Materials Science and Metallurgy Engineering, 2013, Vol. 1, No. 2, 31-36
Available online at http://pubs.sciepub.com/msme/1/2/4

DOI:10.12691/msme-1-2-4

Corrosion Behavior of Nanostructured Tialn and Alcrn Thin Coatings on ASTM-SA213-T-11 Boiler Steel in Simulated Salt Fog Conditions

Vikas Chawla*

Director-Principal, D.A.V. College of Engineering & Technology, Kanina, India
*Corresponding author: vikkydmt@gmail.com

Received July 27, 2013; Revised November 02, 2013; Accepted November 11, 2013

Abstract In this work, TiAlN and AlCrN coatings were deposited on ASTM-SA213-T-11 boiler steel using Balzer's rapid coating system (RCS) machine (make Oerlikon Balzers, Swiss) under a reactive nitrogen atmosphere. The corrosion resistance of the substrate, TiAlN-coated and AlCrN-coated samples in a 5 wt% NaCl solution was evaluated and compared by salt fog (spray) test for 24 hrs, 48 hrs and 72 hrs. The weight loss per unit area increases with the duration of the test. The samples were monitored and analyzed by using Weight loss measurement, XRD and SEM/EDAX techniques. The weight loss per unit area in case of nanosructured thin TiAlN coating is less than as compared to the nanostructured AlCrN coating and uncoated boiler steel in all test conditions.

Keywords: *salt fog test, physical vapour deposition, corrosion, aluminum chromium nitride, titanium aluminum nitride*

Cite This Article: Vikas Chawla, "Corrosion Behavior of Nanostructured Tialn and Alcrn Thin Coatings on ASTM-SA213-T-11 Boiler Steel in Simulated Salt Fog Conditions." *Materials Science and Metallurgy Engineering* 1, no. 2 (2013): 31-36. doi: 10.12691/msme-1-2-4.

1. Introduction

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 [1]. It is important to understand the nature of all types of environmental degradation of metals and alloys as vividly as possible so that preventive measures against metal loss and failure can be economically devised to ensure safety and reliability in the use of metallic components [2]. Uusitalo et al., [3] has also suggested that there is a need to investigate the high temperature corrosion behaviour of thermal spray coated materials in different aggressive environments. Mostly Cr and Al are added to enhance the oxidation resistance of alloys. Besides the oxidation resistance at high temperature, the resistance to pitting corrosion at normal temperature is another important performance of these materials [4]. 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 [5]. The chloride-rich seawater is a harsh environment that can attack the materials by causing pitting and crevice corrosion [6].

Metallic nitrides are widely used nowadays as a barrier thin film in electronics, as hard coatings and special refractory materials [7]. In all cases, corrosion resistance is very important and nitride coatings can significantly improve the corrosion performance of steel. The present work has been focused to compare the corrosion behavior of nanostructured thin (by physical vapor deposition process) TiAlN and AlCrN coatings on ASTM-SA213-T-11 boiler steel by salt spray (Fog) tests.

2. Experimental Details

2.1. Development of Coatings

TiAlN and AlCrN coatings; with a thickness around 4µm, were deposited on low-carbon steel ASTM-SA213-T-11, which has a wide range of applications in boilers, especially when the service conditions are stringent from the point of temperature and pressure. 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 actual chemical composition of the T-11 has been analyzed with the help of Optical Emission Spectrometer of Thrmo Jarrel Ash (TJA181/81), U.S.A make. Normal and actual chemical composition is 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 *1μm* lavigated alumina powder suspension. The specimens were prepared manually and all care was taken to avoid any structural changes in the specimens. The nanostructured thin TiAlN and AlCrN coatings; with a thickness around 4μm, were deposited on the substrates at Oerlikon Balzers Coatings India Limited, Gurgaon, India. A front-loading *Balzer's rapid coating system (RCS) machine (make Oerlikon Balzers, Swiss*) was used for the deposition of the coatings. The grain size of the thin films was estimated by Scherrer formula from XRD diffractogram and by Atomic force microscopy (AFM; Model: NTEGRA, NT-MDT, Ireland). The grain size for TiAlN and AlCrN coatings was found 14 nm and 20 nm respectively. The details of the coating parameters and coating characterization have been reported in another paper (communicated).

