GRAIN BOUNDARY CHARACTER DISTRIBUTION AND INTERGRANULAR CORROSION IN HIGH PURITY ALUMINUM

By

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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Grain Boundary Character Distribution and Intergranular Corrosion in High Purity Aluminum

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ABSTRACT

Corrosion tests at three different concentrations of aqueous HCl (8%, 16% and 38%) were performed in order to investigate the intergranular corrosion susceptibility of high purity aluminum (99.9999%) having different grain boundary character distributions (GBCD's). The grain boundaries in annealed aluminum were characterized according to the coincidence site lattice (CSL) model combined with Brandon's criterion for allowable deviation angles from the exact CSL relationship, using automated orientation imaging microscopy (OIM™) and the semi-automatic electron back scattered diffraction (EBSD) techniques in the scanning electron microscope (SEM). Pole figures were also generated through OIM™ for microtexture examination. It was found that GBCD's were significantly influenced by the crystallographic texture formed in the aluminum samples. Moreover, the GBCD was shown to have a great effect on the intergranular corrosion susceptibility. The results indicated that, at high concentrations of HCl (38 and 16%), only low angle (Σ1) boundaries were shown to be resistant to corrosion while at lower acid concentration (8%), other low Σ boundaries (Σ3–Σ29) were also found to be less susceptible to corrosion as compared to random boundaries. A detailed analysis of corroded CSL boundaries as a function of the deviation angles showed that Brandon's criterion was not applicable for determining their susceptibility to corrosion in high acid concentrations of HCl (38% and 16%). In such cases, a more restrictive criterion such as the Palumbo-Aust criterion would be more appropriate in determining corrosion susceptibility.
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LIST OF ACRONYMS

CSL - Coincidence Site Lattice

EBSD - Electron Backscattered Diffraction

GBCD - Grain Boundary Character Distribution

HVEM - High Voltage Electron Microscopy

OIM™ - Orientation Imaging Microscopy

SEM - Scanning Electron Microscopy
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CHAPTER 1 - INTRODUCTION

Most materials used in today's manufactured products are polycrystalline in nature. The microstructure of a polycrystalline material consists of differently oriented grains which are separated by grain boundaries. Since grain boundaries are considered defects in the material, intergranular degradation phenomena such as corrosion, cracking, cavitation, etc. are strongly associated with the structure of the grain boundary. Therefore, the study of grain boundaries has long been recognized as crucial in enhancing the overall performance of materials. In an early study, Hargreaves and Hills (1929) proposed that different structures could exist for different grain boundaries in metals. Kronberg and Wilson (1949) noted the importance of certain orientation relationships between two lattices adjacent to a grain boundary, which can lead to superlattices with relatively small unit cell, the so-called coincidence site lattices or CSL's. A detailed description of CSL is given in section 2.2.

Numerous studies including an early study by Aust and Rutter (1959) have shown that certain grain boundaries associated with CSL's may possess beneficial physical and chemical properties. Later, Watanabe (1984) introduced the concept ‘grain boundary design and control’ in which it was proposed that the bulk properties of materials could be improved by increasing the frequency of beneficial boundaries in a material, and at the same time, reducing the frequency of non-beneficial boundaries. More recently, it became possible to increase certain CSL boundaries in face centered cubic materials having relatively low stacking fault energies by using special thermomechanical treatments (Palumbo, 1992, Lin et al., 1997).
Intergranular corrosion is an interfacial degradation phenomenon that can be much more detrimental than uniform corrosion (Fontana and Staehle, 1972). Materials susceptible to intergranular corrosion often exhibit considerable reduction in cross section and grain dropping which can lead to significant mass loss, rapid deterioration of structural integrity and unpredictable catastrophic failure. Many factors have been known to affect intergranular corrosion including electrochemical environment (Osozawa et al., 1966), grain boundary structure (Palumbo and Aust, 1990), impurity segregation (Aust et al., 1966) and second phase particles (Erb and Aust, 1984), residual stress (Erb et al., 1982), etc. Recently, the influence of grain boundary character distribution (GBCD) on the overall resistance to intergranular corrosion of polycrystalline materials has been shown to be immense in alloy 600 (Lin et al. 1995), alloy 800 (Palumbo et al., 1998) and lead (Lehockey et al., 1998).

Most of the previous studies on the effect of boundary structure on intergranular corrosion in high purity aluminum have been limited to bicrystal studies using grain boundaries with controlled misorientations and grain boundary planes (see e.g., sections 2.3 and 2.4). Recent developments in processing electron back scattered diffraction (EBSD) patterns with the aid of powerful computers has allowed for rapid measurements of local lattice orientations in polycrystalline materials. This has led to the emergence of a new microstructural analysis technique called orientation imaging microscopy (OIM™) which is particularly suitable for studying intergranular degradation phenomena (Mason and Adams, 1994).

The main objective of this work is to investigate the effect of GBCD on intergranular corrosion of high purity polycrystalline aluminum in HCl. Particular
emphasis will be on the analysis of the susceptibility of various grain boundary types to intergranular corrosion.

This thesis is organized in the following way. The subsequent chapter contains background information relevant to the topic such as an overview of grain boundary structure and a review of previous studies on intergranular corrosions in pure aluminum as well as other systems. Chapter 3 presents the experimental procedures followed in this work including details on OIM\textsuperscript{TM} and description of the equipment used in this study. In chapter 4, the results and discussion of the study will be presented followed by the conclusions in chapter 5. Finally, a few recommendations for future work are suggested in chapter 6.
CHAPTER 2 - LITERATURE REVIEW

§2.1 Localized Corrosion at Grain Boundaries

A grain boundary is the region where two grains meet. Since these grains have different orientations, the two lattices do not normally fit, resulting in a "looser" structure than the grain interior. This creates an opportunity for preferential corrosion attack along the grain boundaries. From the structural point of view, less work would be needed to remove an atom at the grain boundaries than to remove an atom from the interior of a crystal interior where atoms are more firmly held than within the grain boundary region (Evans, 1960). On the other hand, if there is a second constituent present in the metal, it will likely be accumulated at or near the grain boundaries, leaving a zone of appreciable width parallel to the boundary that possesses different electrochemical properties than those of a pure grain-interior. It was shown by Thomas and Chalmers (1955), that even in a material with very small impurity content, there was solute segregation to the grain boundary. They showed that polonium segregates to the grain boundaries after adding only 1 part in $10^{10}$ of polonium into a lead alloy containing 5% bismuth. Therefore, it is expected that in any case of intergranular corrosion phenomena, both structural and compositional effects may be contributing factors.

Another important factor that is of concern for intergranular corrosion in lower purity materials is second phase formation along the grain boundaries. When this occurs, the zone of material close to the grain boundaries can be depleted in some constituent of the alloy and, as a result, changes in the corrosion susceptibility are controlled by local
variations in composition. For example, the importance of this factor was noted in studies by Was (1990), Airey (1970), Erb and Aust (1984). However, since this study is dealing with a material of high purity (99.9999% Al) in which second phase formation is unlikely to occur, studies on second phase effects will not be included in the literature review. Previous intergranular corrosion studies interpreted in terms of solute segregation and structural factors will be summarized in sections 2.3 and 2.4, respectively. Particular emphasis will be on previous studies on aluminum since these are of direct relevance to the present study.

