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Full Length Research Paper

Cyclic oxidation behavior of Ni- and Fe-based superalloys in air and Na_2SO_4-25%NaCl molten salt environment at 800 ^oC

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The present investigation aims to evaluate the high-temperature oxidation and hot corrosion behaviour of Ni-based superalloy (Superni 75) and Fe-based superalloy (Superfer 800H). The superalloy specimens were exposed to air and molten salt (Na_2SO_4-25%NaCl) environment at 800 °C under cyclic conditions. The thermogravimetric technique was used to establish the kinetics of corrosion. X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe micro analyser (EPMA) techniques were used to characterize the corrosion products. The hot corrosion resistance of Ni-based superalloys was found to be better than that of Fe-based superalloys. The formation of scale rich in Cr_2O_3, NiO and spinel $NiCr_2O_4$ has contributed for the better oxidation and hot corrosion resistance of Superni 75, whereas relatively lesser hot corrosion resistance of Superfer 800H is due to the formation of non-protective oxide of iron, and sulphides of iron and nickel.

Key Words: Superalloys, Hot corrosion, Oxidation, Molten salt environment

INTRODUCTION

In many high temperature applications severe degradation of alloys is caused by thin deposits of molten salts especially alkali metal sulfates, alkali metal chlorides and mixtures of these salts (David and Bani, 2004). In harsh environments, such as heat engines and heat exchangers, the structural materials are subjected to high temperature corrosive gases and condensed phases such as NaCl and Na_2SO_4 (Guangming et al., 2005). Under the appropriate conditions these salts deposit on the substrate, leading to severe hot corrosion attack and accelerated degradation of materials (Kofstad, 1988).

Ideally, in a clean environment like air, the normal oxide film that forms at the surface of an alloy acts as an effective barrier to further oxidation. The continuing growth of the oxide film requires the transport of metal species or oxidant species through the film via solid state diffusion. In practice, however, the oxide film often became porous and cracked, allowing much faster transport along these channels and leading to heterogeneous film morphology (David et al., 2004). Molten salt provides a medium for the transport of oxidants inward toward the metal and of dissolved metal ions outward. Moreover, the chemical reactions are generally faster in liquid phase than as solid–solid reactions (Uusitalo et al., 2004). Reactions that form metal chlorides or metal sulfides near the oxide/metal interface will consume alloy elements, especially chromium, that are intended to build or repair the protective scale.

Johnson et al. pointed out that the presence of NaCl in the mixtures of NaCl/ Na_2SO_4 initiates attack in high chromium content alloys. The addition of 10% NaCl in Na_2SO_4 coatings can easily cause the cracking of protective Cr_2O_3 layers and increase the amount of sulphur incorporated into the substrate, accelerating the corrosion of alloys (Charng- Cheng et al., 2005).

In the present investigation, an attempt has been made to evaluate the oxidation and hot corrosion resis-

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Table 1. Nominal chemical composition of the substrate materials.

Alloy (Midhani Grade)	Chemical Composition (wt %)							
	Fe	Ni	Cr	Ti	Al	Mn	Si	C
Superni 75	3.0	77.1	19.5	0.3	-	-	-	0.1
Superfer 800H	43.8	32.0	21.0	0.3	0.3	1.5	1.0	0.1

tance of nickel- and iron-based superalloys, namely Superni 75 and Superfer 800H respectively, in air and in a corrosive environment of molten salt Na_2SO_4-25%NaCl , respectively, at 800^0C under cyclic conditions. These superalloys are mostly used in boilers and turbines where this kind of environment is usually present.

EXPERIMENTAL

Substrate Materials

The substrate material selected for the present study was Ni-based superalloy (Superni 75) and Fe-based superalloy (Superfer 800H), which were procured from Mishra Dhantu Nigham Limited, Hyderabad (India) in the rolled sheet form. The chemical composition of the substrate materials is given in Table 1.