Table 1. Chemical composition (wt %) of T-11 Boiler Steel (ASTM code SA213-T-11)

Elements	C	Mn	Si	S	P	Cr	Mo	Fe
Nominal	0.15	0.3-0.6	0.5-1	0.03	0.03	1-1.05	0.44-0.65	Bal
Actual	0.161	0.441	0.282	0.005	0.013	0.914	0.5125	Bal

2.2. Salt Spray (Fog) Test

The ASTM B117 Salt Fog test was used to evaluate the performance of the uncoated and nanostructured thin TiAlN and AlCrN coatings. The salt fog test is an accelerated corrosion test by which samples exposed to the same conditions can be compared. In the B117 test, the samples are exposed to a salt fog generated from a 5% sodium chloride solution with a pH between 6.5 and 7.2 in salt fog testing set up (HSK 1000, Heraeus Votsch, Germini) as shown in Figure 1. The salt solution employed was prepared with NaCl analytical grade reagent with minimum assay 99.9 % supplied by Qualigens Fine Chemicals, Mumbai, India and deionised water. All the samples were placed in the salt fog chamber for 24 Hrs, 48 Hrs and 72 Hrs. Photographs were taken before and subsequent to exposure to document the surface conditions. Initial weight and dimensions were measured. The uncoated as well as the coated specimens were polished down to 1μm alumina wheel cloth polishing to obtain similar condition on all the samples before salt fog testing.

2.3. Analysis of the Corroded Specimens

After exposure; samples were monitored and analyzed by using XRD and SEM/EDAX techniques.

Visual examination was made after the completion of the tests and the macrographs of the corroded specimens were taken. Surface SEM analysis of the corroded specimens was conducted using Field emission scanning electron microscope (FEI Company, Quanta 200F) with EDAX attachment. EDAX analysis at few points of interest was taken. XRD analysis was carried out for the as coated specimens to identify the various phases present on their surfaces. The X-ray diffraction patterns were obtained by a Bruker AXS D-8 Advance Diffractometer (Germany) with CuK_{α} radiation and nickel filter at 30 mA under a voltage of 40 kV. The specimens were scanned with a scanning speed of 2^{o}/min in 2θ range of 20^{o} to 120^{o} and the intensities were recorded.

Before salt fog testing; the samples were cleaned in acetone, dried, weighed to an accuracy of 1×10^{-5} g using an electronic balance. After exposure; samples were monitored and analyzed by using XRD and SEM/EDAX techniques. Then all the samples were cleaned in running water not warmer than 38°C to remove salt deposits from the surface and then immediately dried with compressed air. The final weight was measured and then the weight loss per unit area was calculated.

Figure 1. Experimental set-up for Salt spray (Fog) testing (a) Salt fog testing set up, (b) Salt fog chamber, (c) Interior view of chamber

3. Results and Discussion

The ASTM B117 Salt Fog test was used to evaluate the performance of the uncoated and nanostructured thin TiAlN and AlCrN coated ASTM-SA213-T-11 boiler steel. The salt fog test is an accelerated corrosion test by which samples exposed to the same conditions can be compared. In the B117 test, the samples are exposed to a salt fog generated from a 5% sodium chloride solution with a pH

between 6.5 and 7.2. All the samples were placed in the salt fog chamber for 24 Hrs, 48 Hrs and 72 Hrs. Photographs were taken before and subsequent to exposure to document the surface conditions. Initial weight and dimensions were measured. After exposure; samples were monitored and analyzed by using XRD and SEM/EDAX techniques. Then all the samples were cleaned in running water not warmer than 38°C to remove salt deposits from the surface and then immediately dried with compressed air.

