CHARACTERIZATION OF NANOCOATIONG ON SS316L BOILER STEEL IN Na_2So_4-60%V_2O_5 ENVIRONMENT AT 900°C UNDER CYCLIC CONDITIONS

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Abstract: **This manuscript is an effort to investigate the effect of coating on microstructure of boiler steel. In the reported study, two types of coatings such as TiAlN and AlCrN were deposited on SS316L boiler steel. Hot corrosion studies were conducted on bare as well as TiAlN and AlCrN coated specimens after exposure to a molten salt environment of Na_2SO_4–60%V_2O_5 at 900°C under cyclic conditions. After the each cycle weight gain was measured and the surface of oxidized samples was visually examined. The thermogravimetric technique was used to approximate the kinetics of corrosion. Microstructure was investigated by Scanning electron microscope (SEM)/ Energy Dispersive X-Ray spectroscopy (EDS), X-ray diffraction (XRD), BSEI and X-Ray analysis. The results of the present study indicated that the performance of AlCrN coated SS316L boiler steel in molten salt was better than the TiAlN coated and uncoated SS316L boiler steel.**

Keywords**: Nanostructured coating, Hot corrosion, Oxide scale, Physical vapor deposition, scale morphology.**

I. INTRODUCTION:

The large number of thermal power plants uses coal as fuel. The coal which is used as fuel is a complex fuel that contains varying amounts of sulphur and a substantial fraction of non-combustible mineral constituents, commonly known as ash [1]. The effect of ash is the degradation of material [2]. Such as erosion, corrosion and oxidation at higher temperatures in aggressive chemical environments. To protect the material from degradation, surface modification is necessary to enhance the life of the material. The best way to extend the performance of material, against hot corrosion and erosion is coating [3]. By selecting proper coating methods and coating materials, we may prolong the service life of the substrate material and increase the commercial value of the products [4]. The most important and commonly used coating technique is Physical vapor deposition(PVD). In hard coatings, the PVD process is used to make a dense adhesive film on material at a low deposition temperature. PVD process offered a better corrosion resistance to substrate [5]. As from literature study chwala et al [6] concluded that the PVD process provided the better corrosion resistance. So in the current study it has been proposed to study the effect of nanostructured TiAlN and AlCrN thin coatings on the hot corrosion behavior of SS316L boiler steel under the cyclic heating condition.

II. EXPERIMENTAL PROCEDURE:

In the current work, two coating powders were selected TiAlN and AlCrN. The coatings were produced by Balzer's rapid coating system (RCS) machine as shown in fig1. SS316L was selected as substrate material with the dimension 20 mm x 15 mm x 4 mm. In SS316L molybdenum was already present, which was more corrosion resistant so it does deal with acidic environments. The chemical composition of the base materials is given in Table 1.

Table 1: Chemical Composition (wt %) of SS316L

S No.	C	S	P	Si	Mn	Ni	Cr	Mo	Fe
1	0.020	0.010	0.035	0.230	1.30	10.130	16.290	2.060	Bal

Two of the six sources were used to deposit a thin and 0.3 μm thick sub layer of TiN sub-layer with the help of the RCS machine which is equipped with 6 cathodic arcs to improve adhesion of coating. Remaining four sources were used to deposit the main layer of coating, which was obtained with the help of customized sintered targets. The compositions of the targets used, coating thickness and the summary of the process parameters are presented in Table 2. For the deposition of coating nitrogen and argon atmosphere was used. By using Argon-ion etching process, the substrate was chemically cleaned, heated and plasma etched.
The coated and bare specimens were analyzed by using Scanning electron microscope (SEM)/ Energy Dispersive X-Ray spectroscopy (EDS), X-ray diffraction (XRD), BSEI and X-Ray analysis.

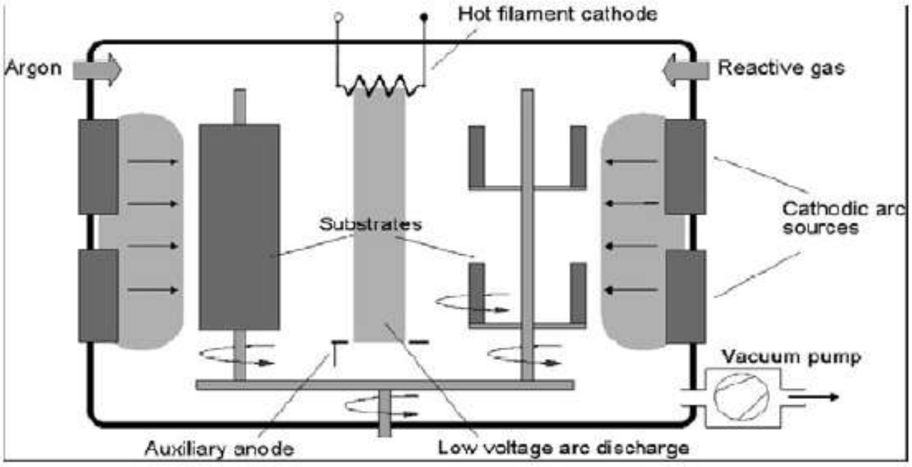


Fig.1: Schematic illustration of the coating device used for the film deposition.

