Chapter V

Corrosion behaviour of Molybdate Conversion Coated aluminium

5.1. Introduction

Molybdate ($\text{MoO}_4^{2-}$) is one of the green inhibitors that are extensively studied as alternatives to $\text{CrO}_4^{2-}$ [1–5]. Both $\text{CrO}_4^{2-}$ and $\text{MoO}_4^{2-}$ are classified as anodic inhibitors. They passivate the metal and shift its potential to nobler values. They have inhibition effect on general and pitting corrosion [6–12].

Besides its environmental acceptability, molybdate gives multimetal protection. It is effective in salt solutions, and is both thermally and chemically stable [13]. The interaction of molybdates with Al and their impact on the corrosion resistance of Al have been the subject of several papers [14–20]. Wiggle et al. [14] studied the effect of molybdates on the pitting behaviour of two aluminum alloys, AA3003 and AA7072 in ethylene glycol/water/molybdate mixtures and found that the corrosion potential becomes more noble, increasing monotonically with the concentration of molybdate anions in the solution. Molybdate treatments have been applied also for decorative and solar absorption functional purposes [21,22].

The inhibitive effect of molybdate on the corrosion of aluminum alloys has long been known. According to kendig et al. [23], it prevents pitting corrosion at pH 7 to 9 by penetrating into an oxide film to a depth of 1500 Å. Both Mo(VI) and Mo(IV) compounds have been detected in the oxide by electronic spectroscopy for chemical analysis; accumulation of molybdenum in pits has been proved by scanning Auger spectroscopy.
According to Stranick [15], implantation of molybdenum in a dose of 
$5 \times 10^6$ ion/cm$^2$ into the surface of the aluminum alloy 3103 reduces the number of 
 cracks in the oxide film and increases its $E_{pi}$ value in 0.1 M NaCl by 0.16 V. The film 
 also contains oxidized molybdenum ($Mo^{4+}$ and $Mo^{6+}$), and the weaker adsorption of 
 chlorides at this film has been attributed to lowering by molybdenum at pH at the 
 point of zero charge (isoelectric point).

Mansfeld et al. [24, 25] has developed a cerium – molybdenum coatings on 
 aluminum alloys. Treatment of copper-free Al alloys in boiling $5\times10^{-3}$ M CeCl$_3$ or 
 $1\times10^{-2}$ M Ce(NO$_3$)$_3$ followed by anodic polarization in 0.1 M Na$_2$MoO$_4$ gives a CC 
 that keeps stable in 0.5 M NaCl for 30 days or in a salt chamber (according to 
 standard ASTM B-117 tests).

Molybdate conversion treatments can be obtained by simple immersion or 
 with cathodic polarization. The pH of the baths and the acids used to adjust the pH 
 seem to have significant influence on the quality of the deposited layer. Nitric, 
 phosphoric and sulfuric acids are currently used [3, 26-29] to adjust pH. The 
 formation of films, providing corrosion inhibition, occurs within the pH range 1–6.

For any kind of acid, for pH values above 6, no apparent conversion coating is 
 formed or the layer does not perform well in corrosion tests. Other deposition 
 conditions such as molybdate concentration, temperature, additives and dipping time 
 may also influence the performance of molybdate conversion coatings but a 
 systematic study has not been made to date.

A literature survey revealed that the most commonly used deposition 
 conditions are a molybdate content between 0.1 and 1.0 M, pH 3–6, bath temperatures 
 of 25– 60°C and dipping times of 1–20 min. In general, although there are many 
 treatments which enhanced the behaviour against pitting corrosion of several
aluminum alloys, data reported to date suggest that, the influence of molybdates is still unclear presenting various handicaps that limit their application on an industrial scale.

In the present work, the investigation was concentrated on producing molybdate conversion coatings from acid bath of sodium molybdate (Na₂MoO₄) by simple immersion. The acidification of the molybdate solutions was done with HNO₃. Further, influence of temperature, dipping time, concentration of sodium molybdate and additives on the performance of molybdate conversion coatings were also tested. The aim of this work is to study the effect of molybdate on the general corrosion behaviour of aluminum metal and to test as an anti-corrosion surface pretreatment for aluminum as an alternative to chromatation.

5.2. Effect of experimental parameters

5.2.1 Effect of temperature

Fig.5.1 reports the dependence of the thickness and growth rate of the molybdate conversion coatings (MCCs) formed by simple immersion method using molybdate bath (80 g/l Na₂MoO₄ + 80 ml/l HNO₃ + 12 g/l (CH₃COO)_2 Mn + 8 g/l Ca(NO₃)₂ + 2 g/l NaNO₃) at various temperatures (30 – 60°C). From the Fig.5.1 it can be seen that, as temperature of the bath increases, the thickness and growth rate of the coatings are found to increase up to 50°C, afterwards they decrease. During these stages, the coatings grew gradually and quickly with increase of temperature. Since the maximum thickness (0.6575μm) and growth rate (0.0328μm/min) were obtained at this temperature, 50°C was considered as the optimum temperature for fabricating better quality coatings (i.e., showing maximum thickness and corrosion resistance). During the process, formation of molybdenum oxyhydroxide and its dissolution in the bath are taking place simultaneously. But at higher temperature
 (>50°C), the liberated heat is high and so the dissolution of Al predominates over the formation of the coatings. So the growth rate and thickness of the coating decrease at higher temperature.

Bairamov et al. [19] found that when Al was exposed to a solution containing sodium molybdate, the film formed was sufficiently thick to mask the Al oxide and metal signal. These results corroborate the earlier work of McCune et al. [17] and the work of Stranick [15], who also found that molybdate was not incorporated into the passive film on Al, but rather was adsorbed onto the Al surface. McCune et al. concluded that it was incorporated into the composition of the film changing from being Mo rich at the surface, to being Al-rich at the metal/film interface.

5.2.2. Effect of treatment time

The effect of the treatment time on the surface properties of the MCCs was also investigated. In order to study the influence of treatment time, the process was carried out on aluminium at various immersion times from 5 to 25 min and its influence on the thickness and growth rate of the coating is given in Fig. 5.2. From the Fig. 5.2, one can observe that, the coating formed in 20 min has more thickness than the others. The black film gradually grew with the increase of immersion time. When the deposition and dissolution of the film reached a dynamic balance, the film is completely formed [30]. The influence of treatment time is compared with surface properties and it is concluded that, the features present are caused by real changes in the topography of the coatings. Thickening of the coatings hinders the access of the solution to the aluminium surface and thus slows down its dissolution.