The macro morphologies of the uncoated and nanostructured thin TiAlN and AlCrN coated T-11 boiler steel exposed to salt fog test for 24 Hrs, 48 Hrs and 72 Hrs; are depicted in Figure 2. The uncoated T-11 boiler steel suffered severe corrosion in all three test conditions i.e. 24 Hrs, 48 Hrs and 72 Hrs (Figure 2.A). The brownish colored corrosion product on the surface of the samples and corrosion pits are visible. The nanostructured coated samples have shown resistance to the corrosion as compared to the uncoated T-11 boiler steel. The nanaostructured TiAlN coatings have shown negligible corrosion products in case of 24 Hrs study, but for 48 Hrs and 72 Hrs studies, it has shown the formation of some corrosion products (Figure 2.B). In case of nanostructured AlCrN coating, the surface of the samples was no longer uniform as before the test in case of salt fog testing for 48 Hrs and 72 Hrs (Figure 2.C). Some corrosion products can also be seen in case of the sample exposed to the salt mist corrosion for 24 Hrs.

Figure 3 shows the surface SEM images of uncoated and nanostructured TiAlN and AlCrN coated T-11 boiler exposed to salt fog test for 24 Hrs. As can be seen in Figure 3 (a), massive corrosion products were accumulated on the surface of uncoated boiler steel.

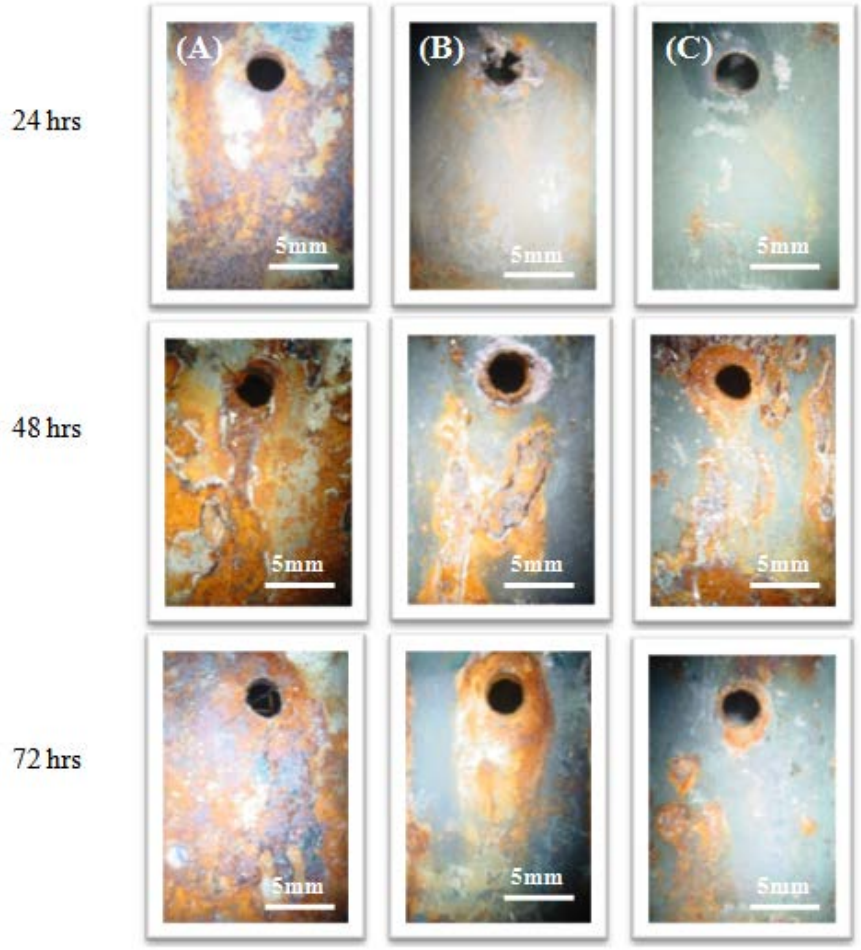

Figure 2. Surface macrographs of uncoated and coated ASTM-SA213-T-11 boiler steel subjected to salt-fog testing (5% NaCl) : (A) Uncoated T-11 boiler steel subjected to 24hrs, 48hrs and 72 hrs testing; (B) Nanostructured TiAlN coating subjected to 24hrs, 48hrs and 72 hrs testing; (C) Nanostructured AlCrN coating subjected to 24hrs, 48hrs and 72 hrs testing

The EDAX analysis at some locations of interest points out the presence of iron and oxygen on the corroded surface (Point 1 and 2 in Figure 3). In case of nanostructured TiAlN coating; very less corrosion products are visible (Figure 3.b). The EDAX analysis (Point 3 and 4 in Figure 3) revealed the presence of Ti and Al as the main elements with small amount of Fe, N, Mo and O. Figure 3(c) shows the SEM image of the nanostructured AlCrN coating. The surface is rich in Al, Cr along with N and negligible amount of Fe and O; as revealed by EDAX analysis (Point 5 and 6 in Figure 3).