Sample Preparation

The specimens, with dimensions of approximately 20 X 15 X 5 mm^3, were cut from the alloy sheets of superalloys Superni 75 and Superfer 800H. These superalloys are developed by Mishra Dhatu Nigam Limited, Hyderabad (India) for high-temperature applications in boilers and gas turbines. They were ground on SiC papers down to 1000 grit. Final polishing was carried out on a cloth polishing wheel machine with 1 m lavigated alumina powder suspension. Subsequently the specimens were washed properly with flowing water, and dried in hot air to remove any moisture.

Oxidation and molten salt corrosion tests

Cyclic oxidation studies were performed in air and molten salt (Na_2SO_4–25% NaCl), with each cycle consisting of 1 h of heating at 800 °C followed by 20 min cooling at room temperature for 50 cycles. The aim of cyclic loading is to create severe conditions for testing. Before performing the corrosion runs, the physical dimensions of the specimens were measured carefully with a Sylvac digital vernier caliper (Swiss make, resolution 0.01), to evaluate their surface areas. Subsequently, the specimens were washed properly with acetone and dried in hot air to remove the moisture. For hot corrosion experimentations, a coating of uniform thickness of 3–5 mg/cm^2 of Na_2SO_4–25% NaCl salt mixture was applied with a camel hairbrush on preheated samples (100 °C). Alumina boats were used to perform the oxidation and hot corrosion runs in the silicon carbide tube furnace. The alumina boats used for these studies were pre-heated at a constant temperature of 1200 ^{o}C for 8 h so that their weight would remain constant during the course of high temperature cyclic study. The weight of boat loaded with specimen was measured at the end of each cycle using an electronic balance (model 06120) with a sensitivity of 1 mg. The spalled scale in the boat was also taken into consideration for the weight change measurements to determine the total rate of corrosion. SEM, XRD and EPMA techniques were used to analyse the corrosion products after subjecting the specimens to oxidation and hot corrosion tests.

RESULTS

Visual observations

Colour of oxide scale formed on the uncoated superalloys Superni 75 and Superfer 800H, after air oxidation for 50 cycles at 800 ^{0}C, was dark grey. Some greenish tinges were observed on the surface of Superfer 800H specimen from the 10th cycle onwards, whereas bluish tinges were observed in case of Superni 75 from 12th cycle while the specimen turned to light blue after 15th cycle of the study. The scale was giving lustrous appearance up to mid cycles of the study, which eventually became dull during subsequent cycles.

A brownish grey scale appeared on the surface of uncoated superalloys Superni 75 and Superfer 800 H during initial cycles of hot corrosion in the molten salt environment at 800 ^{o}C, which turned to dark grey after third cycle. The cracks were developed in the scale and spalling was observed from these regions. The spallation of the scale was mostly confined to edges and corners in case of Superni 75, whereas intensive spalling occurred from the surface of Superfer 800H specimens after 12th cycle.

Corrosion kinetics

The weight gain per unit area results for the substrate superalloys during cyclic exposure to air and molten salt (Na_2SO_4+25%NaCl) environment at 800 ^{0}C for 50 cycles are shown in Figure 1. The superalloys Superfer 800H and Superni 75 show higher weight gain in molten salt environment, which is found to be 1.6 and 1.3 times more, to that gained in air oxidation, respectively. Further, iron- base superalloy Superfer 800H shows higher weight gain in both the environments as compared to that of nickel based Superni 75. It can be inferred from the plots that Superfer 800H reveals almost double and 2.5 times more weight gain as compared to that of Superni 75 in air oxidation and molten salt environment, respectively. Both the superalloys show maximum weight gain during initial cycles, which subsequently becomes gradual. After 30th cycle oxidation rate has become nearly constant. Due to

