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COMPARATIVE HOT CORROSION BEHAVIOR OF HVOF AND PLASMA SPRAYED NI20CR COATED T-22 STEEL IN ACTUAL COAL FIRED BOILER ENVIRONMENT

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ABSTRACT

Thermal spray process is commonly used to protect high temperature corrosions in coal or oil fired boiler due to the effectiveness of the technique. In this study the corrosion resistance of Ni20Cr coating sprayed by two thermal spray processes is compared. The HVOF and Plasma spray processes were used to deposit Ni20Cr coating powder on SA-213 (T22) boiler steel. Studies were performed on coated and bare specimens exposed to actual boiler environment at an average temperature of 700°C under cyclic conditions. The weights gain/lost analysis as well as thickness monitoring of unreacted portion was used to measure the corrosion kinetics in actual boiler environment. The XRD, FE-SEM/EDS and X-Ray mapping analysis were done to characterize the hot corrosion behavior in the given environments. The major phases formed in the Ni20Cr coated specimens are oxides of Ni, Cr, which are suggested to be protective barrier between the corrosive environment and substrate. It is found that Ni20Cr coated specimens offered high resistance to corrosion as compared to uncoated/bare specimen. An overall analysis of thermogravimetric, thickness monitoring, XRD and FE-SEM analysis showed that the HVOF spray process should be the better option for the given environment than Plasma spray process.

Keywords: Hot Corrosion, HVOF, Plasma spray process Thermo Gravimetric technique

I. INTRODUCTION

Materials used in the high temperature environment need to be sufficiently strong and resistant to high temperature corrosion for their safe and reliable usage. Many super alloys are available for these applications [1-4]. Further many surface engineering techniques are available to enhance performance of the materials used in high temperature applications. Thermal spraying is one the surface modification technique which is widely used and is an economical way. Various protective coatings are used on alloys in energy conversion and other high temperature applications to prevent surface from corrosion, erosion and abrasion [5-8]. Wide range of corrosion resistance and specially designed alloys are used for the protection of the surface at high temperatures. Materials rich in oxides formers such as Ni, Cr and Al, are needed to resist in high temperature and corrosive environment because of the formation of protective oxide scales on their surfaces at high temperature. Nickel and Cobalt based coatings are referred to as MCrAlY coatings, where M is the alloy base, it can be nickel, cobalt, or combination of these two. Various thermal spray techniques are available and selection for suitable technique depends upon the various factors like adjustability of the coating material to the intended application technique, level of adhesion, cost and availability of coating equipment [9-13]. Thermal spray techniques such as High Velocity Oxy Fuel (HVOF) and Plasma Spraying are often used to deposit nickel based high chromium coatings on the surface of the boilers tubes to control corrosion by creating a barrier to prevent penetration of hot gases and molten ashes [14-17].

In the present study comparative hot corrosion behavior in actual boiler environment of Ni20Cr powder sprayed by two different thermal spray processes, HVOF and plasma process on ASTM SA213 (T22) boiler steel was observed with the purpose to focus on the influence of the thermal spray process to enhance the hot corrosion resistance under cyclic conditions. Hot corrosion mechanism of coated and bare specimens was studied by

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employing thermogravimetric, X-ray diffraction (XRD), scanning electron microscopy/energy-dispersive analysis (SEM/EDAX) and X-Ray mapping techniques.

II. EXPERIMENTAL

1. Development of the coatings

Substrate material

The Fe-based substrate materials "ASTM-SA 213-A-1(T22)" was selected in this study and was collected from Guru Nanak Dev Thermal Power Plant, Bathinda. The actual and nominal chemical composition of the selected base materials has been provided in Table 1.

Table 1. Chemical composition (wt.%) of "ASTM-SA213 (T22) boiler steel

ALLOY GRADE ⇨	ASTM-SA213 T22	
⇩ Elements	Nominal	Actual
C	0.05-.15	0.15
Mn	0.30-0.60	0.47
Si	0.50 max.	0.35
S	0.025 max	0.021
P	0.025 max.	0.03
Cr	1.90-2.60	2.48
Mo	0,87-1.13	0.92
Fe		Balance

Coating powder

A commercially available 80Ni20Cr (by wt %) powder was used for coating and it was available at ANODE PLASMA LIMITED, KANPUR(U.P.) India. The scanning electron micrograph of the selected powder for coating has been shown in Fig. 1.

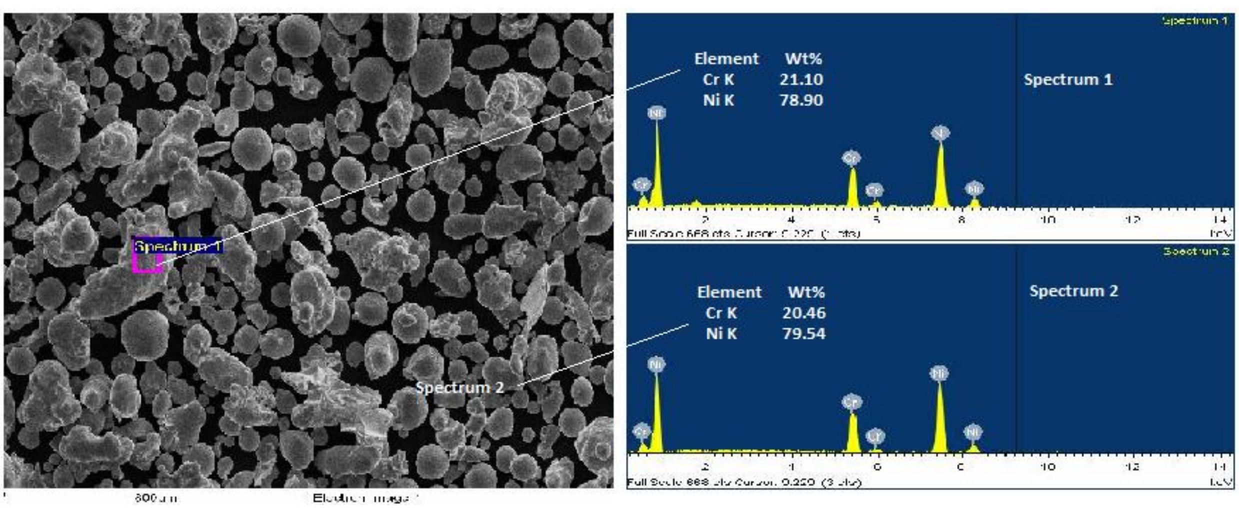

Fig. 1 SEM/EDAX analysis of 80Ni 20Cr coating powder.

