

Performance of Nanostructured Metal Nitride Coated T-22 Boiler Steel in Na_2SO_4 –60% V_2O_5 Environment at 900°C under Cyclic Conditions

Vikas Chawla^{a*}, Amita Chawla^b, D. Puri^c, S. Prakash^c and Buta Singh Sidhu^d

^a Mechanical Engineering Department, F.C.E.T. Ferozepur-152002, India

^b Chemistry Department, Govt. Brijindra College, Faridkot-151203, India

^c Metallurgical & Materials Engineering Department, I.I.T. Roorkee -247667, India

^d Dean (Academics), P.T.U., Jalandhar-144001, India

*Corresponding Author: vikkymt@iitr.ernet.com

ABSTRACT

In this work, TiAlN and AlCrN coatings were deposited on ASTM-SA213-T-22 boiler steel using Balzer's rapid coating system (RCS) machine (make Oerlikon Balzers, Swiss) under a reactive nitrogen atmosphere. Cyclic oxidation studies in molten salt environment were conducted at 900°C temperature in the laboratory using silicon carbide furnace. The weight gain was measured after each cycle and visually examined the surface morphology of the oxidized samples was studied using FE-SEM with EDAX attachment and XRD analysis. The results obtained showed the better performance of TiAlN coated T-22 boiler steels than the AlCrN coated and uncoated T-22 boiler steel.

Keywords: Nanostructured coating, Hot corrosion, Oxide Scale, Physical vapour deposition, Scale morphology.

1. INTRODUCTION

In a wide variety of applications, materials have to operate under severe conditions such as erosion, corrosion and oxidation at higher temperature in hostile chemical environments. Therefore, surface modification of these components is necessary to protect them against various types of degradation [1]. As per the literature review, it is now generally accepted practice to apply coatings to components in fossil fuel energy processes to provide thermal insulation, corrosion and wear resistance, and in chemical process plants or boilers to protect the surface

of structural steels against surface degradation processes such as wear, oxidation, corrosion and erosion [2].

Recent studies show that 80% of the total cost for the protection of metals is related to coating application [3]. Although protective surface treatments are widely used at low temperature, the use of these at elevated temperature is relatively more recent [4]. In many tribological applications, hard coatings of metal nitrides are now commonly used [5]. The major properties required for such coatings are hardness and wear resistance. However, because of severe operating conditions, there is a need to combine mechanical features with corrosion resistance properties.

Physical vapor deposition technique (ion plating, sputtering, and arc evaporation) provides a promising ground for the deposition of these hard coatings by the formation of dense adhesive film at low deposition temperatures. Corrosion protection capability of physical vapor deposited (PVD) coatings is widely reported in literature [6]. Since the commercialization of physical vapor deposited (PVD) TiN coatings in early 1980s, transition metal nitrides based hard coatings have been successfully used for the materials protection particularly to improve cutting tools lifetime [7].

Nanostructured coatings are reported to provide surface characteristics (hardness, wear resistance etc) superior to those of conventional coatings. Despite that several potential advantages have been noted, the technology is yet to be established for use in industrial applications [8]. Present study investigates the effects of nanostructured TiAlN and AlCrN thin coatings on the hot corrosion behavior of T-22 steel under the cyclic heating conditions. Some power plants in India are using T-22 grade as boiler tubes material due to its performance in stringent service conditions of pressure and temperature. A front-loading *Balzer's rapid coating system (RCS) machine* (make Oerlikon Balzers, Swiss) was used for the deposition of the coatings. The purpose of this study is to develop high temperature oxidation, erosion and corrosion resistant materials by thin film coatings.

2. EXPERIMENTAL TECHNIQUES

2.1 Selection of Substrate Material

The substrate material used is: 2.25Cr-1Mo steel ASTM-SA213-T-22 (T-22). This material is used as boiler tube materials in some of the power plants in northern India. T-22 boiler steel has a wide range of applications in boilers, especially where the service conditions are more stringent from the point view of temperature and pressure. The chemical composition of T-22 boiler steel is as reported in Table 1.

Specimens with dimensions of approximately 20mm x 15mm x 5mm were cut from the alloy sheet. Polished using emery papers of 220, 400, 600 grit sizes and subsequently on 1/0, 2/0, 3/0, and 4/0 grades, and then mirror polished using cloth polishing wheel machine with $1\mu\text{m}$ lavigated alumina powder suspension.

Table 1: Chemical composition (wt %) of T-22 Boiler Steel (ASTM code SA213-T-22) :

Elements	C	Mn	Si	S	P	Cr	Mo	Fe
Nominal	0.15	0.3-0.6	0.5	0.03	0.03	1.9-2.6	0.87-1.13	Bal.
Actual	0.165	0.355	0.115	0.00153	0.02026	2.646	0.90275	Bal.

2.2. Development of Coatings

In the present study, the two coatings selected were TiAlN and AlCrN. The RCS system used to apply the coatings is shown schematically in Fig.1. The machine is equipped with 6 cathodic arc sources. Two of the six sources were used to deposit a thin, $0.3\mu\text{m}$ thick TiN sub-layer to improve adhesion of coating. The remaining four sources were employed to deposit the main layer of the coatings, which was obtained using customized sintered targets. The compositions of the targets used, coating thickness and the summary of the process parameters are presented in Table 2.

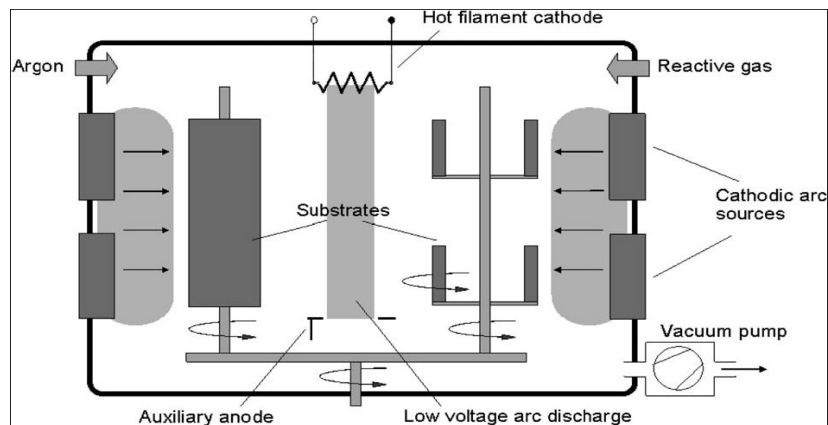


Fig. 1: Schematic illustration of the coating device used for the film deposition [8]

Table 2: Summary of deposition parameters

Machine used	Standard balzers rapid coating system (RCS) machine
Make	Oerlikon Balzers, Swiss
Targets composition	for <i>TiAlN coating</i> : Ti, Ti ₅₀ Al ₅₀ for <i>AlCrN coating</i> : Al ₇₀ Cr ₃₀
Number of targets	Ti (02), Ti ₅₀ Al ₅₀ (04) and Al ₇₀ Cr ₃₀ (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

For all coatings argon (Ar) and pure nitrogen atmosphere was used during deposition. Prior to deposition all the substrates were cleaned in two steps: firstly with Ultrasonic Pre-Cleaner (Imeco, Pune, India) and secondly with Ultrasonic Cleaning Machine with 9 Tanks including hot air dryer (Oerlikon Balzers (India) Ltd.) for 1.5 Hrs.

The characterization of as coated specimens was done and will be reported in another paper i.e. XRD (Bruker AXS D-8 advance diffractometer (Germany) with Cu K α radiation), SEM-EDAX analysis of surface as well as cross-section (FEI, Quanta 200F), surface morphology (2D and 3D) of the thin films by Atomic Force Microscope (AFM, make NT-MDT, Ntegra) and micro hardness. The particle size of the thin films was estimated from Scherrer formula as well as from AFM analysis, which was found to be 18 nm & 22 nm respectively for TiAlN coating, whereas for AlCrN coating was 25 nm & 27 nm respectively.

