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Effect of texture and Zn content on etch morphology of the aluminium alloy EN-AW 6063

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Preface

This project in cooperation with Hydro, SINTEF and NTNU has been carried out at the Department of Materials and Engineering, Norwegian University of Technology and Engineering (NTNU) and SINTEF Oslo in the period from August to December 2008.

The supervisors of this project have been Professor Kemal Nisancioglu¹, Dr. Øystein Bauger² and Otto Lunder³. I am grateful for their interest in this project, and I would like to thank them for their guidance and help.

I would like to give a special thank to Børge Holme³ for the help with White Light Interforometry and Secondary Ion Mass Spectrometry measurements, but at the most I would like to thank him for inspiration and long discussions.

Engineer Kjell Røkke¹ deserves thanks for helping me getting started in the laboratory. Morten Karlsen¹ for helping me with access to the SEM-lab.

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1:NTNU, 2:Hydro Sunndal, 3:SINTEF

Summary

In the industry a surface defect is observed on extruded aluminium alloys called grainy appearance. Earlier investigations have shown that Zn plays a major role contributing to this defect, which is a result of preferential etching of grains. So far the mechanism for this surface defect is still not known. In this project the effect of Zn in the aluminium alloy EN-AW 6063-T6 is investigated.

Correct processing parameters (time, temperature, extrusion speed etc.) in the fabrication of extruded aluminium profiles are important for the surface appearance. The surface defect is a result from etching in alkaline solution, where the surface is treated to obtain uniform even finish and to avoid filiform corrosion. Alluminium alloys have in general very good corrosion resistances due to formation of aluminium oxide.

The influence of texture and Zn on etch morphology (etching in NaOH) is studied with Electron BackScatter Diffraction (EBSD), White Light Interferometry (WLI) and Secondary Ion Mass Spectrometry (SIMS). These techniques give information of crystallographic orientation, topography and chemical composition on the surface respectively.

From crystallographic orientation and topography measurements it is observed higher dissolution rate of grains with {111} orientation compared to {100} and {110} oriented grains. Enrichment of Zn and Cu is found on {111} oriented grains when chemical composition is compared with topography and crystallographic orientations. The preferential etching could be due to potential distinction between grains with different orientation. Selective dissolution of aluminium could be the cause of enrichment.

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1 Introduction

Aluminium is today the worlds second most commonly used metal.^[1] In nature aluminium is occurring as bauxite. The first commercial process for producing aluminium began with Henry Deville in 1854^[2], since then there has been a huge revolution in processing of aluminium and its alloys. Even though the technology is much better today there are still many challenges in the industry; Emission control, waste disposal and energy efficiency are a few. Aluminium recycling began in the early 1900s and the production has today a capital cost 80-85% less than the primary production from bauxite. Recycling of aluminium result in a higher amount of trace elements, and one problem is surface defects after extrusion and anodising.

Spangling effect is an often observed surface defect after the anodising step in the production line. It is proposed divided into three categories; grainy, galvanizing and -sparkling appearance. Grainy appearance is described as grains visible with the eye on the surface after alkaline etching. Whereas galvanizing effect is a surface with a few shiny grains and sparkling appearance is a general shiny surface^[3]. Investigations have shown the phenomenon of grainy appearance is dependent on the chemical composition of the material. During alkaline etching it is observed enrichment of zinc and cupper for Al-Zn and Al-Cu alloy respectively^[4]. Copper and zinc together with a certain grain size, texture and free Zn in the etching bath is believed to increase the susceptibility of grainy appearance^[5].

This investigation is based on previous master thesis performed by Nina Ljones^[3], Siv Malm Nortømme^[6] and David Franke^[7] in cooperation with Hydro. In general it was observed Zn promotes preferential etching of grains. Nina Ljones found by adding Zn to the etching bath resulted in increase of grainy appearance. Siv Malm Nortømme investigated alloys with different amount of Zn and observed higher amount of Zn resulted in higher susceptibility of grainy appearance. The preferential etching of the surface was investigated by White Light Interferometry (WLI) and Electron BackScatter Diffraction (EBSD). Nina Ljones found that {111} oriented grains were etched more compared to other grain orientations, however Siv Malm Nordtømme could not verify this due to lack of {111} oriented grains.

