Effect of Hot Corrosion Behaviour of 20MnMoNi55 and AISI 304 Bare Steel in Molten Salt Environment at 900°C

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Abstract

Hot Corrosion behaviour of 20MnMoNi55 and AISI 304 Steel in Salt solution of 75wt.%Na_2SO_4+25wt.%K_2SO_4 has been studied at a temperature of 900°C under cyclic condition. Thermogravimetric technique has been used to know the corrosion kinetics of 20MnMoNi55 steel and AISI 304 steel in salt at 900°C under cyclic conditions for 50 cycles. Each cycle consisted of 1 hour heating at 900°C followed by 20 min of cooling in air. 20MnMoNi55 steel sample followed somewhat linear rate of oxidation with more weight gain while AISI 304 sample followed the parabolic rate law of oxidation with less weight gain. X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive X-ray (SEM/EDAX) techniques were used to characterise the oxide scales. AISI 304 steel was found to be more corrosion resistance than 20MnMoNi55 steel under salt oxidation for 50 cycles.

Keywords: Hot corrosion; 20MnMoNi55, AISI 304, 75wt.%Na_2SO_4+25wt.%K_2SO_4

1. Introduction

Ferritic steel containing, chromium and molybdenum are well known for their better mechanical properties with high temperature strength and high thermal fatigue life, as well as with good thermal conductivity, weldability, and resistance to corrosion and graphitisation. Due to these characteristics this type of steels have attracted special interest for application in industrial processes related to oil refining, carbochemistry, and energy generation in thermal power plants, where components like, heat exchangers, boilers and pipes operate at high temperatures and pressures for long periods of time, Wortel et al (1992) . Many metals and alloys sometimes experience accelerated oxidation when their surfaces are covered with a thin film of fused salt in an oxidising gas atmosphere at elevated temperatures. This is known as hot corrosion where a porous non-protective oxide scale is formed

at the surfaces and sulphides in the substrate, Singh et al (2004). Alloys that are developed for heat and oxidation typically form a protective layer of chromia or alumina. The more rapidly this layer is established, the better protection is offered. As this layer grows or as it reforms over areas from which the original layer was removed, it must withdraw chromium or aluminium from the metal in order to provide for further scale growth, Link et al (1998). Oxide scale is constituted by a layered structure with compositional and microstructural variations from the substrate to the outer interface, Saeki et al (1998). Among the ferritic steels, modified 9Cr–1Mo exhibited the highest 100h rupture strength at all temperatures, while 2.25Cr–1Mo steel exhibited the lowest rupture strength. The creep strength of modified 9Cr–Mo steel remains higher or equal to that of AISI type 304 austenitic stainless steel up to 899 K .The strength values of plain 9Cr–1Mo steel lie in between of those exhibited by 2.25Cr–1Mo and modified 9Cr–1Mo steels, Baldev et al (2004).

This paper is intended as a contribution to the knowledge of the hot corrosion behaviour of the 20MnMoNi55 (low alloy steel) and AISI 304 in salt (75wt.%Na_2SO_4+25wt.%K_2SO_4) atmosphere under cyclic conditions . In this experimental study emphasis is also given to oxide scales which were separated and fell down in boat while oxidation process was going on.

2. Experimental Material and Procedure

2.1. Substrate steels

The experimental work was performed by using samples of 20MnMoNi55 steel & AISI 304 steel. The 20MnMoNi55 steel was received from BARC, Mumbai, India and AISI 304 steel was received from Jindal Steel, Hissar India. The spectroscopy was done on samples which were taken for experiment, this showed chemical composition in wt. % which is given below:

Table 1. Spectroscopy

Type of steel	C	Mn	Si	S	P	Cr	Mo	Cu	Ni	Al	Fe
20MnMoNi55	0.2000	1.487	0.2669	-	0.028	0.1700	0.5000	0.0725	0.5983	0.0443	Balance
AISI 304	0.1158	1.660	0.6750	0.0006	-	18.000	0.2172	0.7194	6.801	-	Balance