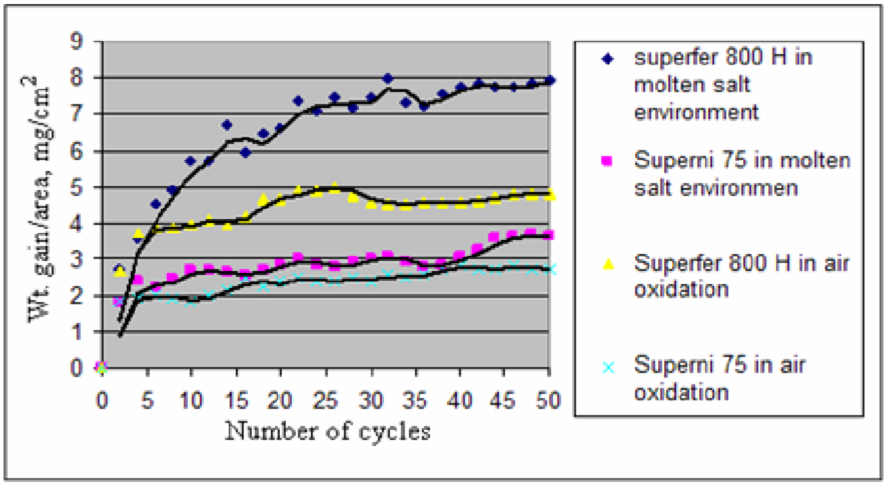

Figure 1. Weight gain/area versus number of cycles plot for the Superni 75 and Superfer 800H Super alloys subjected to air and molten salt (Na_2SO_4-25% NaCl) environments for 50 cycles at 800°C.

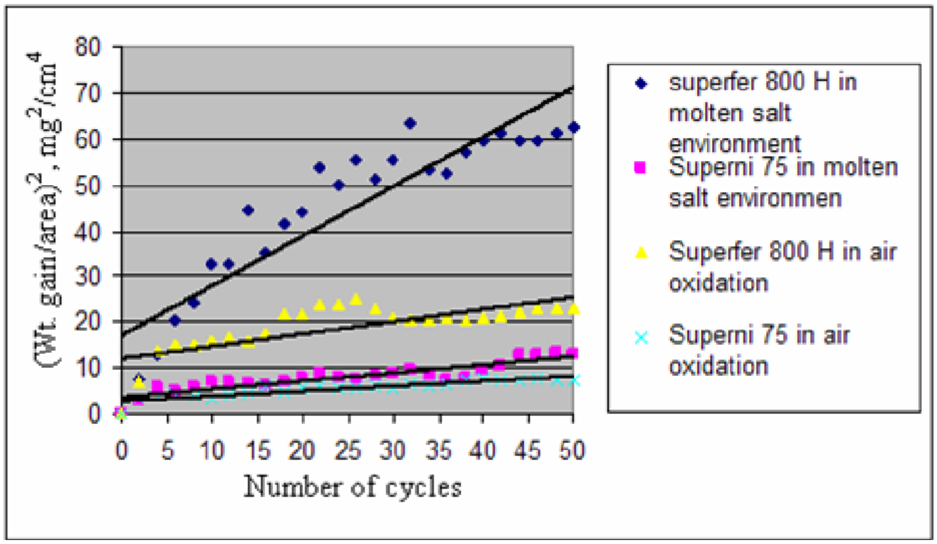

Figure 2. (Weight gain/area)^2 versus number of cycles plot for the Superni 75 and Superfer 800H superalloys subjected to air and molten salt (Na_2SO_4-25%NaCl) environments for 50 cycles at 800^{o}C.

Table 2. Values of Parabolic rate constant, k_p, for bare superalloys

Sample	k_P (g^{2}cm^{-4}sec^{-1})
Superfer 800 H in presence of molten salt	98.6X10^{-10}
Superni 75 in presence of molten salt	71.2 X10^{-10}
Superfer 800 H in presence of air oxidation environment	36.0 X10^{-10}
Superni 75 in presence of air oxidation environment	22.58 X10^{-10}

intensive sputtering of Superfer 800H specimen during cooling period or while keeping the sample inside the furnace, the weight gain by this specimen could not be measured accurately in the molten salt environment, therefore the actual weight gain of this specimen might be higher than what was observed.