1.1 Aim of project

It is known from industry (and N. Ljones master thesis) that Zn in the etching bath can have detrimental effect on the surface appearance. In this project it is desirable to investigate the effect of Zn in the material. The texture and enrichment of Zn on the surface after etching in alkaline solution will be studied on the aluminium alloy EN-AW 6063-T6. Based on earlier investigations, measurements will be performed trying to verify the preferential etching of {111} orientated grains. This will be investigated by using Electron BackScatter Diffraction (EBSD) and White Light Interferometry (WLI) to measure grain orientations and topography respectively. In addition chemical composition of the surface after etching will be emphasised by using Secondary Ion Mass Spectrometry (SIMS) which is a very surface sensitive technique. Understanding the mechanism of how Zn effect the etching morphology is a superior goal.

2 Background

2.1 Production of extruded aluminium profiles

Every step in the production of a finished product influences the final surface appearance. It is therefore important to control the time and temperature profiles in every step in the production line; the temperature sequence for the production line for EN-AW 6063 is shown in Figure 2.1. There are two main routes for producing aluminium; primary from mainly bauxite and secondary from recycled aluminium. Secondary melted aluminium is often added to the primary melt and requires far less energy to produce aluminium than primary aluminium. Here only the primary production path will be considered for extruded profiles due to the EN-AW 6063 extruded profile.



Figure 2.1: Temperature sequence during the production line of aluminium^[8]

2.1.1 Extrusion of aluminium profiles

Bauxite is the starting point and through the Bayer process alumina is produced. Alumina is reduced electrochemical according the Hall-Héroult process to molten aluminium. Then the aluminium is either cast as ingots or extrusion billets at a temperature of approximately 700°C. Ingots are remelted and used for casting whereas the extrusion billets are used for further extrusion processing.

After casting the profiles are homogenised at 580 °C for a few hours. This step is necessary at first to remove solute concentration gradients which are appearing after the supercooling from the casting step. Secondary to reintroduce the crystals and intermetallics formed or precipitated at the grain boundaries into the solid solution.^[2]

In the extrusion process the billets are reheated to 460-500 °C and are forced by hydraulic pressure through an orifice in a die. Extruded profiles are usually rods, foils, bars or hollow sections. The first part of the extruded profile, few mm, has the same structure as the casted material, but during the extrusion the grains are distorted and the constituents aligned in the extrusion direction. Grains are affected by temperature and strain and are therefore hot worked and recrystallized. The temperature should be high enough to allow for micro-recrystallisazation but low enough to avoid eutectic melting. To obtain a good surface finish a high extrusion speed is favourable, but is often limited due to formation of transverse cracks from the die. ^[2]

After extrusion the profiles are artificially aged by heating up to 185 °C for 5 hours. This process strengthens and hardens the material, where the EN-AW 6063 alloy precipitates from a supersaturated solid solution to Mg₂Si having a face centred cubic structure.^[10]

2.1.2 Anodising; Surface treatment and finishing

For different applications of aluminium the right surface treatment is applied to give the wanted surface appearance and serviceability to the final product.

Prior to etching the extruded aluminium profiles are degreased, where oil, grease and other unwanted impurities are removed. This is executed to obtain high degree of uniformity prior to etching. Etching is performed in caustic soda, and additives may be added to the bath depending on the wanted effect (matt, rough surface etc.). The purpose of etching is to remove the natural formed oxide which can contain defects. Aluminium is dissolved according to reactions given in equation 1, exothermic rx, with the formation of hydrogen and alumina.

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

$$2Al + 2OH^- + 6H_2O \rightarrow 2(Al(OH)_4)^- + 3H_2$$
(1)

In long time etchants there will be a build up of impurities in the bath. Only a few p.p.m. of zinc in the solution will give rise to the surface defect galvanizing appearance, see Figure 2.2. This is a preferential grain etching effect, which is prevented by addition of sulphides or chromates.^[11]



Figure 2.2: Galvanizing appearance on etched 6063 extrusion^[11].

During the etching procedure a smut layer (gray-black film) is formed on the surface. It contains elements as silicon, iron, cupper and other alloying elements. This is removed in a nitric acid solution^[12].

In the anodising step the oxide layer on the surface is thickened, up to 20 μ m, by an electrolytic process to improve the corrosion resistance and obtain nice visual surface. Aluminium is used as the anode and lead is usually used as cathode. When current is flowing oxygen reacts with aluminium to produce porous aluminium oxide. The pores have to be sealed to obtain a high quality of the surface; this is performed in hot water (98°C).

