EFFECT OF PRE-TREATMENT ON CORROSION RESISTANCE OF CHROMATE CONVERSION COATED AND ANODIZED AA2219 ALLOY

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ABSTRACT

The study pertains to the effect of prior surface copper removal treatment on the corrosion resistance of chromate conversion coated (CCC) and anodized AA2219 Aluminium-copper alloy. Pre-treatment of test samples was done using AC Polarization in nitric acid to remove the copper rich precipitates from the surface. Pitting resistance of the base metal with and without copper rich phase was evaluated by potentiodynamic polarization test and transmission electron microscopy. Significant improvement in pitting resistance of base metal (T6) was observed after the copper removal. Two layers of organic coatings have been given on chromate conversion coated and normal anodized base metal with and without the copper removal. Zinc rich self etching and strontium chromate based primers are used as under coats. Epoxy based alkyd and polyurethane based finish coats have been used as top coats. Electrochemical impedance spectroscopy has been used to evaluate the corrosion resistance of the coated surfaces. It has been found that CCC is more effective after the copper removal treatment. Lower corrosion resistance of CCC on base metal without copper removal may be attributed to the heterogeneous microstructure and partial covering of CCC on the intermetallic compounds. The copper removal treatment is not effective in improving corrosion resistance of anodized surfaces which has been attributed to possible consumption of base metal and nature of the growth of the anodic oxide layer.

1. INTRODUCTION

Aluminium alloys are widely used in aerospace and defense industries because of their relatively low densities and moderate strength. Aluminium and aluminium alloys are in their passive state in the pH range of 4-8.5 due to a naturally formed barrier oxide film on their surface. This oxide film is 2-3 nm thick and is strongly bonded to the substrate.

The oxide film can re-form immediately when damaged in most environments. However, when exposed to aggressive environments containing halides, aluminium and its alloys are susceptible to localized corrosion, such as pitting and crevice corrosion. Chromate conversion coating (CCC) and anodizing are the most widely used corrosion protection methods for the aluminium alloys.

Chromate conversion coatings are usually applied to aluminium alloys to enhance corrosion resistance and improve paint adhesion. Hughes et al. found that CCCs formed on 2024-T3 alloys were heterogeneous and Cu rich regions were present at the alloy/coating interface. It is obvious that, the heterogeneous microstructure of substrate alloys plays a great role in CCC composition and structure. Recently, Secondary Ion Mass Spectroscopy (SIMS) element mapping revealed that the CCC was heterogeneous, and Cu enrichment was found in the outermost layer of CCC on AA2024-T3 alloy². The CCC only partially covered the intermetallic particles. The authors suggested that, the redistribution of intermetallic dissolution products in the CCC might be attributed to the projection of the intermetallic composition through the CCC toward the CCC surface². Regions of the CCC above intermetallics
were depleted in Cr, but enriched in Cu. Heterogeneous CCC where Cu-rich regions are present may provide paths for selective dissolution and lead to the breakdown of CCC coatings when exposed to the corrosion environment.

Aluminium anodizing is an electrochemical method of converting aluminium into aluminium oxide at the surface of the component being coated. Chromic acid anodizing process is not recommended for high copper and high silicon aluminium alloys. Sulphuric acid anodizing is a method suitable for high copper aluminium alloys, which produces a coating that is normally about 8 μm in thickness and has good corrosion resistance.

In the present work an attempt has been made to investigate the effect of removing copper rich phases at the surface on the corrosion resistance of chromate conversion and anodized surfaces of organically coated AA2219 alloy in T6 condition.

