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COMPARATIVE STUDY OF HOT CORROSION BEHAVIOR OF HVOF AND PLASMA SPRAYED NI20CR COATING ON SA213(T22) BOILER STEEL IN NA_2SO_4-60%V_2O_5 ENVIRONMENT

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ABSTRACT

Material deterioration is a major issue in various high temperature applications. So it is important to understand the mechanism of hot corrosion in metals/alloys at high temperatures and to provide the protective coating for their economic, reliable and safe operation. Nickel based coatings are commonly used for the enhancement of resistance against the hot corrosion. These coatings can be developed by using different thermal spray techniques. The present investigation is an attempt to compare the resistance offered against hot corrosion by Nickel based coating sprayed by two different thermal spray techniques. Coating powder containing 80%Ni20%Cr was deposited on SA-213 (T22) using two thermal spray techniques, HVOF and Plasma spray. Hot corrosion studies were performed in Na_2SO_4-60%V_2O_5 environment at 900ºC under cyclic conditions on bare and coated specimens. Thermo-Gravimetric, Scanning Electron Microscope SEM/EDS and X-ray diffraction tests were performed to examine the hot corrosion behavior. It was found that both thermal spray techniques used in the present study were successful in controlling the hot corrosion of 80Ni20Cr coated specimens. Mass gain in HOVF sprayed coated specimen was minimum, followed by Plasma coating and bare metal. From the results of various analysis techniques used, it may be suggested that the HVOF sprayed coating provided the better resistance to hot corrosion than plasma sprayed coating in the given environment

KEYWORDS: Hot Corrosion, Plasma spray process Thermo Gravimetric.

I. INTRODUCTION

Boiler is an important part of power generation plants. It must be reliable and kept in good working conditions. With increasing raw material costs, maintaining the reliability and consistent performance while minimizing energy costs is a big challenge for any industrial plant. Boiler tubes are generally made of carbon steel, so the chances of hot corrosion are high, which can cause unexpected shutdown of industrial unit [1-4]. Understanding the mechanism of hot corrosion in metals/alloys at high temperatures and providing the suitable solutions has attracted the interest of many scientists long ago. In coal fired boilers hot corrosion is the main problems that occurs at 700 to 750°C, where the corrodents are in liquid form. It is induced by a thin layer of fused sulphate and chloride salts containing alkali metals of sodium and potassium. Sulphur present in coal produces SO_2 which further oxidizes to SO_3 and reacts with metal surface [5-7]. The impurities present in fuel used such as Sulphur, Sodium and Vanadium, causes the material deterioration. Reactions between these contaminants in the presence of oxygen/air causes ash deposits, like sodium sulfate (Na_2SO_4), sodium metavanadate ($NaVO_3$) and vanadium pentaoxide (V_2O_5), which lead to severe corrosion [8,9]. The hot corrosion may cause failure and unsafe operation of boiler. Thus the overall efficiency of power plant is reduced due to high rate of corrosion. To overcome this problem a protective enclosure of materials from the surrounding environment should be created [10-13]. Surfacing is a technique in which a layer of superior material on the substrate of sufficient mechanical strength is deposited to enhance the surface properties like corrosion/ oxidation and wear resistance. Thermal Spray Processing is a rapidly growing field of surface engineering and widely used to protect metal/alloy substrates against hot corrosion [14-17]. Because of incommensurable conditions taking part in converting coal to gas, a complete knowledge of the different factors effecting corrosion is required in the selection of base materials and coatings. Fireside corrosion of boiler tubes in coal fired boilers depends upon the coal chemistry, combustion conditions and operating

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temperature [19, 20]. Nickel based metallic alloy coatings are broadly used because of the high resistance offered by chromium, nickel-chromium alloys against high temperature oxidation and corrosion. Ni-Cr coatings are thermally sprayed in coal fuel-fired boiler tubes and other high temperature applications [21-25]. Corrosion can also be controlled by removing the impurities from the coal, adjustment of firing rate, quantity of extra air, air temperature, amount of recirculating flue gas and effective boiler design [25-28].

In the present study hot corrosion behavior of 80%Ni-20% Cr (by wt.) coatings sprayed by high-velocity oxy-fuel (HVOF) and plasma spray process on ASTM SA213 (T22) boiler steel was observed. There is very less reported literature on comparative hot corrosion behavior of Ni20Cr coating sprayed on the selected substrates by HVOF and plasma spray technique. The purpose of present work is to focus on the influence of the thermal spray process to enhance the hot corrosion resistance of Ni20Cr coating on SA213 (T22) substrate; in an harsh environment of Na_2SO_4-60%V_2O_5 molten salt at 900°C under cyclic conditions. Hot corrosion mechanism of coated and bare specimens was studied by employing thermogravimetry, 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 selected for this study, namely "ASTM-SA 213-A-1(T22)" after consulting the authorities of Guru Nank Dev Thermal Power Plant, Bathinda. The chemical composition of the selected base materials has been provided in Table 1; presenting the nominal and actual composition.

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. The coating powder was available at ANODE PLASMA LIMITED, KANPUR (U.P.) India. A SEM (scanning electron microscope) image of the selected powder for coating has been shown in Fig. 1 showing the powder particles morphology.