2.2 Aluminium alloy EN-AW 6063

The aluminium alloy EN-AW 6063 is one of the most frequently used extruded aluminium alloy. It is used in automotive industry, medium strength purposes in building industry, architectural purposes with good surface finishing and heat transfer applications. The larger variety of applications is due to the good corrosion resistance, surface finish and a superior response to the anodizing step. A low content of magnesium in the alloy gives a good formability but with the expense of mechanical properties, whereas high level of magnesium gives good mechanical properties. Corrosion of aluminium alloy is affected by the alloying elements. Copper is the element with the most negative effect on corrosion resistance, whereas Mn has the lowest effect. Silicon can play a slight role, and together with iron this effect is coming more pronounced^[11]. The chemical composition of the alloy is given in Table 2.1. ^[13] Aluminium has a face centred cubic crystal (FCC) structure,

Figure 2.3.

	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
EN-AW 6063	0.2-0.6	0-0.35	0-0.1	0-0.1	0.45-0.90	0-0.1	0-0.1	0-0.10

Table 2.1: Chemical composition in wt% of EN-AW $6063^{[13]}$.



Figure 2.3: The three different crystallographic planes in FCC structure^[3]*.*

2.3 Corrosion of Aluminium

Aluminium and aluminium alloys have high resistance towards corrosion due to formation of protective aluminium oxide film in the presence of water, see equation 2. The oxide is one of the most stable oxides found in nature. Oxidation of aluminium leads to the reduction of oxygen or production of hydrogen. The oxide is amphoteric; not stable in neither acidic nor alkaline environments. However in neutral, slight acidic or alkaline environments the aluminium has a slight corrosion resistance.

$$2Al^{3+} + 3H_2O \rightarrow Al_2O_3 + 6H^+ \tag{2}$$

The corrosion potential of Al is dependent upon activity of chlorine ions, temperature and alloying elements. If the alloying element is nobler than aluminium the result is selective dissolution of the more active aluminium, leaving behind an enriched noble layer. This enriched layer will behave according to its electrochemical properties^[14].

2.3.1 Galvanic corrosion

If aluminium is in contact with a more noble metal the susceptibility towards galvanic corrosion is large, resulting in breakdown of the passive film. Many types of corrosion of aluminium can be related to galvanic corrosion, either on macroscopic or microscopic level.

Electrical resistance of metal path, conductivity of the electrolyte, cathode/anode ratio and polarisation of the cathode are factors affecting galvanic corrosion^[14].

2.3.2 Filiform corrosion

Attack of the surface beneath coatings is called filiform corrosion^[11]. The surface suffers only a small damage, but the surface appearance is detrimental altered. The susceptibility of filiform corrosion is increased with surface shear during rolling, grinding or machining developing an ultra-fine grained surface structure^[15]. Filiform corrosion can be avoided by etching and anodizing, removing this surface layer^[16].

2.3.3 Pitting corrosion

Pitting corrosion in salt water occurs at weak spots in the oxide film around intermetallic particles and at grain boundaries^[17]. It is dependent on the properties, size and distribution of these intermetallics in the aluminium matrix. They are electrochemical nobler than the Al matrix and act as the cathode. The pH decreases in the pit whereas it increases around the cathodic site leading to etching of Al adjacent to the cathodic site. With the selective dissolution of Al, due to microgalvanic effect, the nobler intermetallics are enriched at the surface. The pits surface will however repassivate due to the detachment of intermetallic particles^{[16],[18]}.

2.4 Electron BackScatter Diffraction (EBSD)

Electron BackScatter Diffraction (EBSD) together with Scanning Electron Microscope (SEM) is used to identify crystallographic orientation in the material. The technique can also be used to identify different phases, dislocations and grain boundaries. It uses a phosphor screen detector which is placed at an angle with respect to the sample, Figure 2.4. The tilt angle is 70° , giving a good spatial resolution.



Figure 2.4: Electron BackScatter Diffraction principe^[19, 20].

