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Salt Fog Corrosion Behavior of Nanostructured TiAlN and AlCrN Hard Coatings on ASTM-SA213-T-22 Boiler Steel

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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 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 vapor deposition; Corrosion; Nanostructured coatings; Pitting

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]. Many methods to modify the surface of a material have existed for a much longer time , but a formal definition of the discipline of surface engineering was given only a decade ago [2]. One only has to think about the fire hardening of wooden spears - the formation of a carbonized surface on the spear tip – a practice already known in the Stone Age. Surface modification technique i.e. coatings provide a way of extending the limits of the use of the materials at the upper end of their performance capabilities, by allowing the mechanical properties of the substrate materials to be maintained while protecting against wear, oxidation and corrosion [3]. Coating technology is one of the more rapidly growing technologies in the field of materials [4].

Deterioration of the materials due to marine salts in coastal regions has been, for many years, a significant and ongoing problem. Marine salts adversely affect the durability of the infrastructure and reduce its service life [5]. The sea spray, composed primarily of seawater along with particles naturally generated by the action of wind on the seawater surface, introduces ionic species into the atmosphere, principally chlorides and sulphates [5]. The air containing sea spray causes accumulative deposition of ions on the external surface of structures that penetrate the interior of the material through ionic diffusion causing its degeneration. Such environments are extremely dangerous to the materials as salts can penetrate and crystallize inside the material, causing deterioration of the physical infrastructure. As reported by Dobrzanski et al., [6]; the chloride-rich seawater is a harsh environment that can attack the materials by causing pitting and crevice corrosion. Every engineering metal or alloy is susceptible to pitting.

As reported by Bao et al., [7]; it seems no research works have been conducted on the corrosion behavior of high temperature corrosion resistant coatings in Cl-containing marine environment. Therefore, it is meaningful to investigate the ambient environmental corrosion behavior of substrate and coatings in accelerating mode, i.e., by salt spray (Fog) tests. Therefore, 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-22 boiler steel, by salt spray tests in 5.0 wt% NaCl solution.

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-22, 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-22 has been analyzed with the help

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of Optical Emission Spectrometer of Thermo 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 18 nm and 25 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-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	0.1658	0.3559	0.1159	0.001	0.020	2.6460	0.9027	Bal.

2.2. Salt spray (Fog) testing:

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. 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 Fig.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.

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.

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 CuKα radiation and nickel filter at 30 mA under a voltage of 40 kV. The specimens were scanned with a scanning speed of 2o/min in 2θ range of 20o to 120o 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.

3. Results and Discussion

All the uncoated and nanostructured thin TiAlN and AlCrN coated ASTM-SA213-T-22 boiler steel 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-22 boiler steel exposed to salt fog test for 24 Hrs, 48 Hrs and 72 Hrs; are depicted in Fig.2. The uncoated T-22 boiler steel suffered severe corrosion in all three test conditions i.e. 24 Hrs, 48 Hrs and 72 Hrs (Fig.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-22 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, these have shown the formation of some corrosion products (Fig.2.B). In case of nanostructured AlCrN coating, some corrosion products can be seen on the surface in all the three test conditions but still very less as compared to the uncoated T-22 boiler steel.