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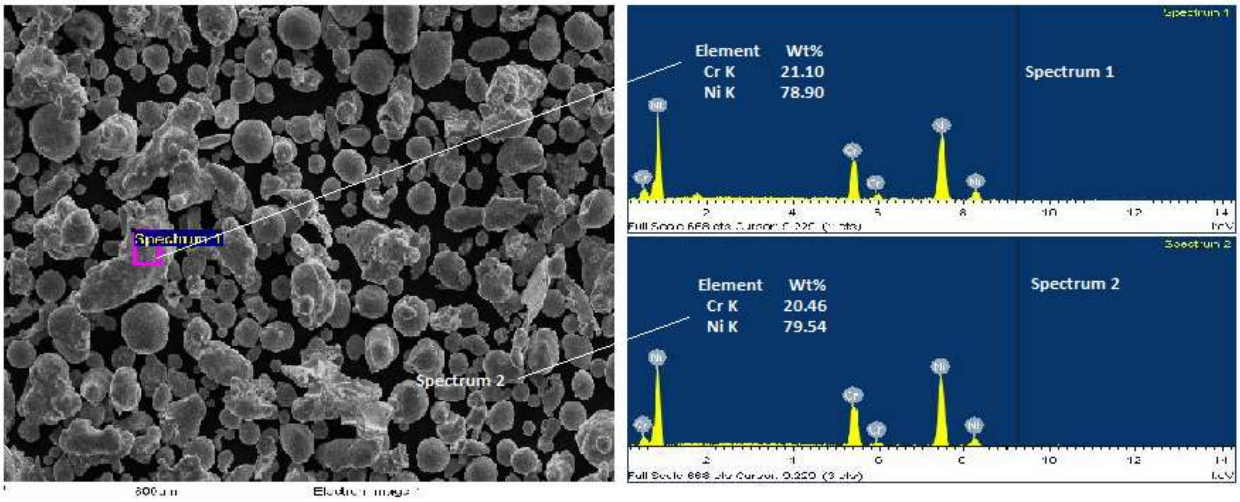

Fig. 1 SEM/EDAX analysis of 80Ni 20Cr coating powder.

Coating formulation

Specimens of size measuring approximately 20mm×15mm×5mm were cut from the boiler tubes and polished using SiC papers of 220 to 600 grit sizes & 1/0 to 4/0 grades. The specimens were then cleaned and grit blasted with Al_2O_3 before application of coating for better adhesion. The deposition of coatings on the substrate using HVOF and Plasma Spray apparatus was carried out at ANODE PLASMA LIMITED, KANPUR (U.P.) India.

2. Characterization of the as-sprayed coatings

PANalytical diffractometer (Netherlands) apparatus was used to perform X-Ray Diffraction tests. The samples were scanned in 2θ range of 20° to 120° with a scanning speed of 3°/min. Further the Scanning Electron Microscope JSM-6510 with EDAX Genesis software attachment and (JEOL6510LV; at Thapar University, Patiala) fitted with an EDAX attachment; were used the surface characterization and with X-ray mapping of the cross-section was also performed. SEM images and EDS were taken with an electron beam energy of 20 keV. For identification of cross-sectional details, the samples of size 15×5×5 were wire cut across its cross-section. Mounting of samples was done by cold epoxy in plastic rings using cold setting resin and hardener in equal proportion and subjected to mirror polishing using SiC papers of 220 to 600 sizes and afterward on 1/0 to 4/0 grades. Alumina powder was used for fine polishing. The samples were then examined using the SEM/EDAX for surface characterization and cross-sectional analysis and compositions of the elements in the coatings.

3. Hot corrosion study in molten salt environment

The polished specimens were exposed to accelerated hot corrosion. A coating of Na_2SO_4-60%V_2O_5, 3 to 5 mg/cm^2 by weight was applied on all the preheated (250°C) specimens (coated/bare) with uniform thickness. Hot corrosion studies were performed up to 50 cycles at 900 °C temperatures in a silicon carbide tube furnace, each cycle was of 60 min of heating at 900°C and then cooling at room temperature for 20 min. Specimen was positioned in an alumina boat (supplied by KUMAR CERAMICS, CHENNAI) and then placed in the furnace. All the specimens the 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. Kinetics of corrosion was analyzed by weight change data. Surface and cross-sectional analysis of all the specimens was performed by using X-Ray Diffraction and SEM/EDS techniques.

III. RESULTS

1. Characterization Of The As-Sprayed Coating

Visual observations of the as-sprayed coating

The 80%Ni20%Cr coating was formulated 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 for both the specimens coated by HVOF and plasma spray techniques.

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Surface morphology of the coating

The SEM images and EDS of HVOF and Plasma sprayed 80%Ni20%Cr coating on ASTM-SA213-T-22 boiler steel as coated, coated specimens undergone through hot corrosion as well as bare boiler steel is shown in Fig.2a-e. The microstructure consist splats of irregular shape and flat appearance. The size of the splats in case of HVOF sprayed coatings was observed as comparatively larger than of Plasma coating. EDS analysis showed that the Ni and Cr on the surface of the coating were present and it is nearly similar to the powder used for coating. In the case of hot corroded bare sample, oxide scale was composed of Fe and O, this show the presence of Fe_2O_3 oxide scale. In case of Plasma spray process the splat is very irregularly shaped, flat and circular. The EDS analysis, the presence of oxides of nickel, chromium and iron is indicated by dark areas on the surface. Particle deformation is due to the high impact during the coating process.