The incident beam must hit the surface at small angel ($\sim 20^{\circ}$) for the possibility of collecting the emitted electrons by the detector and the signal is converted to visual picture with CCD camera. The diffracted electrons are detected as Kikuchi patterns where each line in the pattern is formed according to Bragg's law of diffraction. The specific orientation of these lines corresponds to the crystal structure of the sample and can be mathematically competed to a crystallographic map by scanning the area of interest. Each point on the area of interest corresponds to crystal structure with a specific orientation.^[20]

2.5 White Light Interferometry (WLI)

With the use of White Light Interferometry (WLI) microscope the topography of the surface is determined. A schematically illustration of WLI instrument is shown in Figure 2.5. The technique uses a coherent light source (S1) and the beamsplitter (B1) divides the beam. One beam hits the reference mirror (M1) and is reflected whereas the other is reflected by the object of investigation (O). The beams are recombined at the imaging lens (L3) and the difference in optical path way is recorded by a CCD camera.^[20, 21]



Figure 2.5: Schematic illustration of WLI^[21].

2.6 Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry (SIMS) is a surface analytical technique that can detect low concentrations of impurities and alloying elements. The instrument is build up of a primary ion column, secondary ion extraction system, mass spectrometer and detection system, Figure 2.6. The technique uses a primary ion gun, which can be focused to less than 1 µm in diameter, to bombard the surface in ultra high vacuum. The ion gun can either be oxygen or caesium source. Secondary ions together with atoms and molecules are emitted having variations in energy. Di and triatomic secondary ions have a lower kinetic energy than monovalent atoms. The secondary ions are extracted and analysed in the mass spectrometer. They are separated according to the mass/charge ratio in the magnetic field and are further detected and analysed by phosphorous screen or CCD camera. This gives detailed information on the chemical composition on the surface. Depending on the wanted analysis two different techniques can be used; static or dynamic SIMS. In static SIMS slow sputter rate is used resulting in the removal of only a tenth of an atomic layer. This is used when molecular species is identified. In the dynamic SIMS higher sputter rate is used with the result of a more damaged surface. With this technique quantitative information is obtained, and is the case when depth profiling is performed. The depth profiles are the result of counting the secondary ions of interest as function of sputter time. Instead of depth profiles ion images can be recorded, showing the intensity of secondary ions on the sample surface. The detection limit of the instrument is between 10^{12} and 10^{16} atoms/cm² and is dependent on the performance of the vacuum system.^[22]



Figure 2.6: Schematic illustration of Secondary Ion Mass Spectrometry^[23].

2.7 Previous work

This investigation is based on previous master thesis by Nina Ljones (2006)^[3], David Franke (2008)^[7] and Siv Malm Nordtømm (2008)^[6]. Here are the important results given.

2.7.1 Effect of Zn in the etching bath

From the industry it was belived that Zn had a tremendous effect on the surface defect grainy appearance. The influence of dissolved Zn in the etching bath was therefore investigated by weight loss measurements. Nina Ljones observed that a high amount of dissolved Zn in the etching bath resulted in decrease in weight losses of the samples together with a more preferential etched surface. This indicating some layer of Zn was blocking the further etching of the surface. This was also indicated by the decrease in corrosion potential when etching in solution containing dissolved Zn. The decrease in the potential was found to be 50 mV. From Glow Discharge Optical Spectrometry (GD-OES) analysis, showing weight percent of Al, Si,

Mg, Zn and O as function of sputter depth, it was observed that etched samples in the solution with dissolved Zn had higher amount of Zn on the surface compared with etching in a solution not containing dissolved Zn.

Nina Ljones also observed a more grainy surface appearance was dependent on amount of Zn in the etching bath. Higher amount of Zn lead to higher degree of grainy appearance. Additives from the anodising plant at Hydro Karmøy (HAP-K) added to the etching bath with dissolved Zn resulted in no grainy appearance defect. This indicates that Zn reacts with the additives

2.7.2 Effect of Zn in the alloy

Siv Malm Nortømme investigated the effect of Zn content (0.028, 0.11, 0.22 wt%) in a aluminium alloy. Na₂S (0.0025 g/L) was added to the etching bath to investigate if Zn was deposited from the solution or selectively dissolved from the alloy, however no effect was observed. Siv Malm Nordtømme discussed this was due to low concentration of Na₂S. The effect should be visible by precipitation of white ZnS if Zn was present in the solution. Higher degree of grainy appearance was observed for longer etching time for both alloys containing 0.11 and 0.22 wt% Zn. Indicating that Zn favours grainy appearance. From weight loss experiments Siv Malm Nortømme observed the alloy with lowest amount of Zn in the alloy showed the highest weight loss compared to higher amount of Zn showing less weight loss. The high weight losses she discussed from chance in corrosion mechanism going from pitting attack to galvanic corrosion resulting in preferential etching of grains.

