LOCALIZED CORROSION OF A 2219 ALUMINIUM ALLOY EXPOSED TO A 3.5% NaCl SOLUTION.

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Abstract

This work is focused on the role of intermetallics in pitting corrosion of Al2219 alloy. Second phase particles were characterized by AES, SAM and EDX. Their behaviour in a solution of NaCl was investigated as a function of exposure time. The results confirmed the cathodic nature of the intermetallics with respect to the aluminium matrix. Corrosion products rich in aluminium and oxygen were found to progressively accumulate around the particles and iron was dissolved from the intermetallic, followed by back-deposition. Copper and manganese did not show any major activity. After 32 hours of exposure the larger intermetallics were completely covered.

Keywords: A. Aluminium alloy, A. Intermetallics, B. AES, C. Corrosion

1. INTRODUCTION

Aluminium alloys are widely employed within the spacecraft industry due to the possibility of improving mechanical and corrosion properties based upon the requirements of each particular 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.

Aluminium alloys are more likely to undergo localized corrosion, as a result of the highly protective film which forms on the general surface and the presence of secondary phase particles, pitting corrosion is considered to be one of the principal mechanisms for damage of high strength Al alloys. Heterogeneities present at the surface of such Al alloys include precipitates and constituent particles (intermetallic particles formed by alloying and impurity elements, of 1-30 µm size). At these sites micro-flaws in the oxide film probably exist, and there are potential differences between the particles and the matrix. The micro-flaws and the galvanic couples are responsible for not only the nucleation but also the growth of pits, when the alloy is exposed to an aggressive electrolyte [1].

The general reaction for the corrosion of aluminium is:

In the 2xxx series Al alloys the two major types of precipitates are θ' (Al₂Cu) and S(Al₂CuMg). The θ' is cathodic to the alloy matrix and causes corrosion of the Al alloy at the precipitate/alloy interface [1]. The S phase precipitates are particularly susceptible to pitting corrosion [3,4]. Both Shao et al [3] and Zhu and van Oij [4] found that initially these precipitates are anodic with

respect to the matrix and rapid dealloying of Mg is observed. Later, attack occurs in the matrix at the Al alloy/precipitate interface [3,4], indicating that following this initial anodic dissolution, the change in composition results in the precipitates becoming cathodic with respect to the matrix.

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. 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 to be cathodic with respect to the matrix [3-5]. 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 [3] 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 [4] 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. One of the most widely used pre-treatments in the aerospace industry is Alodine 1200S manufactured by Henkel [6] and it is chromium (VI) based. While this conversion coating enhances the corrosion and adhesion properties of the alloy the presence of Cr(VI) makes it potentially harmful to humans and environmentally undesirable [6,7]. Recent EU restrictions on the use of chromium (VI) have established the legislative requirement to replace Alodine 1200 with a chromium-free conversion coating [8].

This work represents part of an ongoing project to discover a suitable substitute for the chromium based treatment. The behaviour of the 2219 aluminium alloy surface after progressive exposure to a 3.5% NaCl solution has been studied.

Since the main form of corrosion for aluminium alloys is localized corrosion, the combination of high spatial resolution techniques, SEM, Auger, SAM and EDX, has proven to be ideal to investigate the dissolution of inclusions [9,10]. The alloy was immersed in the NaCl solution for different time intervals and the same intermetallics were located and analysis repeated after each exposure. This procedure has been developed in order to monitor changes in shape and composition of inclusions caused by corrosion [11,12,13]. The behaviour of three Al-Cu-Fe-Mn intermetallics was followed. A subsequent paper will deal with the behaviour, following similar exposure, of the alloy treated with a number of conversion coatings including Alodine 1200 and a number of environmentally friendly alternatives.

2. EXPERIMENTAL

One specimen of Al2219 of about 1 cm^2 area was wet ground with 600, 1200, 2500 and 4000 grit silicon carbide papers, and then was polished with diamond paste to a 1 μm finish. Subsequently it was ultrasonically cleaned in acetone and rinsed in ultra pure water. Inclusion sites were identified and marked using a Vickers microhardness tester, to give indentations around the intermetallics of interest. This allowed the inclusion groups to be readily located for subsequent AES, SAM (scanning Auger microscopy) and EDX analysis. Three inclusion groups were chosen, different in size, to observe how the size influences the corrosion process.