Different structures in grain boundaries can lead to different properties of grain boundaries, such as their energy (Aust and Chalmers, 1952) and solute segregation susceptibility (Gleiter, 1970). Therefore, it is not surprising that a large variation for intergranular corrosion susceptibility can exist from boundary to boundary. As was shown in the work of Palumbo and Aust (1990) on polycrystalline nickel and other studies dealing with structure-dependent intergranular corrosion using controlled misorientation bicrystals (as reviewed by Aust and Palumbo in 1986, for example), certain low $\Sigma$ CSL (Coincidence Site Lattice) boundaries are less susceptible to corrosion than high $\Sigma$ and random boundaries. The following section will deal with CSL boundaries.
§2.2 Coincidence Site Lattice (CSL) Boundaries

The coincidence site lattice (CSL) is a 3-dimensional lattice constructed by the common lattice points from two crystals when they are rotated at a certain misorientation. Kronberg and Wilson (1949) first noted the importance of CSL boundaries during a study of secondary recrystallization in copper. An example of a CSL boundary is shown in figure 2.1. The $\Sigma$ value is the parameter used to describe the degree of the coincidence in the CSL. The fraction of lattice points in coincidence at the CSL boundary or the density of coincidence sites is given by the reciprocal of $\Sigma$. Alternatively, the volume ratio of the unit cell of the CSL to that of the crystal is described by $\Sigma$ (Grimmer et al, 1974). Warrington (1979) showed that all grain boundaries could be represented by an appropriate CSL description if $\Sigma$ is allowed to approach infinite values although it was suggested by Watanabe (1985) that the upper limit for ‘special’ properties concerning intergranular corrosion and fracture behavior in polycrystalline materials is $\Sigma 29$. The theory of CSL boundaries was further advanced by Ranganathan in 1966. He formulated an equation which gives $\Sigma$ values of CSL’s for any given rotation axis ([hkl]):

$$\Sigma = x^2 + Ny^2$$  

[2.1]

where $x$ and $y$ are the coordinates of a coincidence site in the plane (hkl) and

$$N = h^2 + k^2 + l^2$$  

[2.2]

and the rotation angle, $\theta$, is given as

$$\theta = (2 \tan^{-1} (y/x))(N^{1/2})$$  

[2.3]
In a cubic lattice, the $\Sigma$ value can only take odd values due to symmetry of the cubic lattice. Thus, if a $\Sigma$ value is even, it is reduced to an odd number by dividing with 2 until an odd number is reached (Brandon, 1966).

Figure 2.1 A coincidence site boundary obtained by a 53.1° rotation across a (100) plane (i.e. about a <100> axis). The reciprocal density, $\Sigma$, of the coincidence sites, shown as large open circles, is 5. Note that the unit cell for CSL is five times larger than that of the primitive lattice (Reed-Hill, 1992).
§2.3 Solute Effects

2.3.1 Grain Boundary Corrosion in Aluminum

One of the earlier studies, which demonstrated the importance of solute effect on intergranular corrosion in aluminum, was published by Roald and Streicher in 1950. They investigated the effect of heat treating aluminum ranging in purity from 99.2 to 99.998% on the corrosion resistance in 20% HCl and 0.30N NaOH, respectively. In this study, intergranular attack in both solutions was shown to be determined by the type and quantity of impurities present and the orientation of the grains.

Perryman (1953) studied the effect of iron content in high purity aluminum on intergranular corrosion. No grain boundary attack after 3 days of corrosion in 0.30N NaOH was observed for water quenched aluminum containing 10ppm of iron. However, as the iron content in aluminum was increased to 370ppm, 90% of all grain boundaries were heavily attacked for samples which had gone through the same heat treatment. Similar results were obtained when both samples were corroded in 10% aqueous HCl. Perryman attributed these results to “equilibrium segregation” of iron impurity along the grain boundaries due to its smaller atom size. Also, he observed that the corrosion occurred in a relatively wide grain boundary zone and the corrosion morphology was similar to a V-shape groove. He specifically reported that the width of the grain boundary grooves was larger than their depth for samples corroded in NaOH, while they were about the same for samples corroded in HCl.

Braun et al. (1958) proposed another contribution of grain boundaries to preferential chemical attack caused by solutes, other than solute enrichment. When
recrystallized aluminum of zone-refined purity was etched in Lacombe and Beaujard's etchant (47% fuming nitric acid, 50% chemically pure hydrochloric acid and 3% pure hydrofluoric acid), the grain boundaries were observed to be resistant to attack immediately after electropolishing, but became susceptible to severe attack after periods of a few days at room temperature. As for the case of 99.99% Al, the etching produced a high density of pits which were uniformly distributed over the surface immediately after electropolishing. After a room temperature anneal of 3 weeks, most of grain boundaries showed continuous troughs. It was suggested that aging at room temperature in-between polishing and etching caused impurities to diffuse along the grain boundaries to the surface due to the high diffusivity along grain boundaries compared with bulk diffusion through the grain interior.

The effect of impurities on intergranular corrosion of aluminum was also noted in Chaudron's work (1962) where significant differences in the intergranular corrosion between 99.997%Al and zone-refined Al in HCl solution were observed. Deep grooves along the grain boundaries developed in aluminum of 99.997% purity after 4 days of exposure to HCl. However, deep grooving was found only after one month of exposure for zone-refined Al.

The effect of copper content on general corrosion of aluminum was examined by Straumanis and Brakss (1939) and interpreted as follows. Copper ions introduced into the acid by dissolution of solid solution are reduced on the aluminum as patches of elemental copper. This enhanced the corrosion rate by providing cathodes of lower hydrogen overvoltage than were originally present. This effect was referred to as an autocatalytic reaction. Arora et al. (1962) showed that the autocatalytic reaction is also
significant in intergranular corrosion of aluminum. They investigated penetration depths of grain boundaries in aluminum samples having different levels of copper ranging from 1 to 600 ppm. After corroding these materials in various concentrations of aqueous HCl up to 37.5%, the rate of boundary penetration was found to increase with increasing copper content; as little as 21 ppm yielded a substantial effect which was greater than that of any other residual elements such as Mn, Ca, Si and Mg. It was concluded that the effect of copper content on intergranular corrosion is similar to its autocatalytic effect on general corrosion.

Aust and Iwao (1974) investigated the intergranular corrosion of zone-refined Al doped with different solutes (Cu, Sn, Ti) in 5-100 ppm range tested in 16%HCl. Crystallographic attack at the grain boundaries revealed \( \{001\} \) type of planes at the walls of the boundary grooves. Both in bicrystal and polycrystalline specimens, increasing amount of solute additions promoted an increase in corrosion at the grain boundaries as well as at the surfaces.

2.3.2 Grain Boundary Corrosion in Other Systems

Bengough et al. (1931) observed that the corrosion attack on high purity zinc in potassium chloride was in the form of geometrical pits in the grain interior with no noticeable intergranular attack. However, when zinc of slightly lower purity was corroded in the same solution, the geometrical pits were absent in the grain interior while the grain boundaries were attacked.

It was shown in Roberts’s study (1952) that impurity elements such as lead, tin, cadmium and bismuth caused Zn-Al die cast alloy to be more susceptible to intergranular corrosion when exposed to steam or to a salt-laden atmosphere.
Beaunier et al. (1978) reported that the addition of small amounts of silicon (up to 0.64 wt%) to nickel produced a significant increase in intergranular corrosion. After examining thin foil specimens using electron energy loss and x-ray spectroscopy in a scanning transmission electron microscope, they observed a strong segregation of silicon to the grain boundaries.

Chaung et al. (1979) demonstrated using Auger electron spectroscopy that sulfur which had segregated to the grain boundaries caused intergranular corrosion in Ni200. Segregated sulfur was shown to catalyze the anodic dissolution kinetics when nickel was exposed to sulfuric acid.
2.4.1 Grain Boundary Corrosion in Aluminum

The early work by Lacombe and Yannaquis (1948a) showed that grain boundary attack by 10% HCl in 99.999%Al depended upon the relative orientations of the grains. For large differences in orientation, the grain boundary suffered rapid attack while low angle or sub-grain boundaries were relatively resistant to attack.

Arora and Metzger (1966) investigated corrosion susceptibilities of tilt and twist boundaries in 16% HCl using 99.999%Al bicrystals of various misorientation angles. The corrosion rates for 23° [001], Σ=13 and 37° [001], Σ=5 tilt boundaries and a 16°[010], Σ=25a twist boundary, were found to be reduced compared to those observed for general high angle boundaries as shown in figure 2.2.