Figure 4 shows the surface SEM images of uncoated and nanostructured TiAlN and AlCrN coated T-11 boiler steel exposed to salt fog test for 48 Hrs. The uncoated T-11 boiler steel has shown severe corrosion as shown in Figure 4.a. Corrosion cracks and corrosion products can be seen on the surface. The EDAX analysis shows the presence of Fe and O as the main elements along with some Mo, Cl and Na. As can be seen in Figure 4.b & c, corrosion cracks were observed on the surface of as-deposited nanostructured TiAlN and AlCrN coatings after salt spray tests. Massive corrosion products were accumulated around the corrosion crevice.

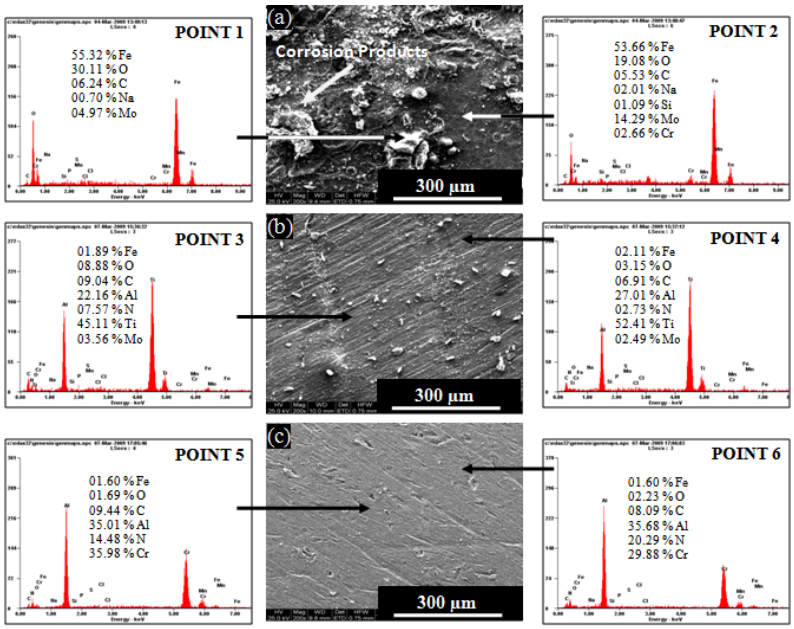

Figure 3. Surface macrographs of uncoated and coated ASTM-SA213-T-11 boiler steel subjected to salt-fog testing (5% NaCl) for 24 hrs: (a) Uncoated ASTM-SA213-T-11 boiler steel (b) Nanostructured TiAlN coating (c) Nanostructured AlCrN coating

Obviously, severer corrosion would proceed in the as-deposited nanostructured thin coatings through the cracks, and cause coating cracking and fracture damage in the subsequent service at elevated temperatures. EDAX analysis (Point 3 and 4) in case of nanostructured TiAlN coating indicates the products were composed of Fe and O. A large number of whiskers like particles can be seen. In case of nanostructured AlCrN coating; EDAX point analysis at a location of interest indicated by point 5 in Figure 4; revealed the presence of Al and Cr as the main element with fewer amounts of iron and oxygen. The corrosion products were found rich in iron and oxygen with negligible amount of Al, Cr and Mo (Point 6 in Figure 4).

The surface SEM images of uncoated and nanostructured TiAlN and AlCrN coated T-11 boiler steel exposed to salt fog test for 72 Hrs; are shown in Figure 5 Massive corrosion products were accumulated on the surface in case of uncoated and nanostructured AlCrN coated T-11 boiler steel after salt fog tests. EDAX analysis (Figure 5) shows the corrosion products were composed of mainly Fe and O in all test samples.

