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Structural characterization and corrosion behavior of nanostructured TiAlN and AlCrN thin coatings in the 3 wt% NaCl solutionVIKAS CHAWLA^{a*}, AMITA CHAWLA^b, BUTA SINGH SIDHU^c, S. PRAKASH^d and D. PURI^d^a Mechanical Engineering Department, F.C.E.T., Ferozepur-152002, India^b Chemistry Department, Government Brijindra College, Faridkot -151203, India^c Punjab Technical University (P.T.U.), Jalandhar -144001, India^d Metallurgical & Materials Engineering Department, I.I.T. Roorkee, Roorkee-247667, India*E-mail: vikkydmt@gmail.com

Abstract

In this work, TiAlN and AlCrN coatings were deposited on low-carbon steel ASTM-SA210 Grade A-1 (GrA1) by using Balzer's rapid coating system (RCS) machine (make Oerlikon Balzers, Swiss) under a reactive nitrogen atmosphere. The coated samples were subjected to optical microscopy (OM), Field emission scanning electron microscope (FESEM with EDAX attachment), AFM analysis and XRD analysis. The corrosion resistance of the substrate, TiAlN-coated and AlCrN-coated samples in a 3 wt% NaCl solution was evaluated and compared by electrochemical potentiodynamic polarization method. It was found that the TiAlN-coating exhibited better corrosion resistance when compared to AlCrN-coating.

Keywords: Physical vapour deposition (PVD), Thin films, Microstructure, Corrosion.

1. Introduction

Physical vapor deposition technique (ion plating, sputtering, and arc evaporation) provides a promising ground for the deposition of 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 [1]. In many applications, the coated parts are

frequently exposed to an aggressive working environment, for instance, a Cl^- containing

corrosive medium which has strong effects in promoting localized corrosion, particularly in marine environment [2]. Recent studies show that 80% of the total cost for the protection of metals is related to coating application [3]. Coatings provide a way of extending the limits of the use of the materials at the upper end of performance capabilities, by allowing the mechanical properties of the substrate materials to be maintained while protecting against wear, oxidation and corrosion [4].

Transition metal nitrides based hard coatings (especially TiN) have been successfully used for the materials protection since the commercialization of physical vapor deposited (PVD) TiN coatings in early 1980s [5]. The use of the ternary system Ti-Al-N as a base for a new hard coating material is one of the most successful new trends in the titanium-nitride technology [6]. In comparison with TiN-based coatings (e.g. TiAlN), CrAlN coatings have been reported exhibiting higher oxidation resistance, as both the chromium and aluminum could form protective oxides which suppressed oxygen diffusion [2]. Many recent reports have shown the improvement made on cutting and drilling lifetime versus speed performance, wear and friction reduction and corrosion resistance when these materials are used in the coating of the tools [6].

In this work, titanium aluminum nitride (TiAlN) and aluminum chromium nitride (AlCrN) coatings were deposited on low-carbon steel ASTM-SA210 Grade A-1 (GrA1) by using *Balzer's rapid coating system (RCS) machine* (make Oerlikon Balzers, Swiss) under a reactive nitrogen atmosphere at Oerlikon Balzers' Coatings, Gurgaon, India. ASTM-SA210 Grade A-1 (GrA1) material is used as boiler tube materials in some of power plants in northern India. GrA1 has a

wide range of applications in boilers, especially in the construction of the water walls. As

reported in literature, mostly Cr and Al are added to enhance the oxidation resistance. Besides the oxidation resistance of the materials at high temperature, the resistance to pitting corrosion at normal temperature is another important performance of these materials. The chloride-rich seawater is a harsh environment that can attack the materials by causing pitting and crevice corrosion. So, the corrosion behavior of the as deposited coatings and substrate in a 3 wt% NaCl solution was tested and compared by an electrochemical method.

2. Experimental details

2.1. Development of coatings

TiAlN and AlCrN coatings, with a thickness around 4 μ m, were deposited on low-carbon steel ASTM-SA210 Grade A-1 (GrA1). The actual chemical composition of the substrate steel analyzed with the help of Optical Emission Spectrometer of Thermo Jarrel Ash (TJA 181/81), USA make. The nominal and actual chemical composition of the substrate is as reported in Table 1.

Table 1

Chemical composition (wt %) of A-1 Boiler Steel (ASTM code SA210-Grade A1) :

Elements	C	Mn	Si	S	P	Fe
Nominal	0.27	0.93	0.1	0.058	0.048	Bal.
Actual	0.2768	0.67257	0.1725	0.00517	0.0093	Bal.

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.

A front-loading *Balzer's rapid coating system machine* was used for the deposition of the coatings (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. For all coatings argon (Ar) and pure nitrogen atmosphere was used during deposition.