David Franke investigated two samples; one with low amount of Zn and Cu (0.00052, 0.00103 wt%) and the other high amount of Zn and Cu (0.04448, 0.03224wt%). They were etched and aged (oil bath at 185°C). He found the alloy containing high amount of Zn was attacked more locally, grain boundaries and certain grains, compared with the alloy with low amount of Zn giving more uniformly attack on the surface. There was also a correlation between the ageing of materials and etching response. Longer aging time up to a certain time resulted in higher etching response on the grain boundaries. He also performed weight loss measurements and found the alloy containing low amount of Zn had higher weight loss.

2.7.3 Preferential etching

The effect of texture on etching response was analyzed by topography measurements and crystallographic mapping by WLI and EBSD respectively. Nina Ljones observed {111} oriented grains were etched more than {100} orientated grains. She proposed a mechanism concerning this result from the packing density of the different grains; {100} oriented grains have lower packing factor and it is energetically favourable for precipitation of Zn on this orientation. From this she discussed that due to the microgalvanic effect between Al and Zn it was expected preferential etching of {111} oriented grains. However the preferential precipitation was not verified.

No correlation between preferential etched grains and orientation was found by Siv Malm Nortømme because lack of {111} oriented grains on the surface.

3 Experimental procedure

The sample in investigation is an experimental alloy based on EN-AW 6063-T6, with a high content of Zn (0.8 wt%). It was provided by Otto Lunder (SINTEF) and was produced at Hydro Sunndal. The performed experimental sequence was polishing, WLI, etching, WLI, SIMS, WLI, electropolishing and EBSD mapping. This showed to give good results. The experiment was only performed on one sample because of only one sample holder in the SIMS, however several sample points were investigated. WLI, SIMS and EBSD were performed at the same location on the sample.

3.1 Peripheral preprocessing

The received samples were cut in small pieces $(2x2 \text{ cm}^2)$ for use in the investigation.

All the samples were first grinded with grit paper from 800 to 4000 and then polished by using diamond paste $3 \mu m$ and $1 \mu m$.

On the final polished sample a scratch was made on the surface, making sure the same area was investigated for later comparison.

3.2 Etching trials

The etching was performed by dipping the sample in 10 wt% NaOH solution (100 mL). The temperature of the etching bath was constant at 60 ± 1 °C and the etching time was 30 seconds.

3.3 Electron BackScatter Diffraction (EBSD)

The EBSD surface analysis was performed with Hitachi S-4300SE. The parameters used in the investigation are presented in Table 3.1.

Electropolishing was performed to obtain good picture in EBSD.

Tuble 5.1. Operating parameters in LDSL	<i>Table 3.1:</i>	<i>Operating</i>	parameters	in	EBSD
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Tilt [°]	70
Working distance [mm]	20
Acceleration voltage [kV]	20
Step size [µm]	5

3.4 White Light Interferometry (WLI)

Topography of the sample was measured after etching and after investigation with SIMS. Height of grains after etching and the sputter depth from SIMS was measured with the software Vision 32. The topography analysis was performed at SINTEF Oslo with WYKO NT-2000 from Veeco Instruments.

3.5 Secondary Ion Mass Spectrometry (SIMS)

Elemental mapping of Cu and Zn and depth profiles on certain grains were obtained by using an oxygen ion source by the dynamic SIMS model CAMECA ims7f, University of Oslo. To find the right isotopes of the elements important for this investigation a mass spectre was performed. It was found the isotopes 1H, 63Cu, 66Zn and 27Al₃ did not overlap with any other possible peaks, so these were used further in the investigation. The depth profiles were performed by finding the wanted grains by the light microscope incorporated in the SIMS and using a raster size of 80x80 nm. Normal sputter time was 250 seconds. The raw data obtained gives the relation between intensity [counts pr seconds] and sputter time. By calculations the sputter time can be given by the sputtering depth. For calculations see appendix A. In the elemental mapping of Cu and Zn the sample was sputtered until a depth of 140 nm was obtained and then the pictures was taken based on the intensities of Cu, Zn and Al.

4 Results

4.1 Grain height distribution and SEM

Topography measurements were performed after grinding down to 4000, polishing down to 1 μ m and after etching. The height distribution is shown in a histogram, see Figure 4.1. What can be observed is that after polishing down to 1 μ m the grains are normal distributed within a region of ±112 nm. This is much better than only grinding to 4000 or polishing down to 3 μ m. After etching the grain height is no longer normal distributed because of the lack of symmetry, and the height varies between ± 1000 nm. Figure 4.2 shows a picture taken in SEM after etching. It can be observed preferential etching of some grains, small pits and particles on the surface.



