CORROSION BEHAVIOUR OF A 2219 ALUMINIUM ALLOY TREATED WITH A CHROMATE CONVERSION COATING EXPOSED TO A 3.5 % NaCl SOLUTION.

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Abstract

This study investigates the formation of a chromate conversion coating at Al-Cu-Fe-Mn intermetallic sites of an Al2219 alloy and the corrosion initiation at these sites in a 3.5 % NaCl solution, using SEM, AES and EDX. Changes in the surface chemistry were monitored after progressive exposures to the solution up to 42 hours. The coating was found to be thinner and more defective on the intermetallic. Initially, Al is dissolved and Al(OH)₃ deposited on and around the intermetallic. After 42 hours of exposure, Al(OH)₃, Fe and Mn oxides and small particles of elemental Cu are deposited as corrosion products.

1. INTRODUCTION

Aluminium alloys are widely employed within the spacecraft industry and they provide the required mechanical and corrosion properties the choice of alloy series depending on application. More specifically the 2xxx series (high copper content) and 7xxx series (high zinc content) are used for structural components due to their high toughness and good fatigue strength. Generally these alloys offer a good corrosion resistance for most environmental exposures. However specific environmental conditions, such as long period storage in humid and salty environments, may trigger corrosion and therefore these alloys require additional protection.

Al2219 has an alloy composition of Al, with Cu 5.8-6.8 wt.%, Mn 0.2-0.4 wt.%, Fe 0.0-0.3 wt.% and trace concentrations of other elements [1]. The major second phase precipitates in these alloys are Al-Cu-Fe-Mn, with a variable composition and size from 1 to 30 µm. Such Al-Cu-Fe-Mn second phase particles are generally accepted as being cathodic with respect to the matrix [2-4]. The corrosion behaviour of Al-Cu-Fe-Mn intermetallics has been the subject of several studies on the 2024 alloys, where the Al-Cu-Fe-Mn phase and the S phase have been found. Shao et al [2] observed significant pitting at the S phase sites but no observable corrosion activity on the Al-Cu-Fe-Mn phase after 2h immersion in a 0.01 M NaCl solution. Zhu et al [3] immersed the alloy for 72 h in a 0.6 NaCl solution and reported heavy corrosion around the S phase particles, but minimal activity around the Al-Cu-Fe-Mn phase.

Numerous conversion coatings have been developed with their main purpose not only being the protection of aluminium from corrosion but also the improvement of paint adhesion [5]. One of the most widely used pre-treatments in the aerospace industry is the chromium (VI) based Alodine 1200S offered by Henkel [6]. It provides a dual function of acting as an anti-corrosive layer and improving the adhesion of paints and adhesives. Grilli et al have reported that the failure of a lap shear joint assembled from an Alodine coated substrate of 6xxx alloy and an epoxy adhesive is essentially cohesive in the adhesive phase [6]. Furthermore, Alodine 1200S is stable over a wide range of pH, and gives the substrate a low surface electrical resistance, this being an important feature for aerospace applications [7]. In the following paragraphs, a description will be given of the mechanisms involved in the deposition of chromate coatings onto pure aluminium and on various second phase particles found in Al alloys. The role of additives as accelerators and the influence of

copper from the substrate will also be described. Finally, some mechanisms of how chromate coatings protect the underlying substrate will be discussed.

Brown et al studied, in detail, the formation mechanism of chromate conversion coatings on high purity aluminium, observing a dependence of the morphology of the coating on the morphology of the substrate [8-10]. They compared the formation of the chromate conversion coating on two Al substrates with different degrees of purity: 99.99% and 99.996 % and the deposition process was described as follows [8-10]: The first step in the coating process, after the immersion of the substrate in the coating solution, is the rapid dissolution of the oxide layer by hydrogen fluoride which reduces the thickness of the passivation layer:

The anodic reaction is the dissolution of aluminium from the bulk:

and the cathodic reaction is the deposition of the coating material:

Liu et al [11] showed that the reduction of dichromate ions to hydrated chromium oxide ($\text{Cr(VI)} \rightarrow \text{Cr(III)}$) occurs on areas of reduced thickness of the film with electrons penetrating the layer by quantum mechanical tunnelling, or local conducting pathways through flaws, such as grain boundaries, impurities or metal ridges. In the early stages of the process it was observed that deposition preferentially occurred at grain boundaries and on the ridges, indicating that the cathodic reaction is more likely to occur with the exchange of electrons at flaws rather than through tunnelling. Increasing the purity of the aluminium substrate results in the surface being more uniform and homogeneous, giving rise to fewer flaw sites and the deposition then occurs mainly by tunnelling. In this case, the coating appears more uniform, without preferential deposition sites. While the coating layer is growing, the distance between the chromate ions in the solution and the alumina layer increases. The gel-like structure of the film facilitates the ionic transport of the reactant to the substrate where the Al oxidation and the Cr reduction take place. The alumina layer retains a thickness of a few nanometres during the process, being continuously dissolved by fluoride on the outer side, and re-formed by Al oxidation on the bulk side. The ageing of the coating in air will reduce any further thickening, due to the loss of water from the film [11].

With regard to the formation of chromate conversion coatings on intermetallic sites in Al alloys, Hagans et al [12] have studied coating formation on a 2024Al alloy. They observed a different deposition rate of the coating on the intermetallics and on the matrix. Juffs et al [13] fabricated macroscopic intermetallic phases and coupled them to aluminium to simulate what happens at the microscopic scale. They observed that the coating on the matrix was 10 times thicker than the coating on the intermetallic phase. Campestrini et al [14] observed that the nucleation of the coating occurs at the second phase precipitates. The intermetallics represent cathodic sites on the matrix, enhancing the rate of the reduction of the chromate species. Furthermore, Campestrini et al noted that the aluminium oxide in the proximity of the intermetallics is known to contain more flaws and defects thus is more easily attacked by the fluoride present in the bath and electron tunnelling is then promoted [14]. After a few seconds the intermetallics are completely coated, consequently they become less reactive and the reduction and deposition of chromium continues in other areas. As a consequence the layer formed is discontinuous with a large number of defects, mainly in proximity of the precipitates, with the result that it is less protective [14].

The coating grows more quickly in the first minutes of exposure of the alloy to the treatment, and after that it slows down. Accelerators can be added to the bath in order to increase the rate of deposition. A common additive to the coating solution is potassium ferricyanide, $K_3Fe(CN)_6$, which acts as an accelerator. The coating solution contains Fe in two states: $[Fe(II)(CN)_6]^{4-}$ and $[Fe(III)(CN)_6]^{3-}$. At first, the proposed mechanism was a competitive adsorption of Fe(III) or Fe(II) cyanide compared to $Cr_2O_7^{2-}$ on the surface of the Cr(III) oxide gel, directing the chromate to react with the substrate surface. More recently, a new model has been proposed. The Fe(II)/Fe(III) couple acts as a catalyst, Fe(III) is reduced to Fe(II) by Al(0), which is oxidized to Al(III), and Fe(II) is oxidized to Fe(III) by Cr(VI), which is reduced to Cr(III). In both models, the presence of the $Cr_4[Fe(CN)_6]_3$ complex is proposed [13]. The couple reacts on the intermetallics as well, suggesting the formation of $CuFe(CN)_6$ [12-13].

The presence of copper in aluminium alloys, such as the 2xxx series, influences the thickness of the conversion coating. Liu et al [15] showed that on binary Al-Cu alloys there is an initial formation of a copper-free coating, then copper starts to be incorporated in the coating and this incorporation leads to a loss of coating material. They suggest that in the early stages of coating formation, only aluminium is oxidised. This produces an enrichment of copper in the alloy underneath the oxide film. When the level of copper is high enough (about 6×10^{15} Cu atoms cm^{-2}) the copper is incorporated in the alumina film and then in the chromate coating. The coating material formed in this manner detaches close to the coating/alloy interface leading to a loss of the outer coating. On a commercial 2014-T6 alloy, Liu et al observed the formation of a thin layer on the intermetallics and a thick one on the matrix, reflecting the difference in copper contents [15]. They indicated that this confirms the influence of copper on the coating formation.