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Coating formulation

Specimens of size approximately 20mm×15mm×5mm were cut from the boiler tubes. The specimens were then polished using SiC papers of 220 to 600 grit sizes, 1/0 to 4/0 grades polishing paper and then grit blasted before applying the coating. The purpose of polishing was for better adhesion between substrate and coating [18-20]. The Ni20Crcoating was deposited by using HVOF and Plasma Spray apparatus at ANODE PLASMA LIMITED, KANPUR, India.

2. Characterization of the as-sprayed coatings

X-Ray Diffraction analysis was performed on PANalytical diffractrometer (JSM-6510) apparatus at Thapar University, Patiala, Punjab, India. The samples were scanned in 2θ range of 20^o to 120^o with a scanning speed of 3^o/min. To understand the surface morphology of as coated specimens, Scanning Electron Microscope (JEOL6510LV; at Thapar University, Patiala) with EDAX Genesis software was used. Elemental compositions (weight %) at selected point/area was obtained by using EDAX genesis software. X-ray mapping of the cross-section was also performed. The area was selected in X-ray mapping in such a way that it can cover substrate, coating and epoxy for identification of cross-sectional details. The samples of size 15×5×5 were cut across its cross-section using wire cutting process. Samples were mounted by using cold epoxy in plastic rings and subjected to mirror polishing . The mounted samples were gold coated in order to have conductivity and then subjected to SEM/EDAX analysis for X-Ray mapping analysis.

3. Corrosion studies in Actual Coal Fires Boiler environment

The actual environment study was performed upto 10 cycles (100 hrs heating and 1 hr cooling) at Guru Nanak Dev Thermal Power Plant, Bathinda, Punjab, India. The specimens were hung in the boiler with the help of Kanthal wire. The temperature of the hanging zone was around 700^oC. All the specimens bare as well as coated were subjected to the given environment. The weight change data was collected after every cycle by using Electronic Precision Balance with a minimum count of 1 mg. The cumulative weight gain after 1000 hrs of exposure in the actual boiler environment was measured for all the specimens exposed to given environment. The remarkable weight gain was observed in bare specimens in actual boiler environment. Kinetics of corrosion was analyzed by weight change data. In actual boiler environment the weight gain may be due to formation of oxide scale or it may be due to deposition of ash particles [21,23]. So in boiler environment corrosion rate was also evaluated by measuring the thickness of unreacted portion of the samples after 1000hrs exposure. The thickness loss is measured in mils per year (mpy). Thickness loss in mm can be converted into mpy as following:

1 mm= 39.37 mils, so mpy = thickness lost in mm x 39.60 x 8760/1000

8760 is total hours in a year and 1000 total exposure time (hrs) in boiler

The specimens were subjected to X-Ray Diffraction, SEM/EDS and X-Ray mapping analysis of surface after the exposure in actual boiler environment.

III. RESULTS AND DISCUSSION

1. Characterization Of The As-Sprayed Coating

Visual observations of the as-sprayed coating

The Ni20Cr coating was deposited on ASTM-SA213 (T22) boiler steel using HVOF and plasma spraying processes. The macrographic appearance of Ni20Cr coated specimens was dark grey in color with smooth, homogenous and crack free in both the HVOF and plasma spray techniques. The macrograph of as coated ASTM-SA213 (T22) boiler steel is shown in Fig.2.

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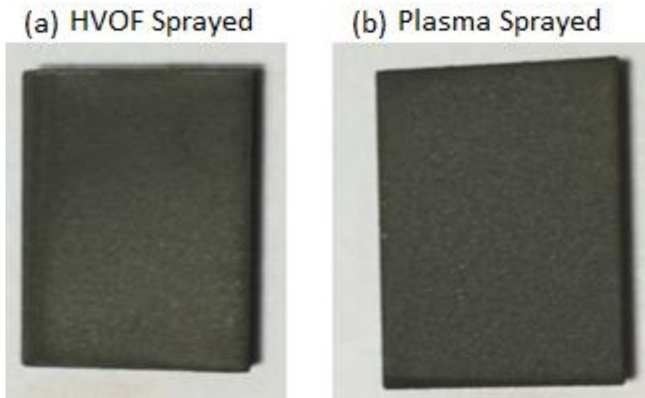

Fig. 2 Macrographs of the (a) HVOF sprayed and (b) Plasma sprayed Ni20Cr coating on ASTM-SA213-T22 boiler steel

Surface morphology of the coating

The SEM/EDS micrographs of HVOF and Plasma sprayed Ni20Cr coating on ASTM-SA213-T-22 boiler steel as coated is shown in Fig.3a,b. The microstructure consists splats of irregular shape and flat appearance. Particle deformation is due to the high impact during the coating process. Larger size splats in case of HVOF sprayed coatings was observed as compared to Plasma coating. Elemental analysis indicated that the presence of Ni, Cr and O on the surface of the coating which is similar to the powder used for coating.