2. EXPERIMENTAL DETAILS

Aluminium-copper alloy AA2219 of the nominal composition Al- Cu-6.3%, Mn-0.38%, Zr-0.2%, V-0.1%, Ti-0.06% made in the form of 3.5 mm thick rolled sheet and heat treated to T6 temper (Solution treated at 808 K, 1 h + aged at 463 K for 36 h) served as the base metal. Copper removal treatment has been conducted by AC anodic polarization technique with optimized parameters of 5 V and 10 mins using 70% nitric acid as an electrolyte in which the material was anodically connected to the AC power supply through Dimmer stat, used for varying the voltage. Authors had optimized the parameters of voltage and polarization time in their earlier study. Stainless steel 304L has been taken as a cathode because it is more passive than the Cu and Al in concentrated nitric acid. The specimen was removed after each treatment, and washed with distilled water and dried. Transmission Electron microscopy (TEM) has been done to find the evidence of copper removal from the surface. Software based PAR Basic electrochemical system was used for conducting potentiodynamic polarization tests to study the general and pitting corrosion behavior of the coated and base metal surfaces using power suit software. All the experiments were conducted in 3.5% NaCl solutions with pH adjusted to 10 at which the transition from passive to pitting region is very sharp. The potential scan was carried out at 0.166 mV/sec with initial potential of –0.25V(OC) SCE to final potential of pitting. The specimen exposed during these experiments was 1 cm². The potential at which current increases drastically is treated as critical pitting potential (E_{pil}). The samples of AA 2219 alloy in T6 condition of 3 mm thickness and size of 50 mm X 100 mm were used for coatings in the present study. All the samples were subjected to degreasing, alkaline pickling and desmutting operations followed by the copper removal treatment. Chromate conversion coating (CCC) of thickness of 1μm and normal sulfuric acid anodizing of thickness 8-9 μm on the both copper leached and unleached base metal were carried out as per the Standards MIL-C-81706 and (MIL – A – 8625) respectively. The organic coatings were applied to the CCC and anodized surfaces with a painting brush in atmosphere of less than 40% humidity. The under coats used were zinc rich self etch primer and strontium chromate based primer. The finish coats were epoxy based alkyd topcoat and polyurethane based topcoat. Software based PAR Basic electrochemical system was used for conducting Electrochemical impedance spectroscopy (EIS) tests to study the corrosion behavior of the coated and base metal surfaces using power suit software. All the experiments were conducted in a solution of 50% sodium chloride, 1% copper chloride and acetic acid was added to maintain the pH of the solution at about 3 as per ASTM standard No: B – 368. The EIS tests were carried out in the frequency range of 100 kHz to 1.0 mHz and the Bode plots were generated. The total impedance value at the lowest frequency was used as the criteria for the corrosion resistance determination.

3. RESULTS AND DISCUSSION

3.1 Base Metal

Ageing produces a microstructure in which there is a uniform distribution of δ' precipitates in α-matrix. On a macroscopic scale it is homogeneous, but on a microscopic scale the precipitate and its immediate
environment represent inhomogeneity. The precipitate sizes are smaller than the relative microscopic features of grain size. The picture becomes more complicated by the presence of the precipitate in preferential locations such as grain boundaries.

The general corrosion and pitting resistance of 2219 alloy in T6 condition is poor which may be attributed to large number of coherent and equilibrium precipitates as evident from TEM study (Fig. 1). Very early establishment of the local-action cells of corrosion between the precipitates and Al-matrix decreases the pitting resistance of the alloy.

Fig. 1: TEM Photograph of base metal-T6 Condition depicting coherent and equilibrium precipitates.

Copper and copper-rich particle clusters were observed to deposit on aging aircraft skin material 2024 alloy after immersion experiments for 5 days in 0.6M NaCl solutions. SEM analysis showed presence of large Cu particle clusters on Fe-rich or Fe-containing areas while a TEM analysis showed wide range of copper deposits exhibiting microdendritic morphologies in basic and neutral environments and nodular morphologies in acidic environments. The plating or cementation of copper from solution as an electrochemical displacement reaction appears to be a major contributor to the pitting corrosion of 2024 aluminium alloy. The desmutting of 2024-T3 aluminium alloy using a rare earth desmutting solution was studied by Hughes et al using SEM and X-ray photoelectron spectroscopy (XPS). It was evident from these studies that during desmutting, there was dissolution and etching of both the intermetallics and basic oxide scale left after alkaline cleaning. In addition copper from the intermetallics was deposited as residue on the surface of the desmuttered alloy. The residue in the form of precipitates ~200 nm in size, proved to be copper with an oxide coating. Mansfeld and Wang developed modified Ce-Mo method to improve the pitting resistance of high copper aluminium alloys such as 2024 and 7075 without the use of chromates. The process involved immersion in boiling Ce(NO₃)₃, anodic polarization in Na₂MoO₄ followed by immersion in boiling CeCl₃. After applying such a pretreatment step, 7075-T6 developed surfaces with high corrosion resistance, which removes copper from the outer surface layers. During exposure in 0.5M NaCl for 30 days no measurable corrosion was indicated. Similarly significant improvement in pitting corrosion resistance of 2024 was also obtained.