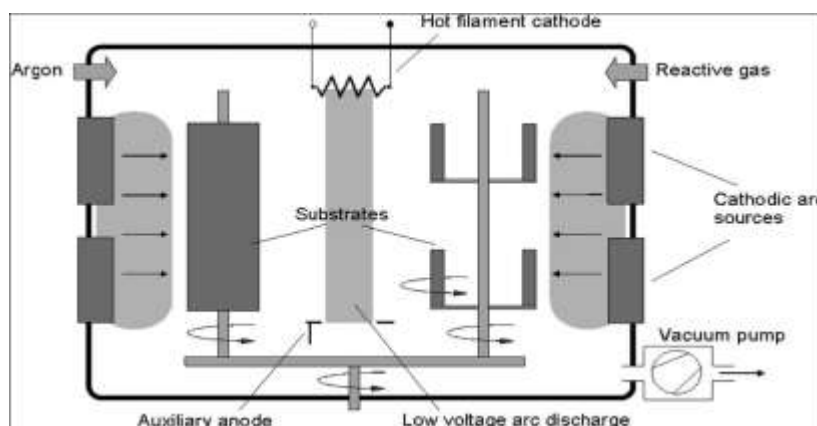


Fig.1: Schematic illustration of the coating device used for the film deposition [7].

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 Ltd. India) for 1.5 Hrs.

Table 2

Summary of coating 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
Total deposition pressure	3.5 Pa
Substrate bias voltage	-40V to -170V
Substrate temperature	450°C ± 10°C
Coating Thickness	4 µm ± 1 µm

2.2 Characterization of the coatings

A Zeiss Axiovert 200 MAT inverted optical microscope, fitted with image software Zeiss Axiovision Release 4.1, was used for optical microscopy. Field emission scanning electron microscope (FESEM, FEI, Quanta 200F Company) with EDAX Genesis software attachment (made in Czech Republic) is used to characterize the surface morphology of the coatings. SEM micrographs along with EDS spectrum were taken with an electron beam energy of 20keV. The surface morphology (2D and 3D) of the thin films was characterized by AFM (Model: NTEGRA, NT-MDT, Ireland) to calculate the surface roughness and particle size.

The coated specimens were subjected to XRD analysis using Bruker AXS D-8 advance diffractometer (Germany) with Cu K α radiation. The scan rate used was 2°/min and the scan

range was from 20° to 120°. The grain size of the thin films was estimated from Scherrer

formula [8]. The porosity measurements were made with image analyser, having software of Dewinter Materials Plus 1.01 based on ASTM B276. A PMP3 inverted metallurgical microscope was used to obtain the images.

2.3 Electrochemical test

In order to evaluate the corrosion behavior of the substrate and coatings, an electrochemical method i.e. potentiodynamic polarization test was conducted in an aerated 3 wt% NaCl solution at room temperature. The electrolyte employed was prepared with NaCl analytical Grade reagent with minimum assay 99.9 % supplied by Qualigens Fine Chemicals, Mumbai, India and deionised water. The potentiodynamic polarization test was carried out using EG&G PAR model 273A potentiostat. The test cell used was having the provisions in the form of circular openings of different sizes to permit the introduction of the two high purity graphite counter electrodes, the working electrode (test specimen) and the Luggin probe capillary tube, which housed the saturated calomel reference electrode (SCE). The tip of the Luggin probe capillary was placed near the sample. The exposed surface area of all specimens was 1 cm² and the remaining portion except the exposed area was painted with good quality nail-paint in order to prevent the initiation of corrosion. Before the electrochemical measurements, samples were allowed to stabilize at their open circuit potential for 30 min. Potentiodynamic polarization measurements were carried out starting from -250 mV_{OCP} to 1600 mV_{SCE} with a scan rate of 0.5 mV/s. The potentiodynamic polarization plots were interpreted using SoftcorrTM III Corrosion Measurement software Version 2.30 provided by EG&G Instruments INC.

3. Results & Discussion

3.1 Microstructural properties

The TiAlN and AlCrN coatings have been formulated successfully by PAPVD (Plasma assisted physical vapour deposition) technique on ASTM-SA210 Grade A-1 (GrA1) steel. The macrographs for TiAlN and AlCrN coatings are shown in Fig.2.