A solution of sodium chloride (3.5%) was prepared from analytical grade NaCl and ultra-pure water. The specimen of Al 2219 was immersed in this solution for different periods of time and after each immersion it was washed in ultra-pure water. The sample was removed from the water,

placed on its side and the water drained onto blotting paper and then analyzed by means of AES, SAM and EDX.

The surface 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 locate 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, leading to a spot size of 155 nm. The AES survey spectra (30 -1700 eV) were recorded with a retard ratio of 4 (1 eV channel width), whilst a retard ratio of 2.8 was used for SAM; the topographic effects were minimised by mapping the ratio $(P-B)/(P+B)$ of each transition, 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 SAM and AES data, Noran System Six was used for EDX. Before the experiment the surface of the specimen was lightly sputtered with argon ions with a 1kV voltage for 5-10 seconds, in order to remove the carbon contamination.

3. RESULTS

Before exposure of the specimen to the 3.5% NaCl solution a visual examination of the surface by SEM, within the Auger microscope, showed the presence of particles of various sizes, from 0.1 to 30 μm . Three second phase particles, different in size, were marked, in order to monitor the development of the corrosion after exposure to NaCl solution. They were first characterized as previously described by SEM, AES, SAM and EDX, then the same set of analysis was repeated after the following immersion times in NaCl solution: 15 minutes, 45 minutes, 2 hours, 4 hours and 8 hours. After 32 hours of immersion none of the marked particles could be located, as a result of the substantial deposition of corrosion products.

Figure 1 and 2 show an example of point analysis performed, before exposure, on the first intermetallic and the surrounding region. Figure 1 is a SEM micrograph of the particle. The dimensions of this intermetallic particle are approximately 30 μm along the major axis and 20 μm on the minor axis. Several points were chosen, on and around the particle and AES and EDX spectra were recorded from them. Auger/EDX spectra from four points are shown in Figure 2. Figure 2 (a) and (b) are AES spectra representative of the matrix. They exhibit large Al *KLL* and O *KLL* peaks at kinetic energies of 1388 and 506-7 eV respectively, and less intense C *KLL* and Cu *LMM* peaks at kinetic energies of 267-8 and 918-9 eV respectively. Figure 2 (c) and (d) are the EDX surveys from the same points. They both show a high intensity Al $K\alpha$ peak and small Cu $K\alpha/L\alpha$ peaks. Figure 2 (e) and (f) are AES spectra from the intermetallic, they exhibit large Cu *LMM* peaks and low intensity O *KLL* and Al *KLL* peaks. The corresponding EDX spectra in Figure 2 (g) and (h) show a strong Al $K\alpha$ peak, the Cu $K\alpha/L\alpha$ peaks are now more intense and small peaks of Fe and Mn are also present. The average composition of the inclusions was 78 at% Al, 16 at% Cu, 5 at% Fe and 1 at% Mn.

Figure 3 shows Al, O, Cu and C Auger maps (first row) and Al, Cu, Fe and Mn EDX maps (second row) before the specimen was exposed to the corrosive medium. The EDX maps show the high intensity of Cu, Fe and Mn over the whole intermetallic, indicating the particle to be comprised of a single Al-Cu-Fe-Mn phase. In the Auger maps, Cu is also strong over the intermetallic region, though it would appear that some of the particle is buried below the surface. In general the Al and O signals are high from the matrix and low on the particle, but there are some small areas where Al and O signals are more intense on the particle. As the Al EDX intensity is low over the whole particle and the regions of higher Auger Al and O intensity on the intermetallic

tend to coincide with cracks or furrows, it is thought that this increase in the Al and O intensity may occur due to some Al becoming trapped at these sites during the polishing process.

Figure 4 shows a high resolution spectrum of Al *KLL* peak of a point on the matrix before the corrosion experiment. Two strong $KL_{23}L_{23}$ components are evident and the energies of the peaks are 1393.6 and 1386.4 eV corresponding to Al metal and Al oxide respectively.