In conversion coating process, dissolution of aluminium also takes place and coating for longer duration leads to vigorous dissolution and so the weight of the deposit as well as rate of coating decreases for longer durations.
The mass gain of the passivation film was almost proportional to the immersion time in the initial stage of immersion, and then it increases slowly after 10 min and begins to decrease after 20 min. The relationship between the Mo content and immersion time is very similar to that between the mass gain versus immersion time. Obviously, the mass loss after 20 min is resulted from the film flaking off, which is visible by naked eye [31].

In conversion coatings, the coating thickens and the aluminium thins with increasing treatment time. The thinning is fastest in the first 3 min of treatment, followed by a slower rate, roughly constant. [32, 33].

5.2.3. Effect of concentration of sodium molybdate

Effect of concentration of sodium molybdate on the formation and properties of molybdate conversion coating was studied by varying it between 60 g/l - 100 g/l at constant concentration of other additives (80 ml/l HNO₃ + 12 g/l (CH₃COO)₂ Mn + 8 g/l Ca(NO₃)₂ + 2 g/l NaNO₃) and the results are presented in Fig. 5.3. As the concentration of sodium molybdate increases in the bath, the formation of Mo⁶⁺ ions also increases, and so thickness increases. At higher concentration of sodium molybdate, the rate of coating decreases. This is due to the increased rate of etching at higher concentration of Mo(VI) ions which attack Al surface more vigorously. So, the growth rate decreases at higher concentration of sodium molybdate (above 80 g/l).

Among the different types of combinations of sodium molybdate, the specimen treated in bath containing 80 g/l Na₂MoO₄ has the maximum thickness (0.6575 m) and growth rate (0.0328 m/min). So, that was chosen as optimum concentration of Na₂MoO₄ for the formation of better quality conversion coatings.

Maximum rate was obtained for 8% Na₂MoO₄. Beyond that concentration, the rate of coating decreases. This may be due to the increased rate of dissolution of Al.
Since Na₂MoO₄ is highly aggressive electrolyte at higher concentration, the aggressiveness of Na₂MoO₄ increases and hence the dissolution increases. So, the coating formation decreases with increase of Na₂MoO₄ concentration.

Moshier and Davis [34] found that the film formed on Al exposed to molybdate is dependent on its concentration and the solution pH. At low molybdate solution concentrations and near neutral pH, the film was thick and consisted of high concentration of MoO₂, whereas at higher molybdate solution concentrations, the film was a thin layer consisting mainly of molybdate.

Shaw et al. [35] indicated that lower concentrations seem to provide more passivation protection than higher concentrations. They also reported the presence of Mo₄, MoO₄²⁻ and MoO₃ species in the passive regions.

5.3. Corrosion behaviour of the molybdate conversion coatings

The corrosion behaviour of the molybdate conversion coatings formed in various conditions were evaluated through potentiodynamic polarization and electrochemical impedance spectroscopy. The corrosion potential (E_{corr}), corrosion current density (I_{corr}) and corrosion rate (R_{corr}) values were determined and the results are presented in the tables.

The simulation fitting procedure was performed using the equivalent circuit of Fig.5.4 and the parameters are R_s, R_p and C, where R_s is the solution resistance, R_p is the polarization resistance and C is the capacitance [36].

The shape of the Nyquist diagram is similar for all samples and the shape is like a semi circle. The impedance data are mainly capacitive. The Nyquist diagram of the coated samples have semi circle with a larger diameter indicating higher corrosion resistance compared to that of the uncoated sample.
Generally, molybdate treatments improve the corrosion resistance due to the formation of protective molydate rich-aluminum oxide films. The corrosion resistance behaviour of molybdate coated aluminum electrodes formed at various deposition conditions are discussed below.

5.3.1. Effect of treatment temperature on the corrosion parameters

Fig. 5.5 shows the Tafel polarization curves of the molybdate conversion coatings formed at various treatment temperatures. The molybdate coated surfaces at various temperatures exhibited significantly lower cathodic current densities and a shift of the potential in the positive direction related to the bare aluminium.

The potential is increased from -1.2 V (SCE) for bare aluminium to -0.6 V (SCE) for the molybdate coated aluminium samples at various temperatures. The corrosion current density for the molybdate coated samples is two orders of magnitude lower than that for bare aluminium. Moreover, the current increasing speed of anodic branch of bare aluminium is slower than that of its cathodic branch, which is just reverse and a passivation behaviour is observed in the cathodic branch for molybdate coated aluminium samples. This indicates that, the addition of molybdate significantly increased the corrosion potential and decreased the corrosive current, suggesting that the corrosion resistance of aluminium could be obviously improved by addition of the molybdate.

The corrosion parameters of the conversion coating as a function of bath temperature are presented in table 5.1. From the table, it can be observed that, the corrosion current density (I_{corr}) and corrosion rate (R_{corr}) decrease, while the corrosion potential (E_{corr}) increases on increasing the bath temperature from 30 to 50 C. This indicates that, on increasing the temperature from 30 to 50 C, the coating formation is rapid and further increase of temperature to 60 C, the values are
reversed. Surface corrosion is initiated at 45 °C and is enhanced at higher temperature. Enhanced surface corrosion is also marked by sudden fall in the coating rate. Hence, the optimum temperature for formation of more corrosion resistant conversion coating is 50 °C. The current density for the molybdate coated samples is two orders of magnitude lower than that for bare aluminium.

Increasing the solution temperature can enhance the corrosion resistance of the molybdate films only to a very limited extent. This is probably a consequence of the fact that, both growth and chemical etching of the molybdate layer are accelerated by an increase in temperature [37].

The Nyquist impedance plots of the uncoated and coated samples formed at various temperatures are shown in Fig. 5.6 and the impedance parameters are given in the table 5.2. On increasing the bath temperature from 30 to 50 °C, the corrosion resistance ($R_p$) increases rapidly (21160 Ω). But for the coating formed at 60 °C, lower corrosion resistance value ($R_p$) is observed (17140 Ω). This is because, the enhanced surface corrosion arises above 50 °C. Since there is fall in the coating rate above 50 °C, the corrosion resistance decreases.