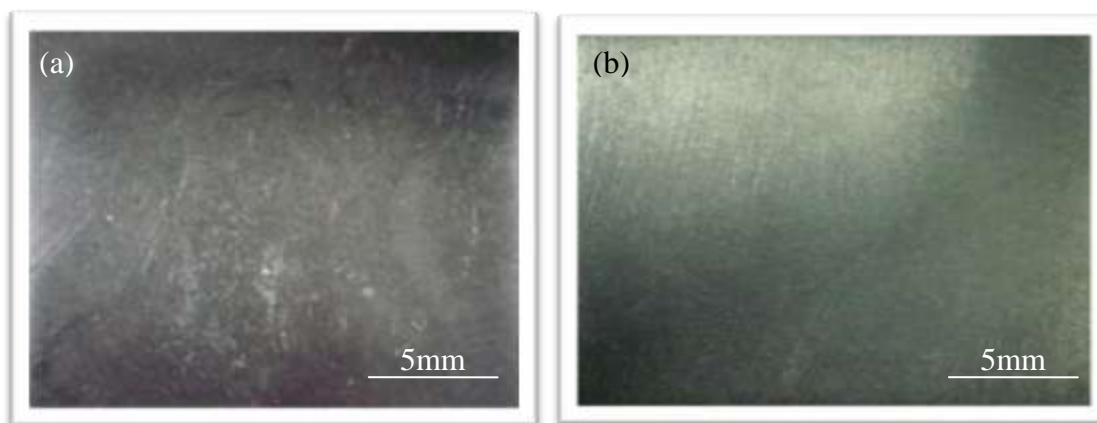


Fig.2: Surface macrographs of (a) TiAlN and (b) AlCrN coatings on substrate (Grade A-1).

The surface appearance of TiAlN coating is violet grey in color and light grey in case of AlCrN coating. Fig. 3 depicts the optical micrographs of the substrate and thin film coatings. The coatings have uniform microstructure. It is evident from the microstructure that the coatings contain some pores and inclusions. The porosity for as coated TiAlN and AlCrN coatings is 0.45 % and 0.42 % respectively and reported in Table. 3.

XRD diffractograms for each coating are depicted in Fig. 4 on reduced scale. XRD analysis for TiAlN coating confirmed the presence of a large percentage of TiN along with AlN. Further, in case of AlCrN coating, the prominent phases are CrN and AlN. From the XRD diffractograms, the grain size of the thin coatings was estimated from Scherrer formula, and reported in Table. 3.

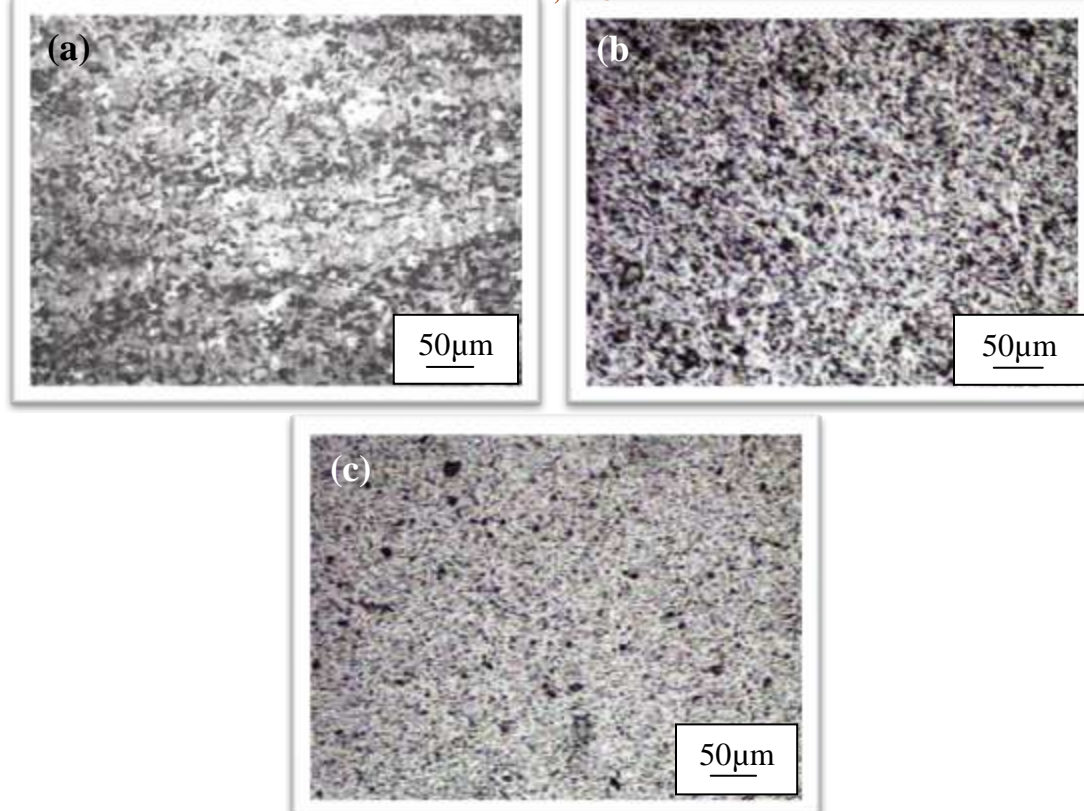


Fig.3: Optical micrograph (200X) of the surface of (a) Substrate, (b) TiAlN coating and (c) AlCrN coating.