First intermetallic group

Figure 5 shows the SEM micrographs and the SAM map sequences of aluminium, oxygen, copper and iron for the particle. Examining the images in a row, morphological and compositional variations due to corrosion progression could be monitored, each micrograph/map representing the intermetallic environment in a specific instant in time during the corrosion process. The SEM micrographs (first row) showed a progressive deposition of corrosion products with time, mainly after the first two hours, which is concentrated around the intermetallic. Considering the Auger data, the Al and O images are similar and indicate that, as expected, there is a general deposition of aluminium oxide based corrosion products as the exposure time increases. However, examination of the point analysis in Figure 6 shows that the Al/O intensity on the matrix shows no change as a function of exposure time, but on the intermetallic the Al/O intensity drops as the exposure time increases (probably due to the formation of other oxide based corrosion products in addition to $Al(OH)_3$). In contrast, the Fe, which prior to exposure exhibited a negligible intensity on the intermetallic, shows an increase in the Fe/O ratio as the exposure time increases. The initial high intensity of Cu on the intermetallic drops to much lower values after 45 minutes, but then shows a relatively constant intensity with exposure time. In Figure 5, the Cl *KLL* peak intensity (at 181 eV) was seen to be negligible after 45 minutes and 4 hours, but after 8 hours Cl intensity was observed in the SAM data. The map shows the aggregation of Cl at the intermetallic site.

Figure 7 shows SEM images again, together with the EDX maps for Al, O, Cu, Fe, Mn. The Al maps are generally unchanged as a function of exposure time, but the area of the intermetallic becomes less well-defined as corrosion products are deposited around this site. Oxygen exhibits an interesting behaviour. After 15 minutes, the O signal is most intense at the periphery of the intermetallic particle, but after 45 minutes, the intensity is more evenly distributed over the intermetallic. Then as the exposure progresses further, the O intensity tends to be associated with the larger fragments of corrosion products which deposit on the matrix close to the intermetallic. However, at the matrix/intermetallic interface where the corrosive attack is most aggressive, the O signal is reduced and the particle is highlighted by a 'narrow halo' of low intensity O. The Cu map shows very little change during the exposure, the Cu intensity remaining intense just at the site of the intermetallic. Fe, on the other hand, at longer exposure times, shows enrichment in the larger corrosion deposits on the matrix.

The Mn signal is generally weak and decreases in intensity with exposure time, but like Cu it appears to remain intense just at the intermetallic site. The Cl intensity is also weak, but unlike Mn increases in intensity with exposure time. The Cl is mostly concentrated on the intermetallic, but for long exposure times, Cl is also observed in the larger corrosion deposits. Although chlorine is clearly detectable in EDX, its peak does not appear in the Auger spectra, since $AlCl_3$ is soluble and it is removed by water when the specimen is washed.

Second intermetallic group

A second intermetallic, smaller in size than the previous, was marked and analysed. The particle is 4.4 μm wide and 18 μm long.

Figure 8 shows the SEM micrographs and the SAM map sequences of aluminium, oxygen, copper and iron for the particle. The first image of the first row corresponds to the intermetallic directly after polishing. The second micrograph corresponds to the same particle after 15 minutes of immersion in the 3.5% NaCl solution. It shows some deposits at its base which point spectra revealed as NaCl, possibly due to an ineffective washing procedure after immersion. After 45 minutes of immersion the sodium chloride deposit has disappeared but corrosion products are now appearing in the surrounding area. More substantial accumulation of deposits can be seen after 2 hours of immersion. After 4 and 8 hours the intermetallic was completely covered by corrosion products. The area could only be identified because one of the four indentation marks was still visible. After 32 hours of immersion none of the marked particles could be located, as a result of excessive corrosion.

The Auger maps show a similar behaviour for Al and O, as for the first intermetallic, with the difference that this time the precipitate is completely covered by corrosion products after 4 hours. A longer exposure (8 hours) does not make any significant difference. Copper from the intermetallic is visible up to 2 hours, but then it is no longer observable in the Auger maps. Iron appears after 15 minutes, its intensity increasing progressively on and around the intermetallic, then also after 2 hours no signal is observed.

Figure 9 shows the EDX map sequences for aluminium, oxygen, copper, iron, manganese and chlorine, plus the SEM sequence again as a reference (first row). Aluminium is detected mainly on the matrix, defining the shape of the intermetallic (lack of Al) up to 2 hours. After 4 and 8 hours three different areas of intensity are distinguished: the matrix, (the most intense), the intermetallic (less intense) and an intermediate intensity area spread around and over the intermetallic.