Copper removal processes are recently being attempted as a pre treatment step in order to avoid the deleterious effects of these precipitates in T6 condition on the corrosion resistance of the alloy. Copper is removed from the outer surface layers without affecting the mechanical properties of the alloy. Effect of copper removal on potentiodynamic anodic polarization of 2219-T6 alloy is as shown in the Fig. 2. Increase in E⁺ by 69 mV(SCE) showed significant improvement in pitting resistance. Thin foil was prepared from the surface layer after copper removal by careful polishing from the bottom side. TEM studies (Fig. 3) revealed clearly that the technique of copper removal process had successfully eliminated copper rich precipitates from the surface layer of the base metal.

Fig. 2: Dynamic polarization curves
3.2 Coated Surfaces

In general organic polymeric coatings contain micro pores, areas of low cross linking density or high pigment volume concentration that provide path for diffusion of corrosive agents such as water, oxygen and chloride ions to the coating/metal interface. Therefore it is necessary to incorporate inorganic/organic inhibitors into the polymeric coating system for corrosion protection. Schematic of the three layered polymeric coating on a metal substrate is as shown in Fig. 4.

The functions of the three layers are as follows: Topcoat is used for camouflaging in addition to imparting corrosion resistance. The primer coat is applied for protecting the material from intergranular corrosion and also offers a good bonding and adds to the adhesion strength of the topcoat to the base metal. The surface modification gives additional corrosion protection and increases the adhesion of the primer and topcoat with the base metal. In the present study, Chromate conversion coating using immersion technique and electrolytic normal anodizing method were used as surface modification techniques prior to the application of organic coatings.

3.3 Chromate Conversion Coatings

Bode plots of EIS studies for the chromate conversion coatings with two primers and two finish coats on the base metal are shown in the Figs. 5 to 8. Tables 1 and 2 summarizes the corresponding impedance values at the lowest frequency (10mHz) for these coating combinations. Increase in the impedance value at the lowest frequency is clear indication of improvement in corrosion resistance of the base metal after the copper removal, which is in agreement with the potentiodynamic polarization test results on pitting resistance. These results also indicated the significant increase in the corrosion resistance of all the coating combinations after the removal of copper-rich precipitates from the surface. This may be attributed to the uniform chromate coating on the alloy surface which is free from the intermetallics and is in agreement with the earlier observations of CCCs on 2024-T3 alloy. Zinc-rich self etching primer is more effective than the strontium chromate due to the self sacrificial nature of the zinc towards aluminium substrate. More water resistant polyurethane finish coat with zinc rich self etching primer is offering more corrosion resistance compared to those of other coating combinations.

3.4 Anodizing

Bode plots of impedance for the anodized surfaces with two primers and two top finish coats are as as shown in the Figs. 9-12. Tables 3 and 4 summarize the impedance values of the anodized coating with other top coating combinations. Results revealed clearly that pre-treatment of copper removal is not having any influence on improving the corrosion resistance. The possible dissolution of base metal surface during the anodization may be the reason for the ineffectiveness of copper leaching on the impedance values obtained for all the coating combinations with anodized surface. However improvement in corrosion resistance with zinc rich self etching primer may be attributed to the self-sacrificial nature of the zinc towards aluminium substrate.