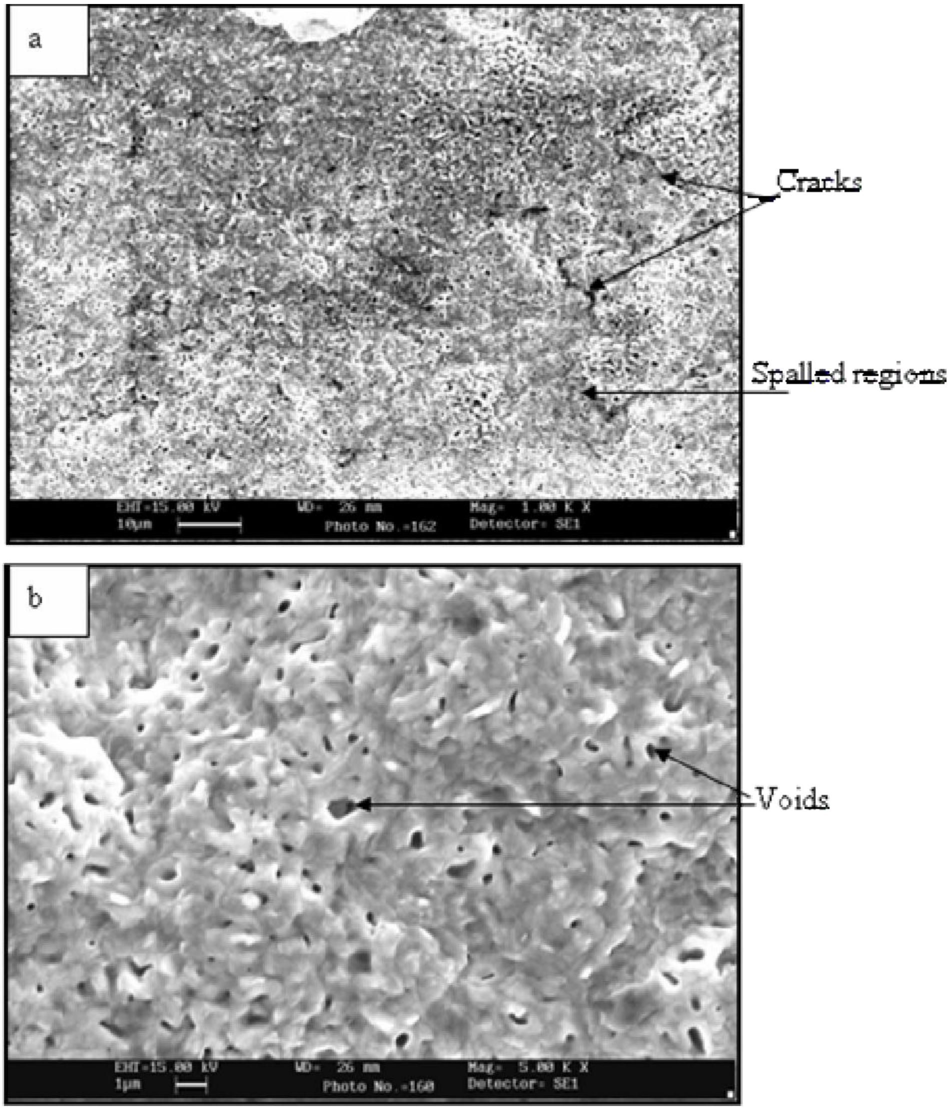

Figure 3. SEM of Superfer 800H after hot corrosion in molten salt environment of Na2SO4+25%NaCl for % 50 cycles at 800°C.

Weight gain square plots shown in Figure 2 reveal that Superni 75 superalloy follows the parabolic rate law of oxidation for the entire 50 cycles of the study, whereas Superfer 800H superalloy shows some deviation from the parabolic laws. The values of parabolic rate constants, k_p, in both the environments are shown in Table 2.

SEM Analysis of the scale

Surface analysis

SEM micrographs showing surface morphology of the corrosion products formed on Superfer 800H specimen are shown in Figure 3. The scale formed on Superfer 800H is found to be fragile in nature. Cracks as well as spalled regions are present in the surface scale (Figure 3a). Voids formed along the grain boundaries can be clearly seen in Figure 3b taken at higher magnification. Superni 75 shows the formation of a regular, homogenous and continuous scale after hot corrosion for 50 cycles at 800 ^{o}C (Figure 4a) . Further, the scale is compact and adherent in nature consisting of irregular size fine grains uniformly dispersed throughout the scale (Figure 4b).