No oxygen was detected before immersion in the solution. After 15, 45 min. and after 2 hours the maps show progressive oxide/hydroxide deposition, at the intermetallic periphery, then around and over the intermetallic. After 4 and 8 hours the intermetallic is completely covered by the oxide/hydroxide deposits. Up to 2 hours of immersion the copper signal is very uniform, located just at the site of the intermetallic. After 4 and 8 hours the intensity distribution, although still located at the inclusion site, is fragmented. Iron is localized on the intermetallic up to 2 hours. After 4 and 8 hours iron seems to be diffused around the intermetallic and the contour of the particle is lost. Manganese is also localized on the intermetallic, but with a lower concentration, and the signal becomes weaker after 2 hours. After 2 hours of immersion Cl is detected on the intermetallic and after 4 and 8 hours the chlorine is spread around the particle.

Third intermetallic group

A third intermetallic was studied, however only commencing the observation after 15 minutes of exposure to the NaCl solution. It was decided that observing the corrosion processes at a particle of a smaller size would make a useful comparison with the behaviour of inclusion groups 1 and 2. This intermetallic had a spherical shape of about 0.8 μm diameter.

Figure 10(a) shows the SEM micrographs and the SAM map sequences of aluminium, oxygen, copper and iron for the particle. The first image set corresponds to the 15 minute exposure. In the SEM image the particle appears smooth. After 45 min exposure there is some deposition of corrosion products on the particle, which is still of the same size, But appears to be corrosively undermined. After 2 hours there is further deposition of corrosion products deposits, and the intermetallic now seems to have been removed from the surface of the specimen.

From the Auger maps it can be seen that aluminium and oxygen signals show some correlation. The Al and O maps after 15 minutes show depletion in intensity on the intermetallic but an

enrichment at its periphery. After 45 minutes and 2 hours exposure the intensity distribution appears disordered. Copper unexpectedly is hardly visible after 15 minutes of exposure. However after 45 minutes the intensity is stronger and is located on the particle. After two hours the intensity distribution is still on and around the intermetallic, but is now more diffuse. Iron is not detected before 45 minutes of exposure. After 45 minutes it appears deposited mainly around the edges of the intermetallic and after 2 hours it is similar to the Cu map, its intensity is weaker and the distribution is more diffuse. After 4 hours of exposition the area could not be located.

Figure 10(b) shows the SEM micrographs and the EDX map sequences of aluminium, oxygen, copper, iron and manganese for the particle. The distinct spherical shape of the intermetallic matches the lower intensity area of the aluminium in the maps recorded after 15 and 45 minutes. After 2 hours of exposure just a halo remains. Oxygen at first is present only on or close to the intermetallic, then after longer expositions (45 min and 2 hours) it accumulates as corrosion products over a wide area. The Cu maps show a high intensity on the inclusion up to 45 minutes exposure, then after 2 hours the elemental distribution is more diffuse around the particle. Iron and manganese can be distinguished only after 15 minutes exposure at the intermetallic site.

Figure 11 shows AES and EDX point analysis spectra of the intermetallic group after 15 minutes of exposition: 10(a) and 10(b) are AES and EDX spectra from the matrix, Al and O peaks can be seen on the surface, while Al and Cu are detected in deeper layers; 10(c) and 10(d) are AES and EDX spectra from the intermetallic, the surface is still characterized by Al and O mainly, the bulk presents higher Cu peak intensity.

4. DISCUSSION

The Al 2219 alloy surface shows the presence of many second phase intermetallics of various sizes with an inhomogeneous distribution. From the EDX spectra the intermetallic bulk contains aluminium, copper, iron and manganese. The surface is rich in copper, with the presence of some aluminium oxide. Three intermetallics were chosen to be monitored during the corrosion experiment, to study the effect of the size on the corrosion behaviour.

First intermetallic group

The SEM sequence in Figure 4 visibly shows the progressive deposition of corrosion products on, but mainly around the intermetallic.

After an exposure to the 3.5% NaCl solution for 15 minutes, the Auger/EDX maps indicate general inactivity of all elements except O. The EDX O map exhibits the deposition of corrosion products in the periphery of the second phase particle, indicating that attack is concentrated at the intermetallic/matrix interface, resulting in the dissolution of the Al alloy close to the intermetallic. Consequently, in agreement with previous work, the SEM and Auger/EDX results show that the Al-Cu-Fe-Mn intermetallic is cathodic with respect to the matrix [3-5].