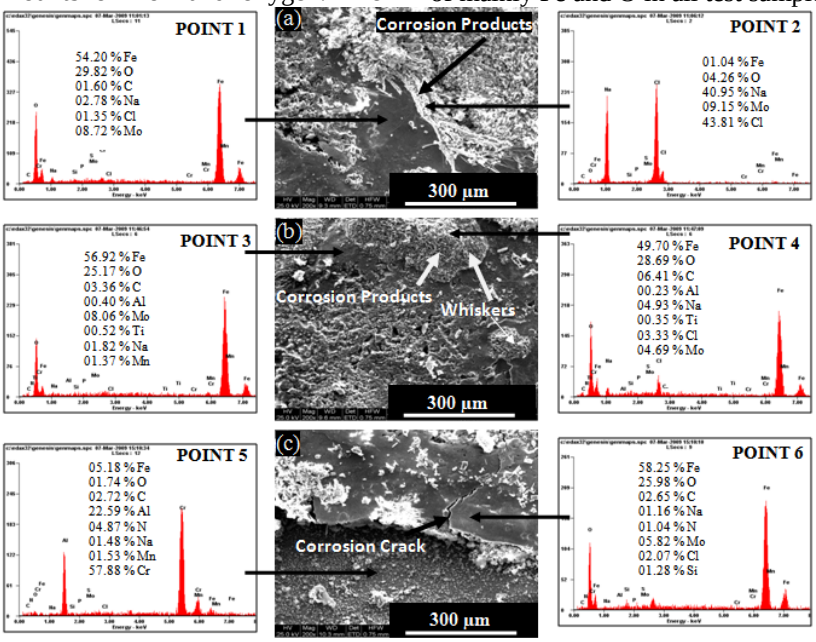

Figure 4. Surface macrographs of uncoated and coated ASTM-SA213-T-11 boiler steel subjected to salt-fog testing (5% NaCl) for 48 hrs: (a) Uncoated ASTM-SA213-T-11 boiler steel (b) Nanostructured TiAlN coating (c) Nanostructured AlCrN coating

XRD diffractograms for coated and uncoated ASTM-SA213-T-11 boiler steel subjected to salt fog tests for 24 Hrs, 48 Hrs and 72 Hr; are depicted in Figure 6 on reduced scale. As indicated by the diffractograms in Figure 6, Fe_3O_4 and with some minor peaks of Cr_2O_3 are the main phases present in the oxide scale of uncoated T-11 boiler steel. In nanostructured TiAlN coating, AlN, TiN and Fe_3O_4 are the main phases revealed with minor phases i.e. TiO_2 and Al_2O_3. Further, the main phases identified for the nanostructured AlCrN coating are CrN, AlN along with Al_2O_3, Cr_2O_3 and Fe_3O_4. The formation of Fe_3O_4 in the scale of corroded specimens in salt spray tests

is found to be in agreement with those reported by Panda, Bijayani et al., [8] and Vera et al., [9]. Salt spray corrosion is an electrochemical reaction process [10]. Generally, the corrosion resistance is influenced significantly by several factors, such as compositions, internal microstructure, and especially the surface condition.

