Morphological and corrosion studies of ammonium phosphate and caesium nitrate treated Al coating deposited by arc thermal spray process

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ABSTRACT

In the present studies, the Al coating deposited by arc thermal spraying process was treated with different concentrations of ammonium phosphate mono basic ((NH₄)H₂PO₄) and caesium nitrate (CsNO₃) to improve the morphology and corrosion characteristics of the coating. As coated (AC) sample exhibits pores and defects onto the surface but once the treatment was carried out, the coating shows reduction in porosity as observed by scanning electron microscopy (SEM). The treated coatings contain caesium aluminum oxide (CAO: Cs₂Al₂O₄) and ammonium aluminum hydrogen phosphate hydrate (AHP: (NH₄)₂Al₂H₃(PO₄)₀.18H₂O) as composite oxides identified by X-ray diffraction (XRD). Electrochemical impedance spectroscopy (EIS) results reveal that as the exposure periods are increased, the resistance to coating/treatment (Rct) and charge transfer resistance (Rct) of AC and 0.5 M NH₄H₂PO₄ and 0.0025 M CsNO₃ (CN2) are increased with exposure periods in artificial ocean water solution. The improvement in total impedance values at 0.01 Hz of AC sample is attributed to formation of corrosion products which fill the pores/defects of coating while CN2 sample owing to the treatment film i.e. AHP and CAO and transformation of AHP into stable form. As the amount of NH₄H₂PO₄ and CsNO₃ is increased up to 1 M and 0.005 M i.e. CN3, the AHP film dissolved and enhances the corrosion reaction. Thus, cracking is observed in corrosion products. The enhancement in corrosion resistance of CN2 sample is attributed to the formation of α-Al(OH)₃ (bayerite) and Al₃(PO₄)₂(OH)₃(H₂O)₉ (Aluminium hydroxide phosphate hydrate: AHPH) in greater amount as corrosion products. These corrosion products of CN2 sample are stable, sparingly soluble and protective.

1. Introduction

Plain carbon steel is prone to corrosion in aggressive environments and causes catastrophic failure of structures. However, the corrosion of steel structure depends on exposure conditions such as atmospheric, splash/tidal, submerged and buried, therefore, coating is required to mitigate the corrosion of steel structure. Coating is providing protection to the steel from corrosion and erosion failure. But the types of coating to be used on the steel substrate depend on exposure conditions. The steel structure immersed in seawater or near to offshore need to be coated by active metal i.e. Al, Zn and Mg which can provide cathodic protection [1].

There are different coating processes to deposit the metallic coating i.e. Al, Zn and Mg onto the steel substrate. However, the thermal spray process is versatile process being used in different industrial sectors and it can be applicable to protect the materials, metals and alloys from corrosion in harsh environments [2–6]. The Al coating deposited by thermal spray process are widely used to protect the offshore, risers, pipes, and ship from corrosion [7,8] in immersed, tidal, splash zone and marine atmosphere [9]. However, Al coating can provide barrier protection for long term exposure as well as cathodic protection to the steel substrate [10–12]. The corrosion resistance properties of Al coating can be achieved by alloying with active metals [13,14].

There are different thermal spray processes such as plasma, arc,
detonation, high velocity oxy-fuel, high velocity air fuel, cold spraying etc. to deposit the Al coating. But among them, the arc thermal spray process is convenient, easy to application compared to other thermal spray processes and the spray gun can be brought to onsite and deposit the coating. The arc thermal spray process is based on melting of twin wires at tip with an electric arc and the melted droplets are propelled by a compressed air towards the substrate to be coated [15–17]. The arc thermal spray process is economical and easy to application than hot dip galvanized, flame spray, high-velocity oxy fuel etc. [15]. However, this process possesses some inherent properties such as porosity and cracks formation on surface attributed to the continuous deposition of coating and sudden cooling of molten metal particles. Although, the porosity in the deposited coating is inevitable. Moreover, it can be controlled by selecting appropriate feedstock material and spraying parameters.

There are different sealants which fill out the porosity of thermal sprayed coating and enhances the corrosion resistance properties of Al coating [18]. The post-treatment or sealing of coating depends on the coating materials and its service life conditions. Wang and Zhou (2019) have used glass powder to seal the pores of Al coating deposited by arc thermal spray process and found that sealed coating exhibited higher corrosion resistance compared to as deposited one in 3.5 wt.% NaCl solution [19]. The most of the often used sealants are epoxide, phenolic, furans, polymethacrylates, silicene, polyester, polyurethanes and polyvinyl ester. Waxes can be used as pore sealing agent but it depends on service temperature. It can be used in cold condition whereas phenolic resin resists up to 150-260 °C and methacrylate up to 150 °C [20]. The organic paint can be used to fill out the pores of Al coating but it causes active corrosion and blistering owing to the acidification underneath of paint where water and Cl⁻ ions can diffuse easily [21,22]. Thus, it is suggested to avoid the use of organic paint to seal the pores of coating.

The inorganic sealants i.e. aluminum phosphate, sodium and ethyl silicates, different sol-gel type solution and chronic acid have been used as sealing agent to fill the porosity of the thermally sprayed coatings. However, through the annealing of coating at melting point, the porosity can be filled, but it may change the microstructure which causes relaxation in residual stress [23]. Therefore, it is utmost required to fill the porosity of coating deposited by arc thermal spray process using proper chemicals. The use of solution based inorganic salt i.e. phosphate as pore sealing agent dissolve in water and applied onto the Al coating by brush. After the application of pore sealing agent, the Al react and form composite oxide which fill the pores of coating and enhance the corrosion resistance properties [24–27]. The phosphate based pore sealing agent has promising properties on morphological and corrosion resistance in aggressive environment. The different concentrations of ammonium phosphate have been used as pore sealing agent and it was found that 0.1 M exhibited excellent corrosion resistance properties but once the concentration is increased, it shows deterioration attributed to the formation of acidic film [24].