Boos and Goux (1970) conducted similar experiments using 99.998% Al bicrystals but in an autoclave containing heated water at 150°C. In the case of (100) tilt boundaries, no cusps were observed in corrosion depth among the different boundaries (figure 2.3). However, the depth of boundary grooves measured for [110] tilt bicrystals clearly showed that the attack was very much reduced for boundaries with misorientation near the 70.5°, Σ=3 and 129.5°, Σ=11 CSL boundaries as shown in figure 2.4.
Figure 3.3  Depth of corrosion in aluminum [100] symmetrical tilt bicrystals with (001) nominal reference surface exposed to 10 days in 16% HCl (Arora and Metzger, 1966).

Figure 2.2  Depth of corrosion in aluminum [100] symmetrical tilt bicrystals with (001) nominal reference surface exposed to 10 days in 16% HCl (Arora and Metzger, 1966).

Figure 2.3  Variation of the depth of intergranular groove formed after exposure to water for 10 hours at 150°C versus the tilt angle of the two crystals about <001>. a, b and c denote the direction measured (Boos and Goux, 1970).
Figure 2.4 Variation of the depth of intergranular groove formed after an exposure to water for 48 hours at 150°C versus the tilt angle of the two crystals about <011> (Boos and Goux, 1970).
2.4.2 Grain Boundary Corrosion in Other Systems

Qian and Chou (1982) studied grain boundary corrosion of niobium bicrystals produced from [0 1 1] oriented single crystals. Two sets of niobium symmetrical tilt bicrystals (having tilt axis of [1 0 0] and [0 1 1]) of various misorientations were corroded in an acid bath containing 70% HNO₃ and 30% HF for 40 seconds. The depths of the boundary grooves, d, were measured with respect to the grain surface using interference microscopy. Figure 2.5 summarizes the results in which d increases with θ, except where cusps appear. In the low angle boundary regime (θ < 15), the correlation between d and θ followed a Read-Shockly type relationship (Read and Shockly, 1950) for both sets of bicrystals. For the high angle boundaries produced from the bicrystals having [1 0 0] tilt axis, the boundary corrosion reached minimum at θ = 21.5° (Σ13) and 28.5 (Σ17). In the case of [0 1 1] bicrystals, a broad cusp appears at θ = 29° which is close to a Σ19 boundary. Qian and Chou concluded that the boundary corrosion correlated with the boundary energy. However, no grain boundary energy values were given in their study for these boundaries.

The correlation between intergranular corrosion and grain boundary structure of 99.999%Cu in a 16% HCl + 1g/l FeCl₃ solution was investigated by Erb et al. (1982). The corrosion rates of about 10,000 boundaries of different structures, which were prepared by sintering single crystal spheres (diameter 60 ± 10μm) onto the {110} surface of single crystal substrates were measured. The higher corrosion resistant boundaries were compared with the boundaries of minimal energy after long annealing time (50h at 1050°C) in the same system. It was found that boundaries of least corrosivity were
boundaries of low energy. However, boundaries deviating even less than 1° from an ideal low energy structure were found to be susceptible to intergranular corrosion as much as random boundaries. The authors concluded that the corrosion occurred as a result of structural defects, e.g. dislocations in the boundary rather than energetic differences since a deviation of less than 1° yields an increase in grain boundary energy of only a few percent (Rutter and Aust, 1967). The corrosion attack observed in this study was assumed to occur when the grain boundary dislocation spacing was less than the geometric dimensions of corrosion channels formed along the boundaries. Boundaries having relatively small angle deviation (θ≈10⁻⁵) were assumed to be resistant to corrosion by preventing a continuous path for corrosion propagation since at this deviation angle, dislocation spacing would be spread more than 10-50μm which was the dimensions of the corrosion channels observed in this study.

The importance of grain boundary dislocations in intergranular corrosion was also noticed in a study by Palumbo and Aust (1990) where electrochemical corrosion tests were conducted on high purity (99.999%) polycrystalline nickel in 2N H₂SO₄ in order to evaluate the CSL boundary corrosion susceptibility. The corrosion channels were found to develop from small isolated pits, which initiated along the boundary at low overpotential. Coalescence of these pits occurred when the overpotential was increased. The intrinsic grain boundary dislocations (IGBD) were interpreted as preferential sites for pitting since they can act as sinks for solute at grain boundaries (Gleiter, 1970). In addition, they could act as preferential sites for accumulation of anions leading to localized destabilization of the passive surface film (Keddam et al., 1987). Palumbo and Aust concluded that immunity against intergranular corrosion was closely related to the
IGBD spacing, i.e. the corrosion susceptibility increased with decreasing IGBD spacing which is a function of deviation angle and $\Sigma$ value. Figure 2.6 shows the structural limit below which immunity to intergranular corrosion was observed.
Figure 2.5  Variation of depth of boundary groove $d$, as a function of misorientation angle $\theta$, in (a) $<100>$ tilt series, (b) $<0 \bar{1} 1>$ tilt series (Qian and Chou, 1982).

Figure 2.6  Schematic representation of the effect of applied overpotential ($E_b$) on the structural field ($\Sigma$, $\Delta \theta$) of immunity to intergranular corrosion (Palumbo et al., 1990).
§2.5 Effect of Grain Boundary Character Distribution (GBCD)

The grain boundary character distribution (GBCD) is a parameter used to quantitatively describe the type and frequency of grain boundaries present in a microstructure. Lin et al. (1995) have recently assessed the effect of GBCD on the bulk sensitization and intergranular corrosion of Alloy 600. The materials were processed using a special thermomechanical process (Palumbo, 1992) to alter the GBCD significantly from the one that is present in conventionally processed material (cold rolled by 65% reduction in thickness and heat treated at 1000°C for 5 min). The specially processed materials showed a higher cumulative fraction of special (i.e., Σ≤29) grain boundaries (i.e., 63-71%), most of them being twin boundaries (46-55%) as compared to 37% of special boundaries found in conventionally processed material. Some of the specimens were annealed at 600°C for 1 hour to induce sensitization to evaluate susceptibility to the sensitization as well. Corrosion tests were conducted by immersing the specimens in 600mL of boiling ferric sulfate (31.25g/L)-50% sulfuric acid solution for 24 hours. It was found that the rate of intergranular corrosion decreased with increasing number of special boundaries in the GBCD as shown in figure 2.7.

More recently, Lehockey et al. (1997) proposed a geometric model in order to predict the effect of special boundary frequency in the microstructure on average depth of attack in cross section of the materials by grain dropping which occurs during intergranular corrosion processes. In this model, it was assumed that special boundaries are immune to corrosion and a material is composed of 14-sided tetrakaidekahedron-shaped grains. The results of this modeling showed that a relatively modest increase in
special boundary frequencies significantly decreased the weight loss by intergranular attack and that grain dropping could virtually be eliminated in materials containing special boundary fractions greater than 50%. The results of these studies offer great potential for the concept of 'Grain Boundary Design and Control', first advanced by Watanabe (1984), who proposed that bulk material properties can be improved by manipulating the GBCD to achieve high fractions of structurally ordered low Σ CSL grain boundaries.

Figure 2.7 Intergranular attack of alloy 600 when immersed in 600mL of boiling ferric sulfate (31.25g/L)-50% sulfuric acid solution for 24 hours as a function of % special boundaries for solution treated (lower curve) and sensitized (upper curve) materials (Lin et al., 1995).
The experimental procedures for this study included basically three distinct steps in the areas of sample preparation, microstructural characterization and corrosion studies. The following sections will deal with these three steps in the order in which they were performed.

§3.1 Sample Preparation

The starting material for this study was zone-refined Al ingot with a purity of six 9's (99.9999%). It was supplied by AESAR in bar form having a cross section of 3.5cm by 3.5cm. Cubes of 3cm in length were cut from the ingot for subsequent recrystallization experiments.