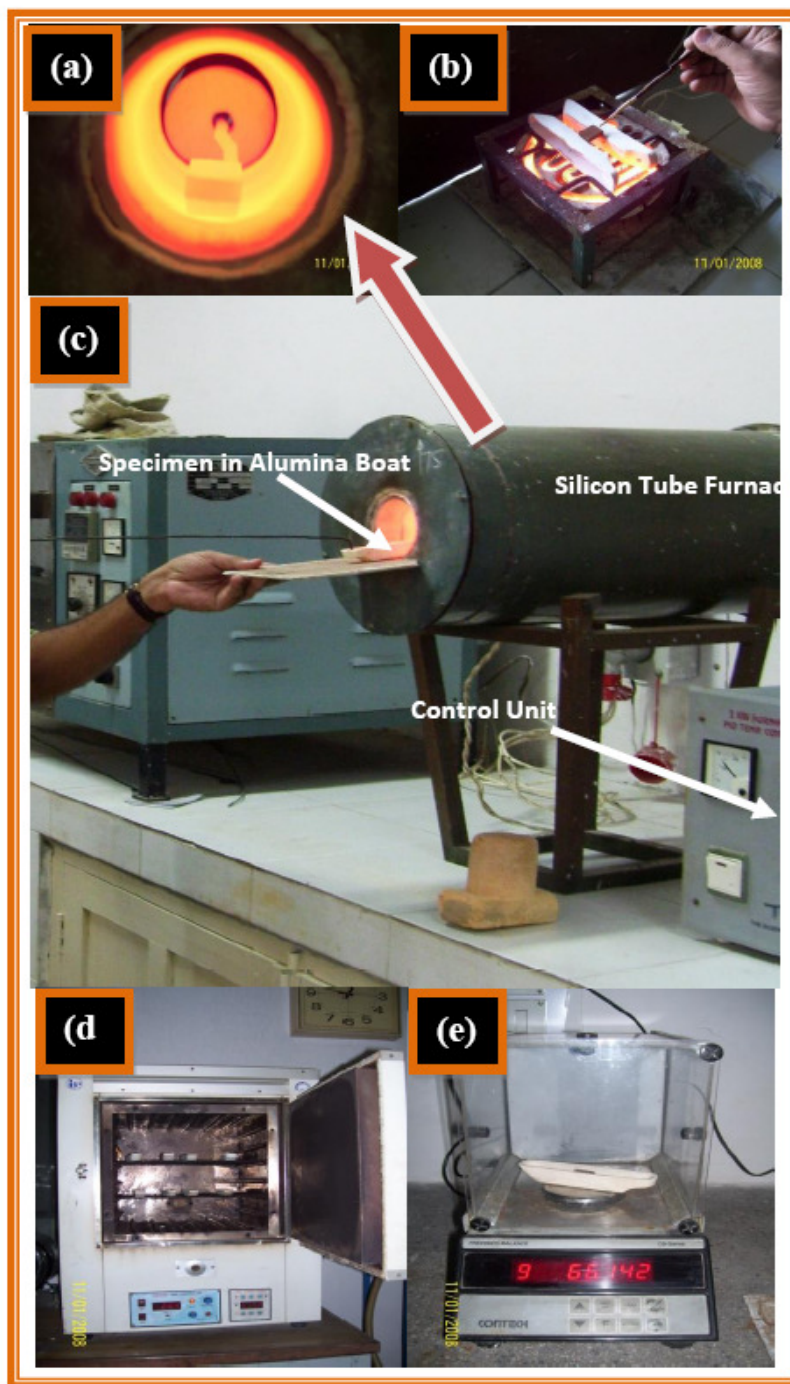
2.3 Hot Corrosion Studies in Na₂SO₄–60% V₂O₅ Molten Salt

Hot corrosion studies were conducted at 900°C in a laboratory silicon carbide tube furnace (make Digitech, India) as shown in Fig.2 (a & c). The furnace was calibrated to an accuracy of ± 5°C using Platinum/Platinum-13% Rhodium thermocouple fitted with a temperature indicator of Electromek (Model-1551 P), India. The bare as well as the coated specimens were polished down to 1µm alumina wheel cloth polishing to obtain similar condition of reaction before being subjected to corrosion run.

The physical dimensions of the specimens were then recorded carefully with 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. The

as coated as well as bare specimens (mirror polished) were then heated in an oven up to 250°C and a salt mixture of Na_2SO_4 -60% V_2O_5 dissolved in distilled water was coated on all the six surfaces of the warm polished specimens with the help of a camel hair brush (Fig.2.b). The salt Na_2SO_4 was obtained from S.D. Fine-chem Limited (Art. 40223), Mumbai and V_2O_5 was obtained from Loba Chemie Pvt. Ltd (Art. 6470), Mumbai. Amount of the salt coating was kept in the range of 3.0 -5.0 mg/cm^2 . The salt coated specimens as well as the alumina boats were then dried in the oven (Fig.2.d) for 3 hours at 100°C and weighed before being exposed to hot corrosion tests. Then each prepared specimen was kept in an alumina boat and the weight of boat and specimen was measured. The alumina boats used for the studies were pre-heated at a constant temperature of 1200°C for 12 hours and it was assumed that their weight would remain constant during the course of high temperature cyclic oxidation/corrosion study. Then, the boat containing the specimen was inserted into hot zone of the furnace maintained at a temperature of 900°C. The weight of the boat loaded with the specimen was measured after each cycle during the corrosion run, the spalled scale if any was also considered during the weight change measurements. Holding time in the furnace was one hour in still air followed by cooling at the ambient temperature for 20 minutes. Following this, weight of the boat along with specimen was measured and this constituted one cycle of the oxidation study. Electronic Balance Model CB-120 (Contech, Mumbai, India) having a sensitivity of 10^{-3} g was used to conduct the weight change studies (Fig.2.e). The specimens were subjected to visual observations carefully after the end of each cycle with respect to color or any other physical aspect of the oxide scales being formed.

All oxidation and hot corrosion studies were carried out for 50 cycles. The reproducibility in the experiments was established by repeating hot corrosion experiments for three cases. The kinetics of corrosion was determined from the weight change measurement. After the oxidation studies, the exposed specimens were analyzed by XRD and SEM-EDAX analysis using Bruker AXS D-8 advance diffractometer (Germany) with Cu $K\alpha$ radiation at the scan rate of 2°/min for 20° to 120° and FE-SEM (FEI, Quanta 200F) respectively. The oxidized specimens were then cut using Buehler's Precision Diamond saw (Model ISOMET 1000, USA make) across the cross-section and mounted for the cross-sectional analysis using SEM/EDAX and elemental X-ray mapping. The kinetics of the cyclic oxidation of coated as well as uncoated specimens was determined using the thermogravimetric analysis and by evaluating the parabolic rate constants.

**Fig. 2**

Experimental set up for high temperature oxidation and hot corrosion studies; (a) Heat Zone inside furnace, (b) Molten salt coating, (c) Silicon tube furnace, (d) Oven for pre heating the specimens, (e) Electronic balance

3. OBSERVATIONS

3.1 Visual examination

The macrographs for uncoated and coated ASTM-SA213-T-22 boiler steel subjected to cyclic oxidation in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C for 50 cycles are shown in Fig.3.

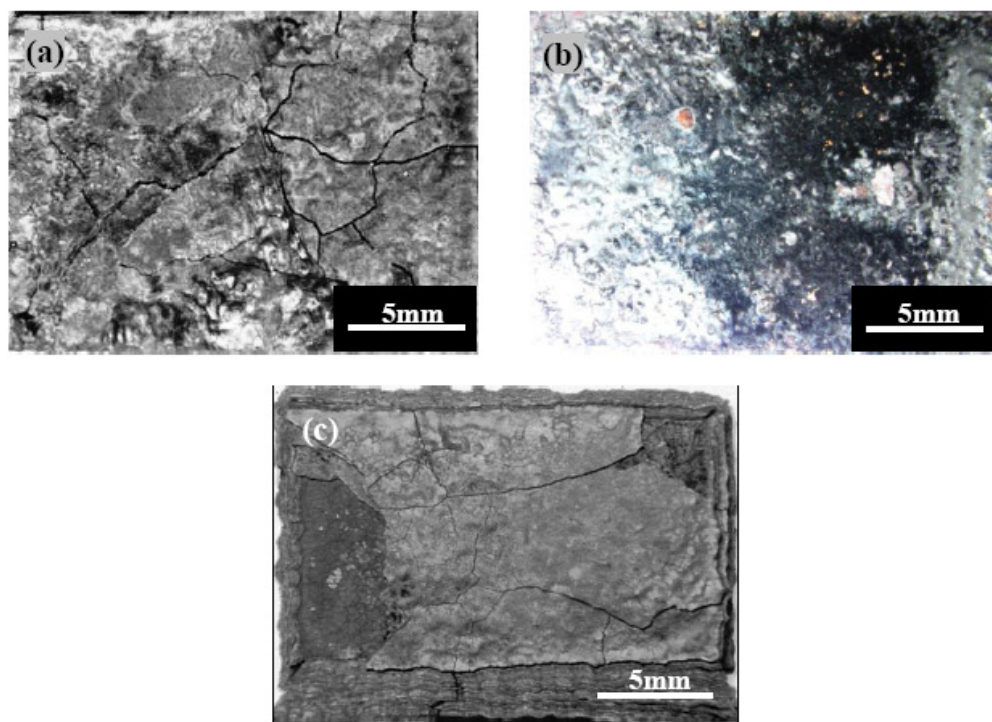


Fig. 3 Surface macrographs of uncoated and coated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles: (a) Uncoated T-22 boiler steel, (b) Nanostructured TiAlN coating, (c) Nanostructured AlCrN coating,

For the uncoated T-22 boiler steel, a grey colored scale appeared on the surface right from the 1st cycle. This bare steel showed spalling of scale just after the 5th cycle, which continued till the end of 50 cycles. At the end of cyclic study, irregular and fragile scale was observed with deep cracks and blackish grey color surface appearance, which can be seen in Fig.3 (a).

Color of the oxide scale at the end of the study was observed to be blackish grey from the middle portion of the sample with light grey sides, in case of nanostructured thin TiAlN coated T-22 boiler steel (Fig.3.b). The dark and light grey spots at some locations were observed after 16th cycle. After 25th cycle hairline cracks were observed in the oxide scale. The scale remains

adherent to the substrate during the course of the study. The nanostructured thin AlCrN coated T-22 boiler steel has shown the formation of fragile scale with cracks, when subjected to cyclic oxidation in Na_2SO_4 -60% V_2O_5 molten salt at 900°C for 50 cycles. Color of the oxide scale at the end of the study was observed to be dark grey, as shown in Fig.3 (c). The scale starts falling in the boat just after 3rd cycle and this trend continued till 50th cycle. New layers of scale were forming and falling in the boat.

3.2 Weight Change Measurements

Weight gain per unit area (mg/cm^2) versus time expressed in number of cycles plot for coated and bare T-22 boiler steel subjected to cyclic oxidation in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C for 50 cycles, is presented in Fig. 4.