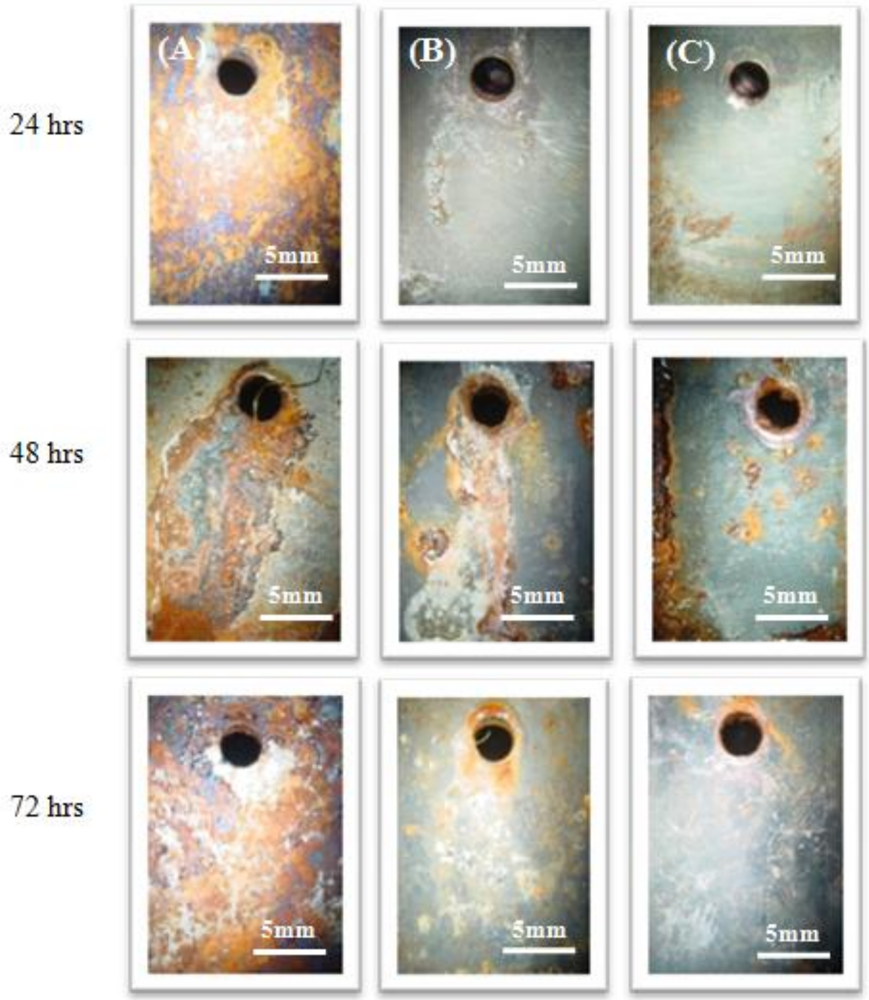

Figure 2: Surface macrographs of uncoated and coated ASTM-SA213-T-22 boiler steel subjected to salt-fog testing (5% NaCl) : (A) Uncoated T-22 boiler steel subjected to 24hrs, 48hrs and 72 hrs testing; (B) Nanostructured TiAlN coating subjected to 24hrs, 48hrs and 72 hrs testing; (C) Nanostructured AlCrN coating subjected to 24hrs, 48hrs and 72 hrs testing.

Figure.3 shows the surface SEM images of uncoated and nanostructured TiAlN and AlCrN coated T-22 boiler steel exposed to salt fog test for 24 Hrs. As can be seen in Fig.3(a), massive corrosion products were accumulated on the surface of uncoated T-22 boiler steel. 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 Fig.3). In case of nanostructured thin TiAlN and AlCrN coatings; no corrosion products were visible (Fig.3.b & c). The EDAX point analysis (Point 3 to 6 in Fig.3) revealed the presence of the coating elements with negligible presence of Fe and O. So, in case of 24 Hrs test conditions; the nanostructured thin coatings have performed well and protected the substrate material.