The corrosion protection offered by the chromate conversion coating is basically twofold: (1) it provides a thick and well attached barrier layer between the alloy and the electrolyte, (2) it acts as a self-healing material [16]. The self-healing mechanism can be described as follows [16]: The coating layer consists of an amorphous and insoluble chromium oxide, with many hydroxyl groups where the formation of Cr(III)-O-Cr(VI) bonds can take place; these act as adsorption sites for chromate ions from the coating bath. The coating is therefore a mix of Cr(III)/Cr(VI) oxide. Where it is in contact with the electrolyte the Cr(VI) migrates to the defects of the layer, more vulnerable to corrosion attack. Then a series of reactions with the corrosion products, or with the walls of the defect can take place, leading to repassivation. It is not clear how ageing of the coating, and the concurrent loss of water, can influence this self-healing mechanism. Hughes et al [17] suggested that in the absence of water the Cr(VI) species could be immobilized, thus become inactive to repair the damage of corrosion. Furthermore it was observed that the ageing process produces a developing network of micro-cracks which a limited Cr(VI) reservoir is unlikely to repair [17]. Lunder et al [18] conducted a SEM and TEM analysis of the section of the 6060 aluminium alloy treated with a chromate conversion coating. They observed the presence of numerous pores and cracks in the chromate layer, which may represent rapid diffusion pathways from the external environment to the aluminium substrate.

In spite of its good performance as an anti-corrosion treatment, the Cr(VI) species employed in the chromating process are well known to be environmentally unfriendly. Many possible replacement coatings are currently under investigation in an attempt to find a treatment which results in a coating with similar properties to chromate and that is safe for the environment [19, 20]. The purpose of this study is to describe the corrosion mechanisms of an aluminium alloy coated with a chromate conversion coating to provide a baseline for assessment of the new replacement coatings. We have previously reported on the corrosion on the untreated alloy, describing the reactions involved, the active sites and the mechanisms [22]. We are now reporting work conducted on the same alloy coated with an Alodine chromate layer.

It should be noted that this work is part of a wider research programme with the aim of assessing the performance of a group of Cr(VI) free coatings [21] and we have also recently published work on the composition and performance of one of these new environmentally friendly coatings: a titanium based coating deposited on the same alloy and exposed in the same corrosion environment [23].

Since the main form of corrosion for aluminium alloys is localized corrosion, the combination of high spatial resolution techniques, scanning electron microscopy (SEM), Auger electron spectroscopy (AES), scanning Auger microscopy (SAM) and energy dispersive x-ray spectroscopy (EDX), has proven to be ideal to investigate the dissolution of inclusions [24, 25]. In this study, these techniques are employed to examine formation of an Alodine 1200S coating on Al2219 at intermetallic sites and on the general matrix. The treated alloy was then immersed in a 3.5% NaCl solution for different time intervals and the same intermetallics were located and analysis repeated after each exposure. This procedure has been used previously to monitor changes in shape and composition of inclusions caused by corrosion [26-28].

2. EXPERIMENTAL

Al2219 specimens of approximately 1 cm² area were wet ground with 600 and 1200 grit silicon carbide papers, in order to clearly observe the intermetallics, then subsequently ultrasonically cleaned in acetone and rinsed in ultra-pure water. The specimens were then treated with a commercial chromate conversion coating (CCC) (Alodine 1200S, Henkel GmbH) by immersion at room temperature, according to the manufacturer directions [29]. Intermetallic sites were identified and marked using a Vickers microhardness tester, to give indentations around the intermetallic particles of interest. This allowed the intermetallic groups to be readily located for subsequent AES/EDX analysis.

A 3.5% NaCl solution was prepared from analytical grade NaCl and ultra-pure water. A specimen of Al 2219 was immersed face down in this solution for different periods of time and after each immersion it was washed in ultra-pure water. (No measures to control the dissolved oxygen level were employed). Each time the sample was removed from the water, it was dried by being placed on its side and the water drained onto blotting paper. It was then immediately introduced into the scanning Auger microscope prior to analysis, and the inclusion group of interest relocated using microhardness intents to regain the exact register required.

AES/EDX analysis was performed using a Thermo Scientific MICROLAB 350 microscope fitted with an integral EDX detector (Thermo Fisher Scientific NORAN System Six). This enabled Auger electron and EDX spectra and images to be acquired from the same regions of the sample without the need to relocate the specimen. An electron beam energy of 10 kV was used for the acquisition of Auger data and 15 kV for the EDX spectra and maps. The beam current was between 6 and 8 nA. The AES survey spectra (30 -1700 eV) were recorded using a retard ratio of 4 (1 eV channel width), whilst a retard ratio of 2.8 was used for Auger imaging. In the Auger images, topographic effects were minimised by applying the (P-B)/(P+B) algorithm (where P is the Auger peak intensity and B is the background intensity). The Thermo Advantage V3.75 datasystem was used for the acquisition and processing of the Auger data and the Noran System Six was used to record the EDX data and process them for phase analysis. Prior to Auger/EDX analysis the surface of the specimen was lightly sputtered with 1kV argon ions (for 5-10 seconds), in order to reduce the level of carbon contamination.