In the present study, the Al coating was deposited by arc thermal spray process which possesses porosity. The porosity of the deposited coating was filled by post-treatment with different concentrations of ammonium phosphate mono basic (NH₄H₂PO₄) and caesium nitrate (CsNO₃) to improve the properties of coating. The corrosion kinetics and mechanism of as coated (AC) as well as treated coatings was assessed in artificial ocean water solution [28] at prolonged exposure periods.

2. Methods and materials

2.1. Process of coating

A 8 cm x 6 cm x 0.1 cm dimensions of plain carbon steel plate containing C=0.20, Mn=0.95, Si=0.26, P=0.02, S=0.01, Cu=0.02, Cr=0.04, Ni=0.03, Fe=balance in wt.% was coated with 1.6 mm diameter of Al (99.95wt.%) twin wires by arc thermal spray process. Prior to deposit the coating, steel plate was polished up to 1200 µm grit paper followed by blasting with 0.7 to 0.8 mm steel balls to make the surface rough for proper adhesion. The coating was deposited by keeping the steel plate 20 cm away from the gun at 6 bars air pressure, 30 V voltage, and 200 mA current [29–31].

The coating thickness was measured by non-destructive Elcometer456 (Japan, Tokyo) at three different locations and their average value was considered as a result. The bond adhesion test of deposited coating was measured according to KS F4716 standard [32] for four different consecutive samples and their average was calculated for the result. The bond adhesion measurement was performed by selecting 16
The post-treatment of the deposited Al coating was carried out with nylon brush by dissolving 0.1 M NH₄H₂PO₄ + 0.001 M CsNO₃ (CN1), 0.5 M NH₄H₂PO₄ + 0.0025 M CsNO₃ (CN2) and 1 M NH₄H₂PO₄ + 0.005 M CsNO₃ (CN3) in distilled water to reduce the porosity and enhance the corrosion resistance properties in the aggressive environment. The pH of respective treatment solutions i.e. CN1, CN2 and CN3 was found to be 4.36, 4.23 and 4.16 at 20°C, respectively. The treatment of Al coating was carried out for 24 hours at every 8 hours of interval (3 times in 24 hours) subsequently kept in humidity chamber at 50 ± 1°C, respectively. The treatment of Al coating was accomplished with different concentrations of NH₄H₂PO₄ and CsNO₃. It was observed that with the increase in concentration of NH₄H₂PO₄ and CsNO₃, the porosity is decreased. The highest porosity is observed at 1 M and 0.005 M, respectively i.e. CN3 exhibits lowest porosity. From Figs. 1a and 2a it can be seen that AC sample exhibits severe defects, porosity, infill and splats particles onto the surface attributed to the sudden cooling of melted metal particles whereas once the post-treatment of deposited Al coating was accomplished with different concentrations of NH₄H₂PO₄ and CsNO₃, they show improvement in the morphology. In Figs. 1a and 2a, the white deposition is infill particles around 1-10 µm whereas chunk morphology exhibited the splats particles around 50 µm and defects as well as pores are found all over the surface. The pores and defects are in deep which are very perilous for corrosion. Through the pores, the aggressive ions and solution pierce and causes the severe corrosion of the coating as well as substrate too. If the coating thickness is high then the penetration of solution can be reduced but in low thickness coating, it may corrode early and the service life of the structure would be decreased. CN1 sample shows compact and dense morphology (Fig. 1b) attributed to the reaction of treatment solution and Al metal which fill out the porosity of coating by forming composite oxides result in slight increment in thickness. The particles size of the coating reduced compared to AC and found to be around 10-20 µm attributed to the formation of composite oxides. These oxides are looks as needle, elongated and attached to each other. Thus, the diameter of needle particles is found around 1-2 µm but the length is around 5-10µm. However, at the periphery it shows few pores (Fig. 1b and 2b) owing to less concentration of NH₄H₂PO₄ and CsNO₃ which was not completely fill the pores/defects of coating thus, there would be some possibility to cause the corrosion in aggressive environment. But, once the concentration of NH₄H₂PO₄ and CsNO₃ is increased i.e. CN2 (Fig. 1c) and CN3 (Fig. 1d), they show agglomeration and dense morphology which cover the coating surface and reduce the porosity of deposited coating. After the post-treatment of the Al coating, the composite oxide particles are petal like having around 5-10 µm in diameter and 5-10 µm in length which uniformly covered all over the surface and make the coating surface defects free (Fig. 2c). Once the amount of NH₄H₂PO₄ and CsNO₃ is increased up to 1 M and 0.005 M, respectively i.e. CN3 exhibits smaller and thin composite oxide particles (Figs. 1d and 2d) which causes space between two particles therefore, there will be a possibility to ingress the aggressive ions result in enhancement in deterioration of coating. The particles of composite oxides are elongated and needle like. The dimension of composite oxides is around 1 µm in diameter and 5 µm in length. However, crack is observed in CN2 (Fig. 1c) and CN3 (Fig. 1d) at the periphery of coating surface attributed to the formation of brittle composite oxide film [24] which allow to penetrate the solution.

The porosity of the coating was determined by ImageJ software at lower magnification SEM images and found to be 47, 27, 16 and 12% for AC, CN1, CN2 and CN3 respectively. The number of treatment solution is increased, the porosity is decreased. The highest porosity is found by AC attributed to the process of coating. However, it is significantly reduced by 42.55, 65.96 and 74.47% for CN1, CN2 and CN3 compared to AC, respectively.