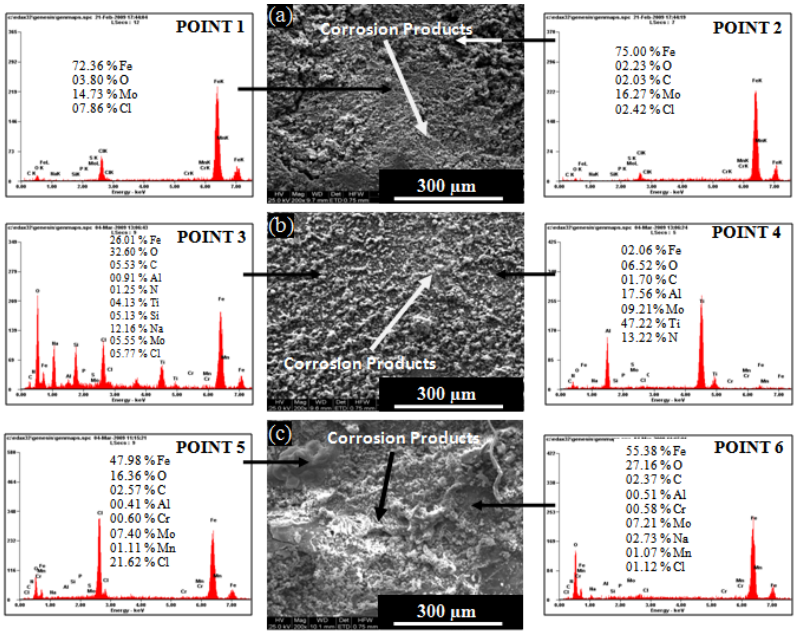

Figure 5. Surface macrographs of uncoated and coated ASTM-SA213-T-11 boiler steel subjected to salt-fog testing (5% NaCl) for 72 hrs: (a) Uncoated ASTM-SA213-T-11 boiler steel (b) Nanostructured TiAlN coating (c) Nanostructured AlCrN coating

Bao et al., [10] have studied the corrosion behavior of as-deposited and pre-oxidized NiCoCrAlYSiB coatings by salt spray test. They have reported that an extra thin salt-containing moisture film would form due to deposition during salt spray test, and the film would adsorb and dissolve more oxygen. These active oxygen atoms would diffuse easily to reach the surface of a specimen. A continuous oxide layer could insulate active oxygen atoms from reacting with the underneath metallic coatings i.e. in case of pre-oxidized coating a thin layer of Al_2O_3 has developed and prevented the active oxygen to enter the substrate. On the contrary in case of as-coated coating, oxidation–reduction will occur easily as the metal confronts with the moisture film directly. The weight loss measurements were carried out for the uncoated and nanaostructured thin TiAlN and AlCrN coated T-11 boiler steel exposed to the salt fog tests for 24 Hrs, 48 Hrs and 72 Hrs. Figure 7, depicts the column chart showing the weight loss per unit area for the uncoated and coated T-11 boiler steel. It can be inferred from the plots that the uncoated T-11 boiler steel has shown maximum weight loss per unit area in all three test conditions i.e. 24 Hrs, 48 Hrs and 72 Hrs tests; as compared to the coated counterparts.

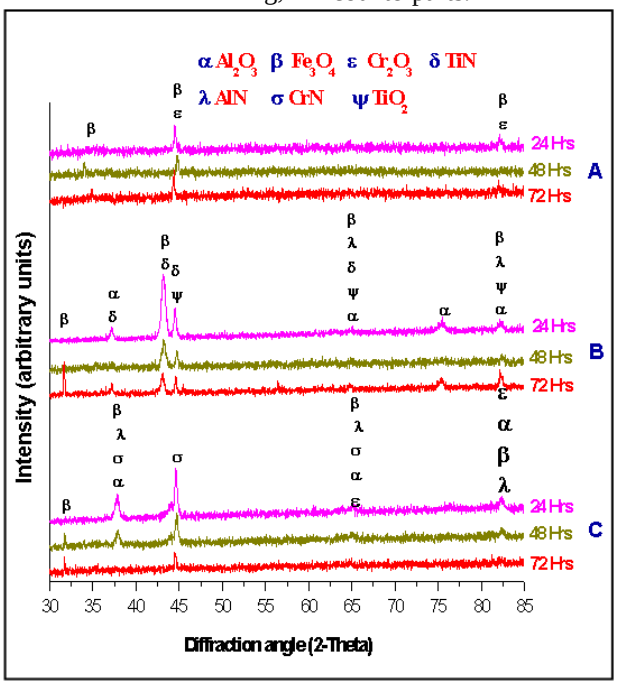

Figure 6. X-Ray Diffraction pattern of uncoated and coated ASTM-SA213-T-11 boiler steel subjected to salt-fog testing (5% NaCl) for 24 Hrs, 48 Hrs and 72 Hrs: (A) Uncoated T-11 boiler steel, (B) Nanostructured TiAlN coating, (C) Nanostructured AlCrN coating

Both the coatings have shown good protection to the substrate in terms of weight loss per unit area. As can be seen in Figure 6 for uncoated and coated T-11 boiler steel; the weight loss per unit area increases with the duration of the test. The weight loss per unit area in case of nanosructured thin TiAlN coating is less than as compared to the nanostructured AlCrN coating and uncoated boiler steel in all test conditions. It can be mentioned based on the present investigation that nanostructured thin TiAlN and AlCrN coatings can provide a very good corrosion resistance when exposed to the simulated marine environment i.e. salt fog test.