3.1.1 Recrystallization

The cubes cut from the ingot were deformed by means of cold rolling to a final thickness of 0.2 cm (corresponding to a 90% reduction in thickness). This was achieved by multipass rolling in a rolling mill (STANAT, model no. TA215). The samples were cooled by immersing into liquid nitrogen between rolling passes to prevent/minimize dynamic recrystallization during rolling.

Two different deformation/heat treatment schedules were used to recrystallize the specimens, labeled schedule I and schedule II, respectively. These will be described in detail in the following:

Schedule I

For the first set of experiments, multipass rolling in which the block was rolled with constant rolling direction was used to deform the samples. They were then annealed
in a tube furnace for recrystallization. After loading the cold rolled sheet in the tube furnace for annealing, the tube was flushed with argon gas for 10 minutes at high flow rate. Then, the furnace was turned on and the sheet was slowly heated (20°C/min) to 300°C. After the final temperature was reached, the samples were pulled out from the hot zone of the furnace and air cooled in the argon gas atmosphere inside the tube. This deformation/heat treatment schedule produced recrystallized materials with non-uniform grain size distribution and crystallographic texture which appeared as distinct bands in the microstructure. This will be further discussed in the results and discussion section.

Schedule II

In order to eliminate the banded structure observed in the first set of experiments, another deformation/heat treatment schedule was designed which allowed for better control of annealing time. Instead of using a tube furnace, annealing was carried out in a molten salt bath (containing 53% potassium nitrate and 47% sodium nitrate) followed by water quenching. The first batch of material was cold rolled as described in schedule I. This material was then recrystallized at 600°C for 5 seconds. The second batch was produced by cross rolling where the rolling direction was changed by 90° between each rolling pass. The rolled sheets were then annealed for 5 seconds at 300 °C and quenched in water. The resulting microstructures of samples produced in both batches exhibited no banding and pole figures showed that grains were more randomly oriented than in samples that were produced from schedule I. Further details will be discussed in the results and discussion section.
3.1.2 Surface Preparation

Square shaped specimens of 1.5cm length were cut from the annealed sheet using a low speed diamond saw. These were successively ground on emery papers (grit sizes of 800 and 1200) using an automatic grinding wheel. Following grinding, the specimens were mechanically polished with 1μm alumina particles suspended in water. In order to produce a mirror-like finish and deformation-free surface, all specimens were electropolished in an electrolyte containing 1 part (by volume) perchloric acid, 1 part glycerol and 8 parts methanol. Electropolishing was performed for about 1 minute at a temperature of less than -20°C using liquid nitrogen as electrolyte coolant. The specimen acting as the anode, was vertically immersed in an electrolyte beaker containing a stainless steel cathode in the form of cylindrical mesh lining the inside of the beaker. A constant voltage of 40 volts DC was applied, and the electrolyte was stirred by a magnetic stir throughout the electropolishing process. The residual film on the surface from electropolishing was removed by immersing in a 10% hydrofluoric acid solution for 1 minute. This removed the residual film that could have had some temporary protective effect during the corrosion test (Arora and Metzger, 1966).
§3.2 Microstructural Characterization of Annealed Samples

The data sets for determining the grain orientations and character of grain boundaries of recrystallized aluminum were obtained from analysis of EBSD patterns. OIM™ was used in conjunction with SEM to form and analyze the EBSD patterns.

3.2.1 Electron Back Scattered Diffraction (EBSD) Pattern Formation

When a beam of electrons is focused on the surface of a specimen, a large number of scattered electrons are generated, travelling in all directions beneath and above the surface. Scattered electrons satisfying Bragg’s condition, will be diffracted by specific planes \{hkl\}. Bragg’s law is stated as follows:

\[ n\lambda = 2d_{hkl}\sin\theta_B \quad [3.1] \]

where \(d_{hkl}\) is the interplanar spacing for a family of planes, \{hkl\}, \(\lambda\) is the electron wavelength, \(n\) is the order of the reflection, and \(\theta_B\) is Bragg’s angle.

Since the scattered electrons are travelling in all direction, diffracted electrons form two cones oriented at Bragg’s angle as shown in figure 3.1. These cones are called Kossel cones and when a detector is placed to intersect the edges of two cones, they appear as a band consisting of two parallel lines. Due to the very small Bragg’s angle, the Kossel cones appear as sets of parallel lines instead of parabolae on a flat detector (figure 3.2). The EBSD pattern is a projection of the lattice planes in the crystal, therefore, one can determine either absolute grain orientations or orientations relative to adjacent grains (called misorientations) when the pattern is indexed properly by noting the symmetry of the zone axis and the whole EBSD pattern symmetry.
3.2.2 Grain Orientation Analysis

A grain orientation may be described by a rotation of a crystal required to bring its crystal axes into parallelism with a set of sample axes. The crystal axes and the sample axes are shown in figure 3.3. The rotation required is described by a 3×3 rotation matrix, R whose elements are direction cosines of angles, α, β and γ.

\[
R = \begin{bmatrix}
    a_{11} & a_{12} & a_{13} \\
    a_{21} & a_{22} & a_{23} \\
    a_{31} & a_{32} & a_{33}
\end{bmatrix} = \begin{bmatrix}
    \cos(\alpha_1) & \cos(\beta_1) & \cos(\gamma_1) \\
    \cos(\alpha_2) & \cos(\beta_2) & \cos(\gamma_2) \\
    \cos(\alpha_3) & \cos(\beta_3) & \cos(\gamma_3)
\end{bmatrix} \quad [3.2]
\]

For instance, the cosines of α₁, β₁ and γ₁ are the angles between (100) and RD, (100) and TD and (100) and ND, respectively. Similarly, the second and third rows are formed from the cosines of angles between sample axes and (010) and between samples axes and (001), respectively. The rotation matrix has the following properties; the sum of the squares of each column or row vector is unity and the vector products obtained between column vectors or row vectors are zero (vectors are orthonormal).

A pole figure is a stereographic projection of either a <100>, <110> or <111> pole from individual grain with reference to sample axes, RD, TD and ND. Thus, in order to plot a pole figure, one needs to obtain the orientation matrix, A, which is given by the multiplication of rotation matrix, R with the pattern matrix, P.

\[
A = RP \quad [3.3]
\]

The pattern matrix is also a 3×3 pattern matrix whose rows are composed of orthonormal axes in an EBSD pattern obtained from a single crystal of known orientation (usually a single crystal of Si is used). Once the orientation of individual grains are determined,
Figure 3.1  Diagram showing the diffracted electrons from Kossel cones centered at P on the diffraction planes (Williams and Carter, 1996).

Figure 3.2  EBSD pattern acquired from a grain in a recrystallized aluminum sample at 20kV.
Figure 3.3  Schematic diagrams showing
(a) the sample axes in EBSD analysis
(b) the relationship between the sample axes and crystal axes, (100), (010), (001).
they can be used to plot a pole figure to investigate the texture or preferred orientation in a material.