The chemical analysis of the coating is determined by EDS and the results are shown in Table 1. From this table it can be seen that AC sample contain only 2.85% oxygen (O) and rest of Al. The O content is very less and it might be coming from atmosphere. This result suggests...
that the coating deposited by arc thermal spray process does not show oxidation of the coating. As the concentration of NH$_4$H$_2$PO$_4$ and CsNO$_3$ is increased, O, P, N and Cs amount increased. This result suggests that these elements came from the treatment solution and some composite oxide has been formed on the coating surface. Thus, it is required to analyze the phases formed onto the coating surface by XRD. In subsequent paragraphs XRD results are discussed.

3.1.3. XRD analysis

The phases formed onto the AC and treated Al coating surface is determined by XRD and results are shown in Fig. 3. The XRD results shown in Fig. 3a reveal the presence of Al, caesium aluminum oxide (Cs$_2$Al$_2$O$_3$: CAO) and ammonium aluminum hydrogen phosphate hydrate ((NH$_4$)$_3$Al$_5$H$_6$(PO$_4$)$_8$.18H$_2$O: AHP) in treated coating [24] while AC sample exhibits only Al. The formation of CAO and AHP is described in Eq. (1).

$$7\text{Al} + 8\text{NH}_4\text{H}_2\text{PO}_4 + 2\text{CsNO}_3 + 22\text{H}_2\text{O} + 3\text{e}^- \rightarrow (\text{NH}_4)_3\text{Al}_5\text{H}_6(\text{PO}_4)_8.18\text{H}_2\text{O} + \text{Cs}_2\text{Al}_2\text{O}_3 + 7\text{NH}_4\text{OH} + 3\text{H}^+$$  \(1\)

AHP CAO

Al react with treatment solution i.e. NH$_4$H$_2$PO$_4$ and CsNO$_3$ and form AHP as well as CAO as composite oxide film which fill the porosity of the Al coating deposited by arc thermal spray process. Moreover, due to the intense peak of Al, the low intensity peaks of AHP and CAO are suppressed at lower scan range. Thus, the XRD results are re-plotted in Fig. 3b from 20=10-30°. The XRD result of AC sample suggests that there is no phase transformation after deposition of Al coating by arc thermal spray. Generally, most of the thermal spray coating processes attributed oxidation of coating which decrease the properties of coating. But, there is no oxidation of Al coating occurred after deposition by arc thermal spray process. This result corroborates the EDS analysis where only 2.85% O present which is not able to form Al$_2$O$_3$ film and detected by XRD. There is possibility that film is very thin and beyond the limitation of XRD to detect the oxide phase. It can be seen from Fig. 3a that the Al peak is very intense and well define in AC sample but once the post-treatment is performed, this peak becomes broad as well as intensity is decreased. It is attributed to the participation of AHP and CAO phases as observed in Fig. 3a and b.

The volume fraction (%) of composite oxides are determined by JADE software built in XRD instrument and the results are shown in Table 2. It can be seen from this table that AC sample contain 100% Al which suggests that there is no phase transformation of Al during coating process. However, as the concentration of NH$_4$H$_2$PO$_4$ and CsNO$_3$ are increased, the volume fraction of AHP is increased while Al is decreased. AHP is highly acidic and brittle in nature, thus, CN3 sample shows cracking in coating as observed in SEM images (Figs. 1d and 2d).

However, CN2 contain higher volume fraction of CAO compared to other treated coatings. The CAO is sparingly soluble and thermodynamically stable. Due to high amount of NH$_4$H$_2$PO$_4$ compared to CsNO$_3$ in CN3, greater AHP has formed.

3.2. Corrosion studies

3.2.1. EIS with exposure periods in artificial ocean water

The corrosion characteristics of coatings are performed in artificial ocean water with exposure periods and the EIS results are shown in
higher amount of acidic film i.e. AHP and cracks onto the coating surface CN3 exhibited lower in magnitude compared to CN2 attributed to the inhibit the ingress of solution and protect the coating from corrosion. formation of greater amount of CAO (Table 2) onto the surface which deteriorate but subsequently fill out the porosity by corrosion products. This finding suggests that CN1 and CN3 neither improve nor decrease the corrosion resistance properties of coating.

As the exposure periods are increased up to 6 d, the magnitude of complex-plane impedance of all samples increased attributed to the presence of heavy defects/pores and inflight particles onto the surface which enhances the deterioration of coating and allow to ingress the solution. The defects/pores work as active site (anode) and profoundly activate the corrosion reaction, thus, lower in magnitude is found. However, once the post-treatment was applied onto the Al coating, the porosity is decreased. Thus, higher in magnitude of complex-plane impedance is observed. CN2 exhibited higher in magnitude owing to the formation of greater amount of CAO (Table 2) onto the surface which inhibit the ingress of solution and protect the coating from corrosion. CN3 exhibited lower in magnitude compared to CN2 attributed to the higher amount of acidic film i.e. AHP and cracks onto the coating surface which influences the corrosion reaction while in case of CN1, some defects/pores are still present after post-treatment which influences the deterioration of coating, thus, lower in magnitude of complex-plane impedance is observed compared to CN2 and CN3.