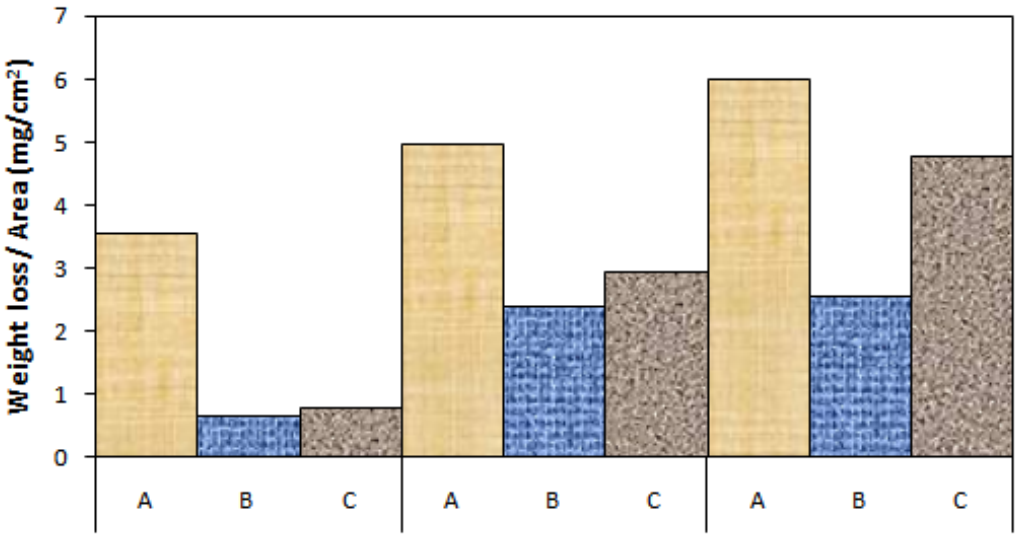

Figure 7. Column chart showing weight loss per unit area for the uncoated and coated ASTM-SA213-T-11 boiler steel subjected to salt-fog testing (5% NaCl): (A) Uncoated T-11 boiler steel subjected to 24hrs, 48hrs and 72 hrs testing; (B) Nanostructured TiAlN coated T-11 boiler steel subjected to 24hrs, 48hrs and 72 hrs testing; (C) Nanostructured AlCrN coated T-11 boiler steel subjected to 24hrs, 48hrs and 72 hrs testing

4. Conclusion

The corrosion behavior of the nanostructured thin (by physical vapor deposition process) TiAlN and AlCrN coatings on ASTM-SA213-T-11boiler steel; has been analyzed by salt spray (Fog) tests (5.0 wt% NaCl). The following conclusions can be made:

1. The uncoated T-11 boiler steel suffered severe corrosion in all three test conditions i.e. 24 Hrs, 48 Hrs and 72 Hrs. The nanostructured coated samples have shown resistance to the corrosion as compared to the uncoated T-11 boiler steel.
2. It can be inferred from the weight loss per unit area plots that the uncoated T-11 boiler steel has shown maximum weight loss per unit area in all three test conditions i.e. 24 Hrs, 48 Hrs and 72 Hrs tests; as compared to the coated counterparts.
3. It can be inferred from the weight loss per unit area plots that the uncoated T-11 boiler steel has shown maximum weight loss per unit area in all three test conditions i.e. 24 Hrs, 48 Hrs and 72 Hrs tests; as compared to the coated counterparts.
4. It can be mentioned based on the present investigation that nanostructured thin TiAlN and AlCrN coatings can provide a very good corrosion resistance when exposed to the simulated marine environment i.e. salt fog test.

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 Mr. Vikas Chawla (corresponding author) and grant under Nationally Coordinated Project (NCP).

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