136
Fig. 5: Bode’s plots of chromate conversion coated base metal before and after copper removal with zinc rich self etching primer and Polyurethane finish coat.
1. base metal before copper removal
2. base metal after copper removal
3. coating before copper removal
4. coating after copper removal

Fig. 6: Bode’s Plots of chromate conversion coated base metal before and after copper removal with strontium chromate primer and polyurethane finish coat.
1. base metal before copper removal
2. base metal after copper removal
3. coating before copper removal
4. coating after copper removal

Table 1
IMPEDEANCE VALUES (KILO-OHMS) OF CHROMATE CONVERTED COATINGS ON 2219-T6 ALLOY WITH POLYURETHANE BASED TOP COAT.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of Primer</th>
<th>Before Cu-leaching</th>
<th>After Cu-leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc rich self etching</td>
<td>69.783</td>
<td>96.466</td>
</tr>
<tr>
<td>2</td>
<td>Strontium Chromate</td>
<td>14.244</td>
<td>44.507</td>
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</table>

Table 2
IMPEDEANCE VALUES (KILO-OHMS) OF CHROMATE CONVERTED COATINGS ON 2219-T6 ALLOY WITH EPOXY BASED ALKYD TOP COAT.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of Primer</th>
<th>Before Cu-leaching</th>
<th>After Cu-leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc rich self etching</td>
<td>5.25</td>
<td>18.105</td>
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<td>2</td>
<td>Strontium Chromate</td>
<td>13.741</td>
<td>37.6281</td>
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</table>
Fig. 7: Bode’s plots of chromate conversion coated base metal before and after copper removal with Zinc rich self etching primer and epoxy finish coat.
1. base metal before copper removal
2. base metal after copper removal
3. coating before copper removal
4. coating after copper removal

Fig. 8: Bode’s plots of chromate conversion coated base metal before and after copper removal with Strontium chromate primer and epoxy finish coat.
1. base metal before copper removal
2. base metal after copper removal
3. coating before copper removal
4. coating after copper removal

Fig. 9: Bode plots of anodized base metal before and after copper removal with Zinc rich self etching primer and proxy finish coat.
1. base metal before copper removal
2. base metal after copper removal
3. coating before copper removal
4. coating after copper removal

Fig. 10: Bode’s plots of anodized base metal before and after copper removal with Zinc rich self etching primer and epoxy finish coat.
1. base metal before copper removal
2. base metal after copper removal
3. coating before copper removal
4. coating after copper removal
SRINIVASA RAO, et al., : EFFECT OF PRE-TREATMENT ON CORROSION RESISTANCE OF CHROME CONVERSION COATED AND ANODIZED AA2219 ALLOY

Table 3
IMPEDANCE VALUES (KILO-OHMS) OF ANODIZED COATING ON 2219-T6 ALLOY WITH POLYURETHANE BASED TOP COAT

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of Primer</th>
<th>Before Cu-leaching</th>
<th>After Cu-leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc rich self etching</td>
<td>41.917</td>
<td>53.279</td>
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<tr>
<td>2</td>
<td>Strontium Chromate</td>
<td>53.27</td>
<td>61.896</td>
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Table 4
IMPEDANCE VALUES (KILO-OHMS) OF ANODIZED COATING ON 2219-T6 ALLOY WITH EPOXY BASED TOP COAT

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of Primer</th>
<th>Before Cu-leaching</th>
<th>After Cu-leaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zinc rich self etching</td>
<td>29.427</td>
<td>93.057</td>
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<td>2</td>
<td>Strontium Chromate</td>
<td>339.82</td>
<td>237.137</td>
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4. CONCLUSIONS

(i) The CuAl₂ precipitates were removed by applying AC anodic polarization technique resulting in an improvement in pitting corrosion resistance.

(ii) Significant increase in the corrosion resistance of all the chromate conversion coating combinations after the removal of copper rich precipitates from the surface, may be attributed to the uniform chromate coating on the alloy surface which is free from the intermetallics.

(iii) Zinc rich self etching primer has been found to be more effective than the strontium chromate in CCCs and it may be due to the self sacrificial nature of the zinc towards aluminium substrate.
(iv) There is no influence of prior copper removal treatment on the corrosion resistance of the anodized surfaces

REFERENCES