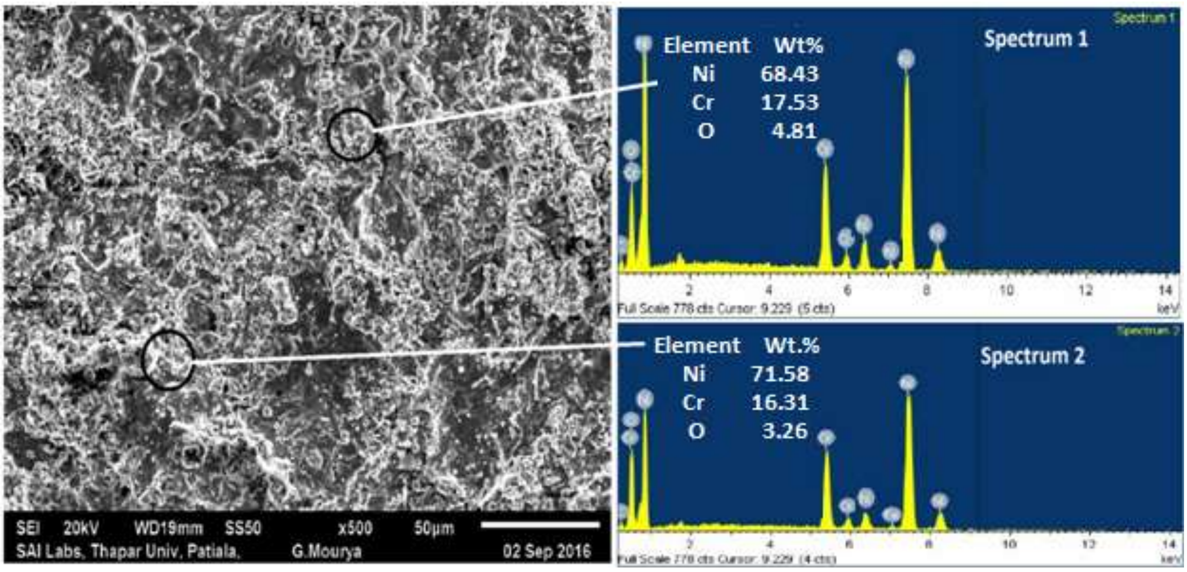

Fig.2a. Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of HVOF sprayed 80Ni20Cr as coated ASTM-SA213-T22 boiler steel

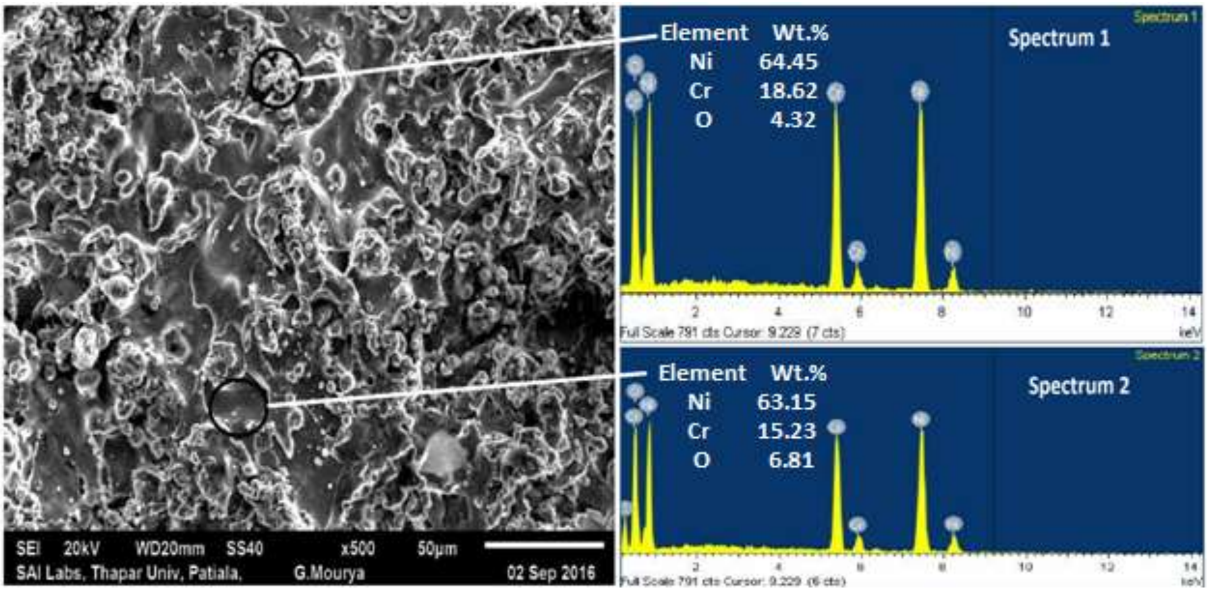

Fig. 2b. Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of Plasma sprayed 80Ni20Cr as coated ASTM-SA213-T22 boiler steel

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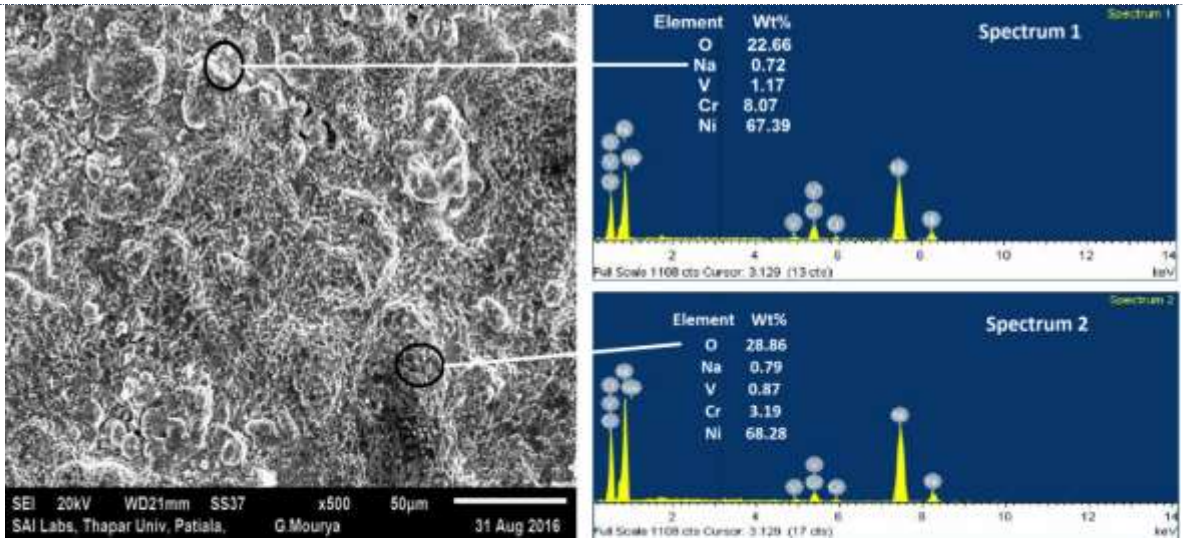

Fig. 2c. *Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of HVOF sprayed 80Ni20Cr coated specimen exposed to given environment.*