As the exposure periods are increased up to 6 d, the magnitude of complex-plane impedance of all samples increased attributed to the formation of corrosion products in pores/defects [12]. The trend in magnitude of impedance plots for the all samples are identical as obtained after 1 h of exposure. There is small tail at lower studied frequency and big semi-circle from high to middle frequency ranges observed which reveal that corrosion process is occurred by dissolution of coating and deposition of corrosion products simultaneously. Therefore, it is necessary to know the corrosion characteristics of coatings at extended exposure periods. It is found by SEM images (Figs. 1 and 2) that CN1 has some porosity while CN2 and CN3 exhibit cracking owing to the formation of greater amount of AHP film. Thus, there is possibility to dissolve the AHP film at prolonged exposure periods and decrease the corrosion resistance properties of the coatings.

Figs. 4-6. The complex-plane impedance plots of coatings after 1 h of exposure in artificial ocean water solution are shown in Fig. 4a. It can be seen from this Fig. that AC sample exhibited lowest in magnitude of complex-plane impedance compared to treated coatings owing to the presence of heavy defects/pores and inflight particles onto the surface while CN1 and CN3 samples while AC and CN2 increased dramatically. This result suggests that CN1 and CN3 neither improve nor decrease the corrosion resistance properties of coating but remain consistent. CN1 sample has not completely fill the porosity of coating while CN2 exhibit cracks and high amount of AHP which dissolved and transformed into another phases. But, simultaneously the corrosion products are deposited onto the surface. Moreover, there is possibility that these corrosion products are not stable and uniform. On the other hand, AC sample initially enhances the corrosion reaction owing to the many active sites (defects/pores) result in dissolution of coating and formation of heavy corrosion products which fill out the pores/defects significantly but it requires some time i.e. 37 days to uniformly deposit the corrosion products onto the surface. This exposure period is significant to dissolve the coating and simultaneously deposit the stable corrosion products onto the surface and pores/defects of coating. These corrosion products fill the porosity of coating and uniformly distributed onto the surface which stifle the ingress of solution. Thus, the higher in magnitude of complex-plane impedance (Fig. 4c) is observed compared to CN1 and CN3. However, CN2 sample exhibited highest in magnitude of complex-plane impedance attributed to the presence of greater amount of CAO as complex oxide after post-treatment of Al coating whereas AHP film start to dissolve and transformed into stable phases. Thus, the highest in complex-plane impedance is observed. In this case, synergistic effect is caused by AHP film which transformed into another phase while CAO itself is protecting the coating from corrosion.

As the exposure periods are extended up to 65 days, the magnitude of complex-plane impedance is increased for all samples attributed to the formation of corrosion products as shown in Fig. 4d. There is an interesting observation found that the magnitude of complex-plane impedance of CN1 is higher compared to CN3 compared to earlier exposure periods owing to the filling of porosity by corrosion products. CN3 contain highest amount of AHP which dissolve and maintain the resistance for corrosion. This finding suggests that CN3 neither improve nor deteriorate but maintain the properties while AC and CN1 samples deteriorate but subsequently fill out the porosity by corrosion products result higher in magnitude. On the other hand, CN2 has formed highest amount of CAO which initially provide protection whereas AHP

Table 1
EDS analysis (wt.%) of coatings.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>O</th>
<th>P</th>
<th>N</th>
<th>Cs</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>2.85</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>Balance</td>
</tr>
<tr>
<td>CN1</td>
<td>12.48</td>
<td>7.63</td>
<td>5.24</td>
<td>0.10</td>
<td>Balance</td>
</tr>
<tr>
<td>CN2</td>
<td>37.51</td>
<td>19.96</td>
<td>6.15</td>
<td>0.12</td>
<td>Balance</td>
</tr>
<tr>
<td>CN3</td>
<td>39.47</td>
<td>26.01</td>
<td>7.36</td>
<td>0.13</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Fig. 3. XRD of coating from (a) 2θ=10-90° and (b) 2θ=10-30°.

Table 2
Volume fraction (%) of phases formed on the coatings.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>AHP</th>
<th>CAO</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>0.00</td>
<td>0.00</td>
<td>100</td>
</tr>
<tr>
<td>CN1</td>
<td>2.30</td>
<td>4.04</td>
<td>93.66</td>
</tr>
<tr>
<td>CN2</td>
<td>30.18</td>
<td>9.13</td>
<td>60.69</td>
</tr>
<tr>
<td>CN3</td>
<td>40.71</td>
<td>7.02</td>
<td>52.27</td>
</tr>
</tbody>
</table>

Fig. 4. (a) shows the complex-plane impedance plots of coating after 37 days of exposure in artificial ocean water solution. It can be seen from this Fig. that there is no improvement in magnitude of complex-plane impedance of CN1 and CN3 samples while AC and CN2 increased.
deteriorates and transformed into another phase result in two phenomena for protection. At longer duration of exposure, AHP completely transformed into stable corrosion products which significantly cover the surface as well as CAO and improve the corrosion resistant properties of coating at longer duration of exposure.