A comparative analysis of the compositions of the surface films obtained from NaCl solutions containing bichromate or molybdate [38] has shown that molybdate prefers adsorption and insertion into oxide. Interaction of molybdate with a passive film on aluminum in nearly neutral solutions (pH 5) has been studied by XPS [19]. According to the results obtained, the amount of MoO$_2$ in an oxide film is not decisive for the enhancement of its protective properties; rather, this is due to adsorbed molybdate anions that hinder the oxide growth and limit the penetration of Cl$^-$ across the film, thus preventing local depassivation. This conclusion agrees with the data
[39] on the improved protective properties of the composite AA6061-T6+10% Al2O3, which have been obtained by treatment in a molybdate solution.

Also, it was reported by many authors that, the corrosion resistance was improved due to passivity enhancement resulting from incorporation of Mo-containing species Mo (VI) and Mo (IV) into the porous Al-oxide lattice [15, 18, 35, 40–43].

It is reported that, treatment at 55°C, decreased the density of corrosion pits and the size of salt tails. Increasing the treatment temperature further to 70 and 85°C, further reduced the number of pits and the size of salt tails observed after corrosion testing [44].

Electrochemical impedance spectra and potentiodynamic scans indicated that, increasing the treatment temperature resulted in a coating that was more electrochemically resistant to corrosion.

Polarization studies by Breslin et al. [45] compared the effects of Na2MoO4 with Na2Cr2O7 on aluminum alloys in NaCl solutions. They observed the formation of Mo, Mo3, and MoO2 species followed by the formation of molybdenum oxides with different oxidation states. The effectiveness of the molybdate solutions was reported to be inhibited by the size and solubility of the oxide, MoO2 species. Sporadic pitting potentials of 100 mV led to the conclusions that, the oxidizing power of MoO42− was not as strong as the dichromate species (Cr2O72−) and the molybdate species was too large to accumulate at flawed areas, therefore unable to effectively passivate the region.

5.3.2. Effect of treatment time on the corrosion parameters

The electrochemical behaviour of the uncoated and molybdate coated samples obtained in various time intervals (5, 10, 15, 20 and 25 min) were studied by
recording the anodic and cathodic potentiodynamic polarization curves and reported in Fig. 5.7. For bare aluminium, the current increases in the anodic region, which is characteristic of an active state and dissolution of the aluminium alloy. This correlates with observed fluctuations in the corrosion potential curve of the untreated sample. For the untreated sample, a passive plateau is observed at a potential of -1.2 V (SCE). The samples coated with molybdate exhibit a large passivation plateau compared to the sample without molybdate. So the molybdate coated samples are stable and protective in a domain of potentials between -6.0 to -1.1 V (SCE).

Samples treated for longer times or higher temperatures exhibited less salting and better electrochemical properties than those subjected to shorter times or lower temperature sealing processes.

The corrosion resistance of the samples with and without molybdate conversion coatings is evidently different. In contrast to the bare aluminium, the samples with molybdate conversion coatings all had the positive corrosion potential and lesser corrosion current density which is shown in Fig. 5.7.

The curves of the molybdate coated aluminium rise to a higher potential of -0.6 V (SCE), whereas the uncoated aluminium remained at the low potential of -1.23 V (SCE), as illustrated in Fig. 5.7. A shift of the Tafel line toward the upper right of the diagram indicates an increase in corrosion current density and a decrease in corrosion behaviour. The current density for the molybdate coated samples at various immersion times is two orders of magnitude lower than that of bare aluminium indicating greater corrosion resistance.

The corrosion parameters of the conversion coating as a function of immersion time are presented in table 5.3. From the table, it can be observed that, corrosion current density ($I_{corr}$) and corrosion rate ($R_{corr}$) decrease and corrosion potential ($E_{corr}$)
increases on increasing the treatment time from 5 to 10 min. On increasing the immersion time from 5 to 20 min, there is rapid decrease in corrosion rate \( R_{\text{corr}} = 3.967 \times 10^{-02} \text{ mpy} \). On further increasing the immersion time to 25 min, the corrosion rate increases \( R_{\text{corr}} = 9.057 \times 10^{-01} \text{ mpy} \). Lowest corrosion rate \( R_{\text{corr}} \) is obtained for 20 min time of immersion.

Increasing the immersion time up to 20 min increases the corrosion resistance; longer conversion times on the contrary decrease the corrosion resistance. These results can again be explained in terms of simultaneous molybdate layer growth and Al etching. After immersion of the Al sample in the molybdate solution, the thickness of the molybdate layer initially increases with time as Mo(VI) is converted to Mo(III) and precipitates as Mo-oxy hydroxide on the Al surface. Thickening of the molybdate layer hinders the access of the molybdate solution to the Al surface and slows down its dissolution. A decrease in the rate of the anodic reaction necessarily slows down the corresponding cathodic reaction, resulting in a decrease in the rate of growth of the molybdate layer. Kendig et al. [46] observed a decrease and eventually a cessation in the growth rate of molybdate layers with increasing processing time.

Similar to the effects of temperature, corrosion performance was also affected by post-treatment duration. A treatment for 10 s at 85°C showed fewer pits and less tailing than an as-deposited sample. As post-treatment time increased, the number of pits and tails also decreased [44].

The Nyquist impedance plots of the uncoated and coated samples obtained at various immersion times at 50°C are shown in Fig. 5.8 and the impedance parameters are given in the table 5.4. From the figure and table, it can be seen that, the corrosion resistance is very much higher for the coated samples than for the bare aluminium as expected. On increasing the treatment time from 5 to 10 min, the corrosion resistance
(Rₚ) increases from 3279 to 7200. On continuous immersion of the sample in the treatment bath to 20 min, the corrosion resistance (Rₚ) increases rapidly and reaches to 21160, afterwards it decreases. Hence, the optimum treatment time is 20 min for the formation of molybdate conversion coatings with better corrosion resistance.