After the TiAlN and AlCrN PVD thin coating the samples were placed in a laboratory carbide tube furnace at 900°C for the hot corrosion study. First of all the specimens were washed with acetone and to remove moisture dried in hot air. After that the specimens were heated in an oven up to 250°C. All the surfaces of warm specimens were coated with a mixture of salt Na_2So_4-60%V_2O_5 with the help of a camel hair brush. After that the samples were placed in alumina boats and these boats along with specimens were placed in furnace at 900°C for one hour and 20 minutes in air for cooling. After that the weight of the boat along with specimen was measured. The samples were placed in a furnace for 50 cycles and the weight of the boat along with specimen was noted after each cycle. After the end of each cycle a careful visual observation of each sample with respect to color or any physical change was noted as heat treated specimens are shown in fig 2.

Fig. 2 Surface micrograph for the SS316L steel exposed to molten salt Na_2So_4-60%V_2O_5 at 900°C for 50 cycles (a) uncoated, (b) TiAlN coated, (c) AlCrN coated.

Table 2: Summary of deposition parameters

Machine used	Standard balzers rapid coating system (RCS) machine
Make	Oerlikon Balzers, Swiss
Targets composition	for TiAlN coating: Ti, Ti 50Al50 AlCrN coating: Al70Cr30
Number of targets	Ti (02), Ti 50Al50 (04) and Al70Cr30 (06)
Targets power:	3.5 kW
Reactive gas	Nitrogen
Nitrogen deposition pressure	3.5 Pa
Substrate bias voltage	-40V to -170V
Substrate temperature	450°C ± 10°C
Coating Thickness	4 µm ± 1 µm

III. RESULTS AND DISCUSSION:

A. *Thermogravimetric analysis*

The thermo gravimetric analysis was done for uncoated and coated SS316L steel for high temperature oxidation. The weight gain per unit surface area (mg/cm^2) was plotted against the number of cycles as shown in Fig.3. Further, weight gain square (mg^2 / cm^4) data were also plotted as a function of the number of cycles as shown in Fig.3. It can be inferred from the plots that the uncoated and TiAlN coated SS316L boiler steels have shown the initially high rate of oxidation as compared to AlCrN coated SS316L steel, followed by a nearly constant rate. After the 20th cycle, the oxidation rate in the case of TiAlN coated sample increased abruptly up to the 50th cycle. The cumulative weight gains after completion of 50 cycles of oxidation are found to be 880, 861, 342.4 mg/cm^2 for the uncoated as well as TiAlN and AlCrN coated SS316L boiler steel, respectively as shown in fig 4.

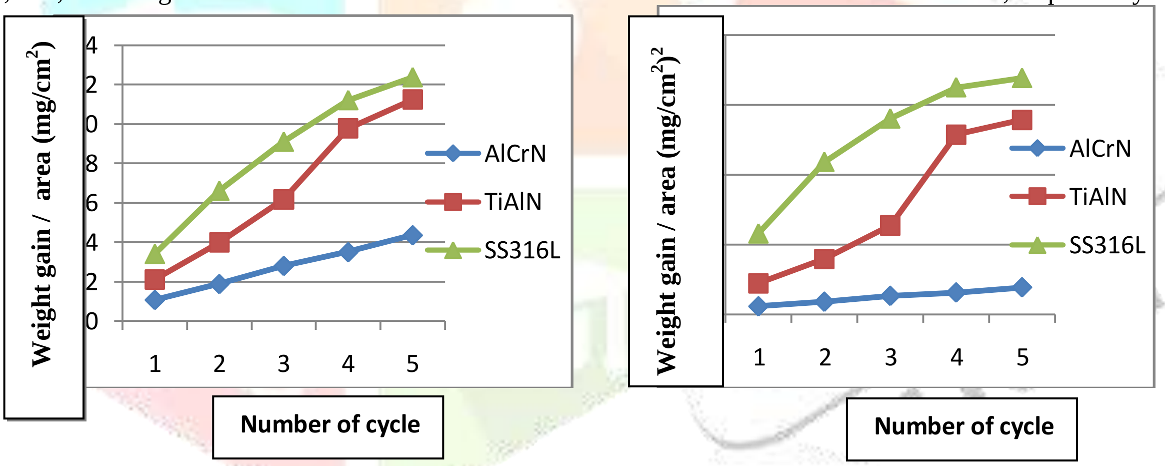


Fig.3: Weight gain per unit area vs. number of cycles and (Weight gain per unit area)^2 vs. number of cycles plot for coated and uncoated SS316L.