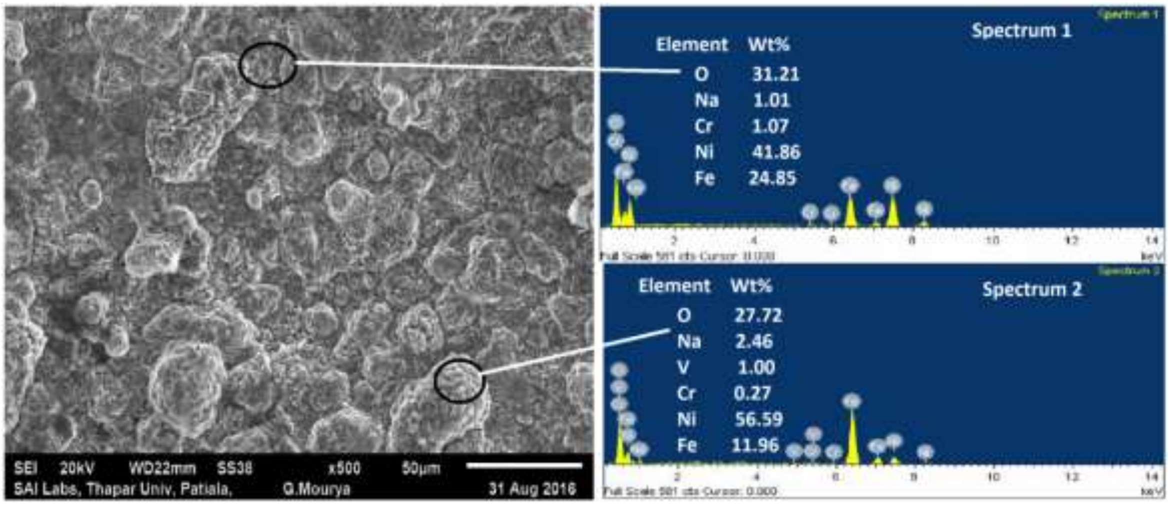

Fig. 2d. *Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of Plasma sprayed 80Ni20Cr coated specimen exposed to given environment.*

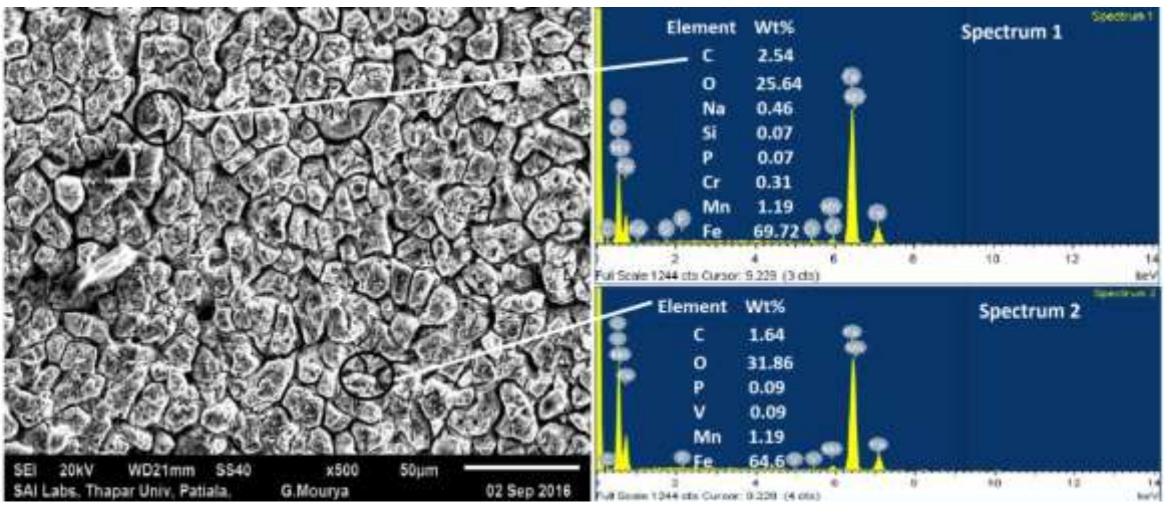

Fig. 2e. *Surface scale morphology and EDS analysis showing elemental composition (wt%) at selected points of bare ASTM-SA213-T22 boiler steel after hot corrosion*

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X-Ray Diffraction Analysis

The XRD diffraction graphs of the as coated, coated specimens undergone hot corrosion as well as bare boiler steel, HVOF-sprayed and Plasma sprayed Ni–20Cr coated SA213 (T22) steel exposed to given environment have been depicted in Fig. 3a–b respectively. It is observed that the scale of the bare metal consist of Fe_2O_3 phase as the main phase and some weak peaks for FeV_2O_4 and Cr_2O_3 can also be seen. In coated specimens, the presence of NiO, Cr_2O_3 and $NiCr_2O_4$ oxides can be observed.