3.2.3 Grain Boundary Characterization - CSL Classification

When the orientations of two adjacent grains are known, the character of the grain boundary, classified using the CSL model, between these two grains can be deduced by noting the misorientation or the difference between the orientations. The misorientation matrix, $M_{12}$, is calculated from two orientation matrices ($A_1$ and $A_2$) as follows:

$$M_{12} = A_1^{-1}A_2 \quad \text{[3.4]}$$

In this study, all the grain boundaries were categorized by giving the $\Sigma$ value of the boundary ($\Sigma$ being the coincidence index number, see section 2.2). Any boundary that has a $\Sigma$ value greater than 29 is designated as a random boundary. In order to determine the $\Sigma$ values for each boundary, the deviation angle matrix ($\Delta M$) from the exact CSL misorientation matrix ($M_{\text{CSL}}$) up to $\Sigma = 29$, tabulated by Mykura (1979), was calculated by

$$\Delta M = M_{12}M_{\text{CSL}}^{-1} \quad \text{[3.5]}$$

Since $\Delta M$ is a $3 \times 3$ matrix, the deviation angle is computed from $\Delta M$ as

$$\Delta \theta = \cos^{-1}\{(\Delta M_{11} + \Delta M_{22} + \Delta M_{33} - 1)/2\} \quad \text{[3.6]}$$

Finally, those grain boundaries for which the deviation angle is within Brandon's criterion (Brandon, D.G., 1966), were designated as the CSL boundaries with proper $\Sigma$ value. Brandon's criterion is stated as

$$\Delta \theta \leq 15^\circ \times \Sigma^{-1/2} \quad \text{[3.7]}$$
3.2.4 Orientation Imaging Microscopy (OIM™) System Configuration

OIM™ is a fully automated technique, capable of plotting a map containing all crystallographic information for an area of interest in the sample. There are various hardware components that are integrated or attached to the SEM to perform the OIM™ analysis. These include a specially designed sample stage, a phosphor screen, a low light camera, a camera control unit, a workstation and OIM™ software (see figure 3.4). The sample stage for OIM™ is tilted by 70° to minimize the electron absorption into the lattice and maximize the amount of scattered electrons into the direction where they are detected by a detector. A phosphor screen serves as the electron detector, which is mounted near the specimen inside of the SEM vacuum chamber. The EBSD pattern is formed on the phosphor screen and captured by the fiber optically linked low light camera, which sends the signal to a camera control unit where it provides a TV output video signal. The on-line EBSD pattern can therefore be viewed on a TV monitor after the contrast in the diffraction pattern is enhanced by image processing (involving "background subtract" routines) in the camera control unit.

OIM™ software version 2.0, written by TSL Co., and the Silicon Graphics SPARCstation computer were used in obtaining the crystallographic data from the EBSD pattern for the area of interest during the automated scan. The automated scan involves moving the beam on a point by point basis to the next position from its starting position according to the given step size. Every time the beam moves to a different location, the computer captures and indexes the pattern thereby storing the orientation data and the location where the data came from. Upon completion of the automated scan, the OIM™ software allows the orientation data to be presented in many different ways. One way to
Figure 3.4  Schematic diagram showing a typical setup for OIM.
present the data is through generating what is called the 'orientation image map'. An example of an orientation map and the optical micrograph showing the corresponding region for an annealed aluminum sample are given in figures 3.5(a) and 3.5(b), respectively. This map contains all the orientation measurements including Σ values for the grain boundaries present for the area shown in the optical micrograph. The grain in the orientation image map is defined in the software as the collection of all connected points that are oriented within the tolerance angle of five degrees. Another way of presenting the orientation data is through plotting the pole figure as shown in figure 3.5(c).

3.2.2 Semi-automatic EBSD Analysis

Following an OIM scan, the orientation image map was obtained and was closely compared with the optical micrograph of the corresponding area. After a sample was etched with diluted HF to remove the residual film from electropolishing, most of the grain boundaries were visible in the micrograph except for some of the low angle boundaries (e.g. the arrow in figure 3.5(a)). This allowed a visual inspection to be made. For areas which were not clearly defined as in Area I of figure 3.5(a) (e.g. high density of points), manual EBSD analysis was performed to characterize the grain boundary. Manual EBSD analysis involved placing the electron beam on the grain of interest, indexing the EBSD pattern, moving the beam across the grain boundary to the adjacent grain and indexing the second EBSD pattern. Calculations determining the grain orientations and the character of the grain boundary (i.e. calculating the Σ value and deviation angle) were performed using OIM software.
Figure 3.5
(a) Orientation image map obtained by performing OIM scan on an annealed aluminum sample.
(b) Optical micrograph of the region corresponding to the orientation image map shown in (a).
(c) (100) pole figure of the region shown in (a).
§3.3 Corrosion Tests

Prior to insertion in the SEM for OIM analysis, a marker in form of a scratch was purposely introduced on the surface of each specimen with a sharp blade in the vicinity of the area to be analyzed by OIM. This marking of the area was necessary because after the corrosion test, especially in high concentration of HCl, the microstructure of the sample was severely attacked by the acid, making it difficult to find the same area on the sample in order to assess the corrosion behavior.

Corrosion tests were carried out at 3 different HCl concentrations, 38, 16 and 8%. Each of the samples was degreased by ultrasonic cleaning in ethanol and was placed in a 250 ml beaker. For corrosion testing in 38% HCl, concentrated reagent grade HCl was directly used without dilution. For the 16% and 8% HCl, the acid was diluted with distilled and deionized water.
CHAPTER 4 - RESULTS AND DISCUSSION

§4.1 Corrosion Behavior of Material Produced by Schedule I

Figure 4.1 is an optical micrograph showing the microstructure of material produced by schedule I (see section 3.1.1 for the details of schedule I sample preparation) followed by a corrosion test in 38% HCl for 2 hours. It was observed that the recrystallized microstructure has two areas showing a distinct difference in the corrosion behavior which appeared as distinct bands aligned parallel to the rolling direction as shown in figure 4.1. These bands are marked as area I and area II. The grain boundaries in area II were more readily etched and, as a result, they are more easily seen while area I was still immune to corrosion. When the sample was further corroded in 38% HCl, the contrast in corrosion between area I and II became more visible. Figure 4.2 is an optical micrograph showing the microstructure of a sample after a 3.5 hour corrosion test. As the corrosion time increased, the corrosion which started initially along the boundaries in area II extended to the interior of grains causing severe damage to the grains. Some grains may have completely dropped out as a result of intergranular corrosion.
Figure 4.1 Optical micrograph showing the microstructure of aluminum at the early stage of corrosion testing (2 hours in 38% HCl). The sample was prepared according to the schedule I.

Figure 4.2 Optical micrograph showing more contrast in corrosion behavior after 3.5 hours in 38% HCl.
§4.2 Microstructural Characterization of Material Produced by Schedule I

From the OIM\textsuperscript{TM} scans in areas I and II, the GBCD's in terms of length fraction of CSL boundaries are shown in figures 4.4 and 4.6, respectively. In addition, the corresponding (110) pole figures for areas I and II are shown in figures 4.3 and 4.5. The length fractions ($L_f$) were calculated as follows:

$$L_f = \frac{L_{GB}}{T_{GB}} [4.1]$$

where $L_{GB}$ is the total length of each boundary type and $T_{GB}$ is the total length of grain boundary. Grain boundaries were characterized by $\Sigma$ values and $R$ denotes a random high angle boundary with $\Sigma > 29$.

From the 110 pole figures and bar charts (figures 4.3 ~ 4.6), it is evident that each of the bands has quite different crystallographic texture and GBCD. In area I, low angle ($\Sigma 1$) boundaries are found to be the most abundant boundaries (65%) whereas the length fraction of random boundaries is the highest in area II (67%). A high length fraction of $\Sigma 1$ boundary in area I is due to the strong cube texture described as (100) [001], prevailing in that region. When a material has strong texture, most of the grains are identically oriented and the boundaries separating these grains would be low angle boundaries. Conversely, when the grains are oriented more randomly, i.e. deviating further away from a certain texture component, fewer low angle boundaries would result because of a greater variation in grain orientations. This is well demonstrated in the (110) pole figures and corresponding length fractions of $\Sigma 1$ boundaries in each area (figures 4.5 and 4.6). High fractions of low angle boundaries in strongly textured materials were also reported in copper (Mishin, 1998) and annealed Fe-6.5%Si (Watanabe et al., 1989).
Figure 4.3  (110) pole figure showing a strong cube texture in area I.

Figure 4.4  Bar chart and table showing GBCD in area I.