Table 3

Micro structural and mechanical properties of the coatings

Coating	Surface Roughness (nm)	Hardness* (HV 0.05)	Particle Size (nm) <i>Scherrer Formula</i>	Particle Size (nm) <i>AFM Analysis</i>	Porosity (%)	Friction* coefficient against steel (dry)	Coating color
TiAlN	03.75	3300	16	18	0.45	0.30-0.35	violet-grey
AlCrN	06.10	3200	26	28	0.42	0.35	light-grey

*Data supplied by at Oerlikon Balzers' Coatings, Gurgaon, India.

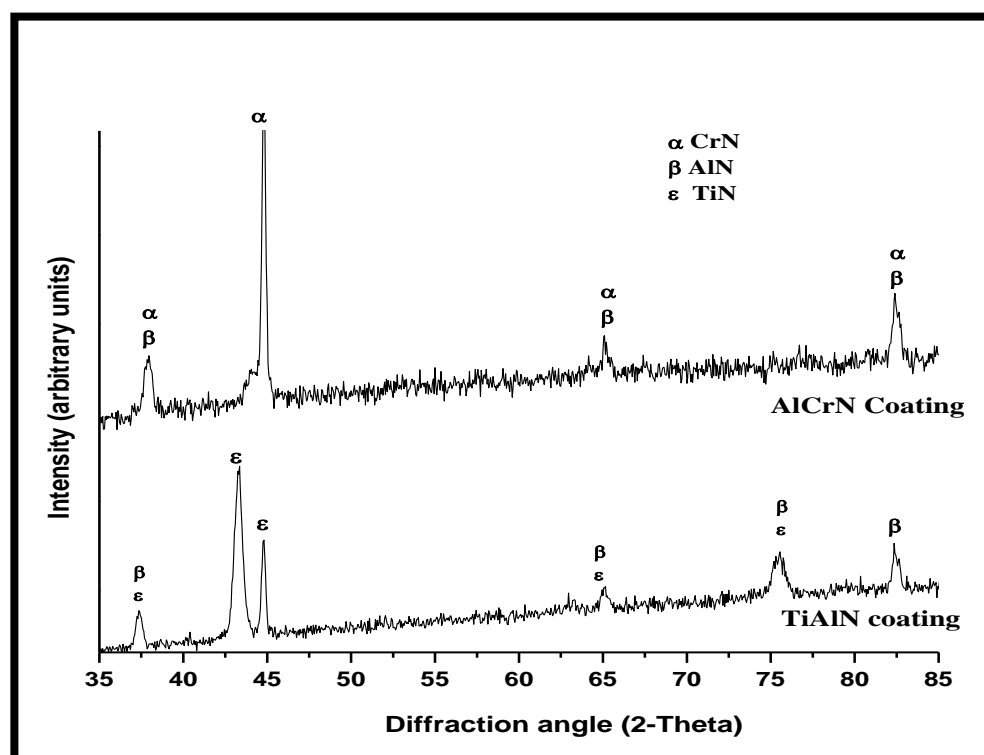


Fig.4: X-ray diffraction pattern for TiAlN and AlCrN coatings on boiler steel substrate (Gr A-1).

The grain size in case of TiAlN coatings (16 nm) is less than that of AlCrN coating (26 nm). Oerlikon Balzers Ltd. India provided the data regarding hardness and the friction coefficient against steel (dry), along with the coating parameters (Table.3). The coated layer on the steel substrate has provided higher hardness as compared to the substrate. In particular, TiAlN coating showed higher hardness value than AlCrN coating.

SEM micrographs along with EDAX analysis for as coated TiAlN and AlCrN coatings are shown in Fig.5. In case of TiAlN coating, the EDAX point analysis (Fig. 5.a) shows the presence of Ti (46.69 %) as the main phase along with Al (24.46 %) and N (24.90 %). A very small amount of O, Fe and C is present, which may be due to the micro voids or pores present in the coating.