Figure 4.1: Histogram showing height distribution of grains from WLI measurement. Black curve: grinding to 4000, red curve: polishing to 3 um, blue curve: polishing down to 1 um, green curve: after etching in 10wt% NaOH.



Figure 4.2: SEM picture after etching in 10 wt% NaOH at 60°C for 30 s.

4.2 Topography and grain orientation

The topography picture shown in

Figure 4.3 gives the relative height of grains after etching. Dark blue grains are low grains whereas red grains are high grains. Low grains are etched more than higher grains. In

Figure 4.4 is the crystallographic orientation taken from the same area as the topography map. The inverse pole figure indicates grains with {111} orientation are blue, {100} oriented grains are red and {101} oriented grains are green. By comparing these two figures (notice that these pictures are tilted compared to each other, and some grains in the EBSD map is etched to the same height) the low grains from the topography map is recognized as {111} oriented grains. The indexing of the same grains gives this relation.



Figure 4.3: Topography map showing grain height after etching (WLI)



Color Coded Map Type: Inverse Pole Figure [001]

Aluminum



Figure 4.4: EBSD-SEM picture showing crystallographic orientation of grains.

4.3 Depth profiles from Secondary Ion Mass Spectrometry (SIMS)

Figure 4.5 shows the same topography area as Figure 4.3. The difference is the dark blue squares located within specific grains, indicating the location of the depth profiles. The crater K (Figure 4.5) was sputtered at longer time (818 seconds) compared to the normal sputtering time (250 seconds). This was performed as to find the relation between sputter times and sputter depths (Appendix A). From each depth profile the intensity of the elements is found as a function of sputter time (sputter depth), this is shown in Figure 4.6 for crater (a). The intensities are all relative to the bulk aluminium signal (calculations in Appendix A). The intensity of H, Zn and Cu decreases with sputter depth, whereas the intensity of Al is increasing with sputter depth.



Figure 4.5: Topography map with depth profiles (WLI)



Figure 4.6: Typical SIMS depth profile graph showing the relative intensities of the elements H, Cu, Zn and Al as function of sputter depth.

In Figure 4.7 and Figure 4.8 the intensities of Zn and Cu are plotted as a function of the sputter depth. The different graphs are related to one certain depth profile within a grain. Only a selection of the comparison of heights is shown (all depth profiles are given in Appendix B). The grain height of the grains was measured from the topography map taken before the SIMS depth profiles were performed. Low grains show a higher intensity of both Zn and Cu than higher grains. This trend is observed at a sputter depth from approximately 100 nm to 175 nm. The relation between the intensity of Zn and Cu is plotted as function of grain height. This relation is shown in Figure 4.9 for Zn and Figure 4.10 for Cu at certain sputter depths (94, 122 and 152 nm). The correlation between Zn and Cu on the surface as function of the grain height is rather poor. However it can be observed better correlation at sputter depth of 152 nm than at 93 nm, this is given by the linear deviation value R. Ideally this should be close to one, indicating good correlation.



Figure 4.7: Comparison of the relative intensities of Zn with sputter depth (sputter time) from depth profiles.



Figure 4.8: Comparison of the relative intensities of Cu with sputter depth (sputter time) from depth profiles.



Figure 4.9: Correlation between Zn on the surface and height of grains after etching.



Figure 4.10: Correlation between Cu on the surface and height of grains after etching

4.4 Elemental mapping from Secondary Ion Mass Spectrometry (SIMS)

From the elemental mapping in SIMS the images b), c) and d) in *Figure 4.11* were obtained. Image a) is the topography map of the same area and the grains are indexed for easier comparison. High intensities of Al, Zn and Cu is represented with brighter colour, and is an indication of amount of the respective elements found on the surface. The grains G7 and G2 are low grains and have {111} orientation. These grains are easy to recognize in image b), with dark brightness indicating lower intensity of Al (EBSD map in Appendix C for the same are of investigation). The same grains have a high brightness in the Zn and Cu image and it can therefore be said these grains contains higher amount of Zn and Cu.



Figure 4.11: Elemental mapping from SIMS; a) Topography map b) Al map c) Zn map d) Cu map. Brighter colour represents higher intensities of the respective elements.