Length fractions of each boundary present in area I

<table>
<thead>
<tr>
<th>Type of boundary</th>
<th>Length fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Σ1</td>
<td>0.6462</td>
</tr>
<tr>
<td>Σ3</td>
<td>0.0107</td>
</tr>
<tr>
<td>Σ5</td>
<td>0.0201</td>
</tr>
<tr>
<td>Σ7</td>
<td>0.002</td>
</tr>
<tr>
<td>Σ9</td>
<td>0.0047</td>
</tr>
<tr>
<td>Σ11</td>
<td>0.0033</td>
</tr>
<tr>
<td>Σ13a</td>
<td>0.014</td>
</tr>
<tr>
<td>Σ13b</td>
<td>0.0094</td>
</tr>
<tr>
<td>Σ17a</td>
<td>0.006</td>
</tr>
<tr>
<td>Σ19a</td>
<td>0.0033</td>
</tr>
<tr>
<td>Σ25a</td>
<td>0.0127</td>
</tr>
<tr>
<td>Σ27a</td>
<td>0.0007</td>
</tr>
<tr>
<td>Random</td>
<td>0.2869</td>
</tr>
</tbody>
</table>
Figure 4.5 (110) pole figure showing a more random texture in area II.

Length fractions of each type of boundary present in area II

<table>
<thead>
<tr>
<th>Type of boundary</th>
<th>Length fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Sigma 1$</td>
<td>0.2673</td>
</tr>
<tr>
<td>$\Sigma 3$</td>
<td>0.0171</td>
</tr>
<tr>
<td>$\Sigma 5$</td>
<td>0.0055</td>
</tr>
<tr>
<td>$\Sigma 7$</td>
<td>0.0041</td>
</tr>
<tr>
<td>$\Sigma 9$</td>
<td>0.0034</td>
</tr>
<tr>
<td>$\Sigma 11$</td>
<td>0.0007</td>
</tr>
<tr>
<td>$\Sigma 13a$</td>
<td>0.0062</td>
</tr>
<tr>
<td>$\Sigma 13b$</td>
<td>0.0022</td>
</tr>
<tr>
<td>$\Sigma 15$</td>
<td>0.0041</td>
</tr>
<tr>
<td>$\Sigma 17a$</td>
<td>0.0014</td>
</tr>
<tr>
<td>$\Sigma 19a$</td>
<td>0.0102</td>
</tr>
<tr>
<td>$\Sigma 21a$</td>
<td>0.0007</td>
</tr>
<tr>
<td>$\Sigma 23$</td>
<td>0.0027</td>
</tr>
<tr>
<td>$\Sigma 25a$</td>
<td>0.0082</td>
</tr>
<tr>
<td>$\Sigma 25b$</td>
<td>0.0007</td>
</tr>
<tr>
<td>$\Sigma 27b$</td>
<td>0.0014</td>
</tr>
<tr>
<td>$\Sigma 29a$</td>
<td>0.0022</td>
</tr>
<tr>
<td>Random</td>
<td>0.685</td>
</tr>
</tbody>
</table>

Figure 4.6 Bar chart and table showing GBCD in area II.
§4.3 Corrosion Behavior of Low Angle Boundaries and Cubic Oriented Grains

Based on the GBCD reported in section 4.2, the intergranular corrosion observed in area II is due to higher corrosion susceptibility of random boundaries as compared to low angle ($\Sigma 1$) boundaries. The high resistance of $\Sigma 1$ to grain boundary corrosion was pointed out by many authors including Lacombe and Beaujard (1948b). They considered that the boundary has a transitional structure which is more nearly that of the perfect lattice when the orientation of the two grains is closer to one another. The beneficial property of the $\Sigma 1$ boundary was also observed in intergranular stress corrosion cracking studies. Yamashita et al. (1988) observed in Cu-9at.% Al bicrystals that $\Sigma 1$ boundaries not only had a lower dissolution rate in an etchant consisting of 2mlBr$_2$, 60mlCH$_3$COOH, 20mlHCl, 100mlH$_2$O, but they also had a significantly greater intergranular stress corrosion crack resistance in a solution of NH$_4$OH and NaOH than random high angle boundaries. In addition, Crawford and Was (1992) investigated the intergranular cracking of Ni-16Cr-9Fe in argon at 360°C and high-purity water. No boundary cracks were observed along $\Sigma 1$ boundary in either environment.

Reduced surface corrosion attack for cube oriented grains as observed in Area I agrees with the results of earlier studies including the study by Braun et al. (1958). In a corrosion study of zone-refined purity aluminum in Lacombe and Beaujard's etchant (47% fuming nitric acid, 50% chemically pure hydrochloric acid and 3% pure hydrofluoric acid), they observed the lowest pit densities for the grains parallel to (100) planes while the highest pit densities were found for the grains parallel to (111) direction.
§4.4 Origin of Bands in Material Produced by Schedule I

The origin of the banded structure where each band has distinct crystallographic texture and GBCD in recrystallized samples produced following schedule I treatment was further investigated by examining the microstructure of the as-received aluminum ingot before the sample preparation procedure. Figure 4.7 shows the macrostructure of a block from the ingot polished on three different faces. The material has a typical as-cast structure where a region close to the mold wall consists of smaller equiaxed grains. The microstructure changes to one of larger elongated grains (or columnar grains) with further distance from the mold wall. Also, the long axis of the columnar grains is parallel to the heat-flow direction (normal to the mold walls). A comparison shows that the width of bands in the recrystallized structure following schedule I is about the same as the width of coarse grains in the starting material. Therefore, it is assumed that the bands observed in the recrystallized samples are a microstructural feature remenent from the cast structure. The textures observed in the bands could depend on the orientation of the initial coarse grains with respect to the rolling direction. Differently oriented grains can lead to different rolling and recrystallized textures (Hjelen et al., 1991).
Figure 4.7  Optical macrographs showing the structure of zone-refined Al.
§4.5 Microstructural Characterization of Material Produced by Schedule II

In order to eliminate the banded structures observed in materials prepared by schedule I and described in section 4.1, a different sample preparation method (schedule II) was employed.

For the first batch of material produced by schedule II which involved unidirectional rolling and salt bath annealing at 600°C for 5 seconds, the microstructural characteristics are shown in figure 4.8. The optical micrograph (figure 4.8(a)) and the (110) pole figure (figure 4.8(b)) show that neither distinct bands nor a strong texture were associated with this thermomechanical treatment. This material has a GBCD consisting of 65% random boundaries and 35% special boundaries of which about 19% were Σ1 (low angle) grain boundaries (figure 4.8(e)). This material was chosen for the corrosion test in 38% HCl. Details on its corrosion behavior will be discussed in section 4.7.

The microstructural characteristics of two samples from the second batch of materials produced using schedule II which involved cross rolling and salt bath annealing at 300°C for 5 seconds are shown in figures 4.9 and 4.10, respectively. The (110) pole figures (figures 4.9(b) and 4.10(b)) show that both materials possess random textures. The GBCD's showed about 70% and 71% random grain boundaries, a somewhat lower Σ1 content and enhanced Σ3 content as compared with the unidirectionally deformed material. These samples were chosen for corrosion tests in 16 and 8% HCl, respectively. Details on their corrosion behavior will be discussed in section 4.7.

When comparing the pole figures for schedule I and schedule II samples having different textures (figures 4.3, 4.5 and 4.8(b) ~ 4.10(b)) and the GBCD charts (figures
4.4, 4.6 and 4.8(c) - 4.10(c)), the length fraction of $\Sigma 1$ boundary decreases as the texture becomes more random for the same reason discussed in section 4.2. The length fraction of $\Sigma 1$ was 0.65 in the strong cube textured sample (figure 4.4) and decreased significantly to 0.06 in the highly random textured sample (figure 4.10 (c)). However, the length fractions of other low $\Sigma$ boundaries (3$\leq \Sigma \leq 29$) increased by the schedule II treatment, especially with the samples that were cross rolled. This can be due to cross-rolling preventing the formation of a strong rolling texture that is often observed in unidirectionally rolled aluminum sheets (e.g. Hirsch et al., 1987). Instead, cross-rolled sheets may have contained recrystallization "nuclei" of various orientations which were evenly distributed throughout the sheet. Many authors including Humphreys and Hatherly (1995) showed that in aluminum, the annealing texture was solely determined by the orientation distribution of the recrystallization "nuclei" and their relative rates of growth since twinning in aluminum is very rarely observed and thereby has little influence in annealing texture formation. However, Haasen (1993) observed with high voltage electron microscopy (HVEM) that twinning occurred in 99.998% Al during the early stage of recrystallization. Humphreys and Ferry (1996) also investigated the twinning during in situ annealing of Al-0.05%Si alloy in the SEM and observed that annealing twins were more frequently formed at a free surface than in the specimen interior. They claimed that the observations of Haasen (1993) concerning the role of twinning in recrystallization of aluminum was restricted to the thin foils which Haasen used in HVEM and didn't occur in bulk aluminum.