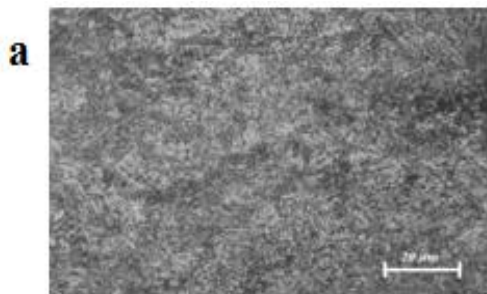### 2.2. Optical microscopy for surface microstructure

The microstructure of the both steel samples, after polishing and etching with marble's reagent (Marble's Reagent = Distilled Water 50 ml, HCl 50 ml & Copper sulphate (CuSO4) 10 grams immersion or swab, etch for a few seconds) is shown in Fig.1(a-b).

The microstructure of 20MnMoNi55 steel revealed ferritic structure i.e. the white spot which is seen in

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microstructure is ferrite and the rest is other phase and the microstructure of AISI 304 sample revealed that some void and pit are present.

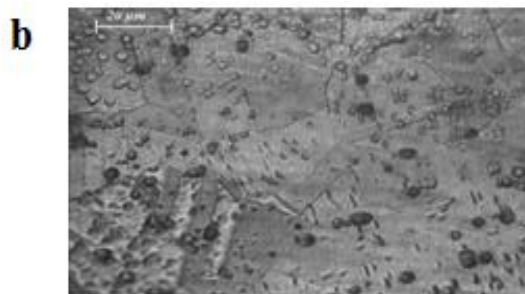Fig. 1. (a) Microstructure of 20MnMoNi55 steel; (b) Microstructure of AISI304 steel at *20x magnification*

2.3. Sample Preparation

The experiment was performed on samples which were made to specified dimensions of approximately 20 x 15 x 3.5 mm from plate sections. The specimens were polished on SiC emery paper down to the 1200 from 120 grades. Polishing was carried out on all six faces. The specimens were degreased (by ultrasonic cleaning in ethanol) and dried, then they were accurately weighed and measured to determine the total surface area exposed to the corrosive environment.

2.4. High Corrosion study in Salt Environment

Hot Corrosion studies were conducted at 900°C in laboratory using silicon carbide tube furnace having PID temperature controller. The samples were subjected to mirror polishing which include cloth polishing which will provide uniformity of reaction while undergoing oxidation process. Then dimensions were accurately measured by digital vernier, so as to calculate area which will be required for plotting of graph of weight gain per unit area verses number of cycle. Finally specimens were cleaned i.e. degreased by ethanol and kept in alumina boat. This alumina boat prior to performing of experiment was kept in oven for 5hr at 250°C in oven and then kept in furnace at 900°C for 2hr so that moisture is totally removed from boat. After this the sample was kept in boat and weight was taken initially and then slowly inserted in tubular furnace.

Samples of 20MnMoNi55 and AISI304 steel were kept in alumina boat and heated in an oven along with alumina boat up to 150°C and the salt mixture of 75wt.%Na_2SO_4+25wt.%K_2SO_4 dissolved in distilled water was coated on the warm polished samples with the help of a camel hair brush. The amount of the salt coating varies in the range 3.0–5.0mg/ cm^2. The salt coated samples were then dried at 250°C for 2 and ½ hrs in an oven to remove the moisture and then weighed, after this sample of 20MnMoNi55 and AISI304 were inserted in different tubular furnace .These samples were kept in furnace for 1 hr at a temperature of 900°C and then they were removed and cooled further for 20 minutes at room temperature and their weight were taken by electronic

balance (make Contech, India) having sensitivity of 0.001 gms. This cycle was repeated for 50 times i.e. 50 cycles were made for each sample. The weight of samples was measured at the end of each cycle and spalled scale was also taken into consideration which used to fall into the boat i.e. the weight was taken along with the boat. This cycle was repeated for 50 times i.e. 50 cycles were made for each sample.