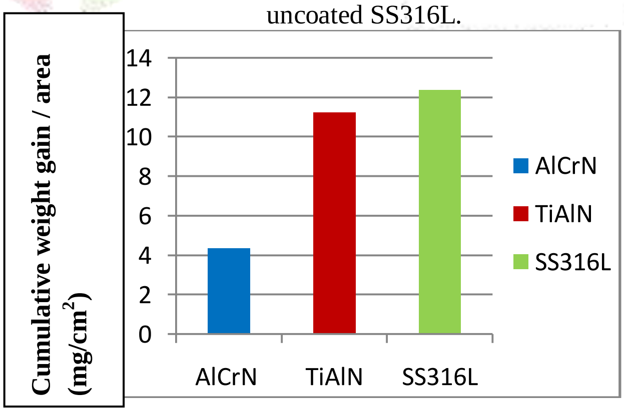


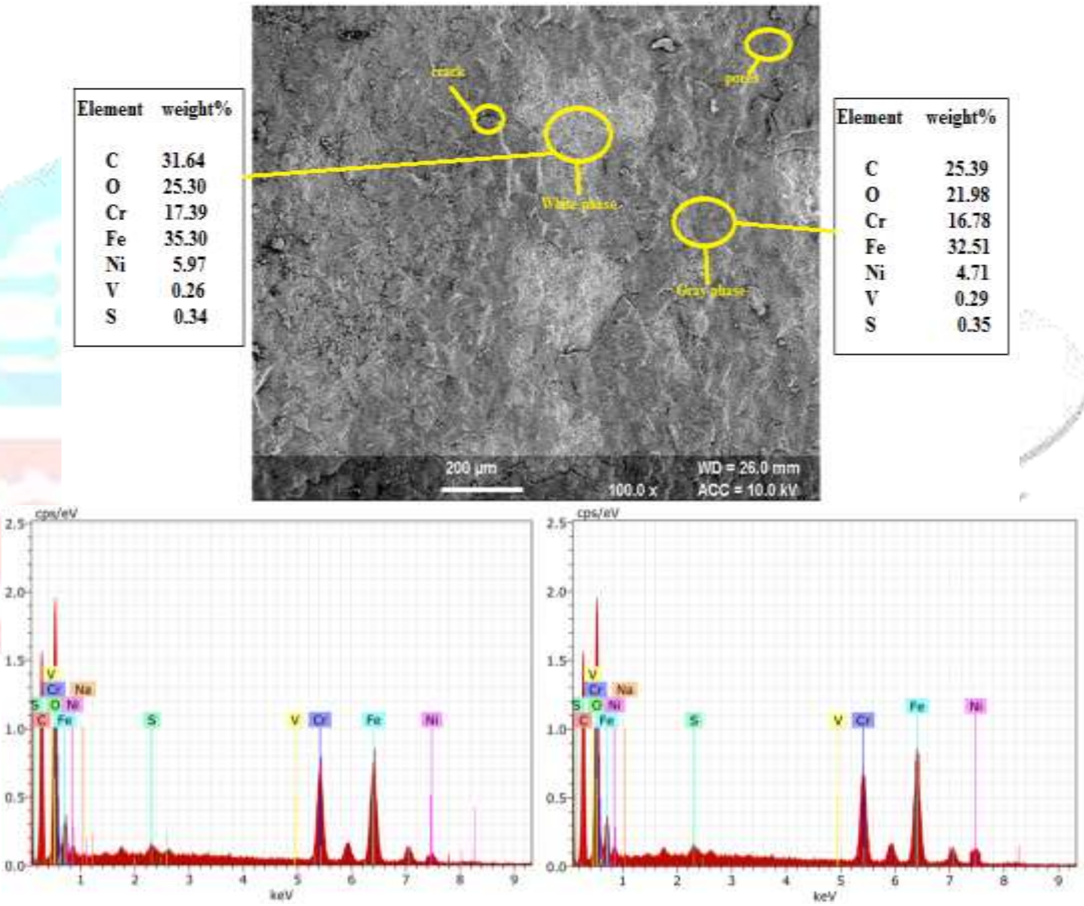
Fig.4.: Bar chart showing a cumulative weight gain per unit area for coated and uncoated SS316L boiler steel subjected to cyclic oxidation in molten salt at 900°C for 50 cycles.

B. SEM/EDS and X-Ray Analysis of salt pieces

The SEM micrographs along with EDS analysis at some selected sites of interest of uncoated and coated SS316L boiler steel subjected to cyclic oxidation in molten salt of Na_2SO_4–60% V_2O_5 at 900°C for 50 cycles is shown in Fig. 5 (a,b,c). The Fractographs of uncoated SS316L specimen indicated the gray phases and white phases. From EDS analysis, there was the presence of Fe, Cr, O, C and Ni. The small amount of S and V were also been noted. The presence of a significant amount of oxygen, Iron, chromium and nickel indicated the possibility of formation of Fe_2O_3, Cr_2O_3 and NiO. The presence of significant amounts of carbon also indicated the possibility of formation of Cr_3C_2 and Ni_3C_2 and CrC. XRD graph for uncoated SS316L boiler steel is shown in fig 5 (a) there was formed of Fe_2O_3, Cr_2O_3 and NiO.

The SEM Fractographs of TiAlN coated specimen mainly indicated the gray phases and Dark gray phases. From EDS analysis, there was the presence of Fe, Cr, O, and Ni. The small amount of C, Nb, S and V were also been noted. The presence of a significant amount of oxygen, Iron, chromium and nickel were pointed out the possibility of Fe_2O_3, Cr_2O_3, TiO_2, Al_2O_3 and NiO along with considerable amounts of Nb_2O_5 and V_2O_3. XRD patterns of the TiAlN coated specimen are shown in fig 5(b). It mainly consists of Fe_2O_3, Cr_2O_3, NiO, Al_2O_3 and TiO_2 phases.

The SEM Fractographs of AlCrN coated specimen mainly indicated Dark gray phases and white phases and also it shows dimple in the surface. From EDS analysis, there a was the presence of Fe, Cr, O, Ni, Al, C and S in sufficient amount. The white region on the gray matrix shows maximum oxygen content. The presence of a significant amount of oxygen and Iron, and chromium and nickel were pointed out the possibility of Fe_2O_3, Cr_2O_3, $Al_2O_3$and NiO. XRD graph for AlCrN coated SS316L boiler steel is shown in fig 5 (c). There was formation of Fe_2O_3, Cr_2O_3, NiO and Al_2O_3.