The plots for all samples shows higher weight gain at initial cycles followed by gradual weight gain except in case of conventional TiAlN coating which has shown abrupt increase in oxidation rate after 21st cycle. The cumulative weight gain per unit area for the coated and uncoated T-22 boiler steel subjected to cyclic oxidation in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C for 50 cycles is shown in Fig. 5. The overall weight gain is highest ($348.5 \text{ mg}/\text{cm}^2$) in case of uncoated T-22 boiler steel. Further, the final weight gain in case of nanostructured TiAlN and nanostructured AlCrN coatings is 73.36 and $345.05 \text{ mg}/\text{cm}^2$ respectively.

Figure 6 shows the $(\text{weight gain}/\text{area})^2$ versus number of cycles plot for all the cases to ascertain conformance with the parabolic rate law. All the coated and uncoated ASTM-SA213-T-22 boiler steel followed the parabolic rate law as evident from the Figure 6. The parabolic rate constant K_p was calculated by a linear least-square algorithm to a function in the form of $(W/A)^2 = K_p t$, where W/A is the weight gain per unit surface area (mg/cm^2) and 't' indicates the number of cycles representing the time of exposure.

The parabolic rate constants for the bare and coated T-22 boiler steel calculated on the basis of 50 cycle's exposure data are shown in Table.3. The ' K_p ' value for the uncoated and nanostructured thin TiAlN coated T-22 boiler steel is higher than in case of other coatings.

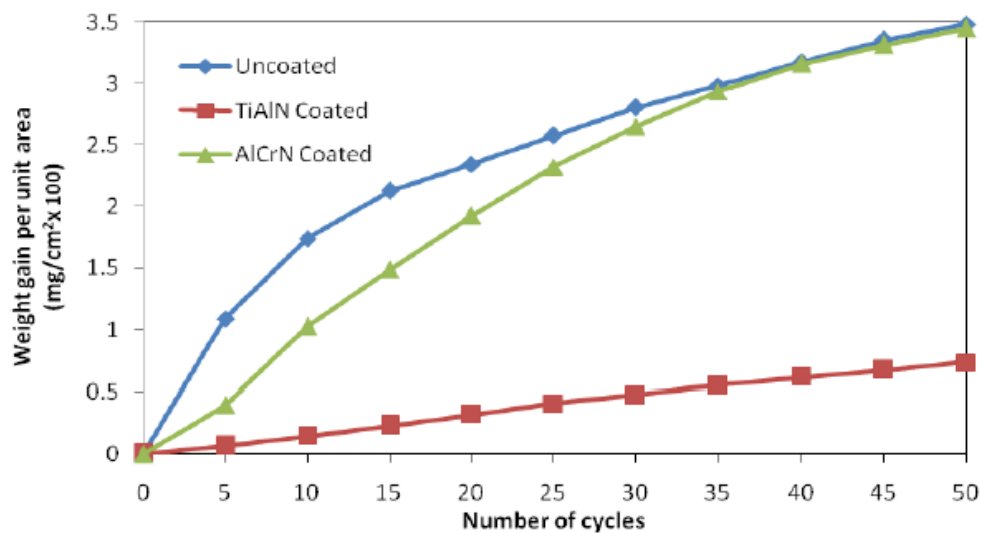


Fig. 4 Weight gain/area vs time (number of cycles) for the uncoated and coated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles

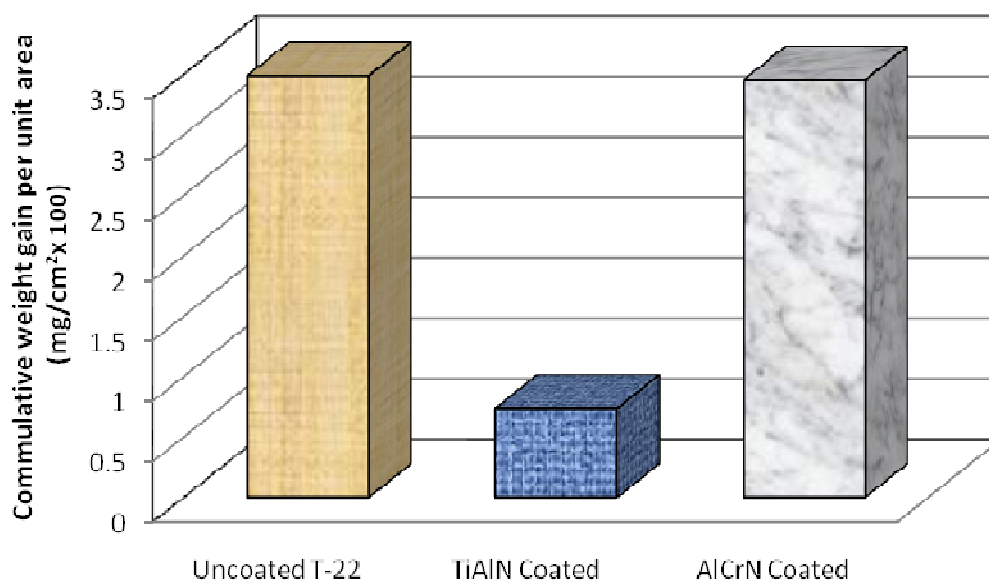


Fig. 5 Bar chart showing cumulative weight gain per unit area for the uncoated and coated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles: (A) Uncoated T-22 boiler steel, (B) Nanostructured TiAlN coating, (C) Nanostructured AlCrN coating

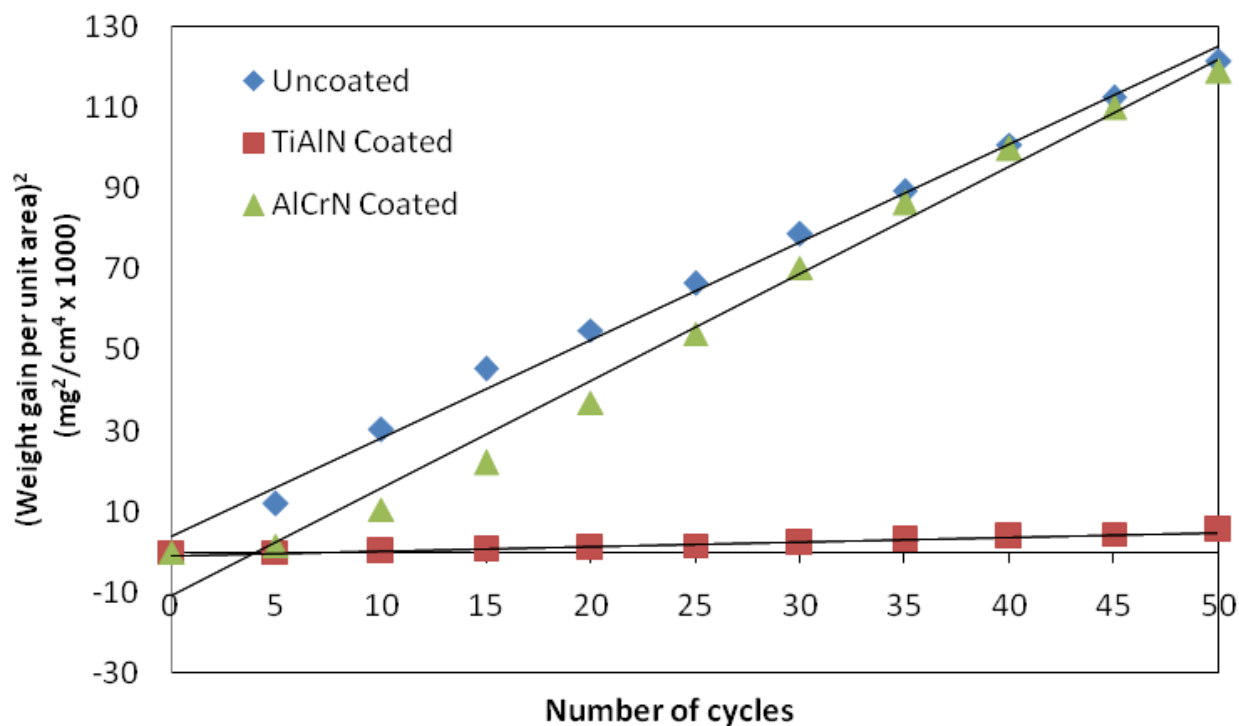


Fig. 6 Weight gain/area square vs time (number of cycles) for the uncoated and coated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles

Table 3 Parabolic rate constant ' K_p ' values of uncoated and coated ASTM-SA213-T-22 boiler steel subjected to cyclic oxidation in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C for 50 cycles

Substrate / Coating	K_p ($10^{-08} \text{ gm}^2 \text{ cm}^{-4} \text{ s}^{-1}$)
Uncoated T-22 boiler steel	67.36
Nanostructured TiAlN coating	03.10
Nanostructured AlCrN coating	73.72

3.3 X-ray Diffraction Analysis (XRD)

XRD diffractograms for coated and uncoated ASTM-SA213-T-22 boiler steel subjected to cyclic oxidation in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C for 50 cycles are depicted in Fig.7 on reduced scale. As indicated by the diffractograms Fe_2O_3 and Cr_2O_3 are the main phases

present in the oxide scale of uncoated and nanostructured thin TiAlN and AlCrN coated T-22 boiler steel. Also, weak peaks of Al_2O_3 are found in case of nanostructured thin TiAlN coating.

3.4 Surface Scale Morphology

SEM micrographs along with EDAX point analysis reveals the surface morphology of the coated and uncoated ASTM-SA213-T-22 boiler steel subjected to cyclic oxidation in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C for 50 cycles are shown in Fig.8. The oxide scale for uncoated T-22 boiler steel indicates the dominance of Fe and O (Fig.8.a). A small amount of Mo, Mn and Cr are also observed in the scale. The surface scale shows distorted and spalled grains like microstructure. The grains are of dark grey color (point 2) and boundaries are whitish in appearance (point 1).