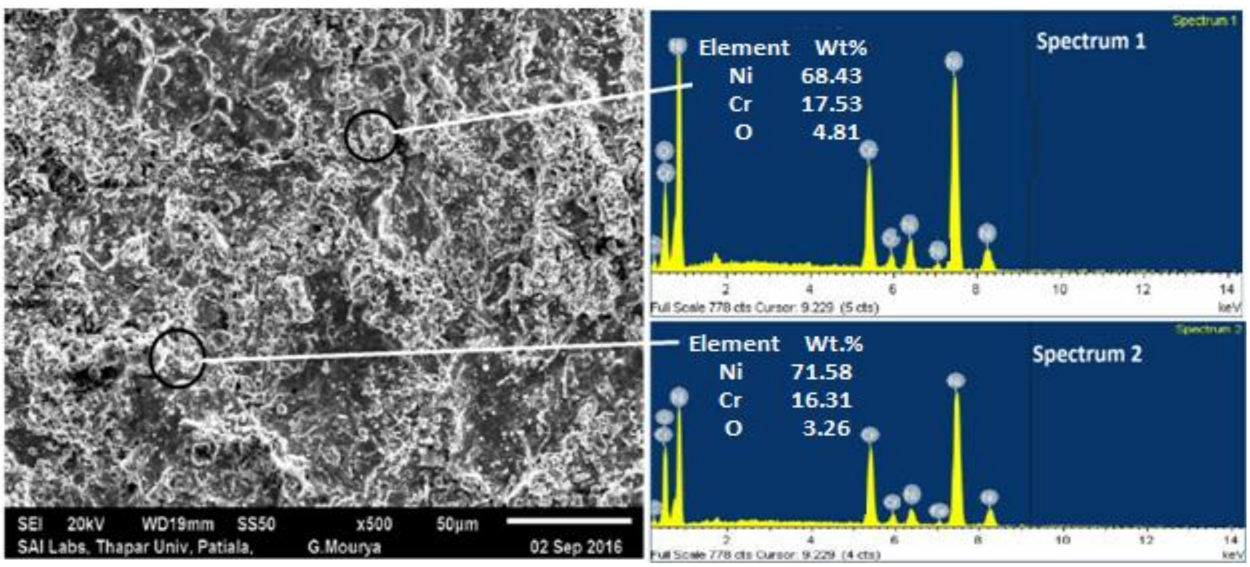

Fig.3a. Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of HVOF sprayed 80Ni20Cr as coated ASTM-SA213-T22 boiler steel

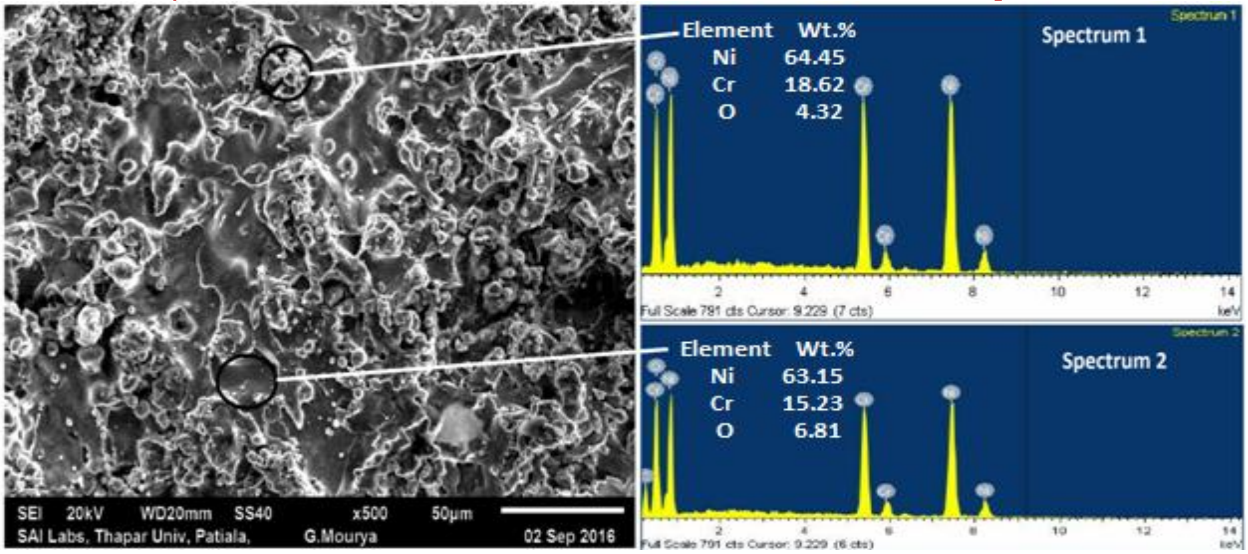

Fig. 3b. Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of Plasma sprayed 80Ni20Cr as coated ASTM-SA213-T22 boiler steel

X-Ray Diffraction Analysis

The XRD diffraction plots of the as coated, bare and Ni20Cr coated specimens subjected to actual environment, SA213 (T22) have been shown in Fig. 4. The main phases of Ni and Cr are revealed in XRD plots of as coated specimens.

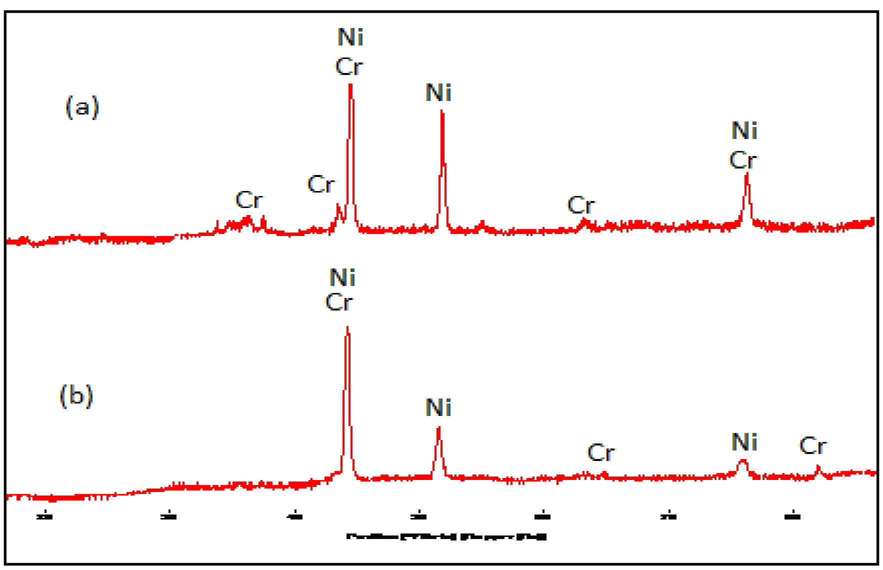

Fig. 4 X-Ray Diffraction pattern of as coated (a) Plasma sprayed and (b) HVOF sprayed Ni20Cr coating on ASTM-SA213-T-22 boiler steel

X-ray mapping analysis

The X-Ray maps across the cross section for HVOF and Plasma sprayed 80Ni20Cr coated on SA213 (T22) specimens as coated are shown in the Fig. 5a,b. Presence of Ni, Cr and O can be observed from the X-Ray maps.