Cross-sectional analysis

BSE images obtained across the cross-section of corroded specimens of Superfer 800H and Superni 75 after exposure to molten salt environment for 50 cycles at 800 ^{o}C are shown in Figure 5. BSE image of Superfer 800H shows the formation of irregular and discontinuous

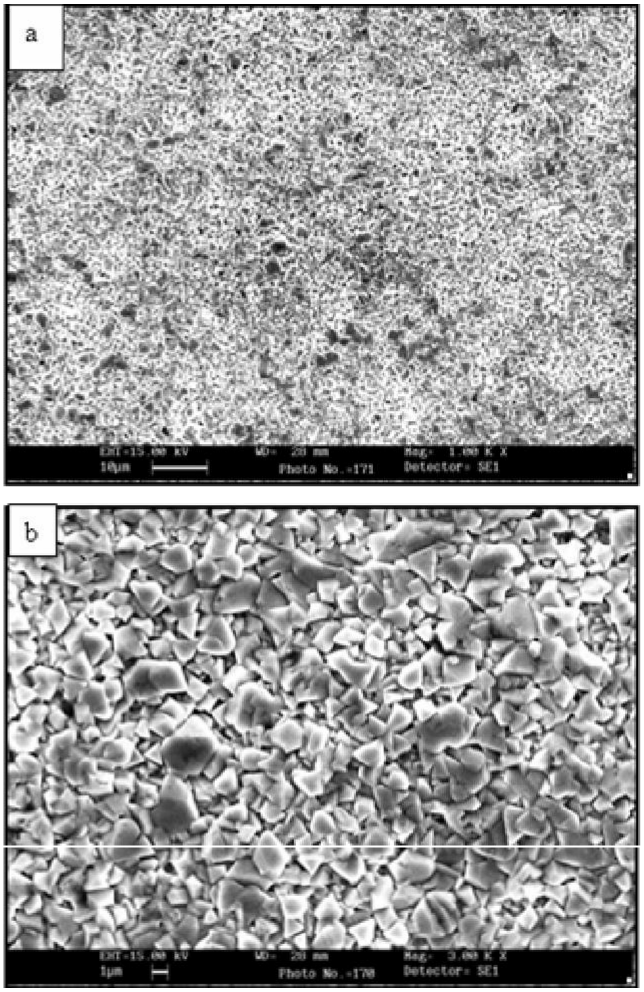

Figure 4. SEM of Superni 75 after hot corrosion in molten salt environment of Na_2SO_4 + 25%NaCl for 50 cycles at 800°C.

fragile scale of about 190 µm thickness (Figure 5a), whereas a continuous, uniform and adherent scale of about 110 µm thick is formed on Superni 75.

XRD analysis of the scale

The XRD patterns of the scale formed on superalloys Superni 75 and Superfer 800H during cyclic oxidation in air and in molten salt environment, are shown in Figures 6 and 7, respectively. The major and minor phases detected at the surface of the specimens are shown in the XRD graph.

EPMA analysis of the scale

Elemental X-ray mappings at the cross-section of Superni 75 superalloy after cyclic oxidation at 800 ^{O}C in Na_2SO_4-25%NaCl environment for 50 cycles are shown in Figure 8. The BSE image indicates the formation of a dense scale consisting mainly of nickel and chromium. Titanium and iron show their existence throughout the cross-section. The upper part of the scale is rich in nickel, whereas chromium forms a dense layer just above the scale-substrate interface. Traces of sodium and sulphur are present throughout the scale.