In the present study, relatively high fractions of twin ($\Sigma 3$) boundaries were found in this study: 0.07 and 0.09, respectively, in the two cross-rolled samples after
considerable depth from the surface was removed by grinding and polishing. This may support Haasen's observation that twinning occurs even for bulk aluminum. According to the Fullman-Fisher theory (Fullman and Fisher, 1951), the high grain boundary energy of high angle boundaries would promote twinning in order to reduce the overall grain boundary energy in the system. Higher number fractions of twin boundaries in the material employed this study (99.9999%) as compared with Al-0.05%Si alloy used by Humphreys and Ferry (7% vs. 3.9%) may be due to the larger impurity level in the Al-0.05%Si. When impurities segregate at grain boundaries, the grain boundary energy can be considerably reduced thereby diminishing the energy difference between different types of grain boundary as was demonstrated by Bolling and Winegard (1958). They showed in zone-refined lead, the addition of 0.1 at.% silver raised the relative interfacial free energy of coherent twin grain boundaries with respect to the average grain boundary to 0.077 ± 0.016 from 0.050 ± 0.014 and interpreted that the average grain boundary free energy was decreased due to segregation of solute at the boundary. This can lead to twinning being less energetically favorable and less likely to occur in the system.
Figure 4.8  
(a) Microstructure of the sample produced by unidirectional rolling and salt bath annealing at 600°C for 5 seconds (etched in 10%HF for 2 min).  
(b) (110) pole figure of the area shown in (a).  
(c) Bar chart and table showing the GBCD of the area shown in (a).
Figure 4.9
(a) Microstructure of the sample produced by cross rolling and salt bath annealing at 300°C for 5 sec (etched in 10% HF for 2 min).
(b) (110) pole figure showing a random texture of the area shown in (a).
(c) Bar chart and table showing the GBCD of the area shown in (a).
Figure 4.10  
(a) Microstructure of the sample produced by cross rolling and salt bath annealing at 300°C for 5 sec (etched in 10% HF for 2 min). 
(b) (110) pole figure showing a random texture in the area shown in (a). 
(c) Bar chart and table showing the GBCD of the area shown in (a).
§4.6 General and Localized Corrosion in Aluminum

All the electropolished aluminum samples were etched in aqueous 10% HF for 2 minutes prior to the corrosion tests in order to remove residual oxide films which could have some temporary protective effect in the beginning of the corrosion process (Arora and Metzger, 1966). Following the HF etch, the grain boundaries appeared as dark lines as shown in figure 4.11(a). From the optical micrograph, they appeared as if the grain boundaries were preferentially attacked. However, a comparison with the SEM image (figure 4.11(b)) taken from the same area revealed the absence of trenches along the grain boundaries. Thus, the dark lines observed in the optical micrograph are due to the step structure produced by differences in the surface dissolution for various grains. For example, the large grain in the bottom center in the box marked on figure 4.11(b) showed the highest dissolution rate leading to a step structure with its neighboring grains. The orientation of this grain is close to (111) as shown in figure 4.11(d) which is consistent with the result obtained by Arora and Metzer (1966). In a corrosion study of high purity aluminum in aqueous HCl, they observed the lowest corrosion rate for grains parallel to (100) planes and increased corrosion for (111) oriented grains. It was suggested that the formation of the passivating film in the acid during anodic polarization would be more perfect on (001) than (111) planes because of the particular atomic arrangement in this surface.

In summary, the initial etch in 10% HF solution did not result in localized corrosion at defect sites such as dislocations or grain boundaries. Only grain orientation-dependent variation in surface dissolution was observed.
Localized corrosion such as preferential grain boundary attack only appeared after the sample was immersed in HCl solution. This is illustrated in figure 4.11(c) which is the same region as shown in figure 4.11(b) but after a corrosion test of 1 hour in 38% HCl. The hydrochloric acid initiated localized attack at some of the grain boundaries and pitting corrosion inside the grains. Faceted attack such as the triangular pits found in the center grain in figure 4.11(c) have been previously observed (Evans, 1960); often they are initiated at dislocations. Mahl and Stranski (1942) have shown that HCl produces etch figures on aluminum whose facets are parallel to the (100) cube faces. Lacombe and Beaujard (1948b) also noted that the morphology of pits was a function of the orientation of the crystal. In the present study, it was observed that the degree of faceting associated with localized attack at grain boundaries and within the grain was strongly dependent on the acid concentration. This can be seen by comparing figure 4.14, 4.15(b) and 4.18; decreasing acid concentration leading to less pronounced faceting and more rounded pitting corrosion attack.

§4.7 Intergranular Corrosion Selectivity in 38%, 16% and 8% HCl

Samples of the two batches of material described in section 4.5 were corroded in 38%, 16% and 8% HCl, respectively. Since the samples experienced considerable grain dropping with increasing corrosion time, the corrosion tests were frequently interrupted to monitor whether grains were lost due to grain boundary corrosion or general surface dissolution. For example, figure 4.12 shows the same sample corroded for 63 hours (figure 4.12(a)), 104 hours (figure 4.12(b)) and 171 hours (figure 4.12(c)) in 8% HCl, respectively. After 63 hours, the grain marked 'x' has been detached from all its neighboring grains due to intergranular corrosion with the exception of the grain.
boundary marked between the two arrows. After 171 hours of corrosion (figure 4.12(c)),
grain 'x' has been lost, very likely due to surface dissolution from the corrosion channels
formed earlier along the other grain boundaries. Thus, the grain boundary between the
arrows can be considered resistant to corrosion whereas the other boundaries surrounding
grain 'x' were highly susceptible to intergranular attack.

Grain boundaries were characterized using OIM and the semi-automatic EBSD
technique and labeled according to $\Sigma$ values using Brandon's criterion as depicted in
figures 4.13, 4.16 and 4.17. In order to determine the intergranular corrosion selectivity
among different types of grain boundaries, the total number of each boundary type and
those that were corroded during the corrosion tests were counted. The results are plotted
in figures 4.19 to 4.21.

Low angle boundaries ($\Sigma 1$) were found to be the most resistant to intergranular
corrosion regardless of acid concentrations. The fraction of $\Sigma 1$ boundaries corroded
decreased slightly from 15.6 to 12.5% as the concentration of acid became more diluted.
As for the corrosion susceptibility of twin ($\Sigma 3$) boundaries, fewer boundaries of this type
compared to random boundaries were found to be corroded in 16% and 8% HCl (figures
4.20 and 4.21); 23% and 35% of the $\Sigma 3$ boundaries versus 53% and 47% of random
boundaries were corroded in 16% and 8% HCl, respectively. For the corrosion test in
38% HCl, the results are statistically inconclusive as only two $\Sigma 3$ boundaries were
observed and both were corroded.
Figure 4.11  (a) Optical micrograph showing the microstructure of 99.9999% Al after etching in aqueous 10% HF for 2 min. (b) SEM image of the same region. (c) Initiation of localized attack after corrosion for 1 hour in 38% HCl. (d) Orientation of grain (marked '+' showing fastest surface dissolution in (c).
Figure 4.12  SEM image (a) and optical micrographs ((b) and (c)) showing the grain removal of 99.9999%Al during the corrosion in 8%HCl by surface dissolution. (a) after 63 hours; (b) after 104 hours; (c) after 171 hours.
The corrosion susceptibility of other low \( \Sigma \) boundaries \( (\Sigma 5-\Sigma 29) \) in high concentrations of HCl (38% and 16%) were found to be just as high as for random boundaries (figure 4.19 and 4.20). However, reduced corrosion susceptibility of other low \( \Sigma \) boundaries \( (\Sigma 5-\Sigma 29) \) was observed in 8% HCl; 31% of these boundaries corroded versus 47% of random boundaries as shown in figure 4.21. This could be attributed to selectivity being also dependent on the driving force for intergranular corrosion. This was earlier demonstrated by Palumbo and Aust (1990) who determined that the selectivity in intergranular corrosion of 99.9999% Ni in 2N H\(_2\)SO\(_4\) was dependent on the electrochemical potential range. This is shown in figure 4.22 where the upper curve represents the lowest overpotential \( (E_c) \), at which corrosion on all grain boundaries except coherent twin boundaries was observed. The lower curve represents the overpotential \( (E_i) \) below which complete immunity for all grain boundaries was observed. The region bounded by the two limits in figure 4.22 is where grain boundary selectivity for other low \( \Sigma \) and random boundaries was noted in the initiation of localized corrosion.