Element	weight%
C	31.64
O	25.30
Cr	17.39
Fe	35.30
Ni	5.97
V	0.26
S	0.34

Element	weight%
C	25.39
O	21.98
Cr	16.78
Fe	32.51
Ni	4.71
V	0.29
S	0.35

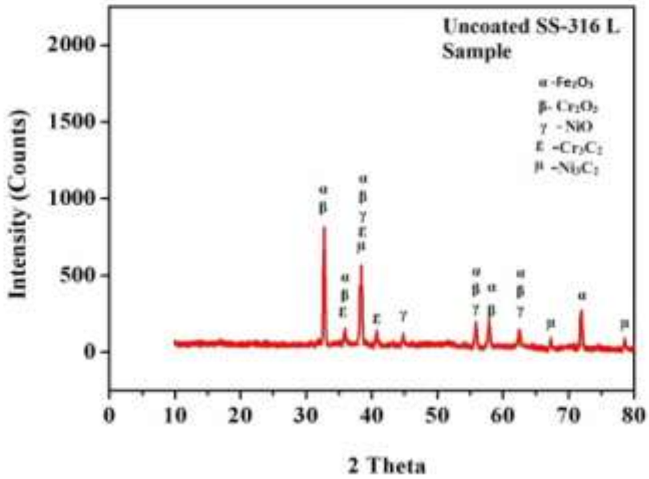
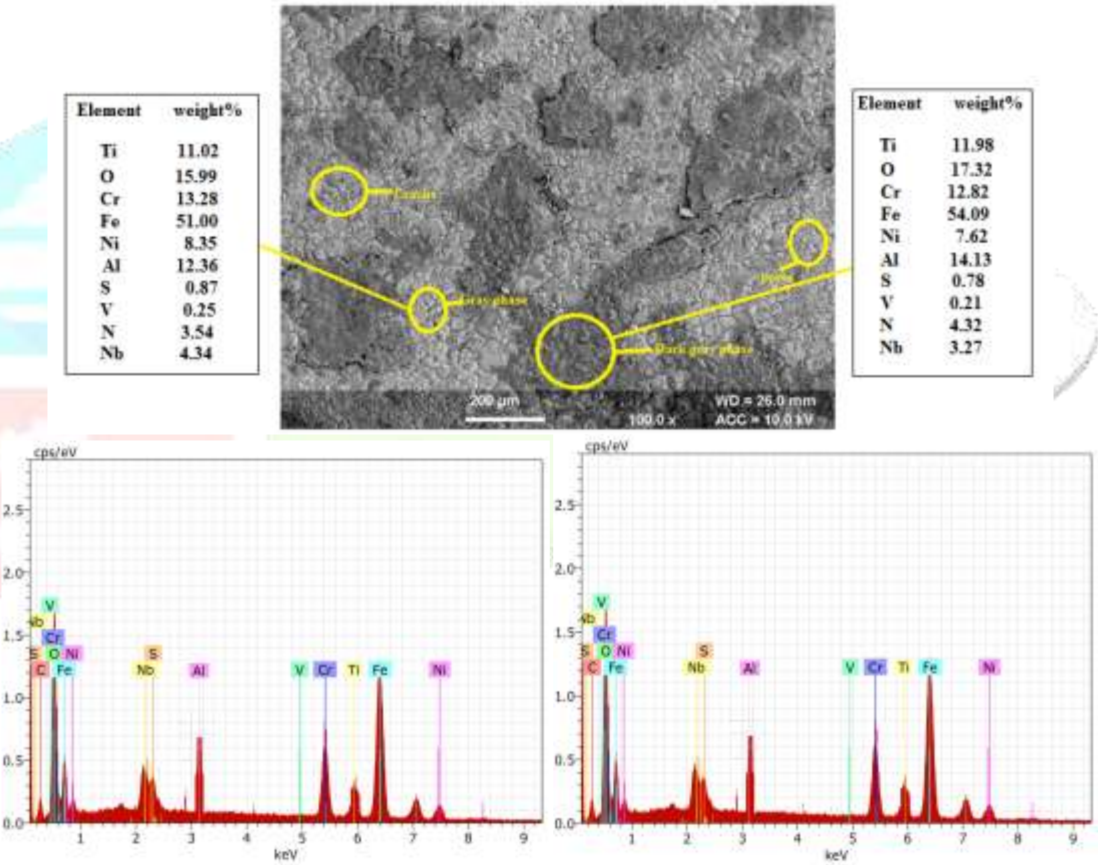


Fig. 5(a): SEM micrograph, EDS analysis and X-Ray Diffraction pattern for uncoated SS316L after oxidation in molten salt Na_2So_4-60%V_2O_5 at 900°C for 50 cycles.



Element	weight%
Ti	11.02
O	15.99
Cr	13.28
Fe	51.00
Ni	8.35
Al	12.36
S	0.87
V	0.25
N	3.54
Nb	4.34

Element	weight%
Ti	11.98
O	17.32
Cr	12.82
Fe	54.09
Ni	7.62
Al	14.13
S	0.78
V	0.21
N	4.32
Nb	3.27