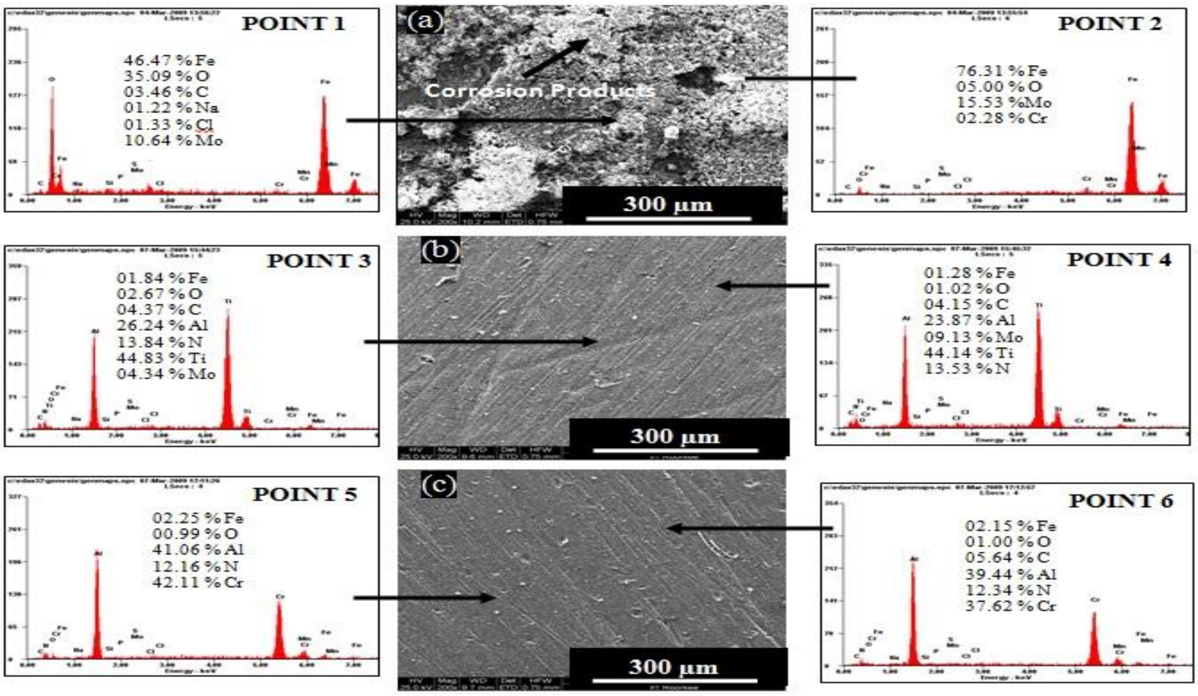

Figure 3: Surface macrographs of uncoated and coated ASTM-SA213-T-22 boiler steel subjected to salt-fog testing (5% NaCl) for 24 hrs: (a) Uncoated ASTM-SA213-T-22 boiler steel (b) Nanostructured TiAlN coating (c) Nanostructured AlCrN coating.

Figure.4 shows the surface SEM images of uncoated and nanostructured TiAlN and AlCrN coated T-22 boiler steel exposed to salt fog test for 48 Hrs. The uncoated T-22 boiler steel has shown severe corrosion as shown in Fig.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 Mn, Cl and Na. As can be seen in Fig.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. 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 Fig.4) in case of nanostructured TiAlN coating indicates the products were composed of Fe and O. The corrosion products in case of nanostructured AlCrN coating were found rich in iron and oxygen with some amount of Al, Cr and Mn (Point 3 and 4 in Fig.4).