XPS measurements were performed using a modified VG Scientific ESCALAB Mk II, equipped with a Thermo Alpha 110 electron energy analyser and a Thermo XR3 digital X-ray source. Al K α X-rays at 340 W power were used, and the electron take off angle was set at 45°. For the high resolution spectra, a pass energy of 20 eV (channel width of 0.1 eV) was used. The unfunctionalised C1s peak, set at a binding energy of 285.0 eV (aliphatic carbon), was taken as reference to correct for any electrostatic charging.

3. RESULTS

A previous study of the corrosion behaviour of polished Al2219 (Cu-rich alloy) by Grilli et al. [22] showed the presence of Al-Cu-Fe-Mn precipitates of different dimensions, from 0.1 to 30 μm in size, with an average composition of 78 at.% Al, 16 at.% Cu, 5 at.% Fe and 1 at.% Mn, as determined by EDX. Figure 1 shows an SEM micrograph of the chromate coated surface. The intermetallic precipitates are still visible by SEM, because of the different morphology of the coating formed on the matrix and on the intermetallic group. The group appears to be formed of two precipitates, the larger precipitate on the right has a diameter of 4-5 μm and the second precipitate, lying fairly to the left, has a diameter of about 2.5 μm . While the coating on the precipitate looks compact and uniform, the coating on the matrix appeared cracked and irregular, typical of a chromate coated surface.

The four points from which AES and EDX spectra were acquired are indicated on Figure 1. The Auger spectra are presented in Figure 2. Figures 2(a) and 2(b) correspond to points 1 and 2 respectively in Figure 1 and are spectra from the two intermetallics. Both spectra show strong Cr LMM and O KLL peaks together with smaller Cu LMM and C KLL peaks. Figures 2(c) and 2(d) are from the surrounding matrix (points 3 and 4 respectively in Figure 1). Figure 2 (c) shows the Auger spectrum from the general chromate coating surface and Figure 2 (d) from one of the many cracks of the chromate coating. In both cases, the spectra are similar, with strong Cr LMM and O KLL peaks and smaller N KLL and C KLL peaks. The Cu KLL is absent. No Al KLL peak (at around 1390 eV) can be seen on the intermetallic or the matrix, indicating a chromate coating thickness greater than the AES depth of analysis (≈ 5 nm) at all points on the surface. Figure 2(e) is an expansion of the area inset in Figure 2(d), showing the peaks more clearly. Table 1 shows the chemical composition derived from EDX spectra acquired from the same four points. It is noted that copper concentration is higher in the intermetallic than in the matrix. The two points on the matrix (points 3 and 4) show different concentrations of chromium, oxygen and iron, the chromium and oxygen signals being higher for point 4, indicating a thicker chromate coating. It should be noted that traces of iron and zirconium were also detected by EDX.

Figure 3 shows high resolution XPS spectra of the Fe 2p_{3/2} and N 1s peaks, acquired from another specimen of Al2219 treated with Alodine 1200S. The Fe peak has a binding energy of 708.8 eV, which is characteristic of the ferrocyanide species ($\text{Fe}[\text{CN}]_6^{4-}$) [30]; the nitrogen binding energy is 398.3 eV, consistent with the presence of ferrocyanide on the surface [30].

Figure 4 shows the SEM micrograph (Figure 4(a)), Auger images (Figure 4(b)) and the EDX images (Figure 4(c)) from the same region of interest. The Auger images were recorded using the C KLL, O KLL, N KLL, Cr LMM, and Cu LMM peaks. The carbon is more intense on the intermetallic than on the surrounding area and on the matrix it reflects the morphology of the coating, being more intense on the general chromate coating surface than in the cracks. The nitrogen distribution is similar to carbon, with the exception that the difference in intensity between the intermetallic and the matrix is less pronounced. Oxygen and chromium have a similar distribution, being more intense on the coating than on the intermetallic, and on the matrix they both seem to be more intense in the cracks (though this may simply be due to the slightly lower carbon overlayer intensity

in the cracks). It should be taken into account that the chromium distribution is influenced by the intensity of oxygen, since the O *KLL* and Cr *LMM* peaks partially overlap. Cu can be seen to have a high intensity at the intermetallic site.