The total impedance of coating with exposure periods are shown in Fig. 5. AC samples exhibited lowest in impedance attributed to the presence of many active sites (pores/defects) which influences the corrosion while CN2 shows highest in impedance values at 0.01 Hz (Fig. 5a). The post-treated coatings show greater in impedance values owing to the filling of pores/defects by composite oxides i.e. AHP and CAO. However, once the exposure periods of coatings are increased in artificial ocean water up to 6 days, the total impedance values of all samples are gradually increased as shown in Fig. 5b owing to the deposition of corrosion products onto the surface. In case of AC sample, initially coating enhances the corrosion reaction owing to the presence of active sites but once the exposure periods are extended, the corrosion products simultaneously deposited into the defects/pores which reduce the active sites resultant increase in impedance values. Moreover, the treated coating exhibited AHP as well as CAO film where AHP is acidic in nature and started to dissolve and transformed into another phases therefore, there is possibility to deteriorate the coating at faster rate but at the same time CAO film at the coating surface reduces the deterioration. Due to the presence of CAO film, the coating exhibited protection and the corrosion products of AHP film deposit onto the coating surface, thus, impedance is increased up to 6 days of exposure. As the exposure periods are increased up to 37 days, the total impedance values are increased (Fig. 5c). There is not ample increment in total impedance values of CN1 and CN3 compared to 6 days of exposure while AC and CN2 increased significantly. In case of AC sample, the impedance is increased owing to the greater filling ability of pores/defects by corrosion products. Initially AC samples corroded very fast but as the exposure periods are increased, the dissolution of coating decreased attributed to the deposition of corrosion products onto the surface. Nevertheless, the active surface area is decreased resultant increase in total impedance values. CN1 is found to be lowest in total impedance values among all samples after 37 days of exposure attributed to the presence of defects/pores on surface (Fig. 1b) as well as presence of AHP film which make the surface brittle and acidic while CN3 contain highest amount of AHP which make the solution acidic result in deterioration of coating. But, subsequently, CAO protect the surface from corrosion and AHP transformed into another phase. CN2 exhibited highest in impedance attributed to the formation of uniform, regular and composite oxides film. AHP dissolved and transformed into another form but CAO provides the protection. The transformed corrosion products and CAO both are present onto the coating surface. Thus, barrier type of protection is exerted by the corrosion layer. But, as the exposure periods are extended up to 65 days from 37 days, the total impedance values of CN1 and CN3 at 0.01 Hz are remained constant but AC sample increased might be owing to uniform deposition of stable and uniform corrosion products (Fig. 5d). The highest impedance values are observed by CN2 attributed to the deposition of uniform, stable and thick corrosion products which stifle the ingress of solution. CN3 samples exhibit the lowest impedance values owing to the dissolution of AHP film result in studied solution become acidic. On the other hand, CN1 sample shows higher in impedance compared to CN3 might be owing to the less amount of AHP film onto the surface which easily dissolved and transformed into another phases. Due to lowest amount of AHP in CN1, it is
not able to make the solution acidic while during corrosion process, the corrosion products deposited onto the surface result in higher impedance values compared to CN3 after 65 days of exposure.

The phase-frequency Bode plots of coating samples immersed in artificial ocean water with exposure periods are shown in Fig. 6. It can be seen from Fig. 6a that all treated samples shifted the phase angle maxima at higher angle from high to middle frequency ranges while AC shifts at low angle. It is attributed to the formation of composite oxide film after treatment [25] whereas AC sample contain defects which possesses capacitive properties. At the highest studied frequency i.e. 100 kHz, the phase angle of CN2 sample is found to be highest among all samples which infers that barrier type of protection exerted by CAO film [35-38]. As the exposure periods are increased up to 6 days, the phase angle at highest and lowest studied frequencies of all samples found to be about to identical as shown in Fig. 6b owing to the corrosion phenomena is controlled by corrosion products. In treated coating, the treatment film started to dissolved and transformed into the other form as corrosion products while due to the greater in active sites of AC samples, initially formed corrosion products deposit into the pores/defects of the coating. AC sample shows asymmetric peak on 40 Hz at -45° reveal the deterioration of coating whereas CN2 samples cover broader ranges of studied frequency followed by CN3 and CN1 owing to the formation of protective film. As the exposure periods is extended up to 37 days (Fig. 6c), AC samples slightly shifted phase angle towards higher side in middle frequency and the asymmetric peak become broad which infer that corrosion products cover the active sites of coating and reduce the surface area of coating resultant increased in impedance value (Fig. 5c). However, CN2 samples show the broadening in phase angle from 2000 Hz to 0.25 Hz in between -38° to -51° which reveal that surface being strengthened by the corrosion products and cover the surface uniformly. CN1 sample shows the asymmetric peak at -55° on 92 Hz which divulge the deterioration of coating. CN3 sample exhibits the lower in phase angle compared to CN1 but the broadening in peak from 8912 Hz to 0.73 Hz which confirm that the corrosion products are providing the protection and uniformly cover the surface and stifle the ingress of aggressive ions towards coating surface. At highest (100 kHz) and lowest (0.01 Hz) studied frequencies, CN2 and AC samples exhibited higher in phase angle maxima shift owing to the corrosion products and coating itself compared to CN1 and CN3, respectively. At lowest studied frequency, CN2 is found the phase angle shift at -19° which is highest followed by AC, CN3 and CN1. This result corroborates with total impedance value at 0.01 Hz where CN1 samples show lowest in its value (Fig. 5c). As the exposure periods reached at 65 days, the broadening in maxima shift of CN2 sample from 1039 Hz to 0.42 Hz around -50° (Fig. 6d) confirm that coating is being protected by corrosion products and cover all over the surface uniformly and strengthen the film. Thus, the highest in impedance is observed after 65 days of exposure (Fig. 5d).

Fig. 5. Modulus-frequency Bode plots of coating after (a) 1 h, (b) 6 d, (c) 37 d and (d) 65 d of exposure in artificial ocean water solution.
studied frequency, it is shifted towards higher angle i.e. -14° (Fig. 6d). The shifting of phase angle maxima at higher angle on 0.01 Hz reveal that coating is providing protection. Initially, the protection to the coating is provided by treatment film i.e. AHP and CAO while at longer duration of exposure by corrosion products and coating simultaneously. In the case of AC sample at longer duration of exposure, the protection is provided by corrosion products while CN2 sample by corrosion products as well as coating surface simultaneously, thus, highest in impedance is observed from initial periods of exposure to 65 days.