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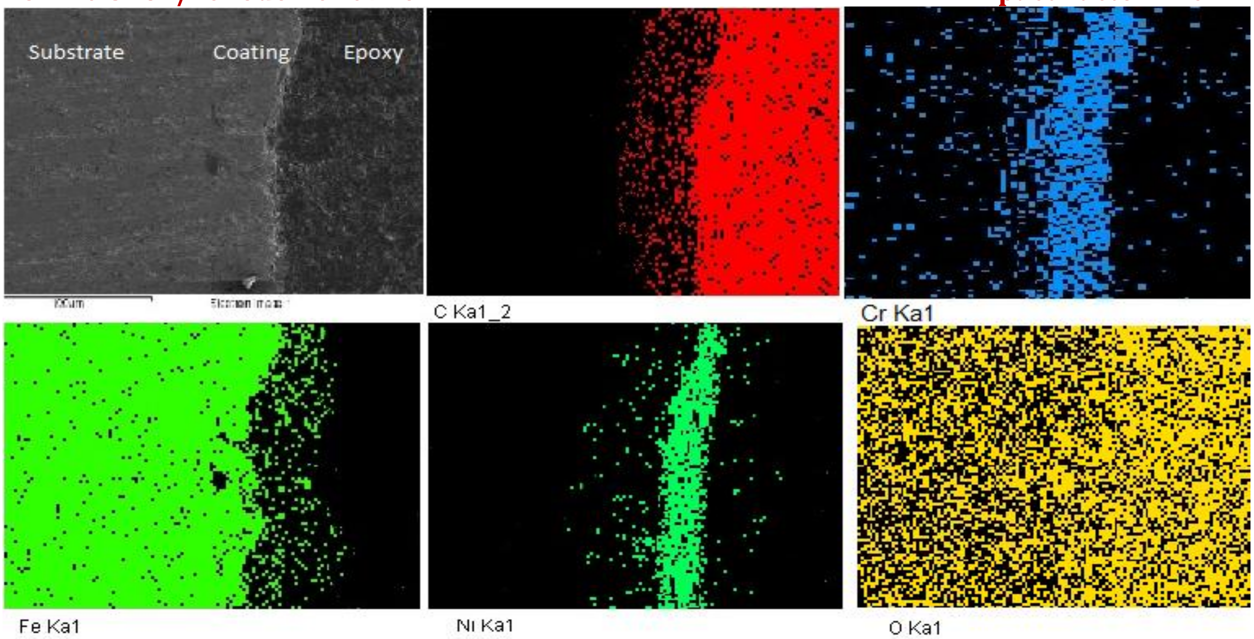

Fig. 5a. SEM micrograph and X-ray mapping along the cross-section of the HVOF sprayed Ni20Cr as coated on ASTM-SA213 (T22) boiler steel.

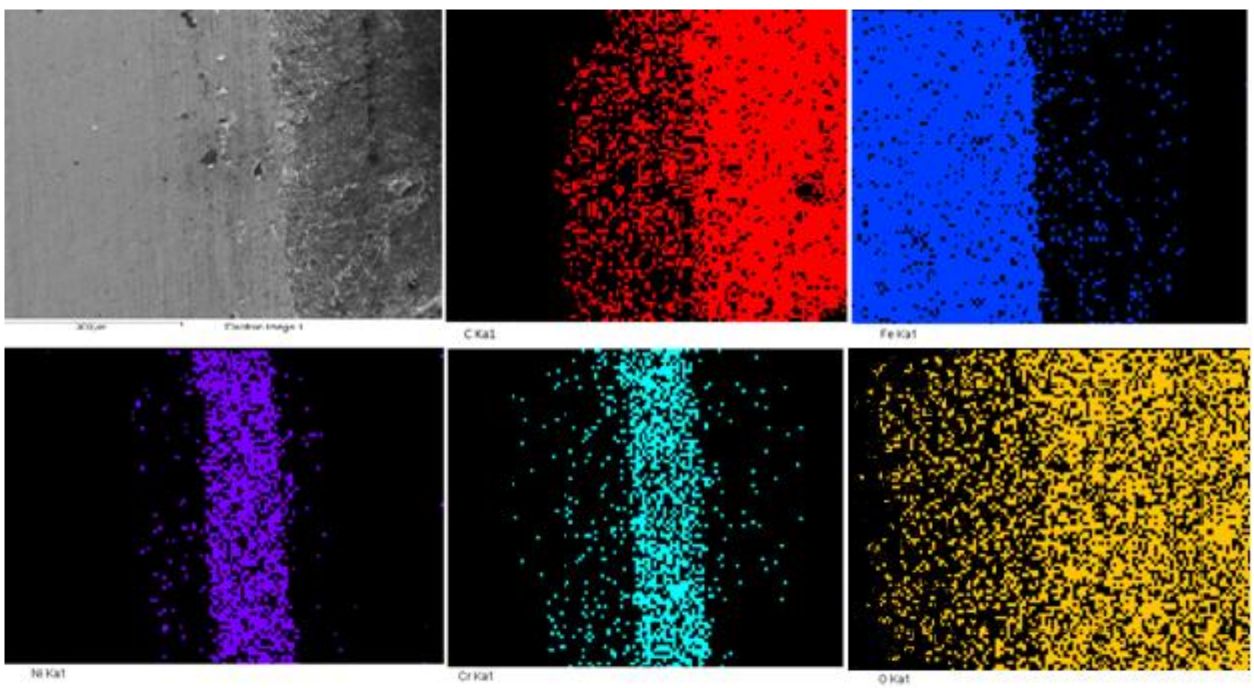

Fig. 5b. SEM micrograph and X-ray mapping along the cross-section of the Plasma sprayed Ni20Cr as coated on ASTM-SA213 (T22) boiler steel.