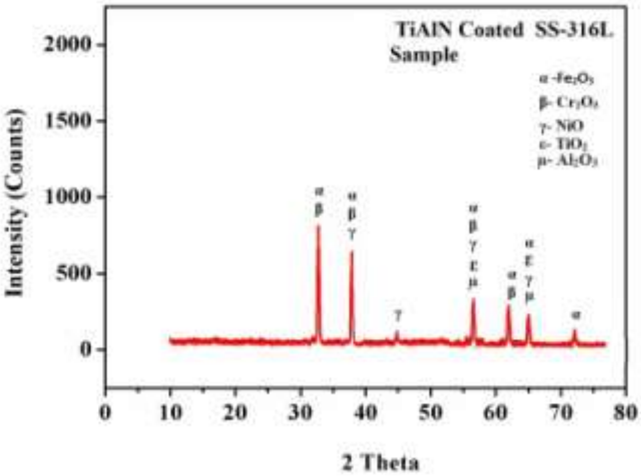
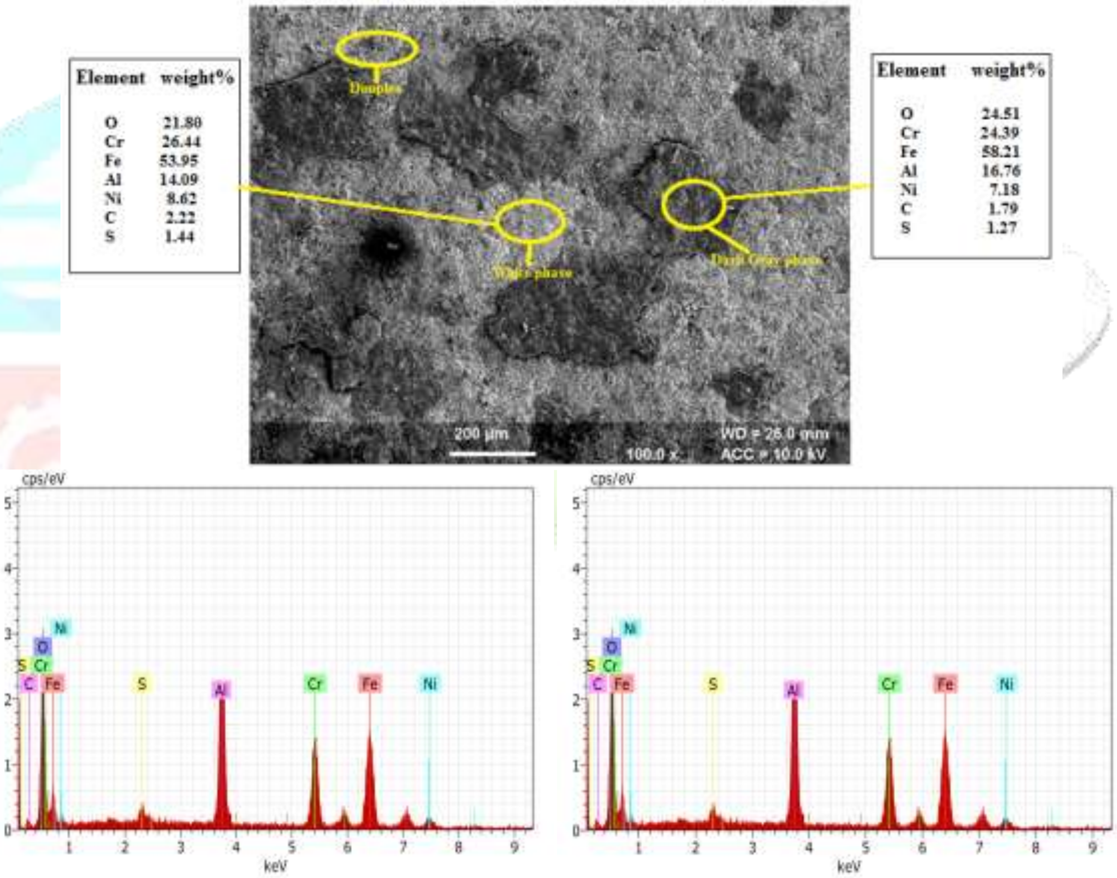


Fig. 5(b): SEM micrograph, EDS analysis and X-Ray Diffraction pattern for TiAlN coated SS316L after oxidation in molten salt Na_2So_4-60%V_2O_5 at 900°C for 50 cycles.



Element	weight%
O	21.80
Cr	26.44
Fe	53.95
Al	14.09
Ni	8.62
C	2.22
S	1.44

Element	weight%
O	24.51
Cr	24.39
Fe	58.21
Al	16.76
Ni	7.18
C	1.79
S	1.27

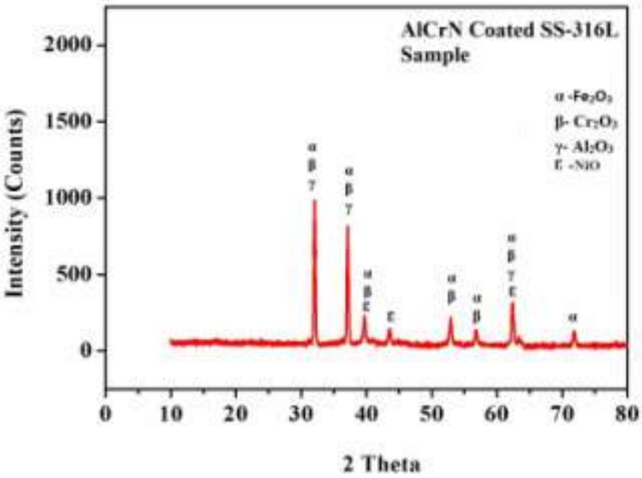


Fig. 5(c): SEM micrograph, EDS analysis and X-Ray Diffraction pattern for AlCrN coated SS316L after oxidation in molten salt Na_2So_4-60%V_2O_5 at 900°C for 50 cycles.