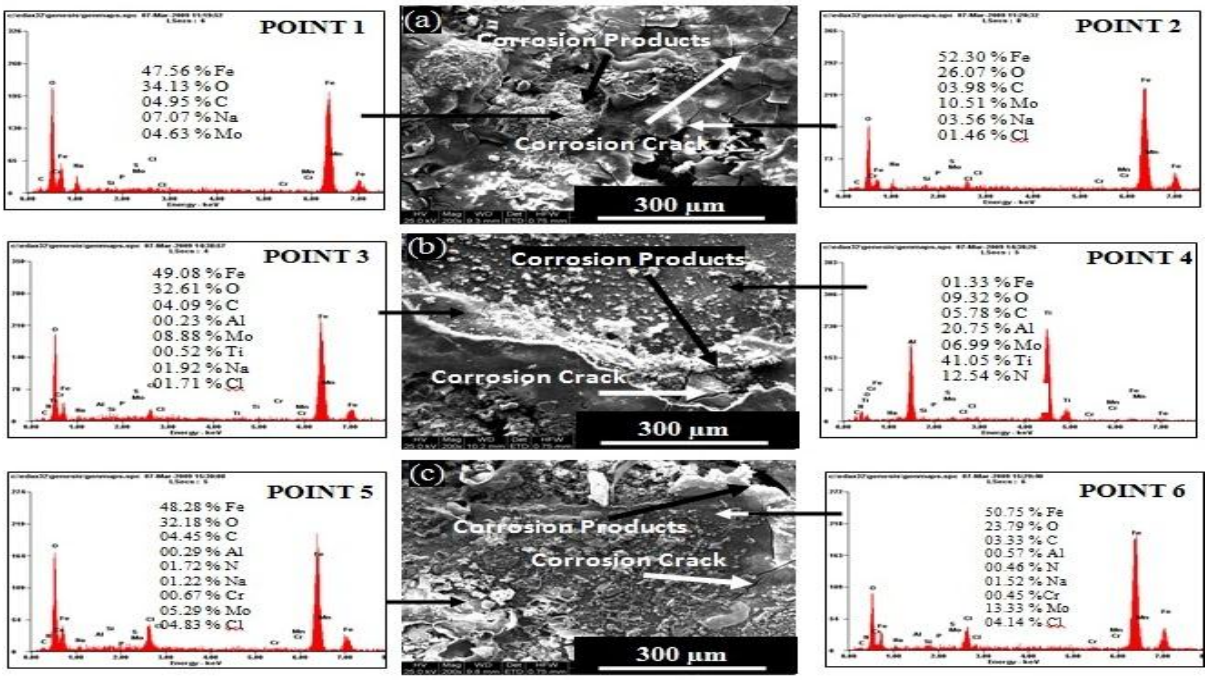

Figure 4: Surface macrographs of uncoated and coated ASTM-SA213-T-22 boiler steel subjected to salt-fog testing (5% NaCl) for 48 hrs: (a) Uncoated ASTM-SA213-T-22 boiler steel (b) Nanostructured TiAlN coating (c) Nanostructured AlCrN coating.

The surface SEM images of uncoated and nanostructured TiAlN and AlCrN coated T-22 boiler exposed to salt fog test for 72 Hrs; are shown in Fig.5. Massive corrosion products were accumulated on the surface in case of uncoated T-22 boiler steel after salt fog tests. EDAX analysis (Point 3 and 4 in Fig.5) in case of nanostructured TiAlN coating indicates the products were composed of Fe and O. In case of nanostructured thin AlCrN coating; EDAX point analysis (Point 5 in Fig.5) revealed the presence of Al and Cr as the main element in the un-corroded area of the surface and Fe and O rich corrosion products (Point 6 in Fig.5).