Corroded Samples were analysed by XRD (BRUKER-binary V3) and FESEM/EDAX and the oxide scale which fell into the boat were also analysed by XRD. Cu radiation was used in XRD at a step of 1°/min and the range of angle was 5-100°.

3. Results

3.1. Behaviour in Salt at Elevated Temperature

The Corrosion of sample which occurred in salt at a temperature of 900°C is shown by plotting a graph. Fig 2. On x-axis "number of cycles" and on y-axis "weight gain/area (mg/cm^2)" was taken. The Hot Corrosion behaviour of 20MnMoNi55 and AISI 304 steel in salt was parabolic as shown in fig. but in 20MnMoNi55 steel after 20th cycle there was more weight gain and also the weight gain of AISI 304 steel was less because the oxide layer which were falling in boat were very thin in size. The graph reveals that AISI 304 steel is better than 20MnMoNi55 steel in molten salt environment (for 50 cycles).
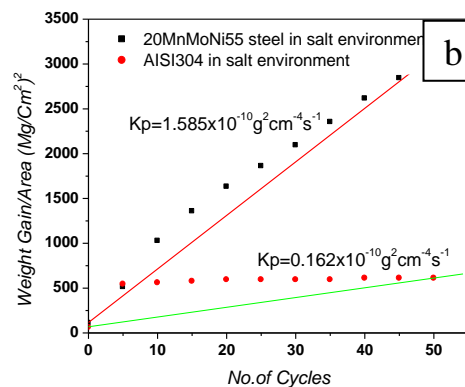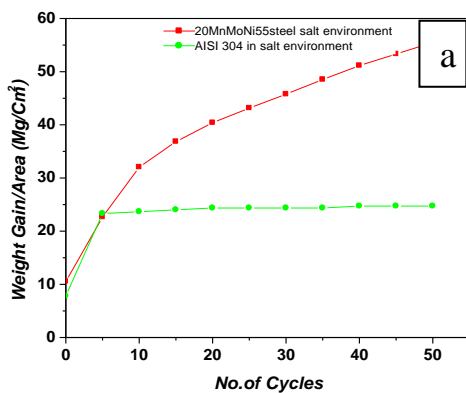

Fig.2.(a-b) Weight gain versus No. of cycles plot for 20MnMoNi5 steel & AISI 304 bare steel exposed to salt environment at 900°C for 50 cycles.

Table 2. Parabolic rate constant (Kp)

Substrate	Kp (10^{-10} g^{2}cm^{-4}s^{-1})
20MnMoNi55	1.585
AISI 304	0.162

The Parabolic rate constant for both steel samples is shown in Table 2. The K_P value of 20MnMoNi55 steel is higher than AISI304 steel. Hence this table indicate that AISI304 steel has better than 20MnMoNi55 steel in salt environment condition at 900^{0}C for 50 cycles. As shown in macrograph AISI

304 salt oxidised sample did not showed much more crack or extrusion of material from substrate and it has crack free scale but 20MnMoNi55 steel has more Corrosion effect. Its layer got separated from substrate and also its oxide scale was thick as shown in Fig.3 (a-b).
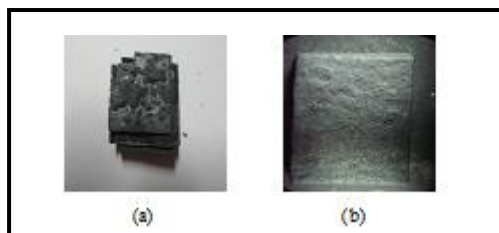

Fig 3. Macrograph of (a) 20MnMoNi55 salt oxidised sample (b) AISI304 salt oxidised sample