With regard to the EDX images, Cu is clearly just located at the intermetallic site. The O and Cr images are again similar to each other, showing a low intensity from the intermetallic region, but (in contrast to the Auger results) now exhibit an enhanced intensity from the chromate coating general surface compared to that in the cracks. The Al image shows a higher intensity from the cracks than from the general chromate coating surface. Hence, it is clear that the chromate coating is thinner in the cracked regions (as suggested by the SEM image).

Figure 5 shows the SEM micrographs and the Auger images for O, Cr, Cu, Al and Mn acquired after 0, 0.75, 4, 26 and 42 hours in 3.5 % NaCl solution. Data acquired after exposures of 15 minutes, 2 hours and 8 hours are not shown because they do not display significant variation from the previous exposure. Figures 6-8 show the corresponding Auger spectra from points 1 (intermetallic) and 3 (matrix) after 4, 26 and 42 hours and should be considered together with the images. After 45 minutes of exposure Cu is no longer detected, the Al and O signals are more intense around and on the intermetallic site and the Cr signal correspondingly reduced in these areas. After 4 hours, only Al and O (and C), are detected (beyond 45 minutes of exposure in the NaCl solution, Cr is no longer detected on the surface). After 26 hours, the Cu signal reappears at the intermetallic site and Mn (detected on the surface for the first time) is also observed at the intermetallic. After 42 hours, the Cu signal is more intense and has now spread onto the matrix in addition to the intermetallic. The Mn intensity is now less intense from the intermetallic. It should be noted that Fe was also observed on the intermetallic after 42 hours of exposure (see Figure 7(a)), however no image was recorded.

Figure 9 shows the Al *K α* and Cl *K α* EDX images of the intermetallic after 4 hours of exposure. Although EDX images of all the relevant elements after all exposure times were acquired, only the two which display some variation are shown. Cl was first detected by EDX after 45 minutes, but only after 4 hours was it found to assume the halo shape distribution, being concentrated at the periphery of the intermetallic, as shown in Figure 9. Comparing the Al *K α* image in Figure 9 with the Al image of the as-coated surface in Figure 4(c), it is evident that aluminium intensity distribution has been modified by the presence of Cl on the surface of the intermetallic.

Figure 10 shows EDX spectra of the treated surface (Figure 10(a)), the surface after 4 hours of exposure in the chloride solution (Figure 10(b)) and the surface after 42 hours of exposure (Figure 10(c)). The spectra have been enlarged to highlight Cr *K α* peak (5.4 keV). The intensity of this peak does not show any significant variation through the 42 hours of exposure.

In Figure 11(a), an SEM micrograph of the intermetallic group after 42 hours of exposure is shown. There is no evident difference in morphology from the image in Figure 1, but increasing the magnification in an area just below the large intermetallic where a high intensity of Cu was observed in the Cu Auger image of Figure 5, the presence of very fine particles on the surface is evident (Figure 11(b)). Figure 12(a) shows a higher magnification SEM micrograph of these particles, together with Auger spectra from one of the particles (Figure 12(b)) and from the matrix Figure 12(c). From the Auger spectra, it is clear that these are Cu rich particles being deposited onto the surface from solution.

More information regarding the phase composition of the intermetallic is given in Figure 13. A capability of the software Noran System Six is the extraction of phases from x-ray image data sets through a mathematical procedure based on principal component analysis. As a result, all image

pixels which have a similar composition are presented to highlight an area representing that specific phase composition. In Figure 13, two phases with differing Cu/Al contents were identified over the area of the intermetallic inclusion: the ratios Cu/Al calculated from weight percentages are 0.9 for the phase in Figure 13(a) and 0.7 for the phase in Figure 13(b). The highest local intensity of pixels in Figure 13(a) (in the centre of the two inclusions) can be seen to correspond to depleted areas in Fig. 14(b). The EDX spectra corresponding to the composition of each of the two phases are given and clearly show different Cu/Al intensities. Further phase images were also extracted from the data. The possibility of extracting different phase images from the inclusion shows the inclusion to have a non-uniform composition.

3. DISCUSSION

The SEM, Auger and EDX data from the CCC treated specimen show the presence of the chromate coating on both the matrix and intermetallic, but the EDX images in Figure 4, indicate a thicker coating found on the matrix. This is in agreement with the results of Juffs [13] and Campestrini [14]. The Auger electron spectra in Figure 2 (a) and (b) indicate that Cu is incorporated into the chromate layer on the intermetallic, in agreement with the results of Liu et al [15]. The Cu signal originates from the chromate layer, not from the intermetallic below, since there is no trace of aluminium, which is the main constituent of these intermetallics. Thus, the chromate layer formed on the intermetallic is both relatively thin and defective, and this could lead to ineffective protection against corrosive attack.