The intensities at certain grains were measured by using the same technique as for finding the height of grains from the topography maps. As a result the relation between amount of Zn and Cu on the surface can be related to the height of the grains, shown in *Figure 4.12*. Low grains have a higher amount of both Cu and Zn.



Figure 4.12: Correlation between amount of Cu and Zn and grain height.

5 Discussion

5.1 Discussion of the measuring techniques

In the beginning of this project a different experimental sequence was used; First polishing, electropolishing, EBSD, etching in NaOH, electropolishing, EBSD, WLI and SIMS. Based on this sequence it was observed an even surface origin from the electropolishing step. Hence it was difficult to indentify the grains found in the EBSD map with the topography map (WLI). This also resulted in difficulties in the SIMS measurements due to the lack of finding specific grains with wanted height. The experimental sequence was therefore changed (see chapter 3)

In Figure 4.6 the intensity of H, Zn and Cu decreases whereas the intensity of the Al signal is increasing with sputter depth. The H signal is used as an indication of where the oxide layer is ending and the beam starts to measure on the aluminium surface. In earlier investigations, performed at SINTEF by Børge Holme, of sputter depths on aluminium the intersection of the H signal and the Cu signal was used as the reference of the oxide/alloy interface. This gave quite good relation between intensity of Zn and grain height, however it was observed better correlation at longer sputtering times. Based on this it was decided to use the intersection of the H and Zn signal which is lower in depth (longer sputter time) than the intersection between H and Cu signal. The thickness of the oxide layer together with the smut layer (resulting from etching) is approximately 140 nm. Since the amount of Zn is 0,8 wt% compared to the low content of Cu it is not surprising that the intensity of Zn is higher than the intensity of Cu.

The different result obtained from the depth profiles and elemental mapping can be accounted for by comparing the two measuring techniques. Figure 4.9, Figure 4.10 (depth profiles) and *Figure 4.12* (elemental mapping) show the correlation between amount of Zn and Cu on the surface as function of grain height.. There is much better correlation for the elemental mapping compared with the result from the depth profiles. The reason for this is the difficulty measuring depth profiles and at the same time avoiding the particles observed on the surface (Figure 4.2). The small particles were not recognisable in the microscope in the SIMS. When

the intensity at the grains is measured from the elemental maps these particles are easily avoided resulting in a much better correlation. It would therefore be preferential with cleaning after the etching step to remove these particles. The intensities of Cu and Zn from the elemental mapping are not comparable due to the different intensity scale bars.

5.2 Preferential etching of crystallographic orientation

From the topography measurements (WLI) and crystallographic mapping (EBSD) it was found correlation between etching height and grain orientation. Grains with {111} orientation was etched more than grains with {110} and {100} orientation. E.V Koroleva et.al^[24] found higher dissolution rate of {334} (close to {111}, only 7° tilt) oriented grains of high pure Al in alkaline solution compared to {119} (close to {001}) oriented grains. They observed slight increase in open circuit potential with decreasing dissolution rate of the grains, indicating difference in anodic potential. This difference in potential of grains in the aluminium alloy could therefore promote anodic dissolution of the {111} grains. They proposed that this was due to the microgalvanic effect, although it was the same material. S. Lee and H. White^[25] also found higher dissolution rate of {111} oriented grains in acidic solution when investigating oxide film dissolution on Al.

The preferential etching of {111} oriented grains are in consistence with previous observation done by Nina Ljones.

5.3 Deposition of Zn and Cu

On the {111} oriented grains enrichment of both Zn and Cu was found in exes compared with other grains. From the literature ^{[26],[27]} investigations have observed enrichment of Cu at the alloy/oxide interface. Y. Liu and F. Colin et. al ^[26] suggested that an enrichment of Cu after etching is due to dissolution of the alloy through an amorphous alumina based film. At the alloy/oxide interface the metal atoms are oxidised and migrate through the film into the alkaline solution. In the alloy Cu is in solid solution and can therefore not be oxidised initially due to the higher Gibbs free energy per equivalent for formation of Cu oxide compared to formation of alumina. This lead to an increased Cu concentration in a surface thickness 1-5

nm in the alloy under the alumina based film^[28]. The Gibbs free energy of formation of Zn oxide is higher than for alumina, so this theory can also be related to the deposition of Zn on the surface.