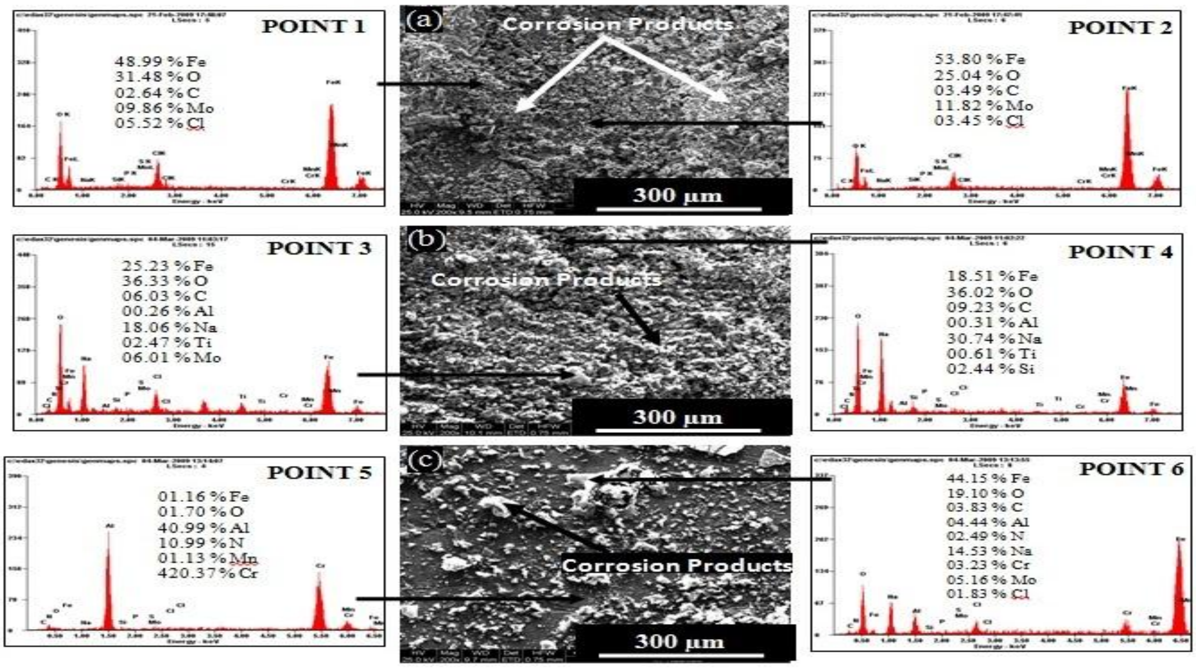

Figure 5: Surface macrographs of uncoated and coated ASTM-SA213-T-22 boiler steel subjected to salt-fog testing (5% NaCl) for 72 hrs: (a) Uncoated T-22 boiler steel (b) Nanostructured TiAlN coating (c) Nanostructured AlCrN coating.

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 Fig.6 on reduced scale. As indicated by the diffractograms in Fig.6, Fe3O¬4 and with some minor peaks of Cr2O3 are the main phases present in the oxide scale of uncoated T-11 boiler steel. In nanostructured TiAlN coating, AlN, TiN and Fe3O4 are the main phases revealed with minor phases i.e. TiO2 and Al2O3. Further, the main phases identified for the nanostructured AlCrN coating are CrN, AlN along with Al2O3, Cr2O3 and Fe3O¬4. The formation of Fe3O¬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].

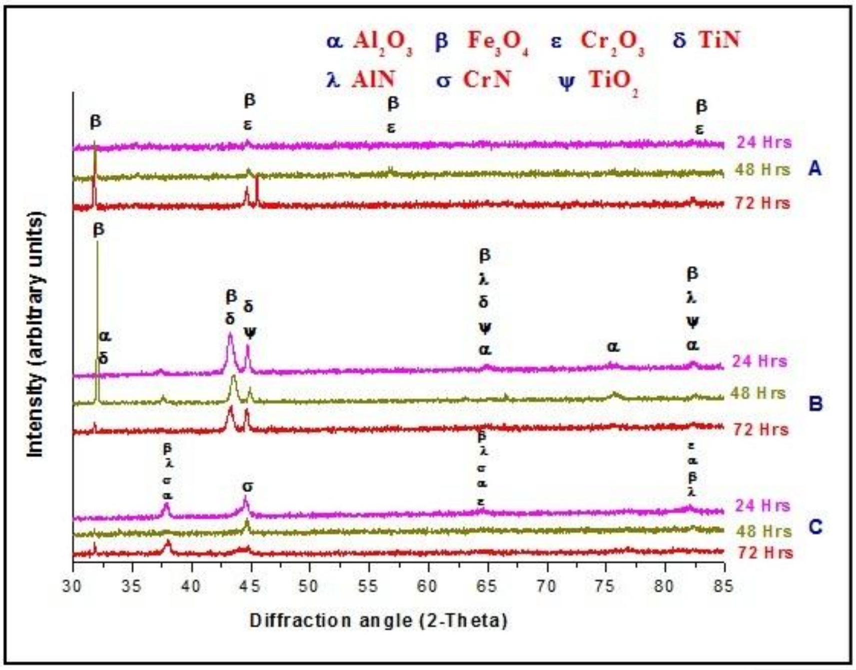

Figure 6: X-Ray Diffraction pattern of uncoated and coated ASTM-SA213-T-22 boiler steel subjected to salt-fog testing (5% NaCl) for 24 Hrs, 48 Hrs and 72 Hrs: (A) Uncoated T-22 boiler steel, (B) Nanostructured TiAlN coating, (C) Nanostructured AlCrN coating.