C. CROSS-SECTIONAL ANALYSIS

1) Scale thickness

During cross-sectional analysis, Very thick scale was observed in case of uncoated SS316L boiler steel as compared with coated SS316L boiler steel. The measured oxide scale thickness for TiAlN coated and AlCrN coated SS316L boiler steel is shown in Table.3.

Table 3: The average scale thickness in mm, values for uncoated and coated SS316L boiler steels.

Type of steel	Thickness (mm)
Uncoated SS316L	1.27
TiAlN coated	0.74
AlCrN coated	0.29

2) Cross-sectional scale Morphology

During analysis the SEM micrograph for uncoated SS316L boiler steel shows a uniform thick scale which can be seen in Fig.6 (a). From EDS analysis graph there was a presence of Fe, Cr, Ni and O elements throughout the scale. The existence of significant amount of oxygen points out the possibility Fe_2O_3 in the oxide scale. Also, the points where Cr content was more shows less Fe and more oxygen as compared to the other points. This shows the possibility of formation of Cr_2O_3 in the scale. BSEI micrograph and elemental variation depicted is shown in Fig.6 (b). The exposed cross-section of TiAlN coated SS316L boiler steel shows the thick, continuous and adherent scale. In the EDS analysis graph of TiAlN coating there was a presence of Fe, Cr, O and Ni throughout the scale. A location at point 4 in the micrograph depicts the increase in percentage of Cr with a decrease in percentage of Fe and Ni. A thick and fragile oxide scale can be seen in case of AlCrN coated SS316L boiler steel Fig.6 (c). The EDS analysis reveals the presence of Fe, Cr, O and Ni throughout the scale. There was a formation of continuous and adherent oxide scale due to the presence of greater amount of Cr. At the scale substrate interface, there was a presence of oxygen due to in flight oxidation of the coating or oxygen might have penetrated during the initial cycles of oxidation run along the intersplat boundaries.

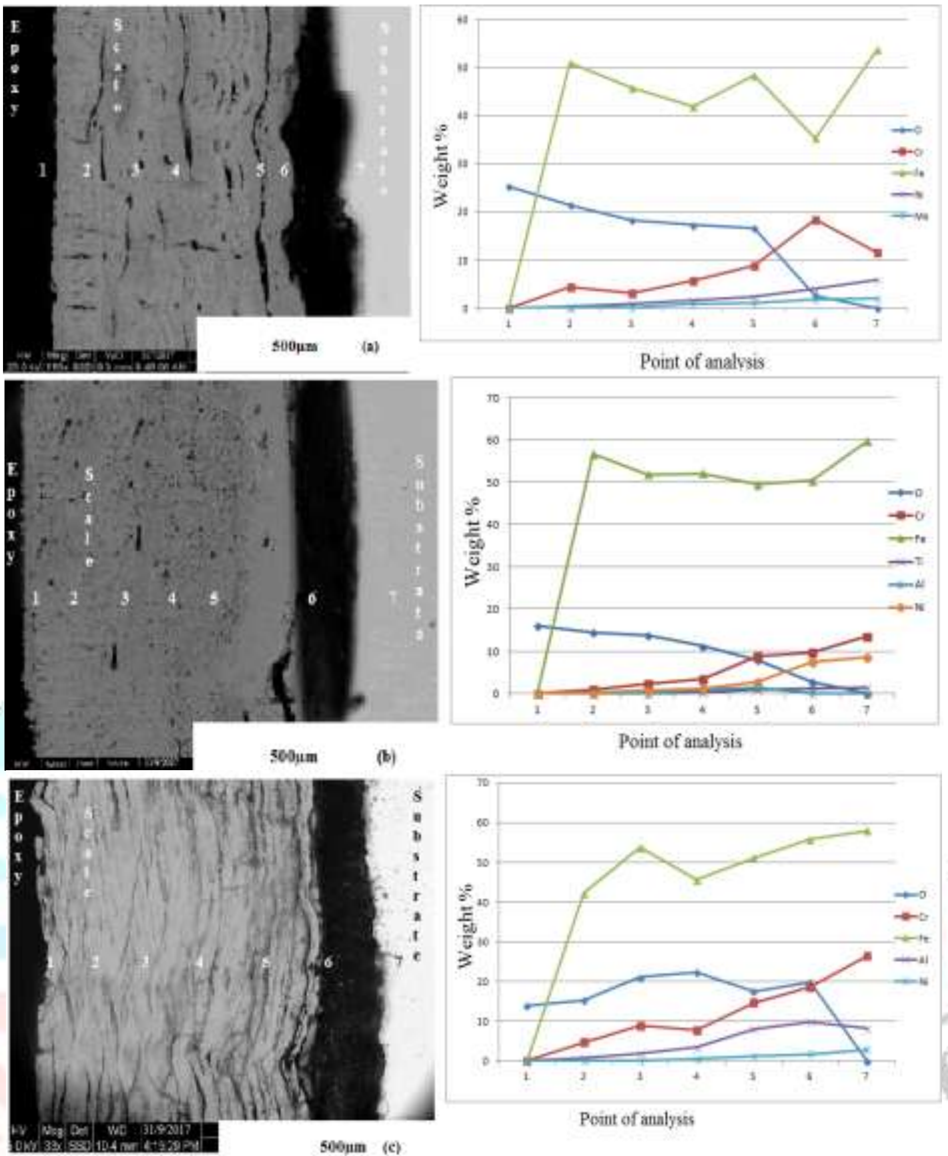


Fig. 6 Oxide scale morphology and variation of elemental composition across the cross- section. (a) Uncoated SS316L, (b) TiAlN coated, (c) AlCrN coated.