After 45 minutes exposure, the SEM images, Auger/EDX maps and spectra show that corrosion products of Al and Fe are being deposited on top of the second phase particle in addition to the area surrounding the particle. Consequently, it is apparent that there is some attack of the intermetallic particle, in addition to the matrix. It is likely that this occurs mainly in the crevice formed between intermetallic and matrix, where the pH will be progressively lowered by accumulation of chloride ions. This attack of the intermetallic in addition to the matrix continues as the exposure time increases. It is interesting to note the different behaviour of the different elements involved.

Al is being deposited as an Al(OH)_3 corrosion product both on top of the intermetallic and the matrix region around the pitting attack. Fe is behaving in a similar manner with the deposition of iron oxide based corrosion products both on the matrix side of the pit (evident from the Fe EDX map) and on the intermetallic (evident from the Auger maps/spectra). For both Al and Fe, dissolution results in the release of Al^{3+} and $\text{Fe}^{2+}/\text{Fe}^{3+}$ ions. Hydrolysis of the Al chloride and Fe chloride corrosion products results in the precipitation of iron oxide/hydroxide and Al(OH)_3 as solid corrosion products around the pit mouth and on the surface of the intermetallic where the pH is raised by reduction of oxygen [14]. Cu exhibits a different behaviour. The Auger/EDX maps and spectra show that both Cu and Cl are observed on the surface of the intermetallic, but not in the corrosion deposits on the matrix side of the pit mouth. Castle has shown that when immersed in a chloride containing solution, a copper cathode can acquire a layer of insoluble cuprous chloride [15]. The negative chlorine ions are attracted initially by the cathodic intermetallic. In contact with copper they will form an insoluble salt, cuprous chloride (CuCl or Cu_2Cl_2), which will form a complex with Cl^- : CuCl_2^- . When the specimen is taken out of the corrosion medium and rinsed with ultra pure water, the mobile Cl^- or complex ions on the outer surface will be washed away, while the complex ions detected in the inner layers are trapped in the pores of the corrosion products.

Second intermetallic group

In this case also the corrosion products deposit on and around the intermetallic. But after four hours of immersion in the NaCl solution the particle is completely covered by the deposits, while the first particle was still visible after eight hours. This difference is probably due to the difference in size of the intermetallics, the smaller one being covered first. An alternative explanation could be a difference in polarity between the two intermetallics, due to a difference in composition. The aluminium and oxygen maps display the same behaviour as the first intermetallic up to two hours of exposure. After 4 and 8 hours the intermetallic is covered in Al(OH)_3 deposits, forming a porous layer over the particle. The copper does not have any activity, apart from the formation of cuprous chloride after 2 hours of exposure. The iron activity is limited to the first stages of the corrosion process, then any further oxidation involves aluminium only. The limiting factor may be the small concentration of the metal in the intermetallic. The manganese seems to be inactive in this particle as well. It appears that the insoluble cuprous chloride required more time to form, compared to the first particle. An examination of AES spectra from the two intermetallics, recorded before any immersion in the corrosion medium, showed that while copper is the main element on the surface of the first particle, on the second its peak is weaker, with Al and O showing stronger intensities. Thus, the reason for a formation of CuCl in the latest stages of the corrosion sequence may be associated with a lower Cu concentration being exposed at the intermetallic surface. After 4 and 8 hours it is evident that the chlorine distribution in the EDX maps is not related to that of copper, but instead is directly correlated with the oxygen distribution around the intermetallic. This may be explained by the fact that an intermediate state of aluminium in the corrosion reaction is the formation of a chlorine complex. While the pH on the intermetallic (cathode) increases as a result of the reduction of oxygen, in the crevice the pH decreases, because of the reaction of Al^{3+} with water. The Al^{3+} released in the crevice by the anodic reaction, plus the increasing concentration of H^+ ions, attracts the highly mobile Cl^- in solution forming the complex $[\text{AlCl}_4]^-$, which becomes trapped in the pores of the deposits around the intermetallic [2]. Comparing the sets of micrographs and maps for the long exposures (4 and 8 hours), it appears that there is no observable activity at the surface in this time interval. This may be consistent with the theory that when the pit is “sealed” by the corrosion products, there is no further exchange of reactants and the localized corrosion stops [2].

Third intermetallic group

This much smaller intermetallic showed very different behaviour mainly as a result of its reduced size. The particle was corrosively undermined after 2 hours of exposure, leaving just some Al, Cu and Fe based corrosion deposits on the surface, and a depression in the surface where the particle has been removed.