The suitable electrical equivalent circuit (EEC) to fit the EIS data is shown in Fig. 7. It can be seen from this Fig. that all EIS data is fitted in one EEC with two times constant at high to middle and middle to lower studied frequencies \[39–42\]. In this EEC, \(R_s\), \(R_{ct}/\), CPE\(_c/t\), \(R_{ct}\) and CPE\(_{ct}\) corresponds to solution resistance, resistance of coating/treatment, constant phase element of coating/treatment, charge transfer resistance and constant phase element for charge transfer, respectively. The first time constant from high to middle frequency is associated to corrosion products which exerted barrier types of protection whereas the second time constant is associated for coating/treatment (top) layer from middle to low frequency. Initially, coating/treatment layer come in contact to solution, thus, corrosion has started at coating/treatment-solution interface while in the meantime, corrosion products deposit onto the coating surface and provided the protection.

After best fitting of EIS in suitable EEC, CPE coefficient \(Q_{eff}\) could be derived on the basis of imaginary impedance \(Z_j\) when CPE exponent \(n\) \(\neq\) 1, by Eq. (2) \[43\]:

\[
Q_{eff} = \sin \left( \frac{n\pi}{2} \right) \frac{-1}{Z_j(f)(2\pi f)^n} 
\]  

(2)

where \(f\) is frequency. But, once \(n\) become 1 then \(Q_{eff}\) becomes a capacitance \(C_{eff}\), therefore, Eq. (2) can be written as:

\[
Q_{eff} = C_{eff} \frac{-1}{Z_j(f)(2\pi f)^n} 
\]  

(3)

However, it is not possible to \(n\) become 1 due to the heterogeneity on the surface of coating/treatment surface where corrosion would start once exposed to solution. Therefore, the blocking characteristics of the coatings/treatments surface by corrosion products between the interfacial capacitance and CPE coefficient \(Q\) can be calculated by Brug’s equation \[44\] and others \[45,46\]:

\[
C_{eff} = Q^{1/n}R_s^{(1−n)/n} 
\]  

(4)

The electrochemical parameter after fitting of EIS plots in suitable EEC is shown in Table 3 and Fig. 8. The \(R_s\) values of coatings at different

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Fig. 6. Phase-frequency Bode plots of coating after (a) 1 h, (b) 6 d, (c) 37 d and (d) 65 d of exposure in artificial ocean water solution.

Fig. 7. EEC of coatings exposed in artificial ocean water solution at different exposure periods.
Table 3
Electrochemical parameters of coatings exposed in artificial ocean water solution at different exposure periods.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Time</th>
<th>Electrochemical parameters</th>
<th>R_{ct} (Ω. cm(^2))</th>
<th>Q_{eff} (1 × 10^{-5})</th>
<th>n_{eff}</th>
<th>R_{ct} (Ω. cm(^2))</th>
<th>Q_{eff} (1 × 10^{-5})</th>
<th>n_{eff}</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>1 h</td>
<td></td>
<td>23.45</td>
<td>17.60</td>
<td>0.52</td>
<td>0.67</td>
<td>31.10</td>
<td>0.55</td>
</tr>
<tr>
<td>CN1</td>
<td></td>
<td></td>
<td>9.03</td>
<td>14.50</td>
<td>0.54</td>
<td>0.74</td>
<td>27.70</td>
<td>0.56</td>
</tr>
<tr>
<td>CN2</td>
<td></td>
<td></td>
<td>14.59</td>
<td>2.74</td>
<td>0.62</td>
<td>0.83</td>
<td>17.86</td>
<td>0.60</td>
</tr>
<tr>
<td>CN3</td>
<td></td>
<td></td>
<td>19.26</td>
<td>3.70</td>
<td>0.60</td>
<td>0.80</td>
<td>23.30</td>
<td>0.58</td>
</tr>
<tr>
<td>AC</td>
<td>6 d</td>
<td></td>
<td>24.77</td>
<td>15.80</td>
<td>0.53</td>
<td>1.09</td>
<td>26.40</td>
<td>0.59</td>
</tr>
<tr>
<td>CN1</td>
<td></td>
<td></td>
<td>19.07</td>
<td>15.10</td>
<td>0.53</td>
<td>1.35</td>
<td>24.30</td>
<td>0.62</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>18.60</td>
<td>1.30</td>
<td>0.64</td>
<td>1.55</td>
<td>14.30</td>
<td>0.68</td>
</tr>
<tr>
<td>CN3</td>
<td></td>
<td></td>
<td>21.22</td>
<td>10.10</td>
<td>0.56</td>
<td>1.44</td>
<td>22.90</td>
<td>0.60</td>
</tr>
<tr>
<td>AC</td>
<td>37 d</td>
<td></td>
<td>21.39</td>
<td>9.20</td>
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<td>2.15</td>
<td>20.30</td>
<td>0.66</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>16.63</td>
<td>18.96</td>
<td>0.52</td>
<td>1.45</td>
<td>23.80</td>
<td>0.62</td>
</tr>
<tr>
<td>CN2</td>
<td></td>
<td></td>
<td>26.22</td>
<td>0.86</td>
<td>0.67</td>
<td>3.25</td>
<td>9.91</td>
<td>0.72</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>23.40</td>
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<td>0.53</td>
<td>2.04</td>
<td>21.30</td>
<td>0.66</td>
</tr>
<tr>
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<td>65 d</td>
<td></td>
<td>26.44</td>
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<td>0.59</td>
<td>4.00</td>
<td>8.20</td>
<td>0.66</td>
</tr>
<tr>
<td>CN1</td>
<td></td>
<td></td>
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<td>0.52</td>
<td>3.16</td>
<td>10.20</td>
<td>0.70</td>
</tr>
<tr>
<td>CN2</td>
<td></td>
<td></td>
<td>15.00</td>
<td>0.61</td>
<td>0.69</td>
<td>4.20</td>
<td>5.36</td>
<td>0.75</td>
</tr>
<tr>
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<td></td>
<td>27.86</td>
<td>16.51</td>
<td>0.51</td>
<td>2.70</td>
<td>18.13</td>
<td>0.69</td>
</tr>
</tbody>
</table>