3.2. X-Ray diffraction analysis

Fig.4 shows the XRD analysis of corroded 20MnMoNi55 and AISI304 steel samples. The results of XRD analysis contained graph indicating peak values (i.e. d values) which were used to identify various phases with the help of inorganic X-ray Diffraction data card from Powder diffraction file of JCPDS. Help of software named Philips X'pert High score and Eva was also taken for finding out compounds at respective peaks.
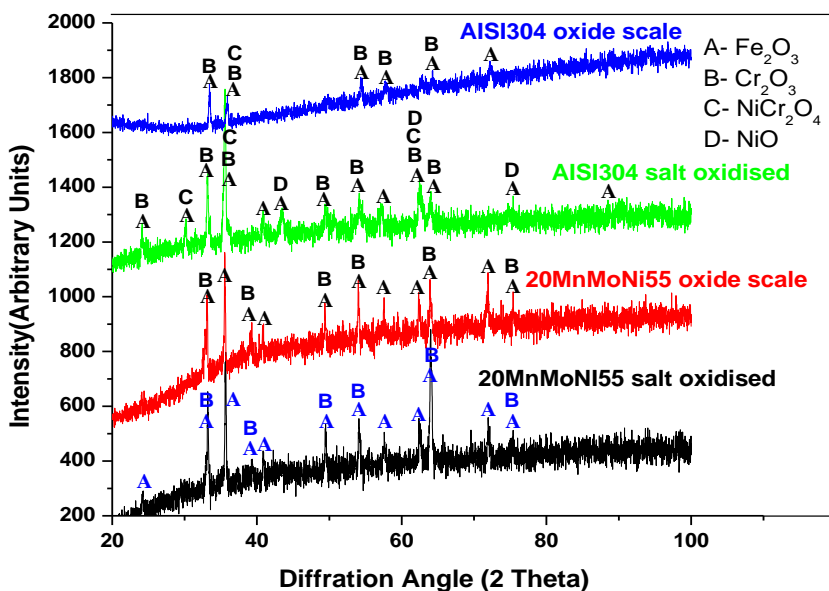
Fig 4. XRD Graph of salt oxidised 20MnMoNi55, AISI304 sample and its oxide scale

From the X-Ray Diffraction analysis it is found that iron oxide (Fe_2O_3), chromium oxide (Cr_2O_3) are major phases which are formed in 20MnMoNi55 steel & in spallation of scale, where as NiO, $NiCr_2O_4$ (Spinel) oxide scale are present besides the Fe_2O_3 and Cr_2O_3 in AISI304 & in spalled scale sample of AISI304. Cr_2O_3 and $NiCr_2O_4$ are more protective oxide layer on the surface due to

which further oxidation is prevented as it acts as barrier for corroding media to substrate but in case of 20MnMoNi55 steel, amount of Cr_2O_3 is very less which is mainly responsible for the corrosion resistance. Also it is found that no spinels are formed due to which it is having less protective oxide layer, this is also major factor which led to accelerated rate of weight gain.