In Figure 12 a schematic diagram of the corrosion process is given. Figure 12a shows the intermetallic just after the alloy was polished a thin layer of aluminium oxide covers the alloy matrix. Figure 12b shows the reactions involved in the corrosion process once the metal is immersed in the solution. The main anodic reaction is the oxidation of aluminium. Iron oxidises also to a smaller extent. The cathodic reaction is the reduction of water in oxygen and hydroxide ions. Figure 12c shows a final state where the intermetallic is completely covered by corrosion deposits. Figure 13 is a representation focusing on the equilibriums in the crevice, which explicate how the chlorine is involved. Not mentioned in the diagram are a series of intermediate reaction products, such as mixed chloride/hydroxide compounds of aluminium.

3. CONCLUSION

1. Three intermetallic groups were identified and marked on an Al 2219 surface after polishing to 1 μm finish. They were very different in size, ranging from $\sim 25 \mu\text{m}$ to $< 1 \mu\text{m}$ in diameter. The surface was exposed to a 3.5% NaCl solution and the behaviour of the particles was observed as a function of time exposure by SEM, Auger and EDX analysis.
2. These Al-Cu-Fe-Mn second phase particles are found to act as pitting initiation sites. They are cathodic with respect to the Al alloy matrix and the pitting attack is concentrated at the Al matrix adjacent to the intermetallic.
3. Initially, after a 15 minute exposure in 3.5% NaCl, just the matrix is attacked, but after 45 minutes and up to 8 hours exposure, the intermetallic is found to also be attacked.
4. Corrosion products of $\text{Al}(\text{OH})_3$, Fe oxide/hydroxide are observed at the Al alloy matrix side of the pit mouth and on the surface of the intermetallic, resulting from the hydrolysis of Al and Fe chlorides. An insoluble cuprous chloride corrosion product deposits directly on the surface of the intermetallic.
5. After 2 hours the smaller intermetallic was corrosively undermined and removed from the surface. After 4 hours the medium size intermetallic is completely covered by corrosion products, while the largest intermetallic needed 32 hours to reach a similar condition.

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Figure 1: SEM image of a recently polished Al-Cu-Fe-Mn intermetallic second phase particle in the 2219 alloy.

Figure 2: AES/EDX point analysis from the area on and around a recently polished Al-Cu-Fe-Mn intermetallic second phase particle in the 2219 alloy.

Figure 3: AES maps of Al, O, Cu and Fe (top row); EDX maps of Al, Cu, Fe and Mn (bottom row) from the area around a recently polished Al-Cu-Fe-Mn intermetallic second phase particle in the 2219 Al alloy.

Figure 4: Auger high resolution spectrum of Al *KLL* from a point on the matrix. The two strong components at 1393.6 and 1386.4 eV correspond to Al metal and Al oxide respectively. The peaks marked as B are bulk plasmon losses.

Figure 5: SEM micrographs (first row) and SAM maps of Al, O, Cu, Fe and Cl at different times of immersion in the 3.5% NaCl solution for the first intermetallic. The scale bar at the bottom of each column is valid for the SEM and SAM images of the column.

Figure 6: Comparison of AES survey spectra recorded after 45 minutes, 4 hours and 8 hours, from a point on the intermetallic (top) and a point on the matrix (bottom) – analysis point marked by a cross on the inset SEM image.

Figure 7: SEM micrographs and EDX maps of Al, O, Cu, Fe, Mn and Cl for the first intermetallic.

Figure 8: SEM micrographs (first row) and SAM maps of Al, O, Cu, Fe and Cl at different times of immersion in the 3.5% NaCl solution for the second intermetallic.

Figure 9: SEM micrographs and EDX maps of Al, O, Cu, Fe, Mn and Cl for the second intermetallic.

Figure 10: Time resolved image sequences for the third intermetallic. (a) SEM micrographs with Auger maps of Al, O, Cu and Fe; (b) EDX maps of the same elements plus Mn.

Figure 11: AES and EDX point analysis spectra of the third intermetallic group after 15 minutes exposure to the NaCl solution: a) AES of the matrix; b) EDX of the matrix; c) AES of the intermetallic; d) EDX of the intermetallic

Figure 12: schematic diagram of a) an intermetallic after polishing, b) corrosion reactions in the NaCl solution, c) after long exposure to the solution.

Figure 13: schematic diagram of the reactions inside the pit.