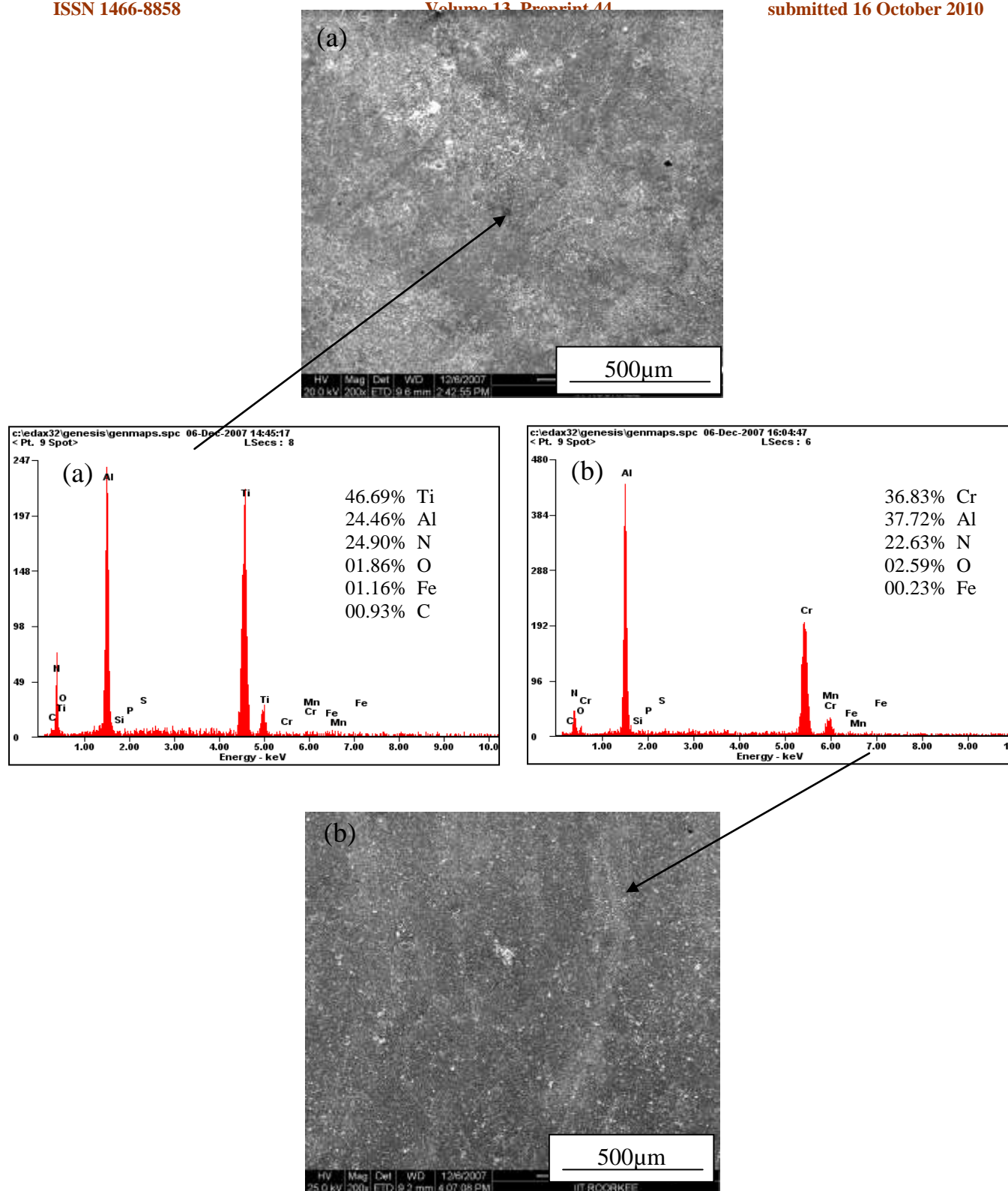


Fig.5: SEM/EDAX analysis along with EDS spectrum for (a) TiAlN (X 200); (b) AlCrN coatings (X 200) on boiler steel substrate (Grade A-1).

Further in case of AlCrN coating, Cr (36.83 %) and Al (37.72 %) are the main phases along with N (22.63 %), as indicated by the EDAX analysis (Fig.5.b).