The weight loss measurements were carried out for the uncoated and nanaostructured thin TiAlN and AlCrN coated T-22 boiler steel exposed to the salt fog tests for 24 Hrs, 48 Hrs and 72 Hrs. Fig. 7, depicts the column chart showing the weight loss per unit area for the uncoated and coated T-22 boiler steel. It can be inferred from the plots that the uncoated T-22 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. Both the coatings have shown good protection to the substrate in terms of weight loss per unit area. it can be inferred from Fig.7 that the weight loss per unit area increases with the duration of the test for all the specimens. 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.

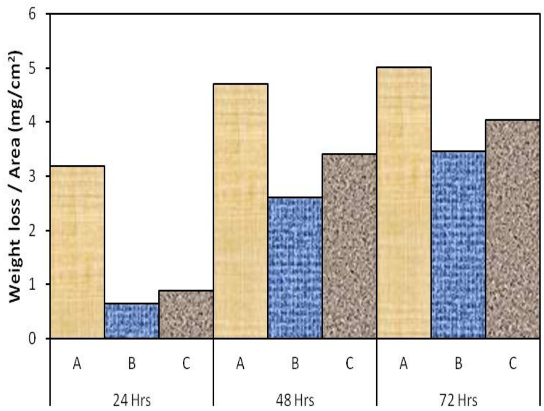

Figure 7: Column chart showing weight loss per unit area for the uncoated and coated ASTM-SA213-T-22 boiler steel subjected to salt-fog testing (5% NaCl) : (A) Uncoated T-22 boiler steel subjected to 24hrs, 48hrs and 72 hrs testing; (B) Nanostructured TiAlN coated T-22 boiler steel subjected to 24hrs, 48hrs and 72 hrs testing; (C) Nanostructured AlCrN coated T-22 boiler steel subjected to 24hrs, 48hrs and 72 hrs testing.

Salt spray corrosion is an electrochemical reaction process [7]. Generally, the corrosion resistance is influenced significantly by several factors, such as compositions, internal microstructure, and especially the surface condition. Bao et al., [7] 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 proposed corrosion mechanism of the as-deposited coated specimen is as explained in Fig.8 which is similar to the one reported by Bao et al.,[7]. Micro-cracks got initiated by residual stress during deposition of coatings. The micro-cracks would be corroded easily and the solution would infiltrate into loose corrosion products and reach crack tip to sustain the internal corrosion, followed by crack propagation (Fig. 8.b and c). This process obeys the rules of crevice corrosion [7]. Acidity in the cracks increased significantly as neutralisation was not easily obtained by exchanging solution between inside and outside the cracks. An ascending acidity accelerates the corrosion attack and results in an unfavourable inner structure. When the acid solution flows across pores, corrosion will take place and enlarge a pore to a corrosion hole (Fig. 8.d).

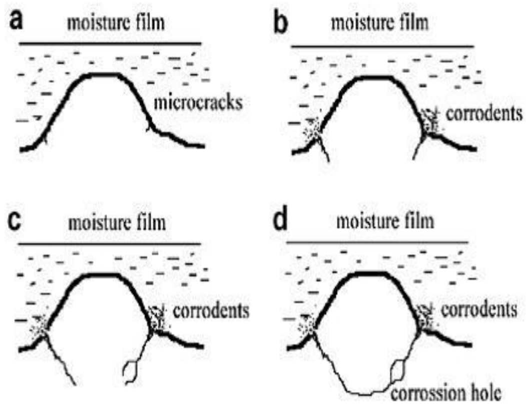

Figure 8: Corrosion evolution of the as-deposited coatings in salt spray test; a: initiation of corrosion micro-crack, b: cracks propagation, c: crack branching, d: formation of corrosion hole [7].

4. Conclusions

The corrosion behavior of the nanostructured thin (by physical vapor deposition process) TiAlN and AlCrN coatings on ASTM-SA213-T-22 boiler steel; has been analyzed by salt spray (Fog) tests (5.0 wt% NaCl). The following conclusions can be made:

- The uncoated T-22 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-22 boiler steel.
- It can be inferred from the weight loss per unit area plots that the uncoated T-22 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.
- 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.

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