3.3 Surface scale analysis

The SEM/EDAX analysis for 20MnMoNi55 sample & AISI304 sample after corrosion in salt for 50 cycles at 900°C is shown in Fig 5 and Fig 6. The oxide scale reveals the dominance phase in scale is Fe_2O_3 and along with this compounds of Fe_3O_4, Cr_2O_3, $NiCr_2O_4$ (Spinel) are also formed. At higher magnification the morphology of scale indicates that the oxide formed are layer wise i.e. one by one layer but the weight wise composition is approximately same. Surface morphology of 20MnMoNi55 sample salt oxidized are shown in Fig 5, indicate that growth of scale has done from inside (having Fe_2O_3 phase) as compare to the other spot and crack in scale has formed in middle. Due to crack and porous scale oxygen penetrates more to the substrate and which in turns oxidation rate is high.
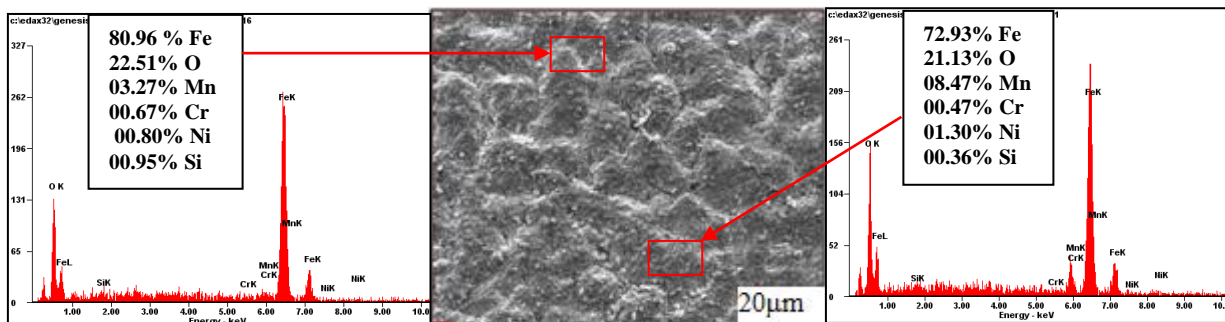
Fig 5. Surface scale morphology and EDAX analysis (wt %) for 20MnMoNi55 sample subjected to the cyclic oxidation at 900°C for 50 cycles in salt environment at scale of 20μm
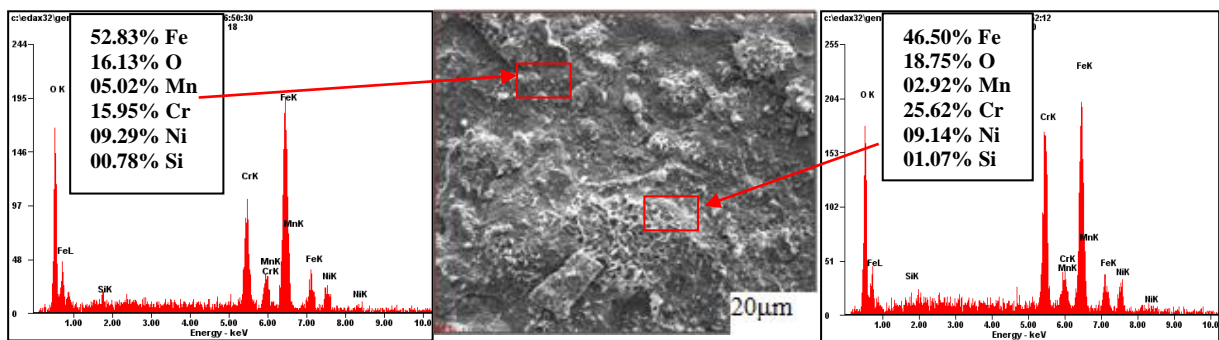

Fig 6. Surface scale morphology and EDAX analysis (wt %) for AISI 304 samples subjected to the cyclic oxidation at 900°C for 50 cycles in salt environment at scale of 20μm.

While surface morphology of AISI 304 corroded sample are shown in Fig 6, indicate that scale is mainly consist of Fe_2O_3, Cr_2O_3, $NiCr_2O_4$ (Spinel) with little amount of Fe_3O_4, and NiO is also

formed as said in XRD analysis and also compact nature of scale is formed . In other word we can say that diffusion of oxygen through scale is less, which

reveals that this substrate has high corrosion resistance as compared to 20MnMoNi55 steel.

3.4. Cross-sectional scale analysis

Fig.7 (a-b) shows the BSEI cross-sectional micrograph of 20MnMoNi55 and AISI304 steel with variation of elemental in scale. In 20MnMoNi55 salt corroded sample shown in Fig.7a shows a very thick oxide layer formed on surface. It shows that up to point 2, Fe is dominated i.e. Fe is more than O, as it is substrate. But at point 3 to 7, O is increasing & Fe is decreasing. At point 3, less amount of ferrous oxide is formed as compared to other point, due to