In addition, impedance measurements showed an unexpectedly large capacitance in the apparent passive region, indicating some kind of adsorption equilibrium at the metal solution interface. This observation led to the suggestion that hydrogen formed in the reduction process during cathodic activation of Mo could diffuse into the metal and cause a limiting oxidation of hydrogen upon positive polarization. The very high capacitance value obtained in our EIS measurements supports the explanation proposed by Raja et al. [47]. In this case, the anodic current density observed in the potential region (up to a small anodic current peak) could be attributed to the hydrogen ionization as well as to the oxidation of low-valent Mo species, i.e. Mo₂O₃ to MoO₂.

Similar results were reported for cerium conversion coatings post-treated for increasing times at 85°C. As the duration of post-treatment increased, more noble pitting potentials and passivation regions were observed as well as higher charge transfer resistances [44].

5.3.3. Effect of sodium molybdate concentration on the corrosion parameters

Fig. 5.9 shows the Tafel polarization curves of the molybdate conversion coatings formed from the bath containing various concentration of sodium molybdate. The molybdate containing layer is very stable and protective over a long range of anodic potential. The potential increased from -1.2 V for bare aluminium to -0.6 V for the molybdate coated aluminium samples for various concentration of sodium molybdate. The current density for the molybdate coated samples obtained from
various concentration of sodium molybdate is two orders of magnitude lower than that for bare aluminium. Moreover, the current increasing speed of anodic branch of bare aluminium is slower than that of its cathodic branch, which is just reverse and a passivation behaviour is observed in the cathodic branch for molybdate coated aluminium samples at various concentration of sodium molybdate.

The corrosion parameters of the molybdate conversion coating as a function of various sodium molybdate concentrations are presented in table 5.5. The corrosion current density ($I_{corr}$) and corrosion rate ($R_{corr}$) decrease and corrosion potential ($E_{corr}$) increases on increasing the concentration of sodium molybdate from 60 g/l to 80 g/l. This indicates that on increasing the concentration, the corrosion resistance increases. Further increasing the concentration of sodium molybdate from 80 to 100 g/l the corrosion current density ($I_{corr}$) and corrosion rate ($R_{corr}$) increase and corrosion potential ($E_{corr}$) decreases.

The Nyquist impedance curves of the coated and uncoated samples formed at 50°C for 20 min are shown in Fig. 5.10 as a function of concentration of sodium molybdate. The impedance parameters are given in the table 5.6. At a lower concentration (60 g/l), the corrosion resistance ($R_p$) is less (8562), but on raising the concentration to 80 g/l, there is rapid increase in corrosion resistance (21160). Further increase in concentration to 100 g/l, the corrosion resistance becomes decreases (14000). This is because, as the concentration of sodium molybdate increases, more number of Mo$^{6+}$ ions are produced near the surface resulting thicker film and so the corrosion rate decreases.

Akiyama et al. [48] reported that the enrichment of Mo in the surface film is significant for Al– Mo alloy with high aluminium contents. Since aluminium oxide is not stable in low-pH environments, its preferential dissolution simultaneously changes
the composition of the oxide layer making it richer in Mo(IV) oxides (MoO₂ and MoO(OH)₂) [49] and/or Mo(IV) oxyhydroxy chlorides (MoOCl₂) [50], which are stable in acidic solutions in the potential region of primary passivity. Therefore, with increasing Mo content in the alloy sample, the enrichment of the oxide layer with oxidized Mo increases indicating better barrier properties and, thus, providing the lower anodic current densities and higher polarization resistance.

5.4. Surface Examinations

5.4.1. Surface Morphological Studies: Scanning Electron Microscopy

Molybdate coated specimens formed in 20 min at various treatment temperature (30-60°C) were analysed by SEM in order to study the growth of molybdate conversion coating as a function of temperature. Figs. 5.11 – 5.14 show the scanning electron microscopic images of molybdate conversion coatings obtained from (80 g/l Na₂MoO₄ + 80 ml/l HNO₃ + 12 g/l (CH₃COO)₂ Mn + 8 g/l Ca(NO₃)₂ + 2 g/l NaNO₃) at different temperatures.

Molybdate coated specimen formed at 30°C is shown in Fig. 5.11. The conversion coated sample revealed the presence of cracks on the coating as well as the presence of cubic crystals. The coating formed at 40°C is shown in Fig. 5.12. Because of the aluminium substrate containing several kinds of metal elements, such as Al and Mn, the outer surface of coated sample have a layered structure being composed of mixture of metal oxides [51]. The particle size is 130-510 nm and a smooth surface is obtained.

The coating formed at 50°C is shown in Fig. 5.13. In this coating, the particle size is very much reduced (90-100 nm). This is the optimum temperature for getting maximum corrosion resistance. It can be seen that the coating covered the whole surface of Al surface as oxidative islands, and some micro-cracks are also found on
the coating. The micro-cracks are not continuous network; this island-like coating is piled up by spherical Mo-rich particles. The crack initiation is dependent on a number of factors, for example pretreatment of desmutting, degreasing and other parameters such as temperature, time of immersion, Mo ions, additives concentration and so on, which would affect the coating composition and morphology [52].

Lin et al. [53] had proposed that cracks in the Mo conversion coating occurred as a result of drying process, and the evaporation of water molecules caused shrinkage in volume, allowing cracks to form. Obviously, the stress as a result of shrinkage increased, and thicker the coating is, larger the stress induced, leading to more severe cracking. From the above statements, the crack of Mo conversion coating is caused by the evaporation of water molecules and more severe cracking appears when the coating is thicker. In addition, pretreatment of the surface is effected on formation of cracks [54].

However, microcracks develop apparently with longer deposition time. Moreover, microcracks probably originated from inhomogeneous deposition on the different surface sites or increasing inter-stress of coating during the rapid drying step.

Fig. 5.14 presents the SEM micrograph of the Al substrates after immersion in molybdate bath for 20 min at 60°C. The molybdate coatings displayed big cracks, which was possibly caused by the release of hydrogen for the chemical reaction during the conversion treatment and/or the dehydration of the surface layer after treating in acidic medium. Cracks of various sizes observable on the surface may have developed during drying out of the initial gel-like coating materials [55]. SEM revealed an almost uniformly distributed molybdate surface layer [39].

The tendency of MoO$_4^{2-}$ for polymerization in neutral media [56] leads to bulky anionic species like Mo$_6$O$_{21}^{6-}$. These species cannot be accommodated easily in
the flawed regions of the surface film [46] and, hence, a relatively higher corrosion rate can be measured for the specimens treated in neutral medium. Conversely, the tendency of MoO$_4^{2-}$ to polymerize into bulky anionic molydate species which appears to be less for the specimens treated in acidic medium. Hence, lower corrosion rates are observed.