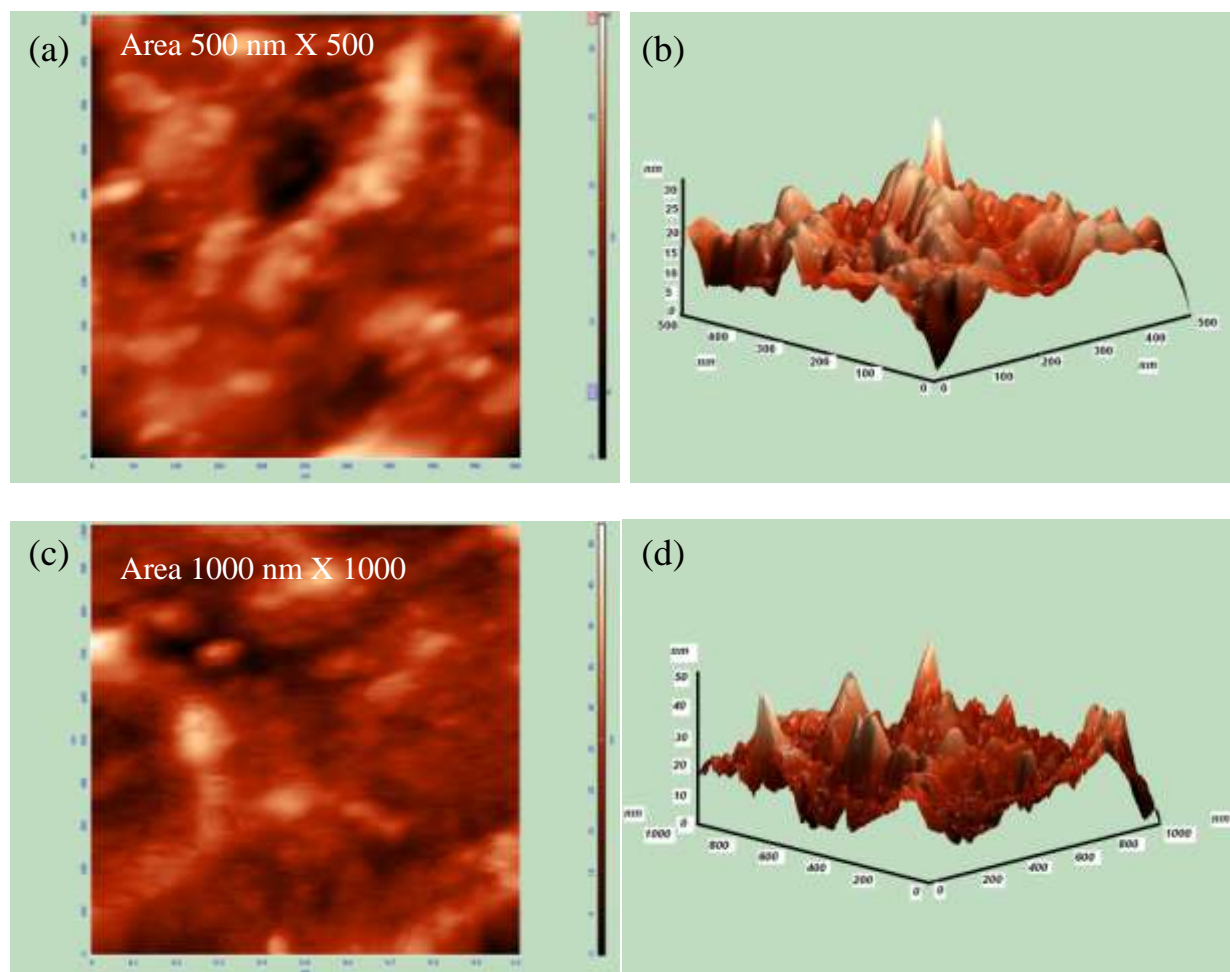


Fig.6: 2D and 3D AFM images of TiAlN [(a) & (b)] and AlCrN [(c) & (d)] coatings on boiler steel substrate (Grade A-1).

Fig. 6 (a-d) shows the AFM surface morphology (2D and 3D) of the TiAlN and AlCrN coatings deposited on ASTM-SA210 Grade A-1 (GrA1) steel. The difference in the morphology between the two coatings can be inferred by comparing the 2D images in Fig. 6 (a) and (c); however a clearer comparison of the coatings is afforded by viewing 3D images in Fig. 6 (b) and (d). As the

axis scale indicates the overall roughness of the TiAlN coating, Fig. 6 (b) is less than that of

AlCrN coating, Fig. 6 (d). The particle size in the coatings was also provided by AFM Analysis, which as reported in Table. 3. The TiAlN coating is having lesser particle size (18 nm) as compared to AlCrN coating (28 nm).

3.2 Electrochemical properties

Potentiodynamic polarization curves of the substrate and each film are shown in Fig.7 and the corrosion parameters in Table 4. The corrosion current density and the corrosion potential were obtained by the intersection of the extrapolation of anodic and cathodic Tafel curves.