 exposure periods in artificial ocean water is found to be in between 9 to 28 Ω.cm\(^2\) (Table 3). This value is very less and does not participate significantly in overall impedance. It can be seen from Fig. 8 that the R_{ct} values of AC and CN2 samples are gradually increased with exposure periods whereas CN3 is almost constant. CN1 sample initially up to 37 days of exposure is decreased but once the duration is increased, R_{ct} is increased. The C_{eff} of AC sample after 1 h of exposure is found to be the highest attributed to the highly defective coating but once the exposure periods are increased, it is decreased. CN2 samples show lowest in C_{eff} value with exposure periods attributed to the deposition of uniform treatment film as well as once the exposure periods are increased, the corrosion products are less defective, thus, the highest impedance is observed in all exposure periods.

The Q_{eff} of the AC sample is found to be highest after 1 h of exposure but once the exposure periods are increased, this value gradually decreased as well as n_{eff} value increased (Table 3). The n_{eff} value of AC samples after 65 days of exposure is found to be 0.59 which suggests that coating is still heterogeneous whereas Q_{eff} value of CN2 samples is found to be lowest from 1 h to 65 days of exposure (Table 3). The R_{ct} and Q_{eff} values of all samples with exposure periods are increased and Q_{eff} is decreased. The n_{eff} value of CN2 samples after 65 days of exposure is found to be 0.75 which infer that corrosion products are homogeneous and cover all over the surface. In this case, treatment film as well as corrosion products both participating in corrosion reaction. Thus, best corrosion resistance performance is shown by CN2 sample.

3.2.2. Potentiodynamic polarisation after 65 days of exposure in artificial ocean water

The potentiodynamic polarization of coatings exposed in artificial ocean water solution after 65 days are shown in Fig. 9. It can be seen from Fig. 9 that CN1 and CN3 samples exhibited higher cathodic current density whereas AC and CN2 are found to be least. An interesting observation can be seen after corrosion potential (E_{corr}) of the coating which anodic current density of CN1 and CN3 samples are abruptly increased suggesting that these coatings possesses pitting corrosion whereas AC and CN2 samples exhibited passive region. The anodic current density of AC and CN2 samples increased gradually after E_{corr} attributed to the formation of stable, protective and uniform corrosion products. The AC sample exhibited limiting current at 6.41 mA.cm\(^{-2}\) from -0.720 to -0.224 V vs Ag/AgCl while treated coatings do not show such behavior. The limiting current tendency in AC sample is attributed to the deposition of thick corrosion products onto the coating surface which causes resistance for penetration of solution [47].

It can be seen from Fig. 9 that all coatings exhibited E_{corr} value greater than -0.870 V vs Ag/AgCl which infer that coatings are providing sacrificial protection to the steel [48]. AC sample shows -1.177 V vs Ag/AgCl which suggests that this coating is deteriorating until 65 days of exposure in artificial ocean water solution even though corrosion products are deposited. There is possibility that thick corrosion products have formed but these are porous where chances for penetration of solution is significant. The corrosion phenomena are controlled by thick corrosion product which can be confirmed by morphology of corrosion products. In subsequent paragraph, the SEM of corrosion products are
Fig. 9. Potentiodynamic polarization plots of coatings after 65 day of exposure in artificial ocean water solution.

Fig. 10. SEM images of (a) AC, (b) CN1, (c) CN2 and (d) CN3 after potentiodynamic polarization studies exposed in artificial ocean water solution.
3.3. Characterisation of corrosion products

The morphology of corrosion products by SEM are shown in Fig. 10. The AC samples show thick and agglomerated net like morphology (Fig. 10a) which contain micro and nano pores as well as some space between two corrosion particles. Due to the deposition of thick and agglomerated corrosion products, AC samples exhibit higher corrosion resistance compared to CN1 and CN3. On the other hands, the CN1 sample shows horizontal cracks as well as porous corrosion products morphology (Fig. 10b) which are not able to resist the penetration of aggressive ions, solution and moisture towards coating surface. Thus, greater corrosion is observed compared to AC. CN2 sample deposits the fine and globular corrosion products onto the coating surface without any defects as shown in Fig. 10c, thus, protection is provided. However, CN3 shows heavy cracks and porous morphology in corrosion products (Fig. 10d) through which solution can penetrate and start the corrosion of steel substrate. From this figure it can be seen that AC, CN1 and CN3 show heavy corrosion products deposition while CN2 exhibits less amount of corrosion products. This finding suggests that the corrosion process of AC, CN1 and CN3 samples are controlled by corrosion products while CN2 by treated film as well as corrosion products.

The EDS analysis of corrosion products are shown in Table 4. There are many elements present in corrosion products owing to the solution composition, corrosion products and treatment film. This result suggests that corrosion products contain composite oxides. C, Na, Mg, Cl, K, Ca in all samples are coming from solution composition (ASTM D1141) where each element respective salt was dissolved in distilled water. The amount of N, P and Cs in corrosion products of treated coating is decreased owing to the dissolution of coated compared to after treatment (Table 1). Cs is very less amount in corrosion products of treated coating.

