrosion of Nimonic alloys. Its effect is significant in the spectacular denudation of alloying elements from the alloy matrix and thus destroying the alloy.

CONCLUSIONS

1. The presence of NaCl either as a liquid or in the vapor state is detrimental to Nimonic alloy 90.
2. The addition of even small amounts of NaCl to Na_2SO_4 are much more harmful than either NaCl or Na_2SO_4 .
3. NaCl preferentially removes Cr, Co, Ti, and Al from the alloy matrix and leaves a nickel-rich surface with a network of voids. On the contrary, depletion of nickel occurs in the presence of Na_2SO_4 .
4. Maximum attack occurs in the presence of mixed corrodants in the temperature region 750–800°C, where the salt mixture exists in the solid + liquid form.
5. The presence of partially molten corrodant either in pure form or in combination with other salt is highly aggressive.

6. The end reaction products identified with NaCl attack are CoCl_2 , Na_2CrO_4 , and Cr_2O_3 and, with the mixture, sulfides of chromium and nickel form in addition to the above products.

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