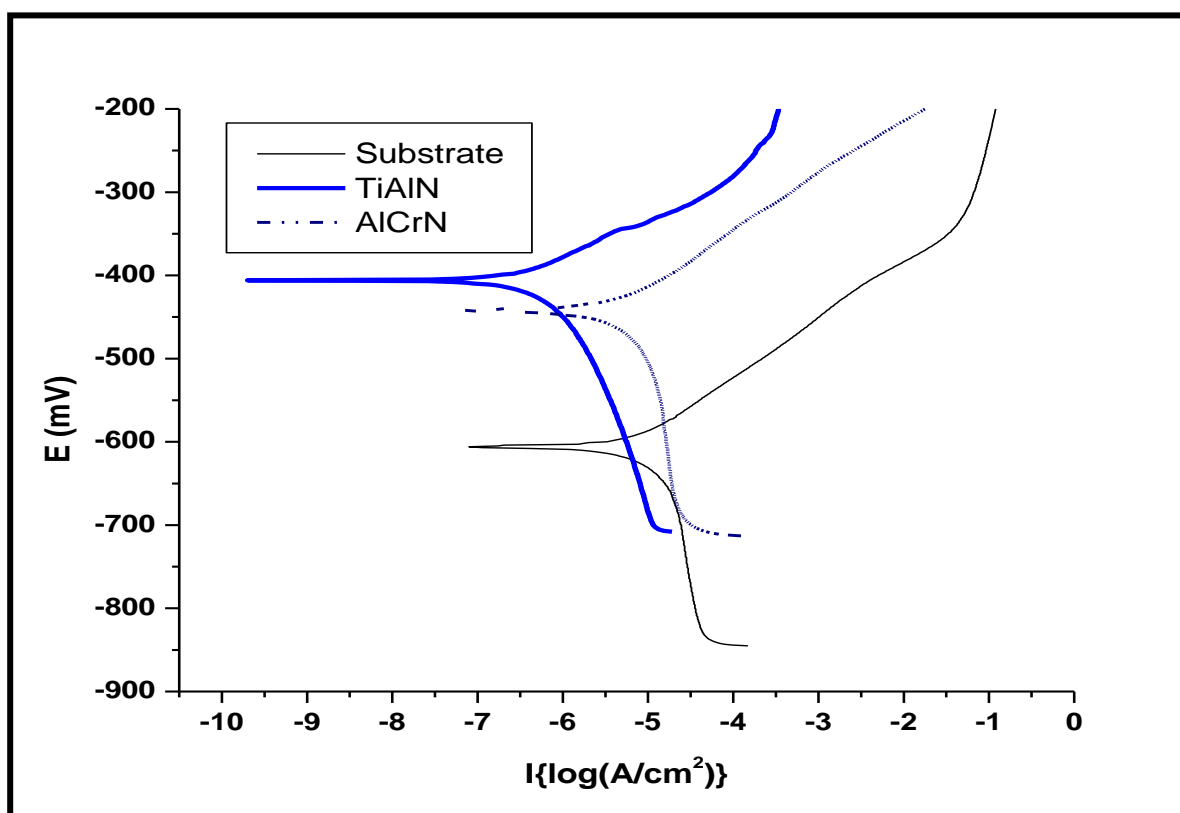


Fig.7: Potentiodynamic Polarization Curves.

Table 4

Results of potentiodynamic polarization tests

Specimen	E_{corr} (mV)	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (V/decade)	β_c (V/decade)	R_p ($\text{k}\Omega\text{-cm}^2$)	P_i (%)	F (%)
Substrate	-606.0	9.498	0.0759	0.3089	02.78	--	--
TiAlN	-405.6	0.676	0.0642	0.2136	40.38	92.87	0.015
AlCrN	-442.1	5.982	0.0735	0.3790	04.46	37.01	0.432

The corrosion current densities of the films were found much lower than that of the substrate steel. The TiAlN coating has performed very well and showed best corrosion resistance as evident from corrosion current density and polarization resistance.

The corrosion rate (i_{corr}) of the specimens was obtained using the Stern-Geary equation [9].

$$\frac{1}{i_{\text{corr}}} = \frac{1}{i_{\text{corr}}^0} \left(\frac{\beta_a \beta_c}{\beta_a + \beta_c} \right) \left(\frac{R_p}{R_p + R_s} \right) \quad (1)$$

Where β_a = anodic Tafel slope, β_c = cathodic Tafel slope, R_p = polarization resistance and, Z is a function of the Tafel slopes.

From polarization test results, the protective efficiency, P_i (%) of the films can be calculated by

Eq. (2):

$$P_i = \left(\frac{i_{\text{corr}}^0}{i_{\text{corr}}} \right) \left(\frac{\beta_a \beta_c}{\beta_a + \beta_c} \right) \left(\frac{R_p}{R_p + R_s} \right) - 1 \quad (2)$$

Where i_{corr} and i_{corr}^0 indicate the corrosion current density of the film and substrate, respectively [10]. The calculated protective efficiencies and polarization resistances are presented in Fig.8.