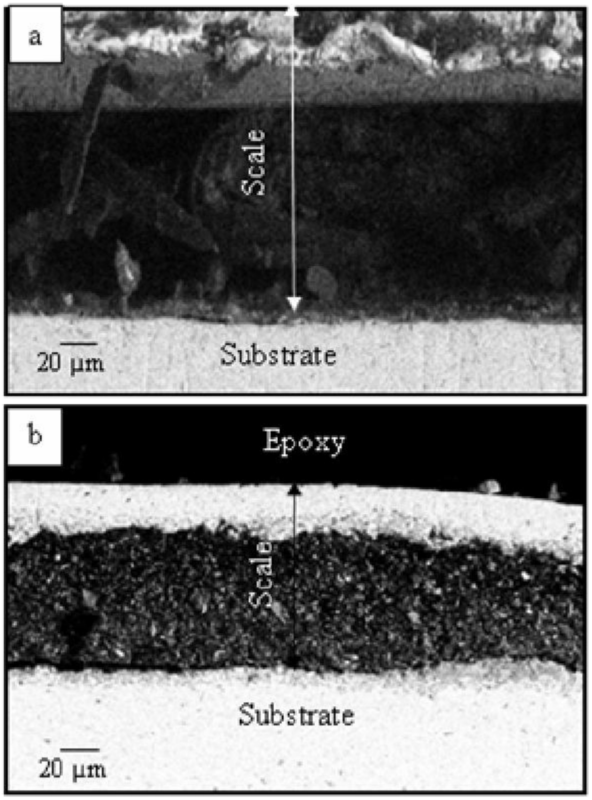

Figure 5. BSE images across the cross-section of hot corroded superalloys after subjecting to molten salt (Na2SO4 + 25 % NaCl) environment at 800C for 50 cycles: (a) Superfer 800H (b) Superni 75.

DISCUSSION

The weight gain of nickel based superalloy Superni 75 is almost half of that gained by iron based superalloy Superfer 800H during oxidation study in air at 800 ^{O}C for 50 cycles. The superalloy Superni 75 also perfectly follows the parabolic rate law of oxidation as indicated by $(weight/area)^2$ plots shown in Figure 2, whereas Superfer 800H shows some deviations from parabolic law of oxidation. Therefore, it can be inferred that the relative oxidation resistance of Superni 75 is greater than that of Superfer 800H. The superior oxidation resistance of Ni-based superalloy, Superni 75, has been attributed to the formation of oxides of nickel and chromium and their spinel $NiCr_2O_4$, as detected by the XRD analysis shown in Figure 6. The EPMA analysis also shows the presence of oxides of chromium and nickel in the scale (Figure 8).

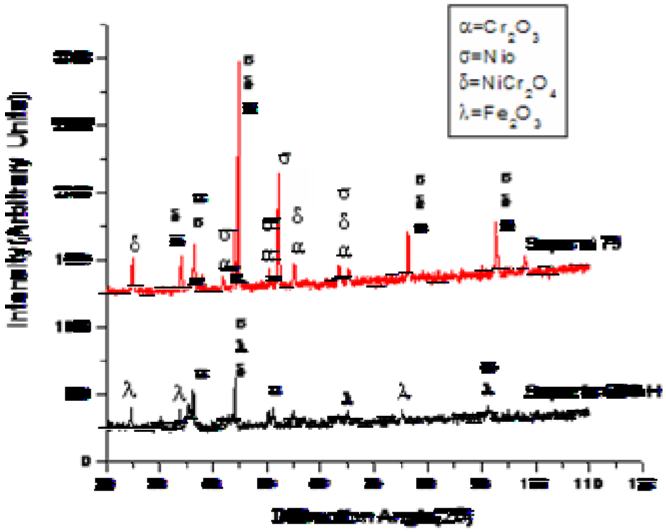

Figure 6. XRD of corroded superalloys after exposure to air oxidation for 50 cycles at 800°C.