The nature of corrosion products formed onto the coating surface was determined by XRD after 65 days of exposure in artificial ocean water solution. The XRD pattern of corrosion products formed onto the coating surface are shown in Fig. 11. From Fig. 11a it can be seen that all samples exhibited Al and NaCl phases. Al comes from the coating whereas NaCl from the ASTM D1141 solution where 24.53 g/l NaCl was added in distilled water. NaCl was deposited onto the coating surface, therefore, it was observed in corrosion products. However, at lower scan angle i.e. 2θ=10–30° exhibited some small peaks which is suppressed by highly intense peaks of Al and NaCl. Thus, it is replotted from 2θ=10–30° and results are shown in Fig. 11b. It can be seen from this Fig. that α-Al (OH)₃ (bayerite) is formed on all coatings while on treated coating contain bayerite along with Al₃(PO₄)₂(OH)₃(H₂O)₉ (Aluminium hydroxide phosphate hydrate: AHPH) due to the transformation of AHP during corrosion process [24]. The bayerite and AHPH are thermodynamically stable and sparingly soluble.

The volume fraction (%) of each phases i.e. Al, NaCl, bayerite and AHPH are calculated by JADE software and the results are shown in Table 5. It can be seen from this table that the corrosion products formed onto CN2 sample contain highest amount of AHPH as well as second highest bayerite among all sample and accountable for reduction in corrosion. It can be seen that the corrosion products formed onto the CN3 sample mostly contain NaCl attributed to the affinity of AHP film with NaCl thus, severe corrosion is shown by this coating (Fig. 10d). AC sample contain 8.83% bayerite which is highest among all sample thus,

Table 4

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Elements (wt. %)</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Na</th>
<th>Mg</th>
<th>P</th>
<th>Cl</th>
<th>K</th>
<th>Ca</th>
<th>Cs</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td></td>
<td>5.23</td>
<td>0.00</td>
<td>48.57</td>
<td>2.23</td>
<td>1.57</td>
<td>0.09</td>
<td>3.62</td>
<td>0.40</td>
<td>1.22</td>
<td>0.00</td>
<td>37.16</td>
</tr>
<tr>
<td>CN1</td>
<td></td>
<td>8.60</td>
<td>1.62</td>
<td>29.01</td>
<td>1.75</td>
<td>0.80</td>
<td>4.53</td>
<td>4.81</td>
<td>0.47</td>
<td>1.28</td>
<td>0.04</td>
<td>47.09</td>
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<tr>
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<td>7.48</td>
<td>2.02</td>
<td>40.05</td>
<td>0.89</td>
<td>0.50</td>
<td>8.14</td>
<td>6.63</td>
<td>0.35</td>
<td>0.97</td>
<td>0.06</td>
<td>32.91</td>
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<tr>
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<td></td>
<td>6.43</td>
<td>2.66</td>
<td>44.08</td>
<td>0.51</td>
<td>0.15</td>
<td>13.68</td>
<td>8.44</td>
<td>0.29</td>
<td>0.46</td>
<td>0.09</td>
<td>23.21</td>
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</table>

Table 5

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Volume fraction (%)</th>
<th>AHPH</th>
<th>α-Al(OH)₃</th>
<th>NaCl</th>
<th>Al</th>
</tr>
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<td>8.83</td>
<td>19.44</td>
<td>71.53</td>
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</tr>
<tr>
<td>CN1</td>
<td>6.96</td>
<td>2.36</td>
<td>14.97</td>
<td>75.70</td>
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<tr>
<td>CN2</td>
<td>9.74</td>
<td>8.61</td>
<td>14.65</td>
<td>67.00</td>
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<td>CN3</td>
<td>8.69</td>
<td>7.50</td>
<td>35.08</td>
<td>48.73</td>
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</tr>
</tbody>
</table>
higher corrosion resistance is observed by this sample compared to CN1 and CN3.

4. Conclusions

From above results and discussion, it can be concluded that post-treatment of Al coating deposited by arc thermal spray process with NH₄H₂PO₄ and CN₃ has positive influence on morphology and corrosion resistance. AC sample exhibited defects and pores whereas once the coating was treated with NH₄H₂PO₄ and CN₃, the pores and defects are filled uniformly and porosity is reduced dramatically from 47% (AC) to 12% (CN3). It was observed by XRD that treated coating contain AHP and CAO as composite oxides. CN2 samples exhibited highest Rs and Rr with exposure periods in artificial ocean water solution attributed to the treatment film and transformation of AHP into stable and uniform corrosion products. The formation of Aluminum Hydrogen Phosphate Hydrate (AHPH) and α-Al(OH)₃ (bayerite) as corrosion products onto the treated coating stifle the ingress of solution therefore, enhancement in corrosion resistance is observed. The morphology of corrosion products formed onto the CN2 samples after 65 days of exposure show compact and less porous while CN3 shows heavy crack and porous morphology.

Authors’ contribution

Jitendra Kumar Singh: methodology, data curation, investigation, formal analysis, writing-original draft and writing-review and editing. 
Hyun-Min Yang: methodology, formal analysis, writing-original draft and writing-review and editing. 
Han-Seung Lee: Conceptualization, supervision, funding, writing-original draft and writing-review and editing. 
Sumit Kumar: formal analysis, writing-original draft and writing-review and editing. 
Rayed Lyousef: formal analysis, writing-original draft and writing-review and editing. 
Hisham Albduljabbar: formal analysis, writing-original draft and writing-review and editing.

Declaration of Competing Interest

All authors declare that there is no conflict of interest.

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Supplementary materials


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