Corrosion study performed by I. Milosev and A. Minovicon^[29] on Cu-Zn alloy in alkaline solution showed simultaneously dissolution of Cu and Zn at open circuit potential. With increasing immersion time preferential dissolution of Zn was observed. From the SIMS elemental mapping results it was observed that Cu and Zn follow each other; which could be due to the simultaneously dissolution. From the study of I. Milosev and A. Minovicon they also found that the preferential dissolution of Zn decreases as the electrode potential becomes more positive. The preferential enrichment of Zn on {111} oriented grains, which from above study indicates to have lower open circuit potential, could therefore have a higher preferential dissolution of Zn. From the depth profiles measurements the intensity of Zn is higher than Cu at the specific grains.

Nina Ljones proposed an enrichment of Zn on the {100} oriented grains leading to microgalvanic effect and hence higher dissolution rate of {111} oriented grains. In this investigation Nina Ljones proposed mechanism is rejected by the observation of Zn enrichment on {111} oriented grains.

Cu and Zn are both nobler than aluminium and in alkaline solution there will be a selective dissolution of Al. The higher dissolution rate of {111} oriented grains, due to potential difference between grain orientation, could leave behind thicker layer of the nobler elements. Therefore an enrichment of these grains relative to the other grains can be observed and is due to the lower dissolution rates of these grains. This proposed mechanism assumes selective corrosion is the cause and not dissolved Zn in the etching bath.

6 Conclusion and outlook

In topography and crystallographic orientation measurements it is observed preferential etching of {111} oriented grains.

From elemental mapping of Zn and Cu higher intensities of both elements are found on {111} oriented grains.

The mechanism for preferential etching and enrichment of Cu and Zn on these grains needs to be further investigated. The open circuit potential of the different orientation should be investigated to confirm the difference in anodic potentials. It would be interesting to add Zn in the etching bath and thus observe if more Zn is found on the surface using depth profiling. Adding Na₂S to the etching bath would help to observe if Zn is deposited from the solution or diffuses from the solution.

The investigation techniques used for determining the effect of Zn in the material gave good results. SIMS elemental mapping was better to use in this case than depth profiling due to the observed smut particles on the surface. For future investigations it would therefore be advantageous to clean the surface after alkaline etching.

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Appendix A

Time and intensity (I) are the output raw data files from the SIMS. Calculating the depth from the time is obtained by finding the relation between sputter depth and sputter time. The sputter depth is found by topography measurements of the craters (from SIMS depth profiling). This relation gives a polynomial equation, where y is the depth and x is the time, and the depth at all times can be calculated.

$$y = 0.00106x^2 + 1,40027x$$



Figure A.1: Relation between sputter depth and time

The intensities of Cu, H and Zn is corrected due to the aluminium bulk intensity signal. First is the Al signal corrected for a small change in the ion beam intensity during the scan. This is done for every crater.

Prim beam intensity @t=0 (nA)	102,2
Prim beam intensity @t=end (nA)	102,5

$$I_{corrected} = 112608 \frac{(102, 5 + (105, 2 - 102, 2)(\frac{y}{412}))}{102, 5}$$
(A2)

Table A.1: Calculated depth and the corrected Al bulk signal.

	Corrected		
	27AI3	Al signal	
Time[s]	Depth[nm]	l[c/s]	l[c/s]
9	12	28187	112288
18	25	26763	112299
27	39	27874	112309
36	52	31632	112320
46	66	37498	112331
55	80	44823	112342
64	94	52277	112353
73	108	60056	112365
82	122	67562	112376
92	137	76492	112388
101	152	83164	112400
110	167	89088	112412
119	182	94159	112424
128	197	99577	112436
138	213	103739	112448
147	228	107472	112461
156	244	108865	112474
165	260	110208	112486
174	276	110967	112499
184	293	111856	112512
193	309	111915	112526
202	326	112629	112539
211	343	112320	112552
220	360	112563	112566
230	377	112798	112580
239	395	112608	112594
248	412	112679	112608

The intensities of Cu, H and Zn relative to the Al signal is found by dividing the intensity of the element on the corrected Al bulk signal.

Appendix B

The indexing of the grains from a-k corresponds to the height of the grains after etching. The specific location can be found in Figure 4.5.



Figure B.1: Comparison of the relative intensities of Zn of varying grain heigh.



Figure B.2: Comparison of the relative intensities of Cu of varying grain height

Appendix C



Figure C.1: Crystallographic map of the same area as Figure 4.11