void and porous and at point 7 there is more ferrous oxide and at point 1 no oxygen but more amount of ferrous as it is substrate material. In AISI304 salt oxidised sample shown in Fig.7b shows a very thin and compact oxide layer on the surface. It shows that at point 7 i.e. outer edge, ferrous oxide is formed along with chromium oxide and spinel but at point 3ferrous oxide seems to be decreasing as compare to other points due to voids.
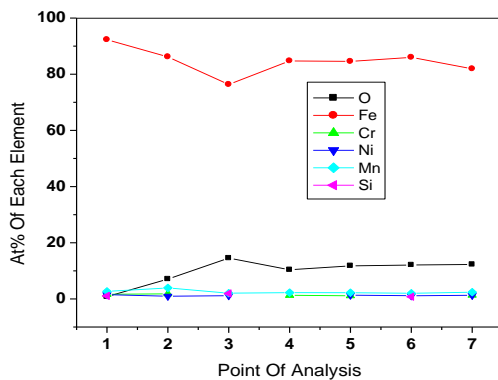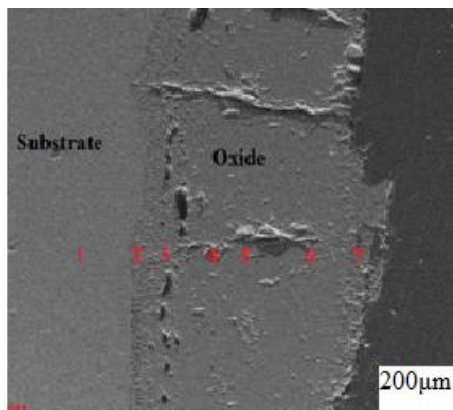

Fig 7(a).Oxide scale morphology and elemental variation across cross-section of 20MnMoNi55 exposed to salt environment at 900°C for 50 cycles.
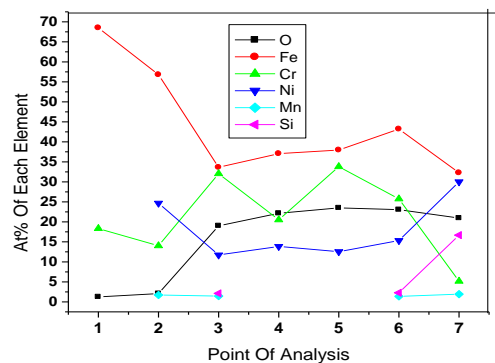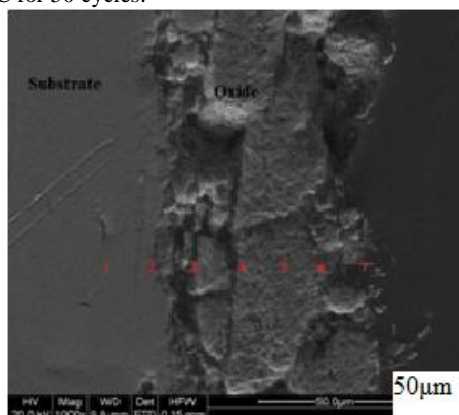


Fig 7(b).Oxide scale morphology and elemental variation across cross-section of AISI 304 exposed to salt environment at 900°C for 50 cycles.