5.4.2. Elemental Analysis: Energy Dispersive X-Ray Spectroscopy

Fig. 5.15 shows the EDX spectra of molybdate conversion coating obtained from the bath containing 80 g/l Na$_2$MoO$_4$ + 80 ml/l HNO$_3$ + 12 g/l (CH$_3$COO)$_2$Mn + 8 g/l Ca(NO$_3$)$_2$ + 2 g/l NaNO$_3$ at 50°C in 20 min. The element contents (%) of different coatings can be determined from EDX results and the results are given in table 5.7. From the table, it can be seen that, the molybdate coatings are all contain C, O, Ca and Mo (came from solutions) and Al (came from substrate). This indicates that the conversion coatings mainly composed of compounds of aluminium, molybdenum oxides and calcium. EDS analysis of the crystals indicated the presence of high concentrations of calcium as well as oxygen. This information can be interpreted as evidence of the presence of calcium nitrate on the coating [57]

5.4.3. Phase Compositional Analysis: X-Ray Diffraction Method

Fig. 5.16 – 5.19 show the XRD patterns of molybdate conversion coatings prepared from (80 g/l Na$_2$MoO$_4$ + 80 ml/l HNO$_3$ + 12 g/l (CH$_3$COO)$_2$Mn + 8 g/l Ca(NO$_3$)$_2$ + 2 g/l NaNO$_3$) in 20 min under various temperatures.

The XRD patterns of molybdate conversion coating formed at 30°C is shown in Fig. 5.16. For the coating prepared at 30°C, aluminium molybdenum (Al$_2$Mo) phase appears at 10.048° (d spacing=8.79) [JCPDS card= 65-1144, hexagonal/primitive, a4.933 c43.980] with preferred orientation of (0 0 5). Sodium molybdenum oxide (Na$_9$Mo$_6$O$_{17}$) phase appears at 38.581° (d spacing=2.3317)
JCPDS card= 86-1683, monoclinic/end-centered, a12.98 b5.518 c9.591; β89.940] with preferred orientation of (3 1 3). Sodium molybdenum oxide hydrate (Na₂Mo₅O₉(H₂O)₅) phase is also observed at 44.786° (d spacing=2.022) [JCPDS card= 87-1785, monoclinic/end-centered, a17.17 b3.775 c10.857; β115.41] with preferred orientation of (7 1 1). Molybdenum oxide (β-MoO₃) phase is observed at 65.273° (d spacing=1.4283) [JCPDS card= 89-1554, monoclinic/primitive, a7.122 b5.366 c5.566] with preferred orientation of (3 3 0). Molybdenum (Mo) phase appears at 78.684° (d spacing=1.215) [JCPDS card= 88-2331, cubic-face centered, a4.03] with preferred orientation of (3 1 1).

The XRD pattern of molybdate conversion coating formed at 40°C is shown in Fig. 5.17. If we increase the temperature to 40°C, sodium molybdenum oxide (Na₂Mo₂O₇) phase appears at 44.75° (d spacing=2.0235) [JCPDS card= 73-1797, orthorhombic/end-centered, a7.164 b11.83 c14.713] with preferred orientation of (2 0 6). Molybdenum oxide (β-MoO₃) phase is observed at 65.273° (d spacing=1.4283) [JCPDS card= 89-1554, monoclinic/primitive, a7.122 b5.366 c5.566; β92.01] with preferred orientation of (3 3 0). Molybdenum (Mo) phase is observed at 78.684° (d spacing=1.215) [JCPDS card= 88-2331, cubic/face centered, a4.03] with preferred orientation of (3 1 1).

The XRD pattern of molybdate conversion coating formed at 50°C is shown in Fig. 5.18. If we increase the temperature to 50°C, molybdenum oxide (Mo₄O₇)₁₁ phase appears at 38.475° (d spacing=2.3378) [JCPDS card= 89-8980, orthorhombic/primitive, a24.47 b6.751 c5.457] with preferred orientation of (4 1 2). Sodium molybdenum oxide (Na₂Mo₂O₇) phase appears at 44.75° (d spacing=2.0235) [JCPDS card= 73-1797, orthorhombic/end-centered, a7.164 b11.83 c14.713] with preferred orientation of (2 0 6). Molybdenum oxide (β-MoO₃) phase is observed at
65.273° (d spacing=1.4283) [JCPDS card= 89-1554, monoclinic/primitive, a7.122 b5.366 c5.566; β92.01] with preferred orientation of (3 3 0). Molybdenum (Mo) phase is observed at 78.684° (d spacing=1.215) [JCPDS card= 88-2331, cubic/face centered, a4.03] with preferred orientation of (3 1 1).

The XRD pattern of molybdate conversion coating formed at 60°C is shown in Fig. 5.19. In this coating, sodium molybdenum oxide (Na₂Mo₂O₇) phase appears at 44.75° (d spacing=2.0235) [JCPDS card= 73-1797, orthorhombic/end-centered, a7.164 b11.83 c14.713] with preferred orientation of (2 0 6) and β-Molybdenum oxide (β-MoO₃) phase appears at 65.273° (d spacing=1.4283) [JCPDS card= 89-1554, monoclinic/primitive, a7.122 b5.366 c5.566; β92.01] with preferred orientation of (3 3 0). Molybdenum (Mo) phase is observed at 78.684° (d spacing=1.215) [JCPDS card= 88-2331, cubic/face centered, a4.03] with preferred orientation of (3 1 1).