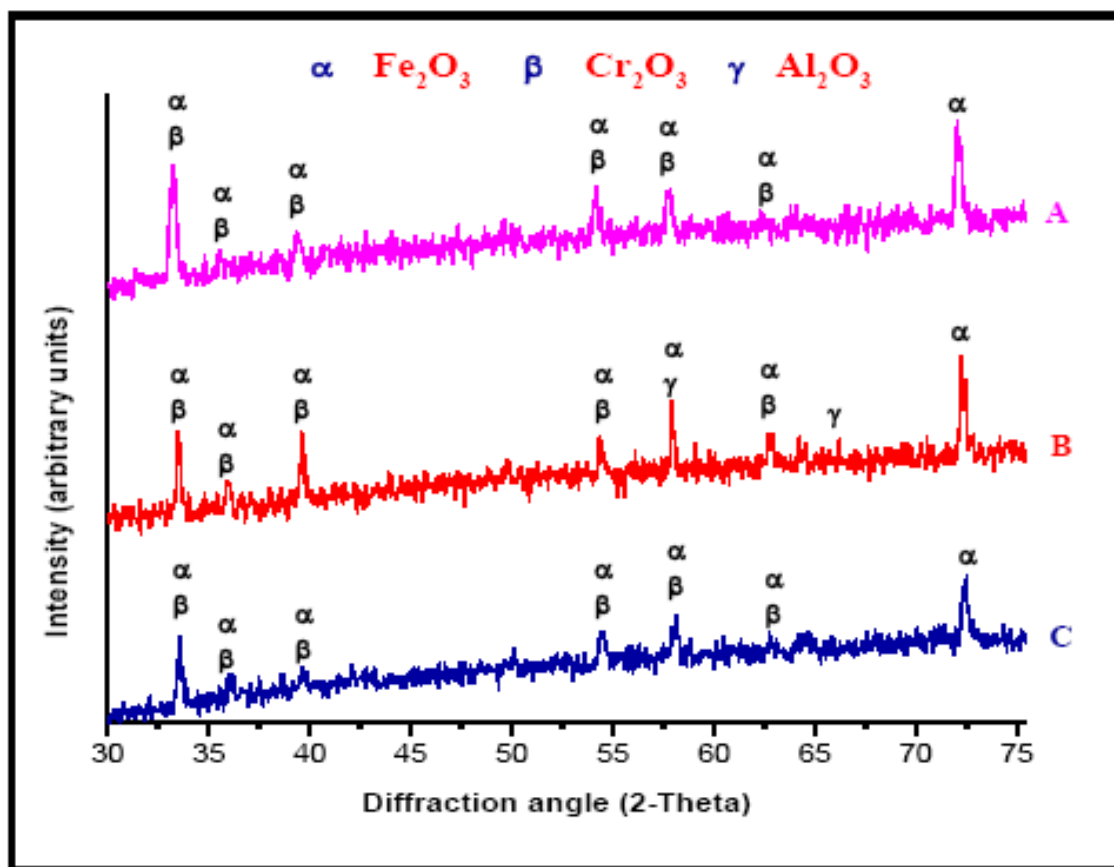


Fig. 7 X-Ray Diffraction pattern of uncoated and coated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles: (A) Uncoated T-22 boiler steel, (B) Nanostructured TiAlN coating, (C) Nanostructured AlCrN coating

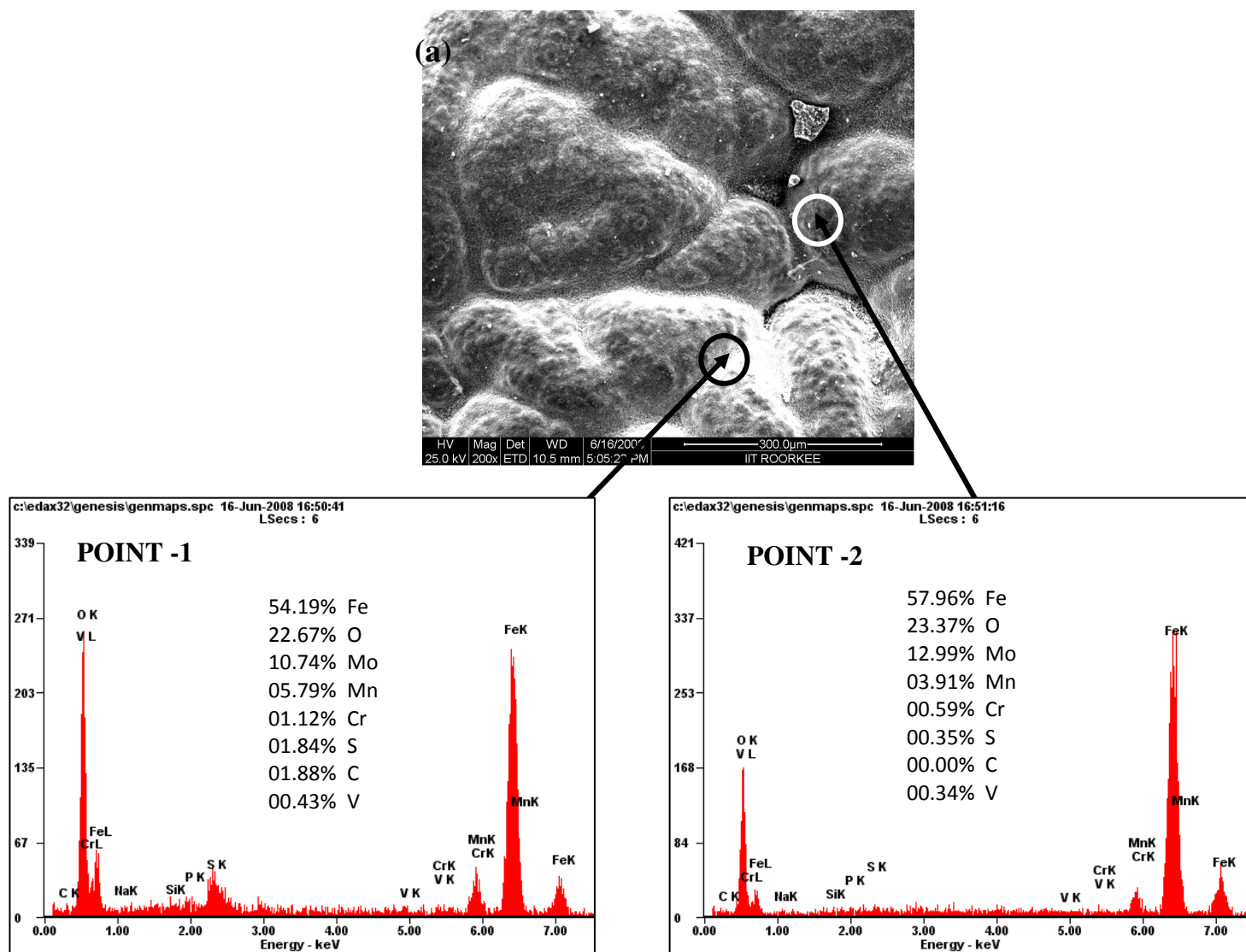


Fig. 8. SEM/EDAX analysis along with EDS spectrum for coated and uncoated T-22 boiler steel exposed to Na_2SO_4 -60% V_2O_5 at 900°C for 50 cycles, (a) Uncoated (X 200); (b) TiAlN coated (X 200); (c) AlCrN coated (X 200).