4. Discussion

The results which were obtain till now states that corrosion resistance property of AISI 304 steel is better than 20MnMoNi55 steel as weight gain is more. Due to the mismatch in coefficient of thermal expansion in oxides scale from that of coating, internal oxidation further led to the cracking of the scale as said by Niranatlumpong et al. (2000). As there are various elements and each have different thermal coefficient of expansion hence there will be more stress generated which will lead to more cracking. Through these cracks, corrosive gases can penetrate to the base material and will thus allow significant grain boundary corrosion attack, Danyluk et al (1979). In spite of cracking, in some cases, little weight gain has been recorded. Extrusion of materials from beneath and oxide protrusions are believed to be due to the greater specific volume of oxides similar to the findings of Bornstein et al (1975). The better corrosion resistance of AISI 304 steels may also be attributed to the less amount of formation of a NiO layer in the scale. During EDS analysis it was observed that, very less amount of NiO layer was seen in the oxide scale of AISI 304 steel as compared to spinal phase. This layer has been suggested to be loose-structured by X. Wu et al (2001), which may not be able to provide effective protection, Niranatlumpong et al. (2000) have also suggested increase in the pore size of Ni and Cr scale with increase in exposure time, which allows the degrading species to penetrate through the coating there by resulting in the oxidation of substrate steels.