Molybdenum forms hard intermetallic compounds with Al, which greatly increase the strength of the material. Al–Mo alloys are potential candidates for coating materials to improve the surface hardness and wear resistance of Al-based light alloys. The majority of authors [58–63, 47, 49, 50] agree that, the passive state of Mo in acidic solutions is caused by the formation of Mo–oxygen compounds of variable oxidation states, depending upon the applied potential. In a slightly acidic solution, Wang et al. [62], used surface-enhanced Raman spectroscopy (SERS) and observed that MoO₂ was the main component of the passive film on molybdenum. According to the electron spectroscopy for chemical analysis (ESCA) of Urgen et al. [63], the passive film of Mo contains mostly Mo(III) species, whereas Mo(VI) is the major species in transpassive films. Based on XPS data, Lu et al. [49] reported that the passive film was found to be comprised of MoO₂ and MoO(OH)₂, whereas HMoO₄ was detected in the analyte of the transpassive region. XPS data on passivated
pure Mo in 4 M HCl solution [50] suggested the possible formation of a thin insoluble Mo oxychloride film or oxyhydroxide chloride salt complex and a relatively large amount of bound water in the outer part of the passive film. An alternative explanation for Mo passivation in acid solutions has been given by Raja et al. [47]. Their combined XPS and electrochemical measurements showed that the commonly used cathodic activation was insufficient to reduce the air-formed film. Thus, the anodic current in the so-called passive region could be due to oxidation of low valent oxides on the surface.

5.5. Effect of additives

Oleinik et al. [64] tried to obtain a protective conversion coating (CC) from a basic Na₂MoO₄ solution (in this medium, the aluminum surface is very active because of its amphoteric properties). The potentials of aluminum or its alloys are negative enough to allow reduction of MoO₄²⁻. Unfortunately, this technique was ineffective without special additives, facilitating the formation of an oxide CC and enhancement of its protective properties [65]. At the same time, they have developed a basic molybdate CC on the AMT-3 alloy, which is not inferior to the chromate CC in thickness or protective properties. Further investigations [66] have revealed the ability of oxidants (ammonium nitrate, hydrogen peroxide, and sodium m-nitrobenzoate) added to a molybdate-carbonate conversion formulation (CF) to stimulate the formation of CCs on AMT-3 and increase their porosity. Some additives usually found in chromating [67] and phosphating [68] baths, such as NaF, NaNO₂ and NaNO₃ were used in 0.1 M solutions.

In the present study also, some additives such as 12 g/l (CH₃COO)₂ Mn, 8 g/l Ca(NO₃)₂ and 2 g/l NaNO₃ were added. The coating obtained without any
additives were not effective. The additives played an important role which is given below.

The addition of Mn may play a critical role on the magnetic properties of the bulk amorphous steels (BASs). To date, however, few data on the magnetic property and corrosion resistance of these BASs have only been published [69].

Fedrizzi et al. [70] have found by secondary ion mass spectrometry that, the molybdenum content of the resulting CC increases with an increase in the concentration of the additive.

The manganese addition to the zinc phosphate bath enhanced the adhesion properties due to the porous nature of Mn and the zinc phosphate system. The phosphate coatings obtained in the presence of Mn\(^{2+}\) increased the bonding between the paint and the metal due to the enhanced adhesion [71].

Unlike the other oxidants studied, KMnO\(_4\) inhibits the dissolution of the aluminum alloy, although not preventing the formation of a CC on it. Addition of KMnO\(_4\) to a molybdate–carbonate CF (conversion formulation) makes the resulting CCs less porous, especially at elevated temperatures of the solution. The CCs obtained in the presence of KMnO\(_4\) are comparable in protective properties with coatings obtained from nitrate-containing CFs (conversion formulations) and filled in hot water [72, 73].

Higher manganese concentrations provide better corrosion resistance since the increased dissolved Mn shifts the matrix potential cathodically while the increased Mn:Fe ratio in the intermetallic particles shifts their potential anodically, leading to an overall lower potential difference between matrix and intermetallics [74].
Various ion additives like $\text{NO}^2_-$, $\text{NO}_3^-$ and $\text{NH}_4^+$ in NaOH solution were applied in the AC treatment. They increased the generation rate and crystallinity of the passive layers [75].

5.6. Mechanism of MCCs

Based on these experimental results, it could be supposed that the growth mechanism of Mo coating was a corrosion/precipitation process as follows: metal ions such as $\text{Al}^{3+}$ were first electrochemically etched from the Al substrate on micro-anodic area. Meanwhile, metal ions in conversion bath with positive charge, such as $\text{Ca}^{2+}$, $\text{Mn}^{2+}$ etc., and $\text{Al}^{3+}$ tend to become micro-cathode and further reacted with $\text{MoO}_4^{2-}$ to form insoluble metaphosphate and deposited on Al surface after a short incubation time. The surface coverage increased quickly with the rapid growth of individual crystals on Al surface, resulting in a mixed protection on the surface of aluminium.

It has been proposed by Vukasovich and Farr [76] that, the inhibiting effect of $\text{MoO}_4^{2-}$ on the active dissolution of stainless steel is due to the formation of insoluble lower valent molybdenum oxide. In addition, Wanklyn [77] has shown that the inhibition of corrosion by Mo(VI) involves a reduction reaction. Devasenapathi and Raja [78] claim that, during stress corrosion cracking, a further mechanism of corrosion inhibition by molybdate species may be possible due to its ability to react with chloride according to

$$\text{MoO}_4^{2-} + 4\text{H}^+ + 2\text{Cl}^- \rightarrow \text{MoO}_2\text{Cl}_2 + 2\text{H}_2\text{O}$$  \hspace{1cm} \text{(Reaction 5.1)}

Thus, reducing the concentration of chloride at crack sites reduces the susceptibility of stainless steel to corrosion.

Mo(VI) is potentially capable of undergoing a redox reaction with aluminium being reduced to Mo(IV) via
\[ 3\text{Mo}^{6+} + 6e^- \rightarrow 3\text{MoO}^4+ \]  
(Reaction 5.2)

\[ 2\text{Al} \rightarrow 2\text{Al}^{3+} + 6e^- \]  
(Reaction 5.3)

allowing the capacity for repair of flaws in the coating [79].

A number of authors have suggested possible coating formation mechanisms for molybdate conversion coatings on zinc surfaces. Rout et al. [80] have considered that zinc cations may combine with molybdate anions to form zinc molybdate. Similarly aluminium cations (\(\text{Al}^{3+}\)) may combine with molybdate anions to form aluminium molybdenum oxide.