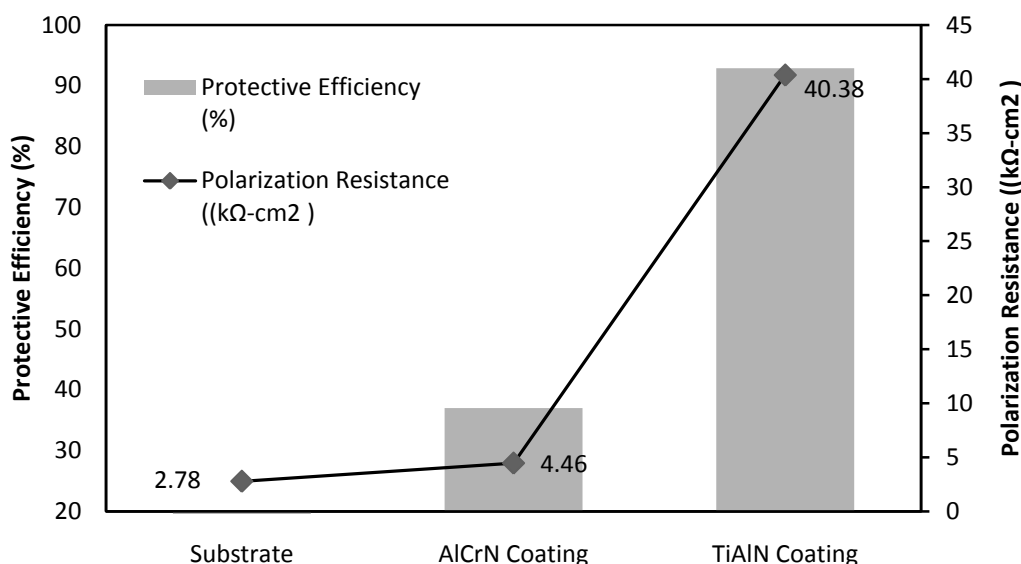


Fig.8: Protective efficiency and Polarization resistance of TiAlN and AlCrN coatings on boiler steel substrate (Grade A-1).

The TiAlN film showed the highest protective efficiency of 92.87% caused by lowest corrosion current density of $0.676 \mu\text{A}/\text{cm}^2$. The observed protection by the TiAlN and AlCrN coatings in an aerated 3 wt% NaCl solution at room temperature, are almost in agreement with the findings of Yun Ha Yoo et al. [10] and Xing-zhao et al. [5].

For further justification the porosity values has also been measured quantitatively by the electrochemical methods according to Eq. (3) proposed by A. Matthews [10] and reported in Table.4.

(3)

Where ΔE_{corr} the corrosion potential difference between the substrate and coating layer, R_p the polarization resistance of the coating-substrate system, β_a the anodic Tafel constant of substrate, R_{pm} is the polarization resistance of the substrate and F represent porosity. The porosity measurement of the coatings is presented in Table 4. The TiAlN film has shown minimum porosity of 0.015 % as compared to AlCrN film (0.43%). In case of AlCrN coating, the porosity measurement by electrochemical test analysis and with image analyser, having software Dewinter Materials Plus 1.01 based on ASTM B276, is having closer results, whereas in case of TiAlN these are different. S. Deshpande et al. [11] have also explained that image analysis (IA) measures both open as well as closed porosity and cannot distinguish between the two, whereas electrochemical test is able to assess pore connectivity in a coating that exists due to the interlamellar pores and intralamellar cracks. So, due to higher porosity in case of AlCrN, the corrosion current density is quite higher than that of TiAlN coating (Table 4.). The more connected the porosity, the higher the corrosion current [11].

4. Conclusion

The nanostructured TiAlN and AlCrN coatings were deposited successfully on low-carbon steel ASTM-SA210 Grade A-1 (GrA1) by using *Balzer's rapid coating system (RCS) machine*. The microstructural morphologies and electrochemical properties of the coatings were investigated in the present work. Both the coatings have been found to possess low porosity (less than

0.5%). The XRD and SEM/EDAX analysis confirmed the formation of the requisite composition

of the coatings. The AFM studies revealed that the overall roughness and particle size of TiAlN coating is less than that of AlCrN coating.

The corrosion current densities of the films in an aerated 3 wt% NaCl solution at room temperature were found much lower than that of the substrate steel. The corrosion resistance of the coatings and substrate followed the sequence:

TiAlN coating > AlCrN coating > Substrate

The TiAlN coating has performed very well and showed best corrosion resistance on the basis of corrosion current density and polarization resistance.

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