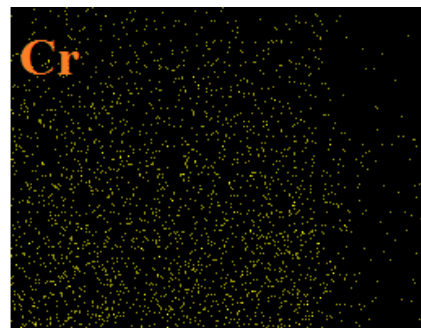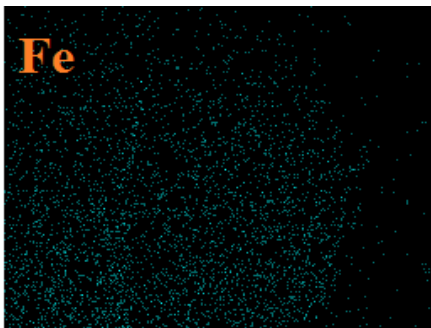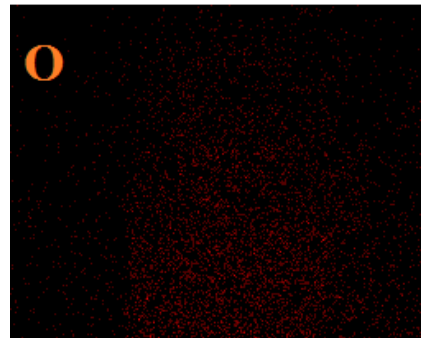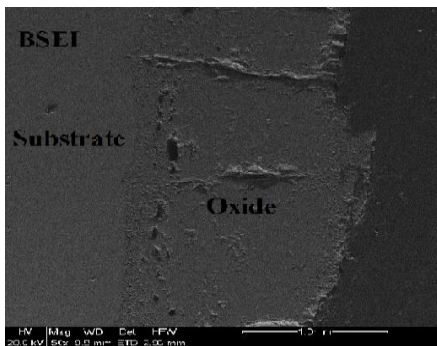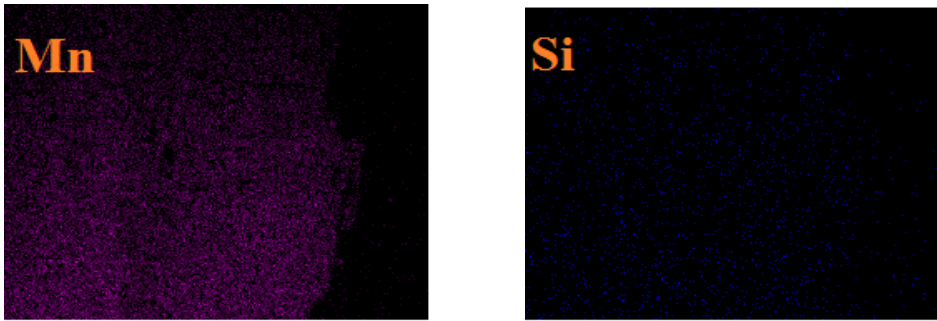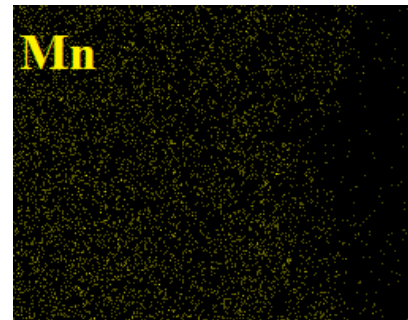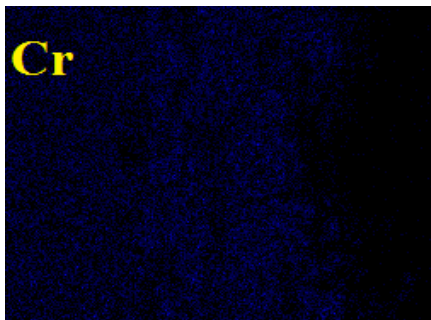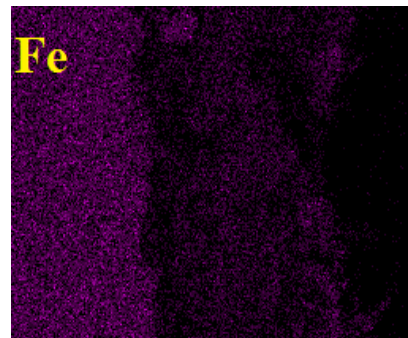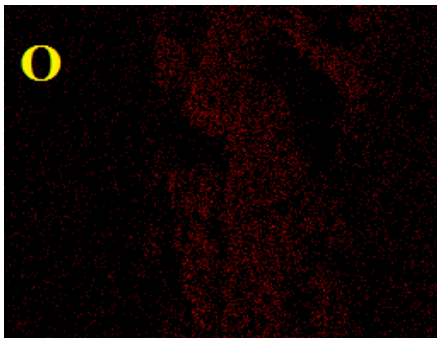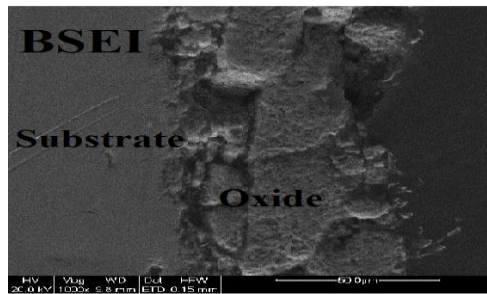
Fig. 8 BSEI and elemental X-ray mapping of the cross-section of 20MnMoNi55 sample exposed to cyclic hot corrosion at 900°C for 50 cycles in salt of 75wt.%Na_2SO_4+25wt.%K_2SO_4
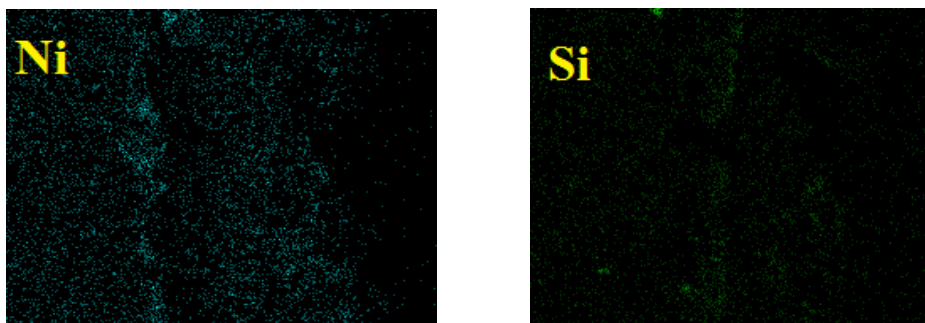
Fig. 9 BSEI and elemental X-ray mapping of the cross-section of AISI 304 sample exposed to cyclic hot corrosion at 900°C for 50 cycles in salt of 75wt.%Na_2SO_4+25wt.%K_2SO_4

5. Conclusion

1. The hot corrosion behaviour of AISI304 steel in salt follow parabolic nature where as in 20MnMoNi55 steel shows rapid increase in weight gain after 20th cycle.

2. In 20MnMoNi55 steel hematite (Fe_2O_3) formed at top surface with less amount of Cr_2O_3. In AISI304 steel Spinel is formed which is more protective layer. This shows that corrosion resistance of 20MnMoNi steel is less than AISI304 steel.

3. The Kp value of AISI304 steel is 0.162×10^{-10} g^2 cm^{-4} s^{-1} much low as compared 20MnMoNi55 steel 1.585×10^{-10} g^2 cm^{-4} s^{-1}.

4. AISI304 steel is found to be superior to 20MnMoNi55 steel and as per the cross section morphology the scale thickness of AISI304 steel is very thin as compared to 20MnMoNI55 steel.

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