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \]  
(Reaction 5.3)

\[ \text{Na}_2\text{MoO}_4 + 2\text{H}^+ \rightarrow \text{H}_2\text{MoO}_4 + 2\text{Na}^+ \]  
(Reaction 5.4)

\[ 3\text{H}_2\text{MoO}_4 + 2\text{Al}^{3+} \rightarrow \text{Al}_2(\text{MoO}_4)_3 + 6\text{H}^+ \]  
(Reaction 5.5)

\[ 2\text{Al}^{3+} + 3\text{HMoO}_4^- \rightarrow \text{Al}_2(\text{MoO}_4)_3 + 3\text{H}^+ \]  
(Reaction 5.6)

In this mechanism, it is basically identical to that of hexavalent chromium ion [81, 82]. It is indicated that, aluminium in acidic environments dissolves to form \(\text{Al}^{3+}\) with an accompanying hydrogen evolution. The float of tiny bubbles when aluminium was immersed in passivation baths confirms the evolution of hydrogen. At the same time, the reduction of hexavalent molybdenum (Mo VI) to tetravalent molybdenum (Mo IV) takes place at the metal–solution interface [83]. Hexavalent molybdenum has been found on the surface as Mo trioxide, which has a complex layered structure where each Mo atom shares the face of an octahedron with another Mo atom [81]. The Mo trioxide could be reduced to form Mo (IV) compounds on the coating surface. The presence of \(\text{MoO}_2\) in the XRD patterns also supports this point. Although some debate still remains over the formation mechanisms, it can be deduced that, the majority of coatings possibly contain Mo in the (IV) and (VI) oxidation state.
Augustynski [18] suggested that the inhibitive nature of the molybdate anion was due to the reduction of the Mo$^{6+}$ in the molybdate to Mo$^{4+}$ during film formation. The reduction of the molybdate anion could provide additional oxygen anions that interfere with the ability of the chloride anion to react at the metal/film interface, possibly by blocking sites through which aggressive anions preferentially penetrate the film.
Figures and Tables

Fig. 5.1 Influence of temperature on thickness and growth rate of the molybdate conversion coatings on aluminium.
Fig. 5.2 Influence of immersion time on thickness and growth rate of the molybdate conversion coatings on aluminium at 50°C.
Fig. 5.3 Influence of concentration of sodium molybdate on thickness and growth rate of the molybdate conversion coatings on aluminium at 50°C.
Fig. 5.4 Equivalent circuit for molybdate conversion coating
Fig. 5.5 Comparative Tafel polarization curves of the molybdate conversion coatings formed at various temperatures (30-60°C).

Fig. 5.6 Comparative Nyquist impedance plots of the molybdate conversion coatings formed at various temperatures (30-60°C).
Table 5.1 Influence of temperature on calculated Tafel parameters of the molybdate conversion coatings.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$I_{\text{corr}}$ (A)</th>
<th>$E_{\text{corr}}$ (V vs. SCE)</th>
<th>$R_{\text{corr}}$ (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>$7.3070 \times 10^{-4}$</td>
<td>-1.2312</td>
<td>$3.131 \times 10^{0.02}$</td>
</tr>
<tr>
<td>30</td>
<td>$4.304 \times 10^{-6}$</td>
<td>-0.7480</td>
<td>$1.846 \times 10^{0.01}$</td>
</tr>
<tr>
<td>40</td>
<td>$1.367 \times 10^{-6}$</td>
<td>-0.8017</td>
<td>$5.862 \times 10^{-01}$</td>
</tr>
<tr>
<td>50</td>
<td>$9.249 \times 10^{-8}$</td>
<td>-0.6200</td>
<td>$3.967 \times 10^{-02}$</td>
</tr>
<tr>
<td>60</td>
<td>$1.472 \times 10^{-7}$</td>
<td>-0.9594</td>
<td>$6.316 \times 10^{-02}$</td>
</tr>
</tbody>
</table>

Table 5.2 Influence of temperature on impedance parameters of the molybdate conversion coatings.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$R_s$ (Ω)</th>
<th>$C$ (F)</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>1.92</td>
<td>$2.182 \times 10^{-3}$</td>
<td>185</td>
</tr>
<tr>
<td>30</td>
<td>$1.617 \times 10^{-6}$</td>
<td>$6.214 \times 10^{-6}$</td>
<td>7206</td>
</tr>
<tr>
<td>40</td>
<td>$4.347 \times 10^{-5}$</td>
<td>$1.367 \times 10^{-6}$</td>
<td>13520</td>
</tr>
<tr>
<td>50</td>
<td>5.457</td>
<td>$1.863 \times 10^{-6}$</td>
<td>21160</td>
</tr>
<tr>
<td>60</td>
<td>0.3019</td>
<td>$2.123 \times 10^{-6}$</td>
<td>17140</td>
</tr>
</tbody>
</table>
Fig. 5.7 Comparative Tafel polarization curves of the molybdate conversion coatings formed in various immersion time.

Fig. 5.8 Comparative Nyquist impedance plots of the coatings formed in various immersion times (5-25 min).
Table 5.3 Influence of immersion time on calculated Tafel parameters of the molybdate conversion coatings.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$I_{\text{corr}}$ (A)</th>
<th>$E_{\text{corr}}$ (V vs. SCE)</th>
<th>$R_{\text{corr}}$ (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>7.3070×10^{-4}</td>
<td>-1.2312</td>
<td>3.131×10^{-02}</td>
</tr>
<tr>
<td>5</td>
<td>1.525×10^{-5}</td>
<td>-0.7234</td>
<td>6.542×10^{00}</td>
</tr>
<tr>
<td>10</td>
<td>2.885×10^{-6}</td>
<td>-0.7376</td>
<td>1.238×10^{00}</td>
</tr>
<tr>
<td>15</td>
<td>1.153×10^{-6}</td>
<td>-1.0539</td>
<td>4.945×10^{01}</td>
</tr>
<tr>
<td>20</td>
<td>9.249×10^{-8}</td>
<td>-0.6200</td>
<td>3.967×10^{02}</td>
</tr>
<tr>
<td>25</td>
<td>2.112×10^{-6}</td>
<td>-0.8122</td>
<td>9.057×10^{01}</td>
</tr>
</tbody>
</table>

Table 5.4 Influence of immersion time on impedance parameters of the molybdate conversion coatings.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>$R_s$ (Ω)</th>
<th>$C$ (F)</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>1.92</td>
<td>2.182×10^{-6}</td>
<td>185</td>
</tr>
<tr>
<td>5</td>
<td>2.119</td>
<td>1.792×10^{-6}</td>
<td>3279</td>
</tr>
<tr>
<td>10</td>
<td>5.457</td>
<td>6.214×10^{-6}</td>
<td>7200</td>
</tr>
<tr>
<td>15</td>
<td>7.838</td>
<td>1.505×10^{-6}</td>
<td>10180</td>
</tr>
<tr>
<td>20</td>
<td>5.457</td>
<td>1.863×10^{-6}</td>
<td>21160</td>
</tr>
<tr>
<td>25</td>
<td>1.098×10^{-6}</td>
<td>1.39×10^{-6}</td>
<td>13950</td>
</tr>
</tbody>
</table>
Fig. 5.9 Comparative Tafel polarization curves of the molybdate conversion coatings formed from various sodium molybdate concentrations (60-100 g/l).