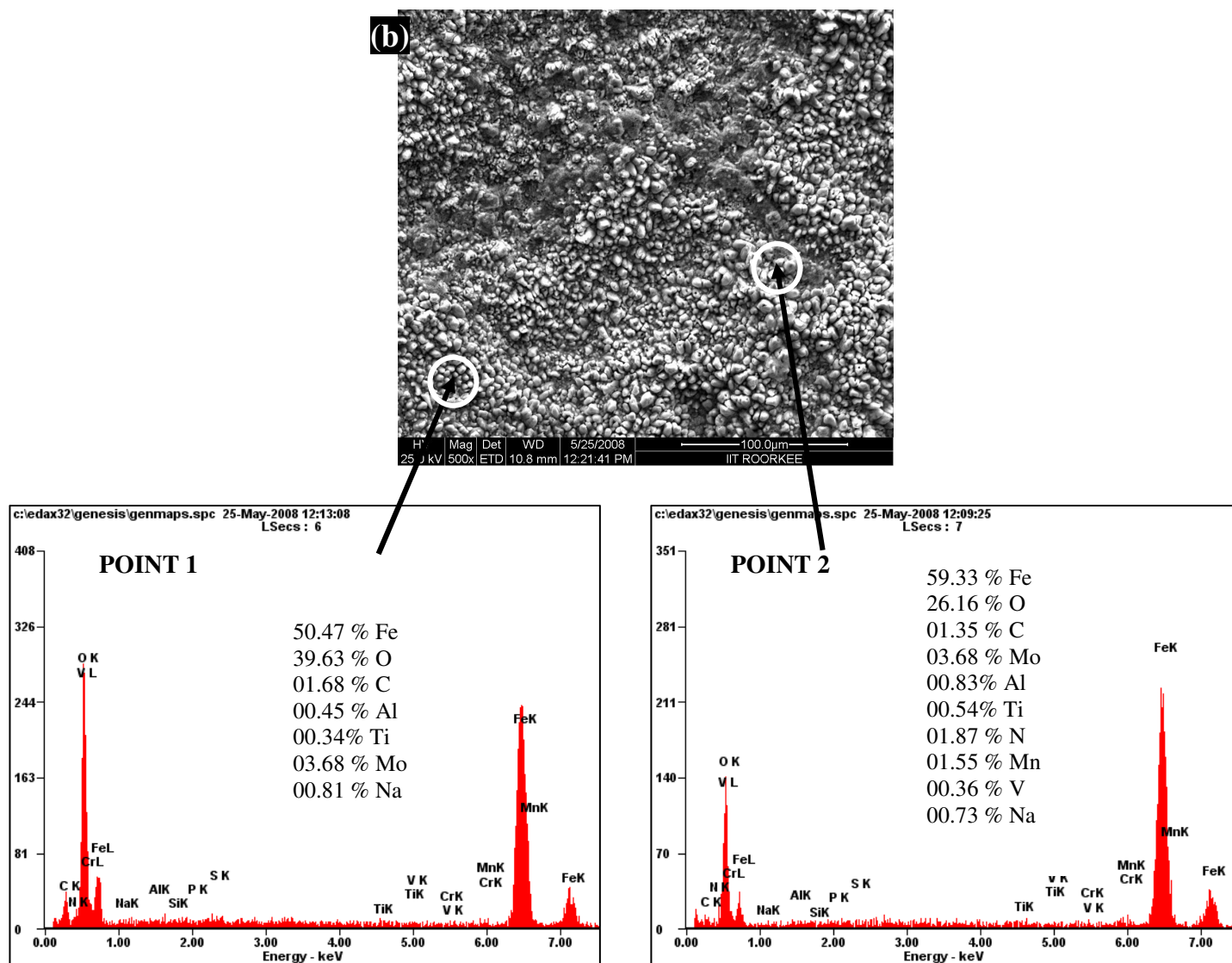


Fig. 8. (Continued).

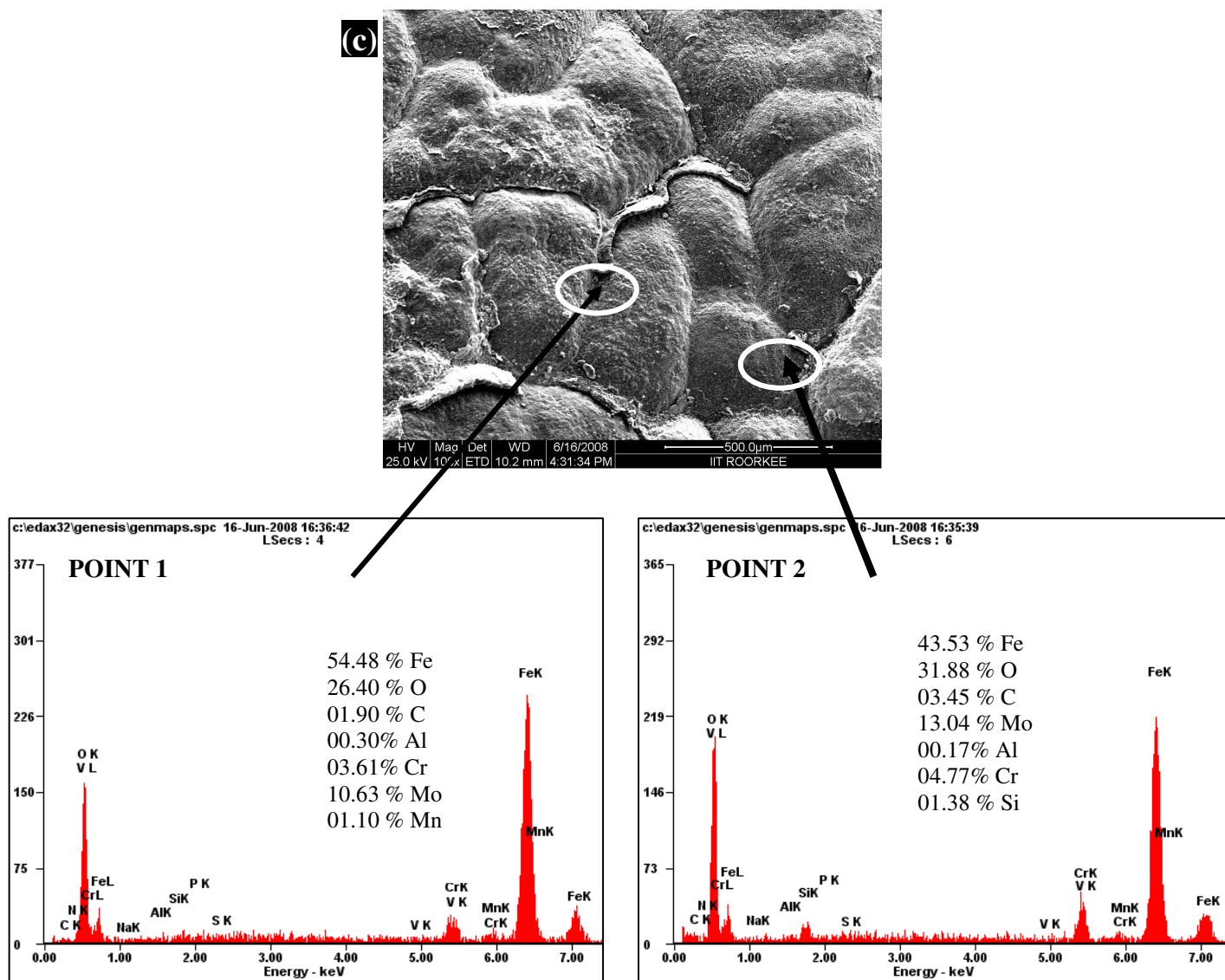


Fig. 8. (Continued).

The SEM micrograph of oxidized nanostructured thin TiAlN coatings is shown in Fig.8 (b). The oxide scale is mainly consisting of dark grey matrix (Point 2) and white needles dispersed in a matrix (Point 1) structure. EDAX analysis shows, the top scale rich in Fe and O with small amounts of Mo, Al, Ti, N, V, Na and Mn. As revealed by the EDAX analysis; matrix contains more amount of iron, whereas the needles like region contains higher amount of oxygen. In case of nanostructured thin AlCrN coated T-22 boiler steel, the SEM micrograph indicates distorted and spalled grains like microstructure as shown in Fig.8 (c). The EDAX point analysis shows the top scale rich in Fe, Mo and O. The small amount of Cr, Mn, Al, and Si are also present. The whitish region (point 2 on Fig.8.c) shows more amount of oxygen as compared to the dark grey area (point 1 on Fig.8.c).

3.5 Cross-Sectional Analysis

3.5.1 Scale thickness

The oxidized samples were cut across the cross section using Buehler Isomet 1000 precision saw and mounted in transoptic mounting resin and subsequently mirror polished to obtain scanning electron back scattered micrographs and X-ray mapping of different elements for coated and uncoated ASTM-SA213-T-22 boiler steel. The scale thickness values were measured from SEM back scattered micrographs as shown in Fig.9. Very thick scale is observed in case of nanostructured AlCrN coated T-22 boiler steel. The measured average scale thickness values for uncoated T-22 boiler steel, nanostructured thin TiAlN and nanostructured thin AlCrN coatings are 895, 738 and 2900 μ m respectively.

3.5.2 Cross-sectional scale morphology

Back Scattered Electron Image (BSEI) micrograph and elemental variation across the cross-section for coated and uncoated ASTM-SA213-T-22 boiler steel subjected to cyclic oxidation in Na₂SO₄-60%V₂O₅ (molten salt) environment at 900°C for 50 cycles are shown in Fig.9. The SEM micrograph in case of uncoated T-22 boiler steel shows uniform thick scale as shown in Fig. 9 (a). The EDAX analysis reveals the presence of iron, oxygen and molybdenum throughout the scale along Cr at some points (points 3 and 6 on Fig.9.a). The existence of significant amount of oxygen points out the possibility Fe₂O₃ in the oxide scale.

Also, the points where Cr content is more shows less Fe and more oxygen as compared to the other points. This is showing the possibility of Cr₂O₃ in the scale. BSEI micrograph and elemental variation depicted in Fig.9 (b), for the exposed cross-section of nanostructured thin TiAlN coated T-22 boiler steel shows the thick, continuous and adherent scale. The EDAX analysis reveals the presence of Fe, Mo and oxygen throughout the scale. A location at points 4 (Fig.9.b) in the micrograph depicts the increase in percentage of Cr with decrease in percentage

of Fe and Mo. A thick and fragile oxide scale can be seen in case of nanostructured AlCrN coated T-22 boiler steel (Fig.9.c). The scale is showing cracking.

3.5.3 X-Ray mapping

X-ray mappings for a part of oxide scale of uncoated and coated ASTM-SA213-T-22 boiler steel oxidized in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C for 50 cycles are shown in Fig.10. In case of uncoated T-22 boiler steel, the micrograph (Fig.10.a) indicates a dense scale, which mainly contains iron and oxygen with some amount of chromium. Presence of thin bands of Cr in the scale indicates the rich and Cr depleted regions. Figure 10 (b), shows X-ray mapping analysis of the scale formed on nanostructured TiAlN coated T-22 boiler steel. The BSEI image and X-ray mapping shows the formation of a dense scale consisting mainly of iron, oxygen and chromium. The X-ray mapping also indicates thick bands of Cr parallel to each other, near the scale/substrate interface. In case of nanostructured thin AlCrN coated T-22 boiler, the BSEI and X-ray mapping are shown in Fig. 10 (c). The scale formed is fragile. The X-ray mapping indicates the presence of iron and oxygen throughout the scale. Few parallel thin bands of Al and Cr can be seen at some locations, where iron is completely absent.