D. X-RAY MAPPING

X-ray mapping for the coated and uncoated SS316L steel which was oxidized in Na_2SO_4-60%V_2O_5 environment at 900°C for 50 cycles are shown in Fig.7. A dense scale was indicated in micrograph of SS316L steel as shown in fig. 7(a). It mainly contains Fe, Cr, and O. As in the case of TiAlN coated specimen as shown in fig. 7(b). The formed dense scale, mainly contains Fe, Cr, Ti, Al and O, throughout the scale. The X-ray mapping of TiAlN coated specimen indicated the thick bands of Cr were parallel to each other, near the scale/substrate interface. As in case of AlCrN coated specimen as shown in fig. 7(c). The formed dense and adherent surface was due to the presence of Fe, Cr, Al, Ni and O throughout the scale.

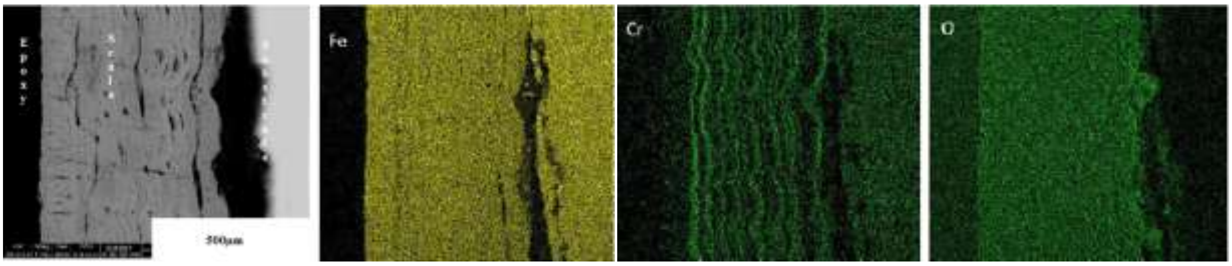


Fig. 7 (a) Composition image (BSEI) and X-ray mapping of the cross-section of uncoated SS316L.

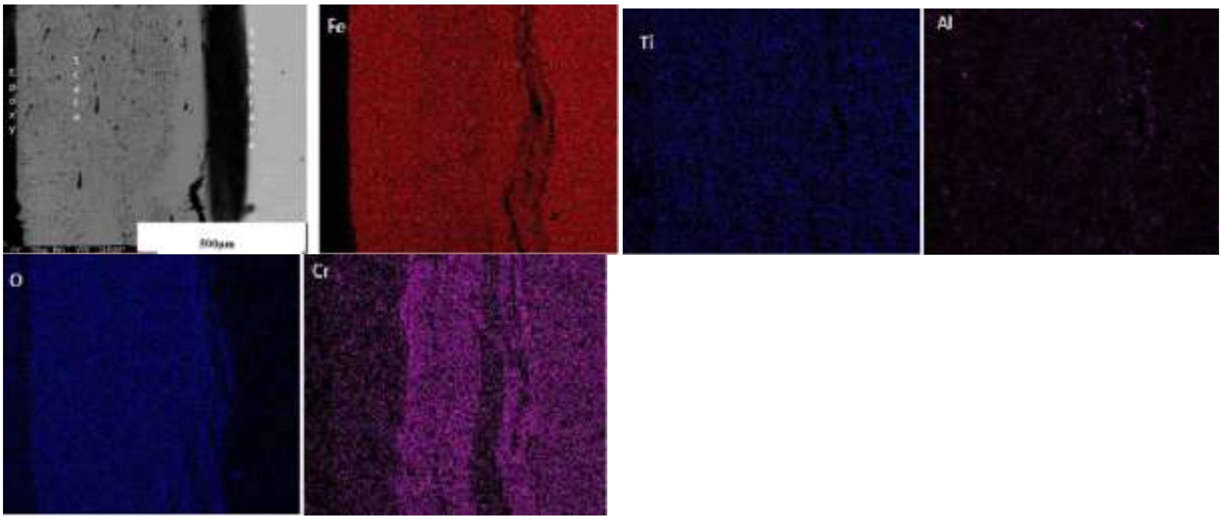


Fig. 7 (b) Composition image (BSEI) and X-ray mapping of the cross-section of TiAlN coated.