2. Corrosion Studies In Actual Boiler Environment

Corrosion Kinetics

Weight Gain/Loss Analysis and Thickness Monitoring

The thermogravimetric as well as the thickness lost analysis was done to investigate the kinetics of the corrosion in the actual boiler environment of the coated as well as bare specimens. In thermogravimetric technique in weight per unit area (mg/cm^2) was measured after every cycles and then cumulated weight gain was calculated at the end of 10 cycles. each cycle was made of 1000hrs heating and 1hr cooling. It was observed that weight gain was maximum in bare T-22 specimen followed by Plasma coated and HVOF coated T-22 specimens in actual boiler environment as shown in the Fig.6a,b.

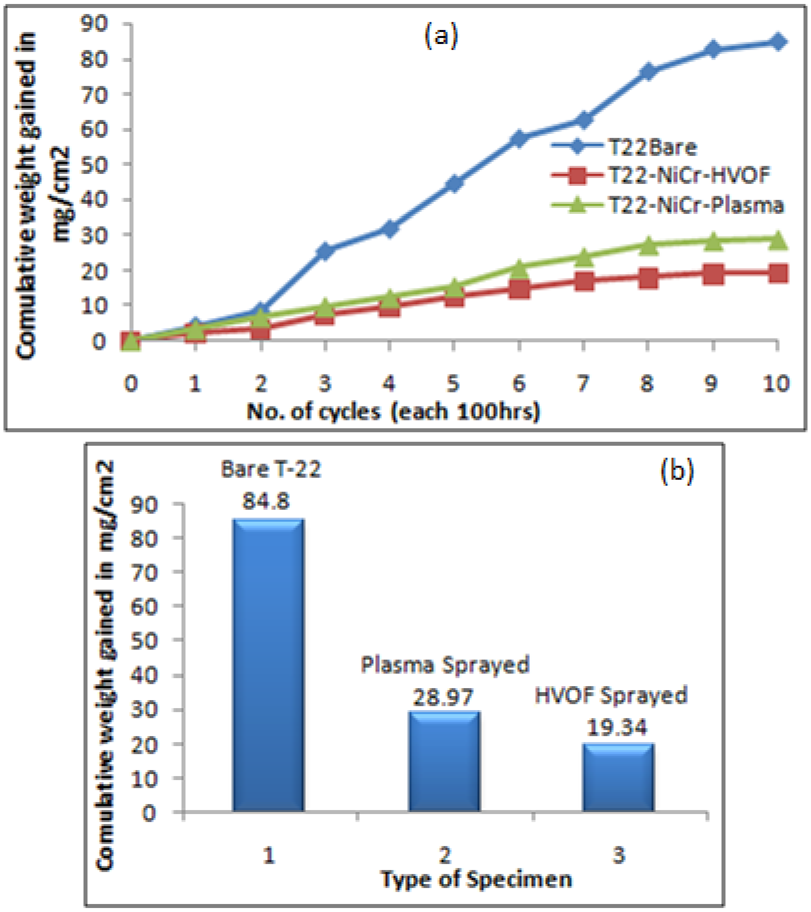

Fig.6. (a) Weight change per unit area vs. number of cycles plot; (b) Cumulative weight gain; for the uncoated, HVOF and Plasma sprayed Ni20Cr coating on ASTM-SA210-A-1 boiler steel subjected to hot corrosion in actual environment.

The weight gains for the bare specimen was reduced by 77.2% in HVOF sprayed specimen and 65.8% in plasma sprayed specimen. Weight change analysis is a good indicator of corrosion rate but in actual boiler environment it is less significant because weight can change due to oxide formation and ash deposition. So in addition to thermogravimetric analysis, thickness of the unreacted portion of all the specimens were also monitored. It was found in the cross sectional analysis that the thickess lost of bare specimen was 0.31mm or 107.63 mpy but in the case of HVOF and plasma coated specimens, no thickness lost was found.

Visual Observation

The macrographs for the bare T-22 and HVOF and Plasma prayed Ni20Cr coating on T-22 after the completion of 10 cycles of each 100 hrs exposure to coal fired boiler are shown in Fig.7.

The scale of the coated specimens was grey in color with brown and greenish stains. The surface of the coated specimens was free of cracks and without any spalling and degradation. In case of bare specimen dark brown colored scale was observed which was sticking out of the surface.

Fig.7. Macrographs of the bare, Plasma and HVOF sprayed specimens subjected to actual boiler environment.

FE-SEM/EDS ANALYSIS

Surface analysis of bare T22, HVOF and Plasma sprayed Ni20Cr specimens subjected to actual boiler environment is shown in Fig.8a-c. It is revealed in the EDS analysis that the oxide scale of the uncoated specimen is mainly consist of Fe, O and C. The large amount of weight gain is due to salt deposition on the surface. Small amounts of Na, Si, S, and P are also observed in the scale, which can be due to boiler environment. In case of coated specimens dense oxide scale was appeared which was mainly consist of Ni, Cr and oxygen. Presence of small amounts of Na, Si, S, C and S is due to the ash content in the scale.

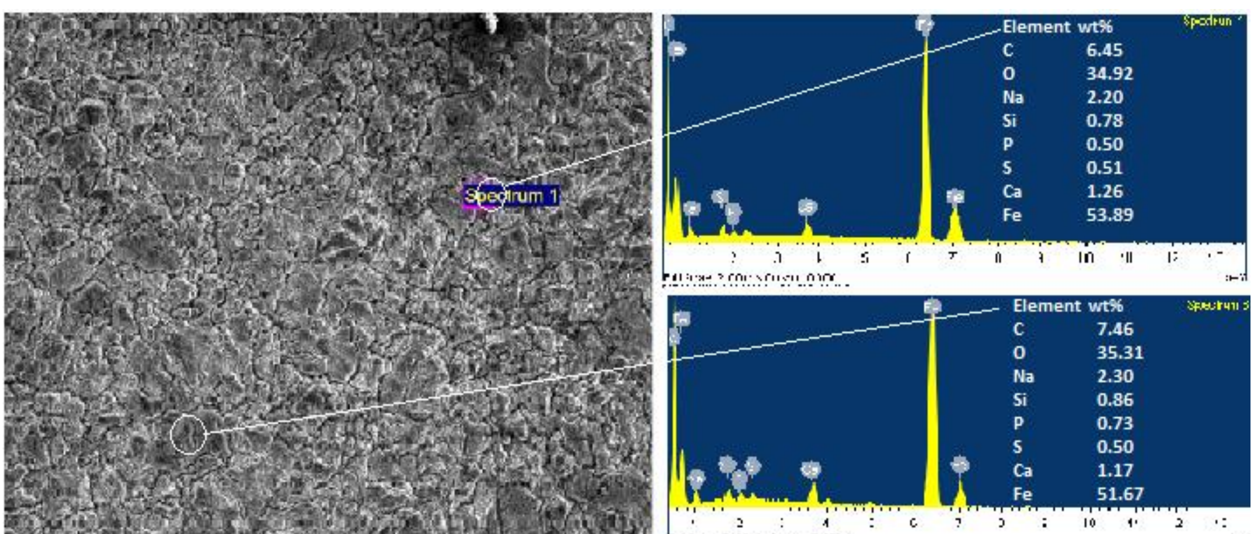

Fig. 8a. Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of bare ASTM-SA213-T22 boiler steel exposed to actual boiler environment