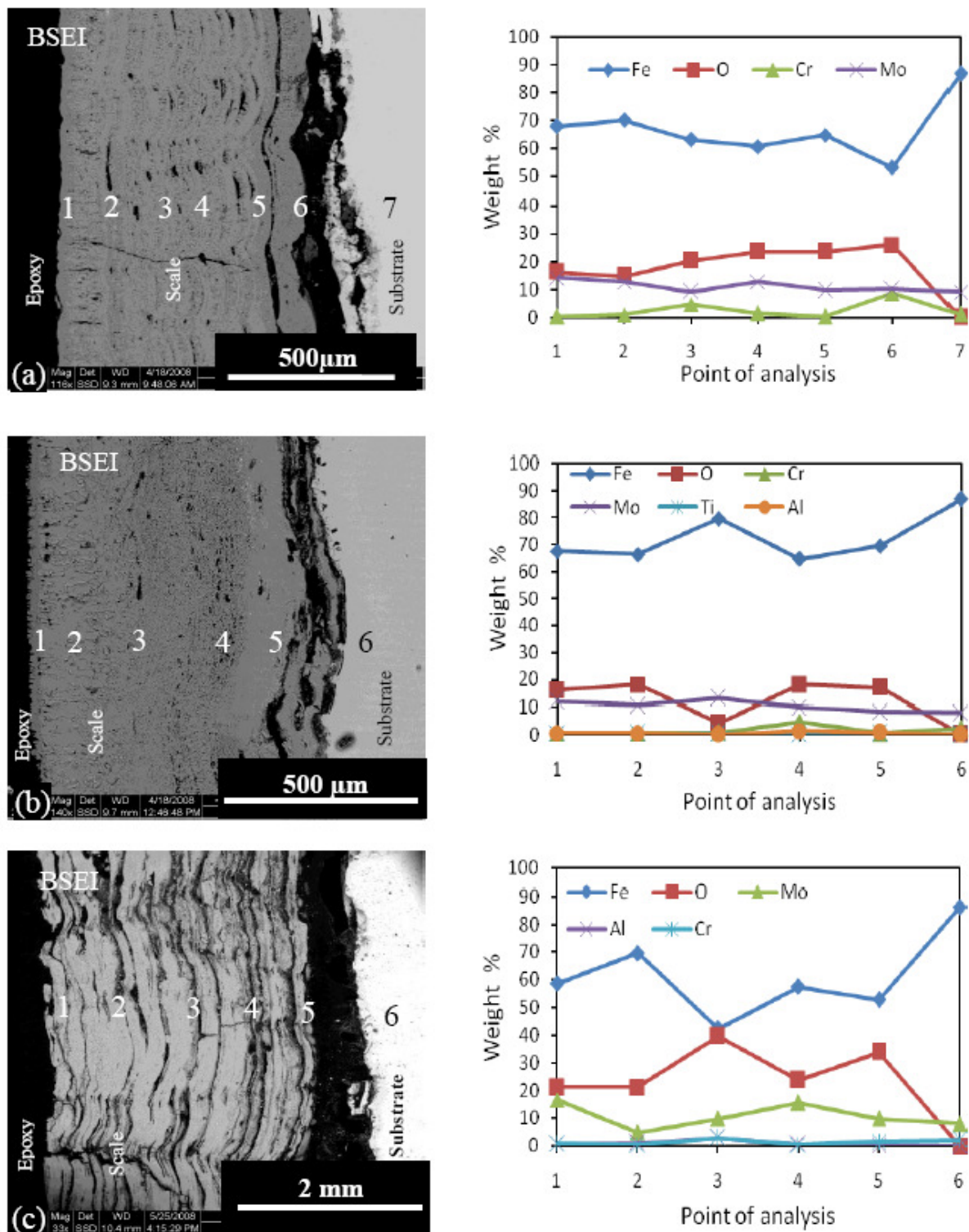


Fig. 9 Oxide scale morphology and variation of elemental composition across the cross-section of the uncoated and coated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles: (a) Uncoated T-22 boiler steel (116 X), (b) Nanostructured TiAlN coating (140 X), (c) Nanostructured AlCrN coating (33 X)

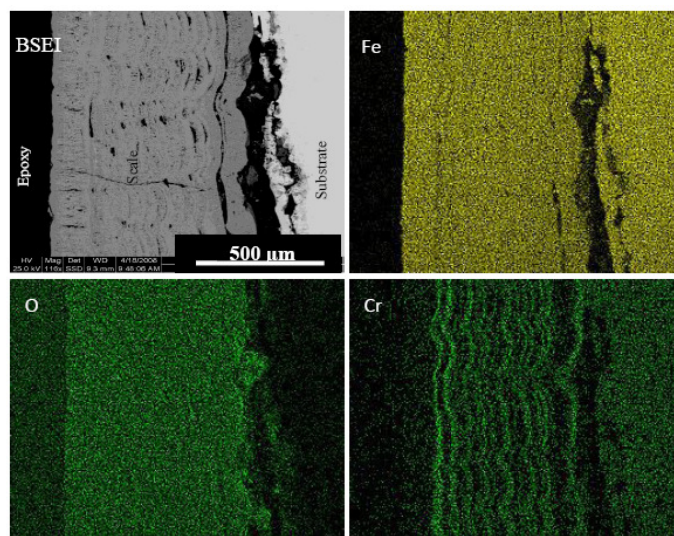


Fig. 10 (a) Composition image (BSEI) and X-ray mapping of the cross-section of uncoated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles

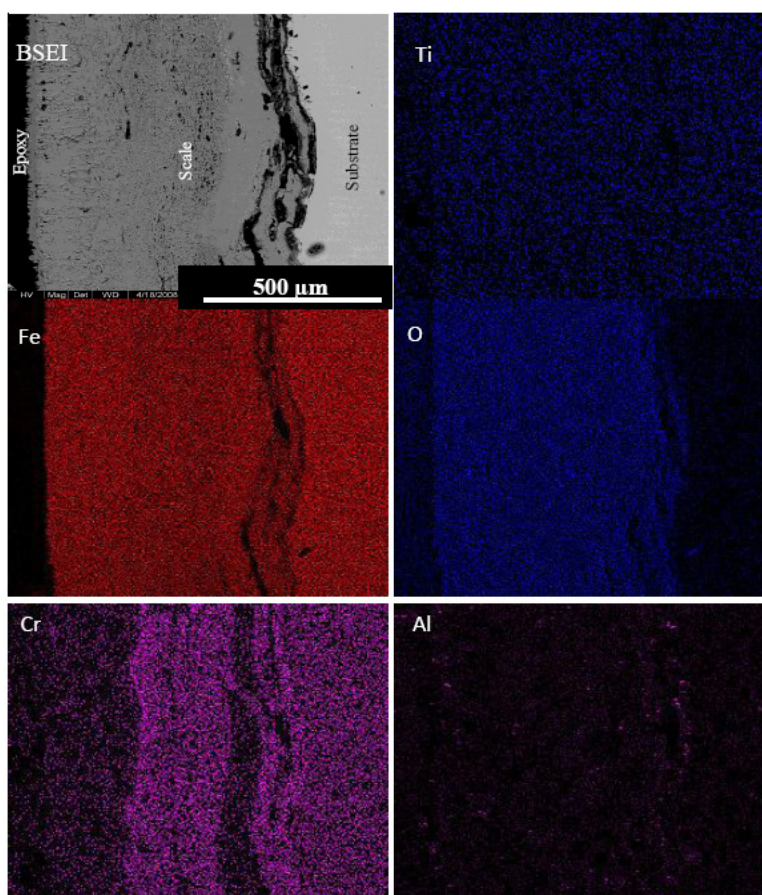


Fig. 10 (b) Composition image (BSEI) and X-ray mapping of the cross-section of Nanostructured TiAlN coated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles

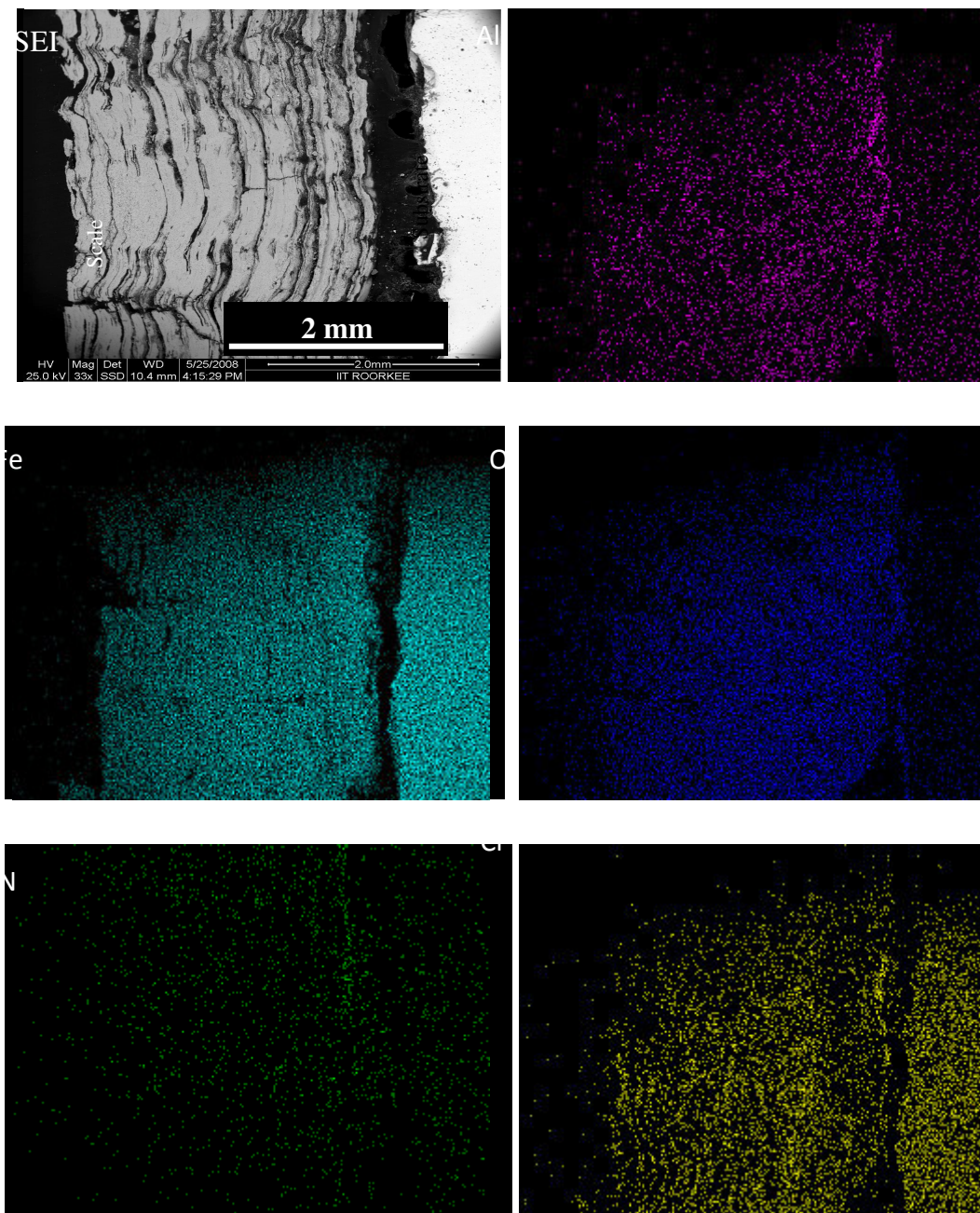


Fig. 10 (c) Composition image (BSEI) and X-ray mapping of the cross-section of Nanostructured AlCrN coated ASTM-SA213-T-22 boiler steel exposed to molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles

4. SUMMARY OF RESULTS

Results obtained after exposure of uncoated and coated ASTM-SA213-T-22 boiler steel to cyclic oxidation in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C for 50 cycles are summarized in Table 4.

Table 4 Summary of the results obtained for uncoated and coated ASTM-SA213-T-22 boiler steel subjected to cyclic oxidation in molten salt (Na_2SO_4 -60% V_2O_5) environment at 900°C for 50 cycles

Coating	Cumulative Weight gain (mg/cm^2)	Parabolic rate constant K_p ($10^{-08} \text{ gm}^2\text{cm}^{-4}\text{s}^{-1}$)	XRD phases	Remarks
Uncoated T-22 boiler steel	348.55	67.36	Fe_2O_3 and Cr_2O_3	A grey colored scale appeared on the surface right from the 1 st cycle. This bare steel showed spalling of scale just after the 5 th cycle, which continued till the end of 50 cycles. At the end of cyclic study, irregular and fragile scale was observed with deep cracks and blackish grey color surface appearance
Nanostructured TiAlN coating	73.36	03.10	Fe_2O_3 , Cr_2O_3 and Al_2O_3	Color of the oxide scale at the end of the study was observed to be blackish grey middle portion of the sample with light grey sides. The scale remains adherent to the substrate during the course of the study.
Nanostructured AlCrN coating	345.05	73.72	Fe_2O_3 , and Cr_2O_3	Color of the oxide scale at the end of the study was observed to be dark grey. The scale starts falling in the boat just after 3 rd cycle and this trend continued till 50 th cycle. New layers of scale were forming and falling in the boat.

5. DISCUSSION

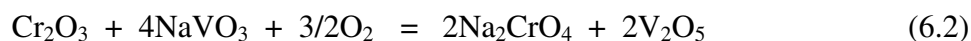
The bare and nanostructured AlCrN coated T-22 boiler steel showed accelerated corrosion in Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C and weight gain was relatively higher as compared to the other coating (Fig.4 and 5). The weight gain graph (Fig.4) for all samples shows higher weight gain at initial cycles followed by gradual weight gain. The weight change plots for the uncoated and coated T-22 boiler steel has shown conformance to parabolic rate law. The parabolic behavior is due to the diffusion controlled mechanism operating at 900°C under cyclic conditions [9]. Small deviation from the parabolic rate law might be due to the cyclic scale growth.

The higher weight gain during the first few cycles might be attributed to the rapid formation of oxides at the splat boundaries and within the open pores due to the penetration of the oxidizing species. Once the oxides are formed at places of porosity and splat boundaries, the coating becomes dense and the diffusion of oxidizing species to the internal portions of the coatings gets slowed down and the growth of the oxides becomes limited mainly to the surface of the specimens. This, in turn, will make the weight gain and hence the oxidation rate steady with the further progress of exposure time [10, 11].

The rapid increase in the weight gain during the initial period of exposure to Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C can also be attributed to the possible formation of NaVO_3 . Kolta et al. [12] proposed that at temperature range of 900°C , the Na_2SO_4 and V_2O_5 will combine to form NaVO_3 , as represented by eq.(6.1) having a melting point of 610°C .



This NaVO_3 acts as a catalyst and also serves as an oxygen carrier to the base alloy through the open pores present on the surface, which will lead to the rapid oxidation of the base elements of the substrate to form a protective oxide scale. There may be simultaneous dissolution of protective oxide Cr_2O_3 in the molten salt due to the reaction [13, 14]:



The Na_2CrO_4 gets evaporated as a gas [15]. The rapid increase in the weight gain during the initial period was also reported by Sidhu et al. [16], Harpreet Singh et al. [17], Tiwari and Prakash [18] and Ul-amid [19] during studies on the hot corrosion of alloys.

Nanostructured TiAlN coatings have been found successful in reducing the overall weight gain of bare T-22 boiler steel. The parabolic rate constant (K_p) was obtained from the slope of the linear regression fitted line (cumulative weight gain/area)² versus number of cycles (Table.3). The parabolic rate constant for the uncoated and nanostructured AlCrN coatings is found to be

higher than the nanostructured TiAlN coatings. The oxidation rate (total weight gain values after 50 cycles) of the coated and uncoated T-22 boiler steel boiler steel follows the sequence as given below:

Bare T-22 > Nanostructured AlCrN > Nanostructured TiAlN

The surface XRD analysis (Fig.7) indicated the formation of Fe_2O_3 as the main constituent of the top scale along with weak peaks of Cr_2O_3 in case of bare, nanostructured TiAlN and nanostructured AlCrN coated boiler steel. The formation of Fe_2O_3 has also been observed by Shi [20] for the oxidation of iron by Na_2SO_4 at 750°C and by Tiwari and Prakash [18] during hot corrosion of Iron-base superalloy in the Na_2SO_4 -60% V_2O_5 (molten salt) environment at 900°C . Weak intensity peaks of Cr_2O_3 in the scale of T-22 steel may due to the presence of some amount of chromium in the alloy steel. The presence of some percentage of chromium in the subscale as revealed by the X-ray mapping analysis (Fig.10) across the cross-section for T-22 steel is in accordance with the findings of Sadique et al. [21]. The authors have reported that Fe-Cr alloys in oxygen at higher temperature (950 - 1050°C) form spinel (FeCr_2O_4) and Cr_2O_3 on the inner side and Fe_2O_3 on the outer side of the scale. This can also be attributed to depletion of iron due to oxidation to form the upper scale thereby leaving chromium rich pockets those further get oxidized to form iron chromium spinel.

The severe spalling and cracking as observed in case of bare and nanostructured AlCrN coated T-22 steels may be attributed to the presence of molybdenum in the steels. Chatterjee et al. [22] have suggested that during initial hours oxidation Fe oxidizes and the oxide scale is protective in nature. With progress of oxidation Mo becomes enriched at the alloy scale interface, leading to the formation of an inner layer of molten MoO_3 (m. p. 795°C). MoO_3 might have further reacted with Na_2SO_4 as per the following reaction resulting in the formation of low temperature melting phase Na_2MoO_4 .



This might have led to the acidic fluxing of the protective oxide scale. This liquid oxide disrupts and dissolves the protective oxide scale, causing the alloy to suffer catastrophic oxidation [23]. Identical results have been reported by Peters et al. [24], Fryburg et al. [15], Pettit and Meier [25] and Misra [26]. The severe spalling of scale identical to the present study for similar type of steel i.e. T-22 type of steel during hot corrosion in medium BTU coal gasifier environment has also been reported by Wanget al. [27] where more than 70% of the scale got spalled during testing. Further Misra [26] reported the spalling of thick external porous scale which spalled off completely on cooling during corrosion experiments at 900°C and 950°C .

Accelerated corrosion observed in the present study in case of bare and nanostructured AlCrN coated T-22 boiler steel up to the end of exposure may be in accordance with the findings of

Misra [26]. The author reported that higher the concentration of Mo, the sooner the melt would attain the MoO_3 activity necessary for the formation of solid NiMoO_4 and this would cause a decrease in the length of the period of accelerated corrosion. Lower percentage of Mo (0.87-1.13%) in the concerned alloy for the present study might have increased the period of accelerating corrosion up to the end of 50 cycles. Probably this factor is responsible for the higher weight gain for bare and nanostructured AlCrN coated T-22 boiler steel.

During cyclic testing, severe cracking in the oxide scale of the bare T-22 boiler steel might be attributed to the different values of thermal expansion coefficients for the scale and the substrate as reported by Sidhu et al. [16], Singh et al. [10], Evans et al. [28], Wang et al. [27] and Niranatlungpong et al [29].