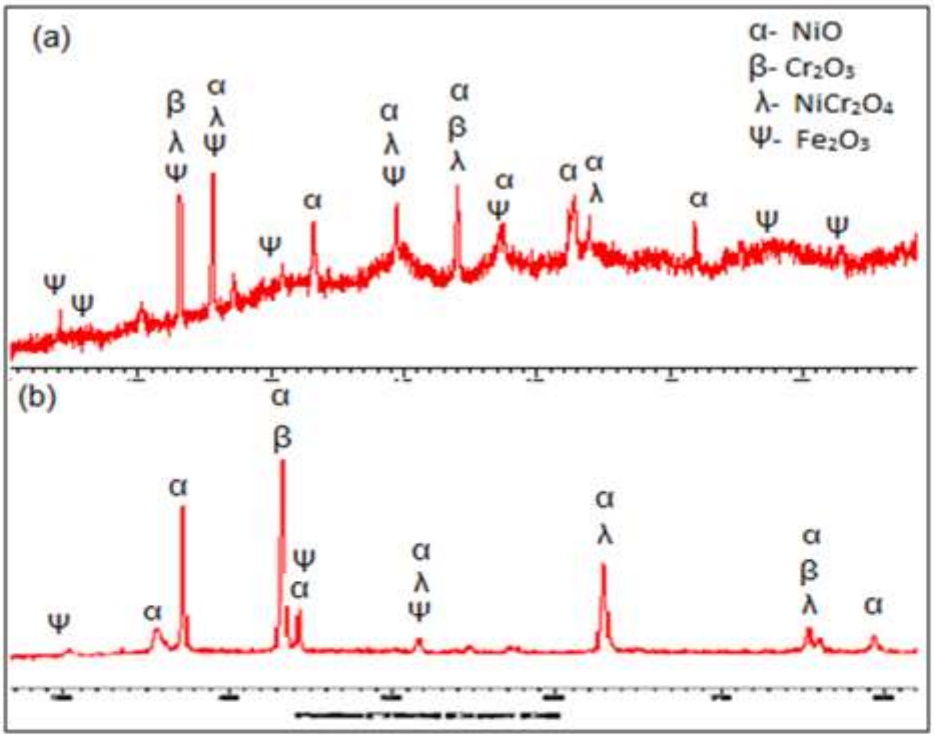

Fig. 3. X-Ray Diffraction pattern of (a) Plasma sprayed and (b) HVOF prayed Ni20Cr coating on ASTM-SA213-T-22 boiler steel exposed to given environment.

X-ray mapping analysis

The X-Ray maps for HVOF-sprayed and Plasma sprayed 80Ni20Cr coated on SA213 (T22) specimens as coated, coated specimens exposed to the given environment and bare specimen are shown in the figures 4a-e. In coated specimens the penetration of oxygen is constrained to coating-substrate interface, indicating the protectiveness of the Ni20Cr coating in the given conditions. The Ni and chromium rich splats are present in the coating which remains unoxidised. It can be observed that uncoated specimen has undergone a severe corrosion.

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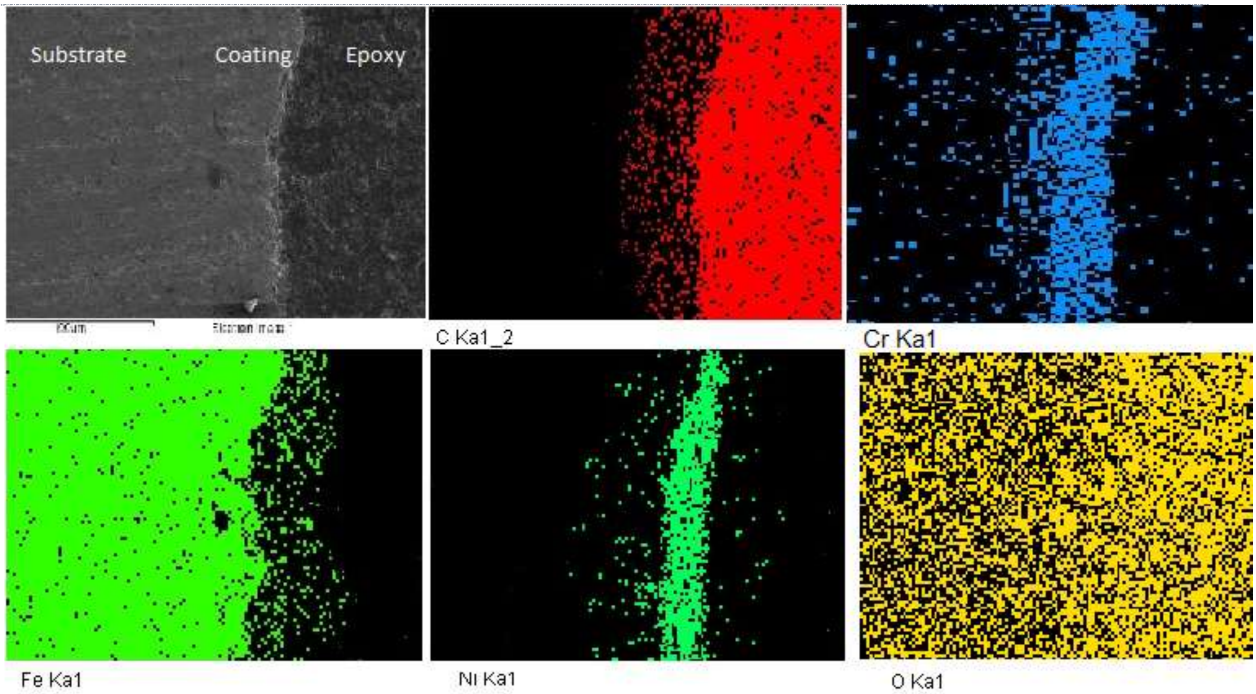

Fig. 4a. ***SEM micrograph and X-ray mapping along the cross-section of the HVOF sprayed 80Ni20Cr as coated on ASTM-SA213 (T22) boiler steel.***