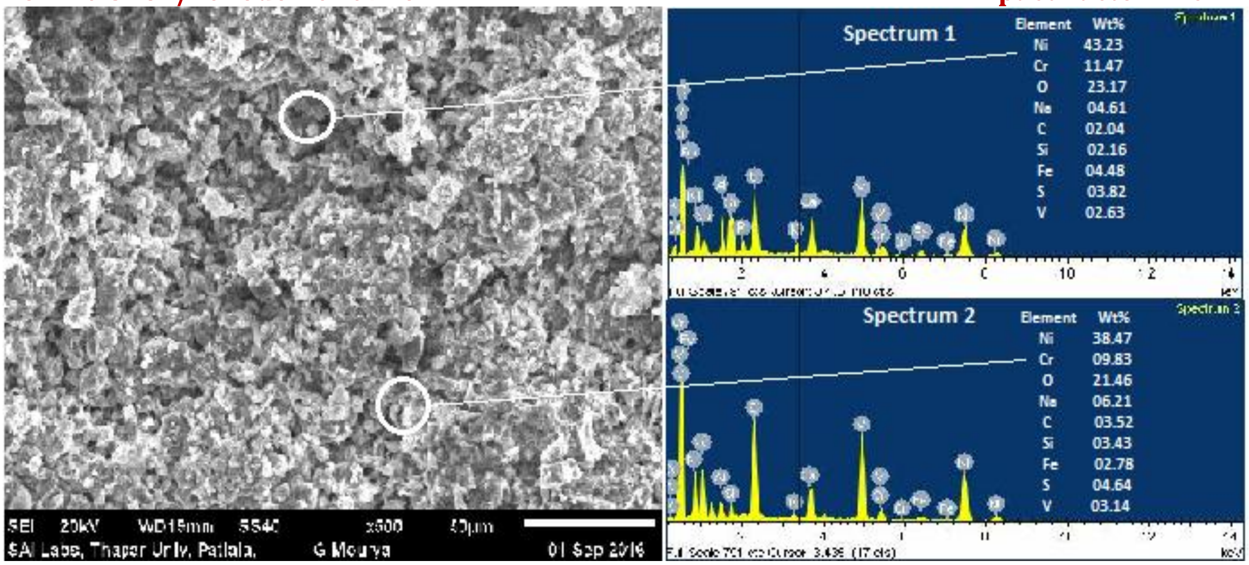

Fig. 8b. Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of HVOF sprayed 80Ni20Cr coated specimen exposed to actual boiler environment

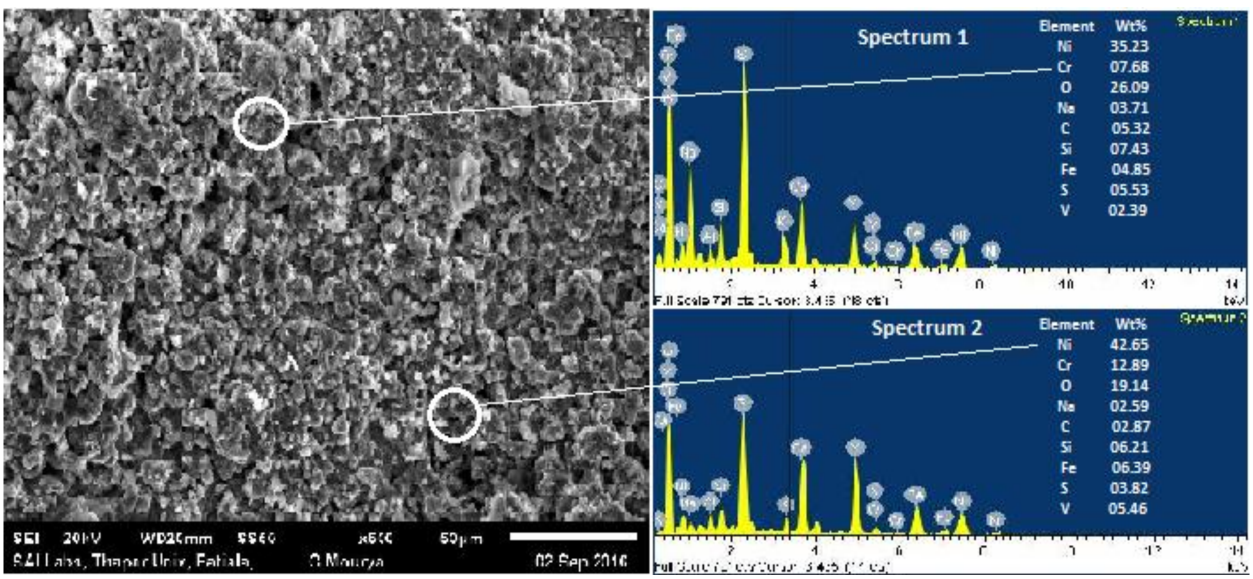

Fig. 8c. Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of Plasma sprayed 80Ni20Cr coated specimen exposed to actual boiler environment

X-Ray Diffraction Analysis

The phases identified in the XRD analysis for HVOF and Plasma sprayed Ni20Cr specimens after the exposure to given environment are shown in Fig. The X-Ray plots of bare metal indicated the strong peaks for Fe_2O_3 and some weak peaks for FeV_2O_4 and C_2O_3. In case of coated specimens strong peaks for NiO, and some medium peaks for Cr_2O_3 and $NiCr_2O_4$ oxides were observed in X-ray diffraction plots.