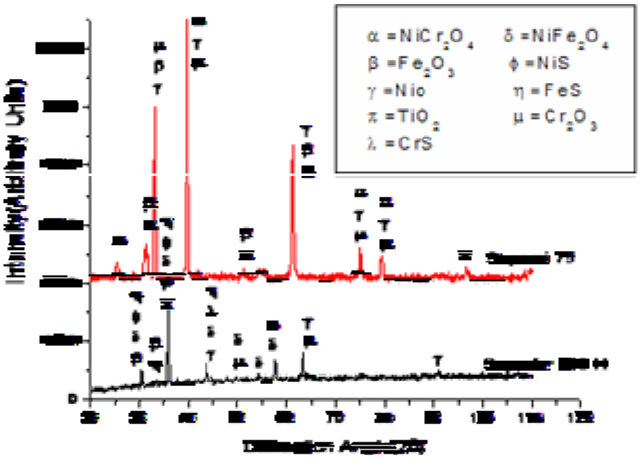

Figure 7. XRD of corroded superalloys after expoasure to molten salt (Na2SO4-25% NaCl) environment for 50 cycles at 800°C.

These oxides act as diffusion barriers for the inward penetration of oxidizing species as has been reported by Goebel and Pettit (1970). The relatively less oxidation resistance of Fe-based superalloy, Superfer 800H, is due to the formation of surface oxide dominated by iron oxide, which is less protective as compared to oxides of chromium and nickel (Pettit and Meier, 1985).

It can be inferred from the weight gain plots (Figure 1) that both the superalloys gain more weight in the molten salt environment as compared to that in air, indicating the occurrence of accelerated oxidation (hot corrosion) in the presence of molten salt environment of Na_2SO_4-25%NaCl at 800 ^{O}C. The presence of large number of oxides of substrate elements in the surface scale formed in the molten salt environment, as detected by XRD analysis (Figure 7), is an evidence of accelerated oxidation of the superalloys. The weight gain data shows that Superni 75 is more resistant to hot corrosion in the given environment as compared to that of Superfer 800H. The surface scale of corroded Superni 75 is found to be rich in protective oxides of chromium, nickel and their spinel $NiCr_2O_4$. The Fe-based superalloy Superfer 800H shows relatively less resistance to hot corrosion and its surface scale is found to be rich in oxide of iron and sulphides of iron and nickel. Malik (1988) has also reported a similar sequence for the hot corrosion rates of Ni- and Fe-based superalloys based on the weight change data for 30 cycles.

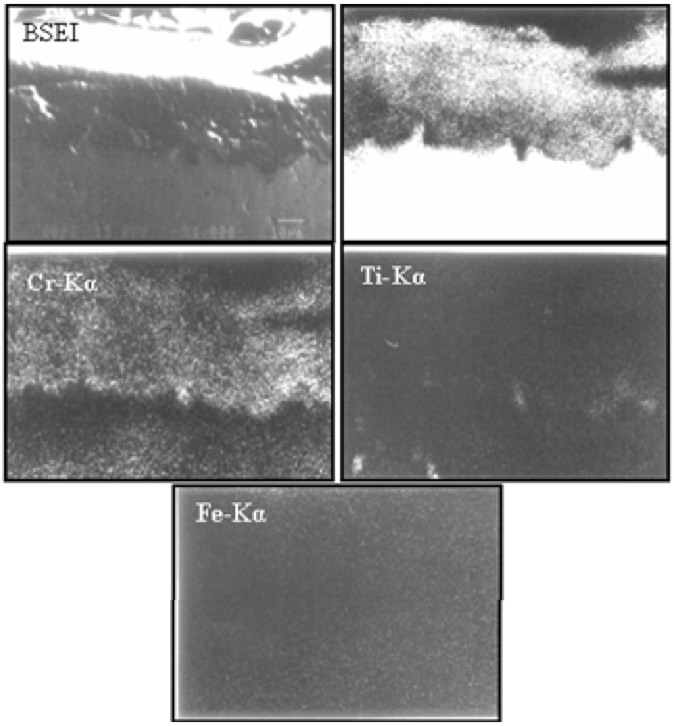

Figure 8. Composition image (BSEI) and X-ray mappings of the cross-section of the Superni 75 subjected to hot corrosion at 800°C in Na2SO4-25%NaCl environment for 50 cycles.