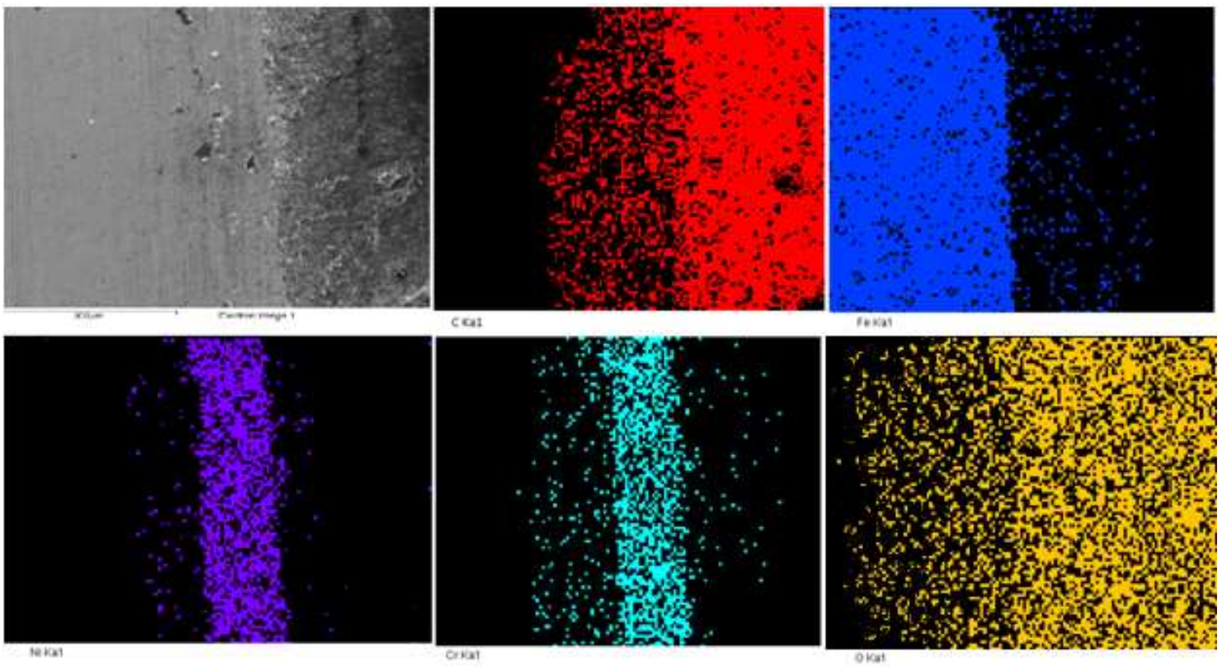

Fig. 4b. ***SEM micrograph and X-ray mapping along the cross-section of the Plasma sprayed 80Ni20Cr as coated on ASTM-SA213 (T22) boiler steel.***

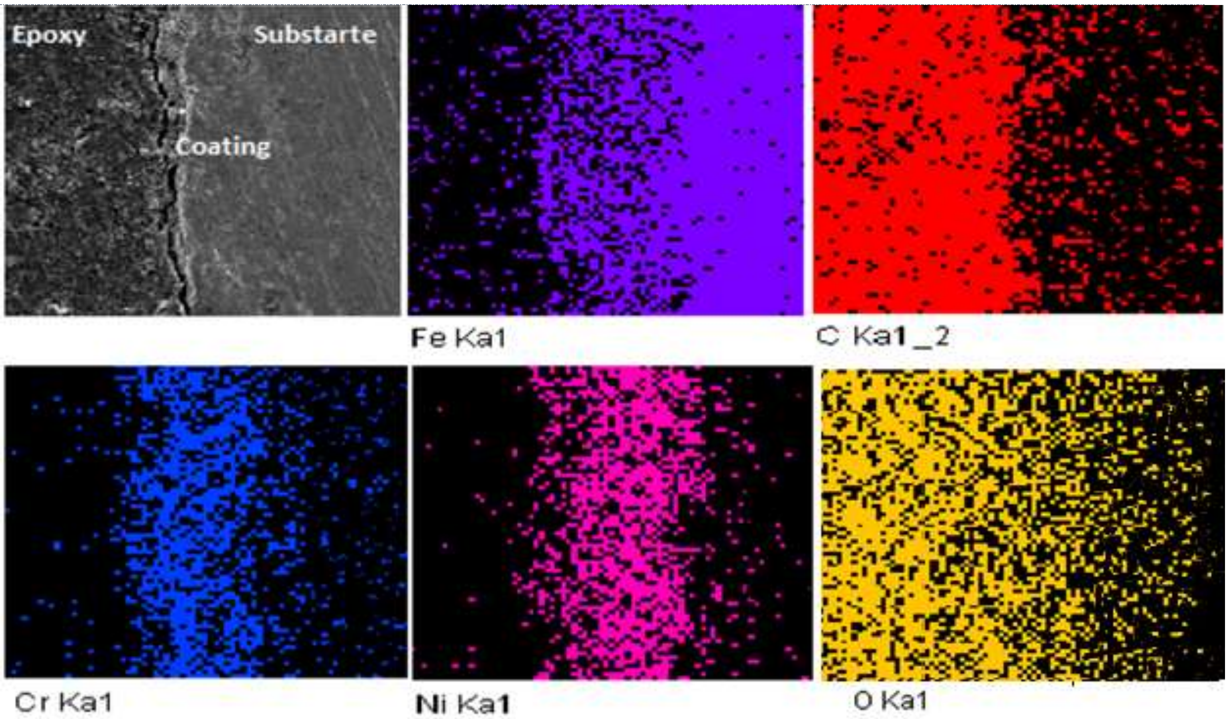

Fig. 4c. ***SEM micrograph and X-ray mapping along the cross-section of the HVOF sprayed 80Ni20Cr coated specimen exposed to given environment.***