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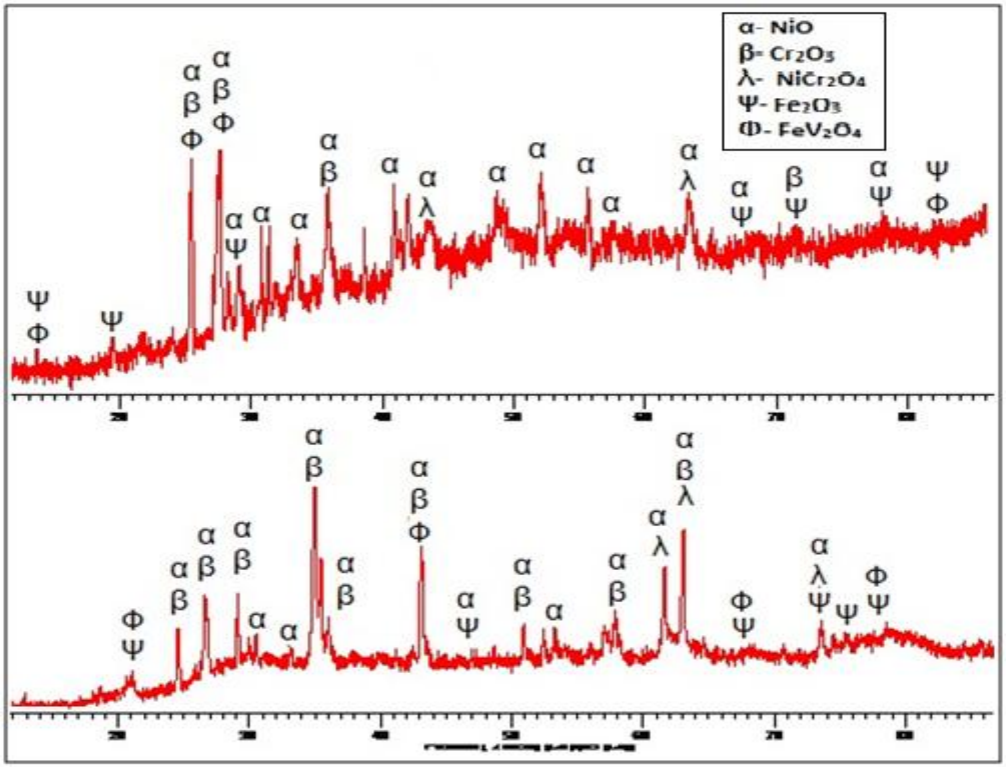

Fig. 9. X-Ray Diffraction pattern of (a) Plasma sprayed and (b) HVOF prayed Ni20Cr coating on ASTM-SA213-T-22 boiler steel exposed to given environment.

X-Ray Mapping Analysis

X-Ray maps for uncoated, HVOF and Plasma Ni20Cr coated specimens after the exposure to actual boiler environment at 700oC for 1000 hrs are shown in Fig.10a-c. In uncoated specimen the presence of Fe and O in the oxide scale indicate the formation of Fe_2O_3. It can be observed in cross sectional analysis that the thickness of unreacted metal has reduced indicate high corrosion rate. In the case of HVOF and Plasma coated specimens the dense oxide scale was observed which was mainly consist of Ni,Cr and O indicating the formation of protective oxide such as NiO, Cr_2O_3 and $NiCr_2O_4$. The presence of small amounts of Na, Si, S, and P can be due to boiler environment.

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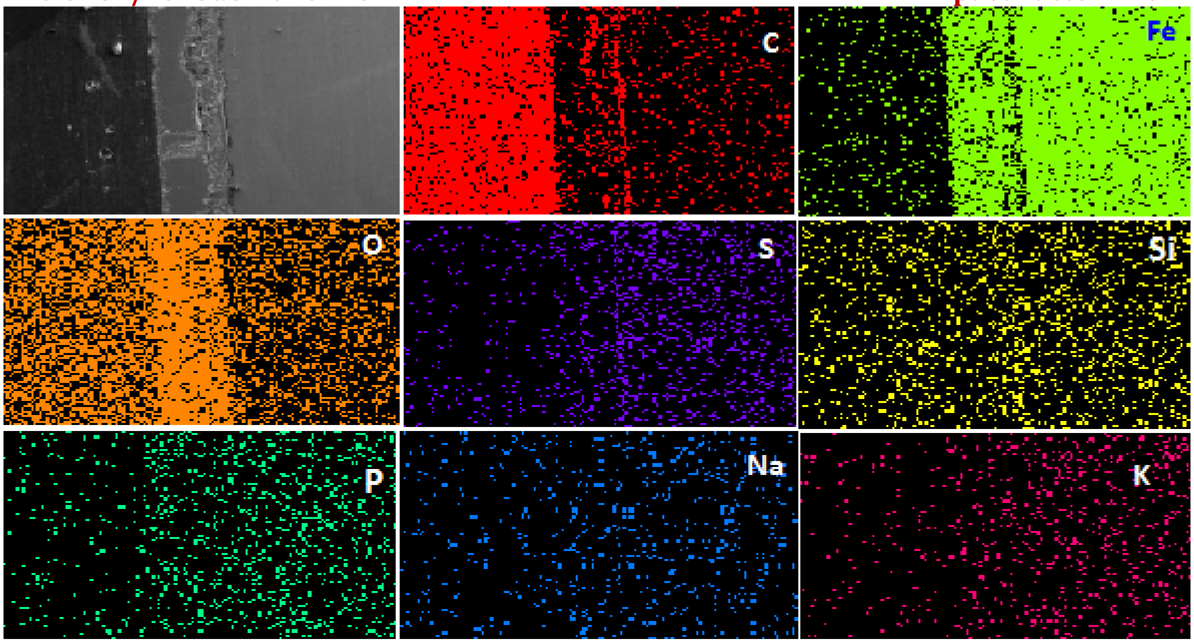

Fig. 10a. SEM micrograph and X-ray mapping along the cross-section of the bare specimen exposed to given environment.