In case of nanostructured thin TiAlN coating, the Fe_2O_3 in the top layer and Fe_2O_3 and Cr_2O_3 in the subscale analyzed by the XRD (Fig.7), SEM-EDAX (Fig.8.b) and X-ray mapping (Fig. 6.10.b). Figure 10 (b) indicated the presence of a thick band of Cr in the subscale along with oxygen and iron. This can be attributed to the depletion of iron due to oxidation to form the upper scale, thereby leaving chromium-rich pockets those have further oxidized to form a regular chromium oxide bands. This band of chromium oxide may have prevented the deep penetration of the reacting environment, as the scale thickness is less in case of oxidized nanostructured thin TiAlN coated T-22 boiler steel than that of uncoated boiler steel. It can be mentioned based on the present investigation that nanostructured thin TiAlN coatings can provide a very good oxidation resistance in Na_2SO_4 -60% V_2O_5 molten salt environment at high temperature.

6. CONCLUSIONS

The high temperature oxidation behaviors of uncoated and coated ASTM-SA213-T-22 boiler steel have been investigated in Na_2SO_4 -60% V_2O_5 molten salt at 900 °C for 50 cycles. The behavior of nanostructured TiAlN and AlCrN coatings was studied and the following conclusions are made:

1. The oxidation rate (total weight gain values after 50 cycles) of the coated and uncoated T-22 boiler steel follows the sequence as given below:
Uncoated T-22 > Nanostructured AlCrN > Nanostructured TiAlN
2. The nanostructured thin TiAlN coatings has shown resistance to oxidation as the overall weight gain is less than as compared to the uncoated T-22 boiler steel.
3. In case of uncoated T-22 boiler steel, the weight gain is highest with thickest scale. Severe spalling and cracking is also observed in case of bare and nanostructured thin AlCrN coated boiler steel.
4. The nanostructured thin TiAlN coatings can provide a good oxidation resistance in Na_2SO_4 -60% V_2O_5 molten salt environment at high temperature.

5. The oxide scale formed is adherent to the substrate in nanostructured thin TiAlN coated ASTM-SA213-T-22 boiler steel. But in case of bare boiler steel, the scale is found to be detached from the substrate after hot corrosion studies.
6. The appearance of cracks/peeling off in the coatings during hot corrosion studies may be attributed to the different values of thermal expansion coefficients for the coating, substrate steel and oxides.

ACKNOWLEDGEMENT

The authors wish to thank All India Council for Technical Education (A.I.C.T.E.), New Delhi, India for providing National Doctoral Fellowship (NDF) to Dr. Vikas Chawla (corresponding author) and Nationally Coordinated Project (NCP).

REFERENCES

- [1] L. Pawlowski; The Science and Engineering of Thermal Spray Coatings; Wiley; New York; 1995.
- [2] B. Q. Wang, G. Q. Geng, A. V. Levy; Surface & Coating Technology; 1992; 54-55; 529-35.
- [3] L. Fedrizzi , S. Rossi , R. Cristel , P.L. Bonora , Elect. Chem. Acta 49 (2004) 2803–2814.
- [4] Harpreet Singh, D. Puri and S. Prakash, International Symposium of Research Students on Materials Science and Engineering, December 20-22, 2004, Indian Institute of Technology Madras, Chennai, India.
- [5] G. Bertrand, H. Mahdjoub, C. Meunier, Surf. & Coat. Technol. 126 (2000) 199-209.
- [6] L. Cunha, M. Andritschky , L. Rebouta , K. Pischow, Surf. & Coat. Technol. 116–119 (1999) 1152–1160.
- [7] Xing-zhao Ding, A.L.K. Tan, X.T. Zeng, C. Wang, T. Yue, C.Q. Sun, Thin Solid Films 516(2008) 5716-5720.
- [8] B.R. Marple, J. Voyer, J. F. Bisson, C. Moreau, J. Mater. Process. Technol. 117 (2001), 418-423.
- [9] Mahesh, R. A., Jayagandhan, R. and Prakash, S., (2008), “A Study on Hot Corrosion Behaviour of Ni-5AL Coatings on Ni- and Fe-based Superalloys in an Aggressive Environment at 900°C,” J. Alloy and Compounds, Vol. 460, No. 1-2, pp. 220-231.
- [10] Singh, H., Prakash, S. and Puri, D., (2007), “Some Observations on the High Temperature Oxidation Behaviour of Plasma Sprayed Ni₃Al Coatings,” Mater. Sci. Engg. A, 444 (2007) 242-250.
- [11] Sidhu, T. S., Agarwal, R. D. and Prakash, S., (2006E), “Hot Corrosion of a NiCr Coated Ni-based Alloy,” Scripta Materialia, Vol. 55, pp. 179-182.

- [12] Kolta, G. A., Hewaidy, L. F. and Felix, N. S., (1972), "Reactions Between Sodium Sulphate and Vanadium Pentoxide," *Thermochim. Acta*, Vol. 4, pp. 151-164.
- [13] Seierdten, M and Kofstad, P., (1987), "Effect of SO₃ on Vanadate Induced Hot Corrosion," *High Temp. Technol.*, Vol. 5, No. 3, pp. 115-122.
- [14] Swaminathan, J., Raghavan, S. and Iyer, S.R., (1993), "Studies on the Hot Corrosion of Some Nickel-base Superalloys by Vanadium Pentaoxide," *T. Indian I. Metals*, Vol. 46, No. 3, pp. 175-181.
- [15] Fryburg, G. C., Kohl, F. J., Stearns, C. A. and Fielder, W. L., (1982), "Chemical Reactions Involved in the Initiation of Hot Corrosion of B-1900 and NASA-TRW VIA," *J. Electrochem. Soc.*, Vol. 129, No. 3, pp. 571-85.
- [16] Sidhu, B.S., Puri, D. and Prakash, S., (2005), "Mechanical and Metallurgical Properties of Plasma Sprayed and Laser Remelted Ni-20Cr and Stellite-6 Coatings," *J. Mater. Process. Technol.*, Vol. 159, No. 3, pp. 347-355.
- [17] Harpreet Singh, Puri, D. and Prakash, S., (2005), "Corrosion Behaviour of Plasma Sprayed Coatings on a Ni-base Superalloy in Na₂SO₄-60%V₂O₅ Environment at 900°C," *Metall. Mater. Trans. A*, Vol. 36, No. 4, pp. 1007-1015.
- [18] Tiwari, S. N. and Prakash, S., (1996), "Hot Corrosion Behaviour of an Iron-Base Superalloy in Salt Environment at Elevated Temperatures," *Proc. of Sympos. Metals and Materials Research*, Indian Institute of Technology Madras, Madras, 4-5th July, pp. 107-117.
- [19] Ul-Hamid, A., (2004), "A TEM Study of the Oxide Scale Development in Ni-Cr-Al Alloys," *Corros. Sci.*, Vol. 46, No. 1, pp. 27-36.
- [20] Shi, L., (1995), "On the Possibility of a Na₂SO₄-Na₂O Eutectic Melt Developing on Metals Coated with Na₂SO₄ Deposit in Oxygen/Air at Intermediate Temperatures," *Corros. Sci.*, Vol. 37, No. 8, pp. 1281-1287.
- [21] Sadique, S. E., Mollah, A. H., Islam, M. S., Ali, M. M., Megat, M. H. H. and Basri, S., (2000), "High-Temperature Oxidation Behavior of Iron-Chromium-Aluminum Alloys," *Oxid. Met.*, Vol. 54, Nos. 5-6, pp. 385-400.
- [22] Chatterjee, U. K., Bose, S. K. and Roy, S. K., (2001), "Environmental Degradation of Metals," Pub., Marcel Dekker, 270 Madison Avenue, New York.
- [23] Lai, G. Y., (1990), 'High Temperature Corrosion of Engineering Alloys,' *ASM Inter. Book*, pp. 15-46.
- [24] Peters, K. R., Whittle, D. P. and Stringer, J., (1976), "Oxidation and Hot Corrosion of Nickel-Based Alloys Containing Molybdenum," *Corros. Sci.*, Vol. 16, pp. 791-804.
- [25] Pettit, F. S. and Meier, G. H., (1985), "Oxidation and Hot corrosion of Superalloys," *Superalloys 85*, Eds. Gell, M., Kartovich, C. S., Bricknel, R. H., Kent W. B. and Radovich, J. F., *Met. Soc. of AIME*, Warrendale, Pennsylvania, pp. 651-687.
- [26] Misra, A. K., (1986), "Mechanism of Na₂SO₄-Induced Corrosion of Molybdenum Containing Nickel-Base Superalloys at High Temperatures," *J. Electrochem. Soc.*, Vol. 133, No. 5, pp. 1029-37.

- [27] Wang, B. Q. and Luer, K., (1994), "The Relative Erosion-Corrosion Resistance of Commercial Thermal Sprayed Coatings in a Simulated Circulating Fluidized Bed Combustor Environment," Proc. of the 7th National Spray Conf., 20-24th June, Boston, Massachusetts, pp. 115-20.
- [28] Evans, H. E. and Taylor, M. P., (2001), "Diffusion Cells and Chemical Failure of MCrAlY Bond Coats in Thermal Barrier Coating Systems," Oxid. Met., Vol. 55, pp.17-34.
- [29] Niranatlumpong, P., Ponton, C. B. and Evans, H. E., (2000), "The Failure of Protective Oxides on Plasma-Sprayed NiCrAlY Overlay Coatings," Oxid. Met., Vol. 53, No. 3-4, pp. 241-256.