The molten Na_2SO_4 + NaCl which was deposited on the superalloy, can cause hot corrosion and flux the normally protective oxides such as Cr_2O_3 (Gurrappa, 2001). In a liquid deposit, the following thermodynamic equilibriums occurs (Rapp and Zhang, 1994).

Na_2SO_4 (l) = Na_2O (l) + SO_3 (g) (1) and

SO_3 (g) = 1 / $2S_2$ (s) + 3 / $2O_2$ (g) (2)

The continuous formation of the oxides on the surface of the alloy will decrease the oxygen potential. Consequently, the activity of sulfur increases, leading to the formation of sulphides. Simultaneously, basic dissolution of oxides occurs by the following reaction:

Cr_2O_3 (s) + 3 / $2O_2$ (g) + $2SO_4^{2-}$ (l) = $2CrO_4^{2-}$ (s) + $2SO_3$ (g) (3)

Therefore, the non- protective oxide (Fe_2O_3, TiO_2) or less protective oxides (NiO) are formed in the surface scale, which allows sulfur diffusion through the scale to the scale/alloy interface, leading to the formation of Cr sulfide.

Addition of NaCl further accelerates the hot corrosion, as it reacts with the oxides thus releasing chlorine which in turn reacts with the oxides to form the volatile chlorides, as per the following reactions (Mckee et al., 1978; Shinata, 1987).

8NaCl (l) + $2Cr_2O_3$ (s) + $5O_2$ (g) $4Na_2CrO_4$ (s) + $4Cl_2$ (g) (4)

Cl_2 is able to penetrate through oxide scales quickly along cracks and react with substrate elements such as Cr. Then volatile chlorides are formed:

Cr (s) + 3 / $2Cl_2$ (g) $CrCl_3$ (g) (5)

The volatile chlorides thus formed tend to diffuse out through the grain boundaries to the surface, and in doing so numerous pits and voids are generated at the grain boundaries, which can be seen clearly in Figure 3b. The chlorides may reoxidize on the surface of the scales:

$2CrCl_3$ (g) + 3 / $2O_2$ (g) Cr_2O_3 (s) + $3Cl_2$ (g) (6)

Cl_2 is then regenerated and the corrosion repeated. Other alloy elements, such as Ni, Ti etc. also follow the above reactions. The pits and voids, produced due to the formation of volatile chlorides, provide paths for the further penetration of corrosive species resulting in internal oxidation and sulphidation of the substrates.

Intensive spalling/sputtering of the scale of the Superfer 800 H superalloy can be attributed to severe strain developed due to the precipitation of Fe_2O_3 from the liquid phase and interdiffusion of intermediate layers of iron oxide as has been reported by Sachs (1958). Further, the presence of different phases in a thin layer might impose severe strain on the film, which may result in cracking and peeling of the scale. Thermal cycles might have also produced cracks in the scale due to different values of thermal expansion coefficients of the substrate and the oxides formed in the scale. These cracks may have allowed the aggressive liquid phase to reach the metal substrate and causes internal oxidation.

CONCLUSIONS

Ni-based superalloy Superni 75 shows higher resistance to oxidation and hot corrosion in the given environmental conditions at 800 ^{o} C as compared to that of Fe-based superalloy Superfer 800H.

The better performance of Superni 75 in both the environments has been attributed for its tendency to form protective oxides of chromium and nickel, and their spinel.

The formation of surface scale rich in less protective oxide of iron is responsible for the relatively lesser oxidation resistance of Superfer 800H. The surface scale rich in oxide of iron, and sulphides of iron and nickel has contributed for its poor hot corrosion resistance in the given environment.

In the hot corrosion attack by Na_2SO_4-25%NaCl molten salt environment, NaCl reacts with the oxides releasing chlorine, which in turn reacts with the oxides to form volatile chlorides. The volatile species thus formed tend to diffuse out of the grain boundaries to the surface and in doing so numerous pits and voids are generated at the grain boundaries, which provides path for the further penetration of corrosive species into the substrate causing internal oxidation and sulphidation of the alloy.

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