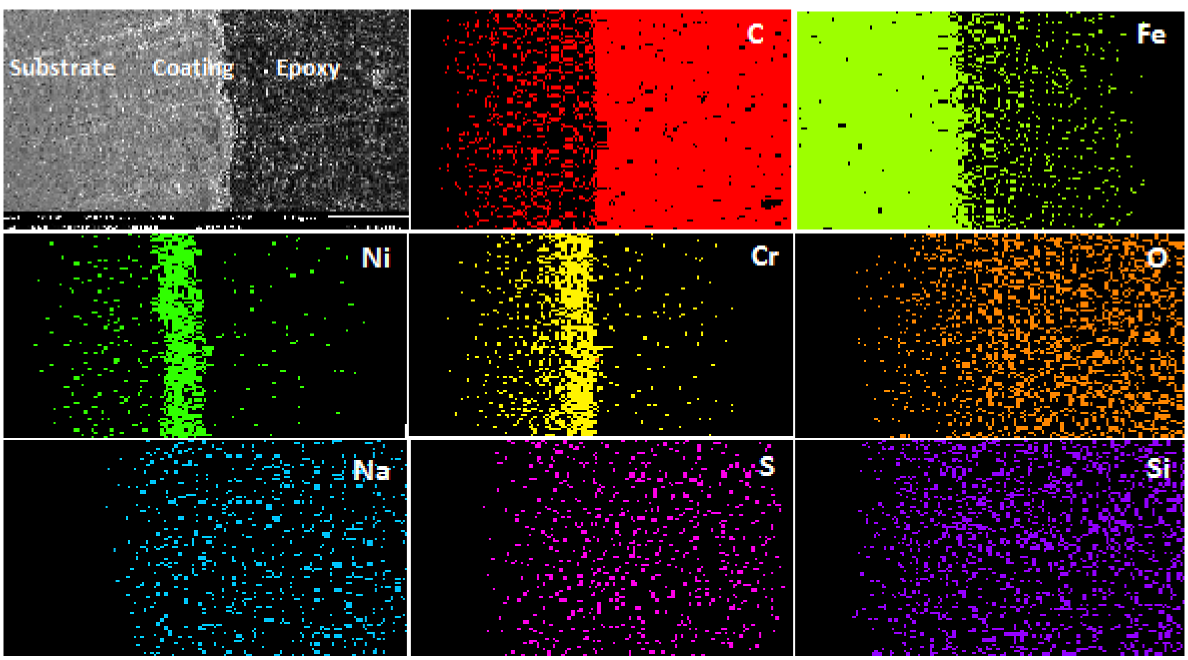

Fig. 10b. SEM micrograph and X-ray mapping along the cross-section of the HVOF sprayed 80Ni20Cr coated specimen exposed to given environment.

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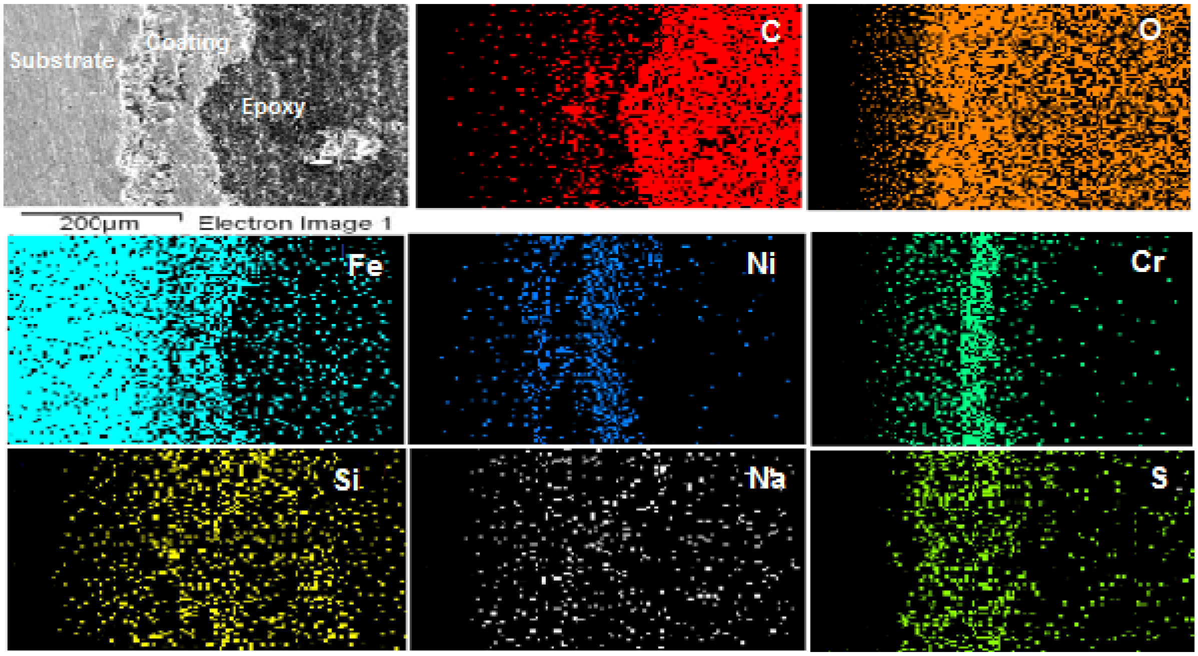

Fig. 10c. micrograph and X-ray mapping along the cross-section of the HVOF sprayed 80Ni20Cr coated specimen exposed to given environment.

IV. CONCLUSION

- The uncoated SA213 (T22) boiler steel showed severe spalling of oxide layer when exposed to actual boiler environment as compared to HVOF and Plasma sprayed Ni20Cr coated specimens. The Thermal Spraying techniques used were successful in controlling the corrosion in actual boiler environment without any spalling.
- In Ni20Cr coated specimens the presence of protective scales NiO, Cr_2O_3 and $NiCr_2O_4$ was confirmed from the phases shown in XRD and EDS analysis when exposed to actual boiler environment.
- The HVOF sprayed Ni20Cr coating has shown the better corrosion resistance in actual boiler environment at 700oC than the plasma sprayed coating . The weight gains for the bare specimen was reduced by 77.2% and 65.8% by applying HVOF and plasma spray coatings respectively.

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