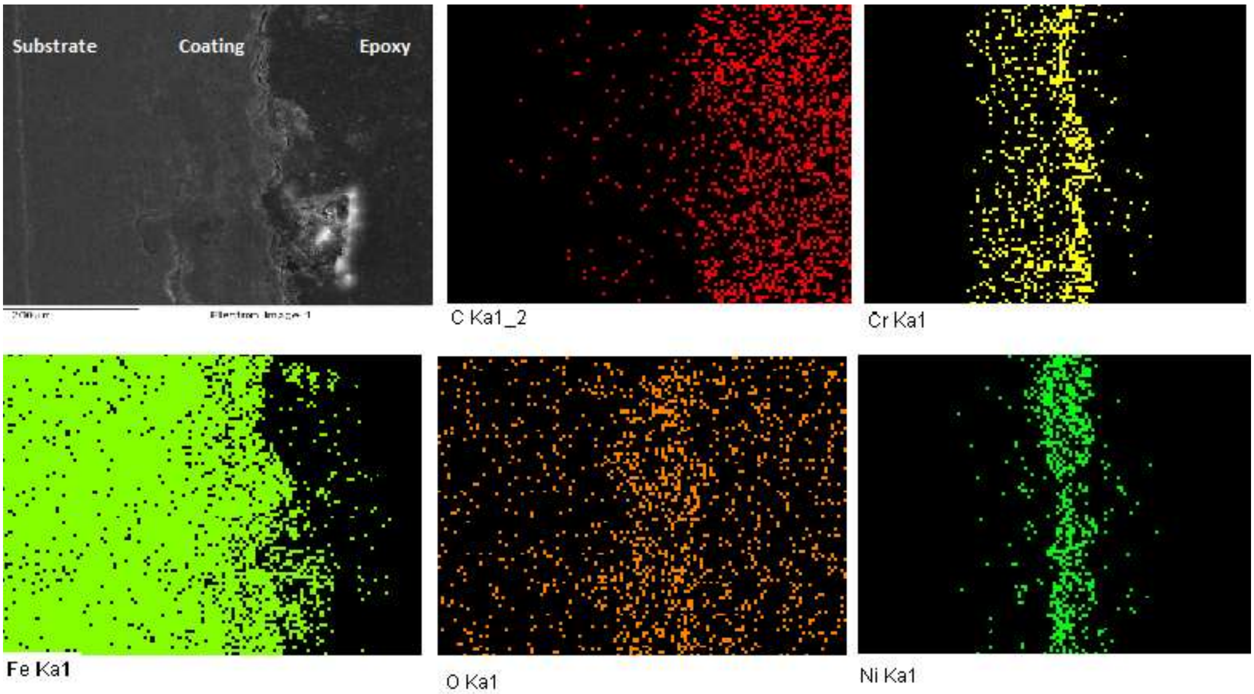

Fig. 4d. ***SEM micrograph and X-ray mapping along the cross-section of the Plasma sprayed 80Ni20Cr coated specimen exposed to given environment.***

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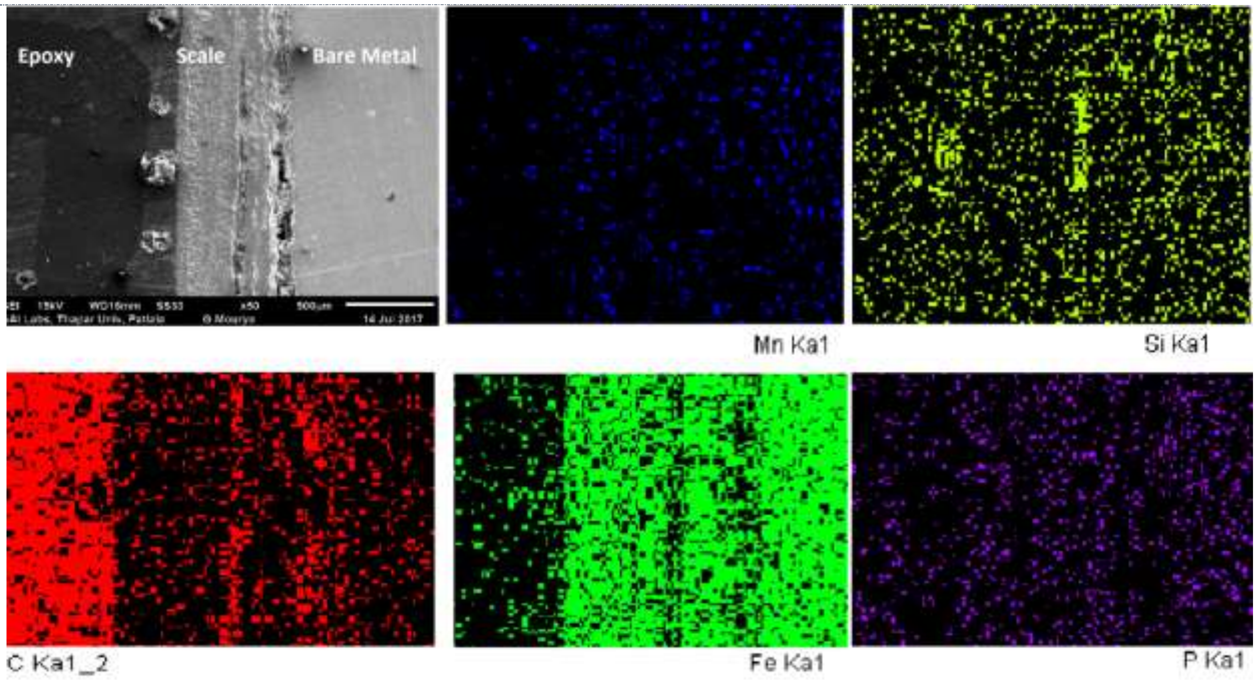

Fig. 4e. ***SEM micrograph and X-ray mapping along the cross-section of the Bare metal ASTM-SA213 (T22) boiler steel specimen exposed to given environment.***

2. Hot Corrosion Behaviour Of Coating In Molten Salt Environment

Corrosion kinetics

The thermogravimetric analysis was used to investigate the kinetics of the high temperature corrosion of the coated and bare alloy substrates. The mass change is an good indicator to examine the corrosion rates in equivalent conditions. Change in weight is monitored as per corresponding number of cycle for HVOF and Plasma spray 80Ni20Cr coating on T22 steel specimens subjected to Na_2SO_4–60%V_2O_5 environment at 900ºC for 50 cycles and compiled in Fig. 5a-b. It is observed from the graphs that the bare specimen has shown much higher weight gain rates and it was continuous till the last cycle as compared to coated. Mass gain in coated specimens have reduced remarkably. However, the HVOF-sprayed specimens showed a higher corrosion resistance than Plasma coated specimens. The steady state of corrosion was achieved in case of HVOF-sprayed specimen, but in Plasma sprayed specimen the reaction rate was little higher after 35th cycle. The weight gains for the bare specimen was reduced by 75% in HVOF sprayed specimen and 61% in plasma sprayed specimen.