Fig. 5.10 Comparative Nyquist impedance plots of the molybdate conversion coatings formed from various concentration of sodium molybdate (60-100 g/l).
Table 5.5 Influence of concentration of sodium molybdate on calculated Tafel parameters of the molybdate conversion coatings.

<table>
<thead>
<tr>
<th>Conc (g/l)</th>
<th>$I_{\text{corr}}$ (A)</th>
<th>$E_{\text{corr}}$ (V vs. SCE)</th>
<th>$R_{\text{corr}}$ (mpy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>$7.3070 \times 10^{-4}$</td>
<td>-1.2312</td>
<td>$3.131 \times 10^{-02}$</td>
</tr>
<tr>
<td>60</td>
<td>$1.354 \times 10^{-5}$</td>
<td>-0.6955</td>
<td>$5.806 \times 10^{00}$</td>
</tr>
<tr>
<td>80</td>
<td>$9.249 \times 10^{-8}$</td>
<td>-0.6200</td>
<td>$3.967 \times 10^{-02}$</td>
</tr>
<tr>
<td>100</td>
<td>$1.493 \times 10^{-7}$</td>
<td>-0.9595</td>
<td>$6.216 \times 10^{02}$</td>
</tr>
</tbody>
</table>

Table 5.6 Influence of concentration of sodium molybdate on calculated impedance parameters of the molybdate conversion coatings.

<table>
<thead>
<tr>
<th>Conc. (g/l)</th>
<th>$R_s$ (Ω)</th>
<th>C (F)</th>
<th>$R_p$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>1.92</td>
<td>$2.182 \times 10^{-5}$</td>
<td>185</td>
</tr>
<tr>
<td>60</td>
<td>$1.738 \times 10^{-5}$</td>
<td>$4.061 \times 10^{-6}$</td>
<td>8562</td>
</tr>
<tr>
<td>80</td>
<td>5.457</td>
<td>$1.863 \times 10^{-6}$</td>
<td>21160</td>
</tr>
<tr>
<td>100</td>
<td>$5.167 \times 10^{-5}$</td>
<td>$1.702 \times 10^{-6}$</td>
<td>14000</td>
</tr>
</tbody>
</table>
Fig. 5.11 SEM image of the molybdate conversion coating formed on aluminium at 30°C.

Fig. 5.12 SEM image of the molybdate conversion coating formed on aluminium at 40°C.
Fig. 5.13 SEM image of the molybdate conversion coating formed on aluminium at 50ºC.

Fig. 5.14 SEM image of the molybdate conversion coating formed on aluminium at 60ºC.
Fig. 5.15 EDX spectrum of the molybdate conversion coating obtained on aluminium at 50°C in 20 min.

Table 5.7 EDX spectrum of the molybdate conversion coating obtained on aluminium at 50°C in 20 min.

<table>
<thead>
<tr>
<th>S.NO.</th>
<th>Element</th>
<th>kev</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>C K</td>
<td>0.277</td>
<td>35.53</td>
</tr>
<tr>
<td>2.</td>
<td>O K</td>
<td>0.525</td>
<td>22.18</td>
</tr>
<tr>
<td>3.</td>
<td>Al K</td>
<td>1.486</td>
<td>41.89</td>
</tr>
<tr>
<td>4.</td>
<td>Ca K</td>
<td>3.69</td>
<td>0.15</td>
</tr>
<tr>
<td>5.</td>
<td>Mo K</td>
<td>2.293</td>
<td>0.24</td>
</tr>
</tbody>
</table>
Fig. 5.16 X-Ray diffraction pattern of the molybdate conversion coating obtained on aluminium at 30°C in 20 min.

Fig. 5.17 X-Ray diffraction pattern of the molybdate conversion coating obtained on aluminium at 40°C in 20 min.
Fig. 5.18 X-Ray diffraction pattern of the molybdate conversion coating obtained on aluminium at 50°C in 20 min.

Fig. 5.19 X-Ray diffraction pattern of the molybdate conversion coating obtained on aluminium at 60°C in 20 min.
References


[57] L. M. Calle and L. G. MacDowell, National Aeronautics and Space Administration, YA-F2-T, Kennedy Space Center, FL 32899, US.


Chapter VI

Corrosion behaviour of Anodized aluminium

6.1. Introduction

The use of aluminum alloys in building and construction industry has increased at the last few decades [1] due to their specific properties such as appearance, low density and high corrosion resistance in combination with relatively good mechanical properties. However, in many instances, inadequate corrosion properties and low surface hardness have greatly restricted their application. Mechanical and corrosion resistance can be further improved when the aluminum substrate is anodized [2–9].

Anodizing [7–9], which is an electrochemical process, consists of converting aluminium into its oxide by appropriate selection of the electrolyte and the anodizing conditions such as current density, voltage and temperature.

Numerous works dealing with anodization were focused on the anodizing treatment conditions and the composition of single acid electrolyte, i.e. solution of sulphuric acid, chromic acid, phosphoric acid or oxalic acid, in order to optimize the properties of the anodic layer such as corrosion resistance, microhardness and abrasion resistance [10–13]. Over the past decades, modified electrolytes were implemented by addition of oxianions having two oxidation states such as the chromates (molybdates, permanganates etc.) [14,15] to improve the properties of the anodic layer and/or to find an alternative of chromic acid anodizing process which will be forbidden by the year 2007.

Montero-Moreno et al. have investigated the effect of the aluminum surface pretreatment [16] and anodizing voltage applied in the first and second anodizing