Carbon seems to be most intense on the intermetallic. Hydrocarbon contamination is well known to be more prevalent on higher energy surfaces and its higher concentration on the intermetallic is probably due to the incorporation of Cu into this oxide, leading to an increased metallic character of intermetallic surface oxide, compared to the pure chromate coating formed on the matrix [31]. In the surrounding area carbon is more intense on the grains than in the cracks. Nitrogen shows the same distribution; in fact the two elements are present together in the ferri/ferrocyanide ion. The presence of the ferrocyanide species was confirmed by the XPS analysis shown in Figure 3. Chromium and oxygen are also related in the $\text{Cr}_2\text{O}_3/\text{Cr}_2\text{O}_7^{2-}$ species. They are more intense in the cracks. This would probably indicate that the ferricyanide activity as a catalyst is confined to the surface of the coating layer, without being incorporated in it. The distribution of Cr and O in the outer layers of the surface is the inverse of that observed in the bulk (EDX maps of Cr and O in Figure 4c show higher concentration on the grains than in the cracks).

After immersion in a 3.5% NaCl solution for 15 minutes, the Auger results (not presented) show that Al appears on the surface of the intermetallic, and after 45 minutes, Cu is no longer detected on the surface, due to the further deposition of aluminium oxide corrosion products at longer exposure times. After 4 hours of exposure, it is evident from Figure 5 that a layer of corrosion products rich in Al and O has been deposited onto the surface on and around the intermetallic. Chloride attack (see Figure 9) is initially leading to preferential dissolution of Al from the intermetallic periphery but, as Al is the most electrochemically active and has the highest concentration of all the elements in the intermetallic, it dissolves also from the inclusion. The results of previous studies on the untreated Al 2219 alloy have shown that the intermetallics act as both cathode and anode sites on the surface, because of their inhomogeneous nature [21]. Al^{3+} ions are reacting to form insoluble $\text{Al}(\text{OH})_3$ corrosion products which are precipitating onto the surface on and around the intermetallic. After 26 hours of exposure, it is evident from Figure 10 that the chromate coating is still present on the intermetallic surface. As the intermetallic is attacked, all the elements are being dissolved into solution. Mn, Fe and Cu are all clearly observed in the Auger spectra from the intermetallic after 48 hours. The Mn and Fe are being precipitated from solution as oxide corrosion deposits. The back deposition of dissolved elemental Cu to form particles onto the surface is a

result of the reduction of Cu^{2+} to Cu, which is to be expected, considering its noble nature. Not so straightforward is the reason why it is dissolving, being a noble metal. Buchheit et al [32] studied synthesized intermetallic particles θ Al_2Cu and Al_2CuMg in NaCl solution, and proposed that after de-alloying the particles undergo nonfaradic release of mechanically and electrically isolated Cu clusters in solution. These clusters, can reach the corrosion potential, and in presence of oxygen they oxidize to Cu^{2+} . Buchheit et al [32] also observed that the formation of the copper chloride complex CuCl_2^- contributes to the dissolution of copper. Cu, being the most noble of the intermetallic elements, dissolves from the Cu rich intermetallic after dissolution of Al, Mn and Fe. Consequently, both $\text{Al}(\text{OH})_3$ and Cu are being precipitated as corrosion products from solution during corrosive attack of the intermetallic.

Our previous work on untreated Al2219 exposed in 3.5% NaCl [22] showed that the intermetallic attack occurs much more rapidly than for the Alodine coated alloy. For the untreated alloy, even after 15 minutes exposure there is the deposition of Fe oxide on the surface of the intermetallic whereas for the Alodine coated sample examined in this work, Fe oxide is only observed after 42 hours of exposure [22]. The Alodine chromate barrier layer is hence substantially improving the localised corrosion resistance of the alloy.