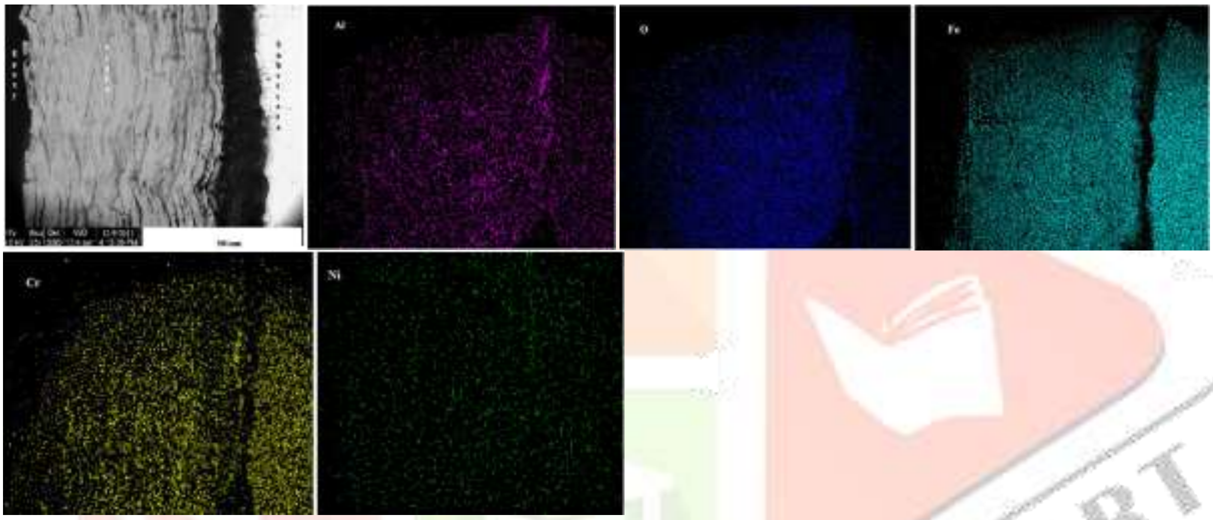


Fig.7 (c) Composition image (BSEI) and X-ray mapping of the cross-section of AlCrN coated.

IV. DISCUSSION

The weight gained was higher in case of bare and TiAlN thin coated specimens as shown by thermogravimetric analysis (as discussed in 2.1). The higher weight was gained during the first few cycles due to the penetration of the oxidizing species in open pores and at splat boundaries. After that the coating becomes denser [7]. During the initial period of Na_2SO_4-60%V_2O_5 environment at 900°C, the weight gained was very rapid due to the formation of $NaVO_3$, as represented by equation having a melting point of 610°C [8].

$$Na_2SO_4 + V_2O_5 = 2NaVO_3\ (l) + SO_2 + ½\ O_2$$

During the initial cycles, $NaVO_3$ acts as a protective oxide scale. $NaVO_3$ behaves like a catalyst and serves as an oxygen carrier to the base metal. This leads to the rapid oxidation of the base metal. Simultaneously the protective scale is destroyed by molten salts as per the reaction:

$$Cr_2O_3 + 4\ NaVO_3 + 3/2\ O_2 = 2\ Na_2CrO_4 + 2\ V_2O_5.$$

By Sidhu et al. [9] The protective scale of Na_2CrO_4 gets evaporated. The direct action of the metal surface is exposed to aggressive environment. Due to the growth of oxides, the weight is gained by the specimen.

The similar observation on uncoated SS316L steel was also given by Jain et al. [10], he concluded that the formation of scale with spalling was higher. The main reasons behind the formation of scale with spalling were precipitation of Fe_2O_3 from the liquid phase, during the cooling period of thermal cycles, and inter diffusion of intermediate layers of iron oxide. From another observation by Shi [11] for coated and uncoated specimens, there was the formation of Fe_2O_3 as the main constituent of the top scale along with weak peaks of Cr_2O_3 at 750°C.

The oxidation and hot corrosion of TiAlN coated SS36L boiler steel may be due to the presence of molybdenum in base metal. By Chatterjee et al. [12] during the initial hour's oxidation, the Fe oxidizes and the oxide scale was protective in nature. At temperature 795°C, the molten Mo becomes an inner layer of MoO_3. This MoO_3 might have further reacted with Na_2SO_4 and formed a phase of Na_2MoO_4.

$$Na_2SO_4\ (l) + MoO_3\ (l) = Na_2MoO_4\ (l) + SO_3\ (g)$$

The oxidation and hot corrosion resistance of TiAlN coated steel at high temperature due to the presence of higher amount of Cr, which may lead to the formation of the Chromium Oxide layer. The presence of Cr_2O_3, NiO and $NiCr_2O_4$ surface oxides, as detected by EDS analysis.

Thermogravimetric analysis shows the weight gain for the AlCrN coated SS316L boiler steel is very less as compared to uncoated and TiAlN coated substrate. By Chawla et al. [13] the presence of higher amount of Cr, which may lead to the formation of the Chromium Oxide layer. The presence of Cr_2O_3, NiO and $NiCr_2O_4$ surface oxides, as detected by EDS analysis, might have contributed to the better hot corrosion resistance of coated steel. Due to strongly flattened splats, the distance from the coating surface to coating/substrate interface along the splat boundary is very long and thus a high corrosion resistance is offered by coating. Further good oxidation resistance to this type of coating has also been observed by Kalss et al. [14].

V. CONCLUSIONS

The high temperature oxidation behaviors of uncoated and TiAlN and AlCrN coated SS316L boiler steel has been investigated in Na_2SO_4-60%V_2O_5 molten salt at 900°C for 50 cycles. The following conclusions were made:

1. The oxidation rate of the coated and uncoated SS316L boiler steel follows the sequence as given below:

   Uncoated > TiAlN coating > AlCrN coating
2. The AlCrN coating has provided good resistance against oxidation in Na_2SO_4-60%V_2O_5 molten salt at 900 °C for 50 cycles and provided the necessary protection to the base metal.
3. The overall weight gain is less in case of AlCrN coatings as compared to the uncoated and TiAlN coated SS316L boiler steel.
4. The TiAlN coating has failed to provide the protection to the base metal during the oxidation in Na_2SO_4-60%V_2O_5 molten salt at 900°C for 50 cycles. This might be due to the formation of oxide scale which is composed of a porous oxide mixture of TiO_2 and Al_2O_3, with the domination of TiO_2.
5. In case of uncoated SS316L boiler steel, the weight gain is highest with thickest scale. Severe spalling and cracking is also observed in case of uncoated SS316L boiler steel.

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