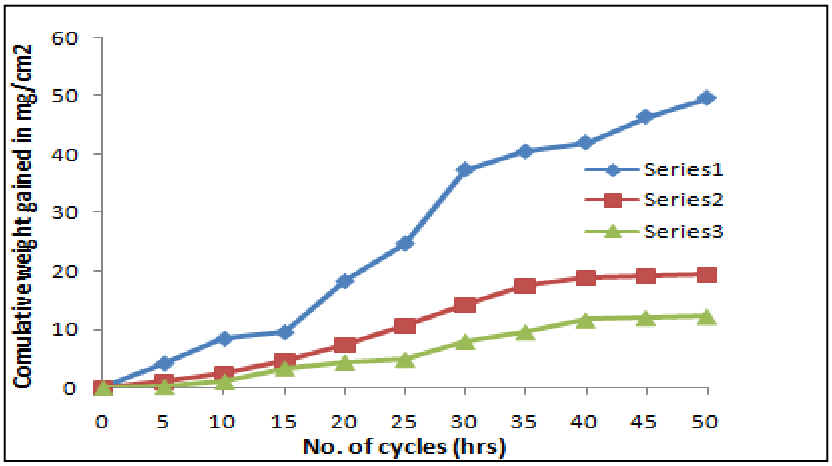

Figure 5a. Weight gain plot for Bare and Ni–20Cr HVOF and Plasma coated steels exposed to Na_2SO_4–60%V_2O_5 at 900°C for 50 cycles.

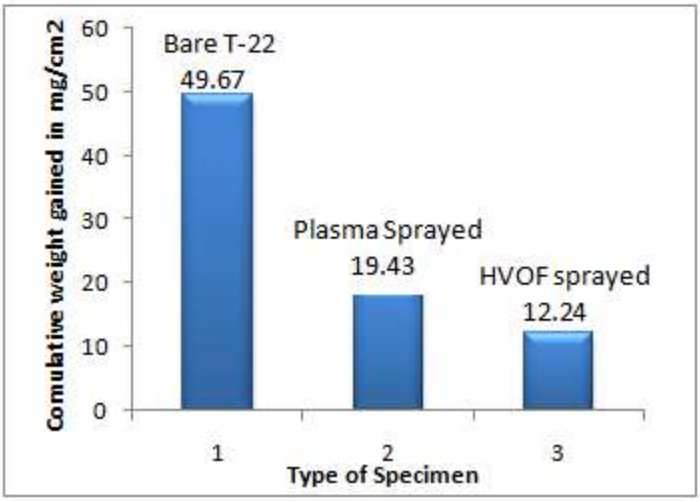

Figure 5b. Weight gain for Bare and Ni–20Cr HVOF and Plasma coated steels exposed to Na_2SO_4–60%V_2O_5 at 900°C for 50 cycles.

IV. DISCUSSION

The 80Ni20Cr coating on SA-213 (T-22) boiler steel by HVOF and Plasma spray were found to be nearly uniform, massive, homogeneous and cracks free(Fig. 2 & 3). Coated specimens have shown good resistance to high temperature corrosion in the given conditions without any spalling. Surface SEM/EDAX of coated samples bring to light that the main composition is of Ni and Cr, which is according to powder supplied. The bare boiler steel showed severe spalling and peeling of the scale because of unprotective Fe2O3 phase as revealed by X-ray diffraction, which is similar to as analyzed by Prakash et al. Major phase detected was NiO, Cr2O3 along with Fe2O4 as a medium and NiCr2O4 as a weak phase for HVOF sprayed NiCr coatings. Cr2O3 and phase NiO have been reported as the prominent phases by the X-Ray Diffraction analysis (Fig. 4) for as-sprayed coating which is further supported by the EDAX analysis which shows the presence of Ni, Cr and O in the coating (Fig. 3). The Phases identified are oxides of nickel, chromium, and spinel containing nickel-chromium type mixed oxides, which are protective in nature. The greenish colour appeared on the surface of the specimens indicate that the chromium oxide is present as a dominating phase. The SEM examination of the interface shows reasonably flawless with minor pores/voids. The X-ray mapping indicates presence of Ni, Cr and O in the surface and no diffusion of iron from the substrate has been observed. (Fig. 3). The weight change plots (Fig.5 a-b) for the bare and coated ASTM-SA213-T-22 boiler steel showed that the oxidation behavior has shown conformance to parabolic rate [22-24]. The HVOF spray coated alloy have offered higher resistance to corrosion than Plasma sprayed followed by bare/uncoated alloy. The HVOF sprayed coatings of 80Ni20Cr powder has provided the good resistance to corrosion in Na2SO4-60%V2O5 environment at 900ºC than the plasma sprayed NiCr coating. The weight gain for the bare specimen was reduced by 78% and 65% with the application of HVOF and plasma spray coatings respectively (Fig. 8.c.). The bare alloy has shown rapid weight gain (Fig. 8.a) when exposed to the selected environment for 50 cycles at 900°C as compared to coated specimen. Therefore, based on the overall analysis it is concluded that the HVOF-spray process is better than plasma spray for the given conditions. HVOF-spray process make it possible for in site applications for larger structures. The weight change graph (Fig. 2.a) shows that the weight increases incessantly in case of the bare alloy. In case of bare metal the weight gain is higher in starting cycles that indicates rapid oxide formation because of oxide formation at pores and splat boundaries.

V. CONCLUSIONS

- The uncoated SA213 (T22) boiler steel showed intense spalling of oxide layer during hot corrosion studies in the aggressive environment of Na2SO4–60%V2O5 at 900oC.
- Both the HVOF and Plasma sprayed techniques used for coating 80Ni20Cr were useful in controlling the high temperature corrosion without any spalling.
- Ni20Cr coated specimens exposed to molten salt at 900oC under cyclic conditions have shown the presence of NiO and Cr2O3 oxides also confirmed by surface XRD and EDS analysis. The phases indicated by XRD analysis are protective oxides of nickle, chromium and spinel containing nickel-chromium type mixed oxides.

- The HVOF sprayed coatings of 80Ni20Cr powder has shown the better corrosion resistance in Na2SO4-60%V2O5 environment at 900ºC than the plasma sprayed NiCr coating. The weight gain for the bare specimen was reduced by 75% and 61% with the application of HVOF and plasma spray coatings respectively.

VI. ACKNOWLEDGEMENTS

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