It is clear from these results that the large Al-Cu-Fe-Mn intermetallics in Al2219 are regions where the chromate coating is thinner and defective. Exposure to chloride containing solutions, results in preferential corrosive attack at these intermetallic sites. Initially, just $\text{Al}(\text{OH})_3$ is deposited and then all the intermetallic elements redeposit corrosion products on the surface in the form of $\text{Al}(\text{OH})_3$, Mn and Fe oxides and elemental Cu. Our previous results on the untreated Al2219 surface, showed that the major corrosive attack occurred at the intermetallic/matrix interface, hence the intermetallic was generally cathodic with respect to the matrix, but that some dissolution of the intermetallic also was occurring [22]. The corrosion of the intermetallic was considered to be due to the pH being lowered in the crevice which formed at the intermetallic/matrix interface [22]. The behaviour of the CCC treated surface presented in this paper, shows again that the intermetallic is being attacked, but in this case, the surrounding matrix is not being severely corroded, due to the presence of a barrier film covering the matrix strongly slowing down the rate of corrosion. The results presented in Figure 13 shows that the intermetallic particle is not homogeneous and that local corrosion cells will be set-up on the intermetallic surface, leading to local regions of anodic and cathodic activity. Consequently, for the uncoated sample, dissolution of the intermetallic occurs mostly as a result of the crevice attack and possibly by the local cell activity on the intermetallic surface (but to a much lesser extent). On the chromate treated specimens, the barrier film prevents severe anodic attack of the aluminium at the intermetallic/matrix boundary and the intermetallic dissolution is occurring as a result of the multi-phase nature of the particle and the local electrochemical cells which are formed at the surface. Finally, however, it should be noted that for the Alodine coated alloy, deposition of aluminium corrosion products on the matrix surface is evidence that the coating is not a total barrier and Al is being dissolved from the matrix surface, confirming the porous and cracked nature of this layer, as observed by Lunder et al [18]. Consequently, crevice attack at the intermetallic/matrix interface may occur after longer exposure times.

3. CONCLUSIONS

1. After the Alodine treatment, the chromate coating is found to be thinner and more defective (due to the incorporation of Cu into the layer) on the second phase particles.
2. On exposure to 3.5% NaCl, chloride attack of the intermetallic initially leads to Al being preferentially dissolved and $\text{Al}(\text{OH})_3$ deposited on and around the intermetallic. Later, (after up to 42 hours) in addition to $\text{Al}(\text{OH})_3$, a very thin layer of Fe and Mn oxides and elemental

Cu droplets are being deposited onto the intermetallic and surrounding areas as corrosion products.

3. The Alodine chromate coating offers a much stronger resistance to corrosive attack of the Al2219 Al-Cu-Fe-Mn intermetallic particles in 3.5% NaCl solution compared to the untreated surface.

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Figure 1: SEM micrograph of the intermetallic group after coating with Alodine 1200S. The positions of the point analysis are indicated.

Figure 2: Auger spectra of the specimen coated with Alodine 1200S; a) point 1 on the intermetallic; b) point 2 on the intermetallic; c) point 3 on the matrix; d) point 4 on the matrix; e) is an expansion of the region in the point 4 spectrum.

Figure 3: XPS high resolution spectra of Fe2p_{3/2}, N1s and C1s of Al2219 alloy coated with Alodine 1200S.

Figure 4: a) SEM micrograph, b) SAM maps and c) EDX maps of the intermetallic group after treatment with the CCC.

Figure 5: SEM micrographs and SAM images of C KLL, O KLL, N KLL, Cr LMM, Cu LMM, Al KLL, Mn LMM after coating and after different exposure times to the NaCl solution. The empty spaces correspond to no detection of the element.

Figure 6: Auger spectra from point 1 (intermetallic) and point 3 (matrix) after 4 hours in NaCl solution.

Figure 7: Auger spectrum from point 1 (intermetallic) after 26 hours of immersion in NaCl solution (left) and a magnification of the area included in the rectangle (right).

Figure 8: Auger spectra from point 1 (intermetallic) and point 3 (matrix) after 42 hours in NaCl solution

Figure 9: EDX maps of Al and Cl after 4 hours in NaCl solution.

Figure 20: x-ray spectra of point 1 on the intermetallic (see Figure 1) a) after treatment with Alodine 1200S; b) after 4 hours in the NaCl solution; c) after 42 hours in the NaCl solution.

Figure 31: a) SEM micrograph of the intermetallic group after 4 hours of exposure; b) magnification of the area in the rectangle.

Figure 42: a) SEM micrograph of an area coated in Copper; b) AES spectrum of the white sphere; c) AES spectrum of the matrix.

Figure 53: Phase analysis for the intermetallic group before immersion in a NaCl solution.