Although the material employed in this study is different, a similar approach can be applied in interpreting the corrosion susceptibility of low \( \Sigma \) boundaries in different concentrations of HCl. For high concentrations of HCl (38% and 16%), the driving force for corrosion would correspond to the region above the upper limit in figure 4.22; most of the boundaries except low angle boundaries are susceptible to intergranular corrosion. As the concentration of hydrochloric acid is diluted to 8%, which would correspond to decreasing the electrochemical overpotential in figure 4.22, the driving force for intergranular corrosion of aluminum would lie in the regime where corrosion selectivity among different types of grain boundaries is noted and therefore, the corroded boundary
The fraction of other low \( \Sigma \) boundaries (\( \Sigma 5 \sim 29 \)) was less than that of random boundaries (31% versus 47%).

The corrosion susceptibility of each CSL boundary in terms of deviation angles from exact \( \Sigma \) values are plotted in figures 4.23 ~ 4.25. The dashed lines show the maximum allowed deviation angles according to Brandon's criterion below which the grain boundaries are considered CSL boundaries.

For the case of low angle (\( \Sigma 1 \)) boundaries, they were almost all immune to the intergranular attack with misorientation angles up to 15°, especially in the 16% and 8% of HCl (figures 4.24 and 4.25). A similar result was reported by Bennett and Pickering (1987) who observed no grain boundary attack for misorientation less than 0<14° during anodic dissolution of stainless steel (Fe-18Cr-10Ni) in 1 N H\(_2\)SO\(_4\).

The fraction of \( \Sigma 3 \) boundaries corroded was found to increase with decreasing acid concentration from 16% to 8% HCl: 23% of the \( \Sigma 3 \) boundaries were corroded in 16% HCl while 35% were corroded in 8%HCl (figures 4.20 and 4.21). This could be attributed to the sample corroded in 8%HCl having \( \Sigma 3 \) boundaries with larger deviation angles from the exact CSL relationship. Seven of the twelve \( \Sigma 3 \) boundaries observed had a deviation angle smaller than 2° from exact \( \Sigma 3 \) relationship while thirteen of fifteen \( \Sigma 3 \) boundaries in the sample corroded in 16%HCl had deviation angle smaller than 2°. Larger deviation angle from the exact CSL means a less ordered structure at the grain boundary, i.e., increased intrinsic dislocation content, which has previously been shown to result in increased susceptibility to intergranular corrosion in Ni (Palumbo and Aust, 1990). Shvindlerman and Straumal (1985) showed, using transmission electron microscopy, that the intrinsic grain boundary dislocation spacing decreased as the
deviation from the exact CSL relationship increased, resulting in a less ordered structure at the grain boundary.

Figures 4.23–4.25 clearly show that with increasing acid concentration more grain boundaries within the angular deviation limit given by Brandon's criterion were found to be susceptible to intergranular corrosion attack. For example, for the sample corroded in 8% hydrochloric acid, 10 out of 28 $\Sigma 3-\Sigma 29$ grain boundaries showed partial or complete corrosion at deviations less than Brandon's criterion (figure 4.25). For samples corroded in 16% HCl, 18 out of 38 boundaries showed corrosion (figure 4.24), while for 38% HCl 13 out of 16 boundaries showed corrosion when the same criterion is applied (figure 4.23). This demonstrates clearly that with increasing acid concentration, Brandon's criterion to predict immunity to intergranular degradation becomes less reliable.

Recently, Palumbo and Aust (1990) proposed a more restrictive criterion for determining CSL boundaries with respect to the deviation angles from exact CSL relationships in a study of intergranular corrosion in 99.999%Ni. They noted that the maximum deviation angle below which selective immunity was observed for each CSL boundary followed a relation of the type:

$$\Delta \theta = 15\Sigma^{-5/6}$$  \hspace{1cm} [4.2]$$

where $\Delta \theta$ is the deviation angle.
Figure 4.13 Optical micrograph showing the microstructure of aluminum etched in 10% HF for 2 min. Grain boundaries are labeled according to $\Sigma$ numbers ($3 \leq \Sigma \leq 29$) with deviation angles. Boundaries marked L are low angle boundaries ($\Sigma 1$) and R are random boundaries ($\Sigma > 29$).

Figure 4.14 Optical micrograph showing the corroded microstructure of the same area as above after 2.5 hours in 38% HCl.
Figure 4.15  Optical micrograph showing microstructure of aluminum (a) before the corrosion test (etched in 10% HF for 2 min) (b) after 24 hours in 16% HCl.

Figure 4.16  Optical micrograph showing the intermediate stage of corrosion in 16% HCl (after 15 hours). Grain boundaries are labeled according to $\Sigma$ values ($3 \leq \Sigma \leq 29$) with deviation angles. Boundaries marked L are low angle boundaries ($\Sigma 1$) and R are random boundaries ($\Sigma > 29$).
Figure 4.17 Optical micrograph showing the microstructure of aluminum before the corrosion test in 8% HCl (etched in 10% HF for 2 min). Grain boundaries are labeled according to $\Sigma$ values ($3 \leq \Sigma \leq 29$) with deviation angles. Boundaries marked L are low angle boundaries ($\Sigma 1$) and R are random boundaries ($\Sigma > 29$).

Figure 4.18 Optical micrograph showing the same area as above after 171 hours in 8% HCl.
Figure 4.19  GBCD and intergranular corrosion susceptibility of different types of boundaries after 2 hours and 30 minutes in 38% HCl (total number of grain boundaries characterized was 154).
Figure 4.20  GBCD and intergranular corrosion susceptibility of different types of boundaries after 24 hours in 16% HCl (total number of grain boundaries characterized was 302).

Figure 4.21  GBCD and intergranular corrosion susceptibility of different types of boundaries after 171 hours in 8% HCl (total number of grain boundaries characterized was 195).
Figure 4.22  The electrochemical potential limits ($E_c$, $E_i$) for intergranular corrosion of 99.999% Ni having different amount of S concentration. The upper curve represents the lowest overpotential ($E_c$), at which comprehensive corrosion on all grain boundaries except coherent boundaries was observed. The lower curve represents the overpotential ($E_i$) below which complete immunity for all grain boundaries was observed. (Palumbo and Aust, 1990).

Figure 4.23  Corrosion susceptibility of CSL boundaries ($\Sigma \leq 29$) after 2 hours and 30 minutes in 38% HCl as a function of deviation angles from exact $\Sigma$ values (x:corroded, o:non-corroded, A: partially corroded boundary).
Figure 4.24  Corrosion susceptibility of CSL boundaries ($\Sigma$<29) after 24 hours in 16%HCl as a function of deviation angles from exact $\Sigma$ values (x:corroded, o:non-corroded, Δ: partially corroded boundary).

Figure 4.25  Corrosion susceptibility of CSL boundaries ($\Sigma$<29) after 171 hours in 8%HCl as a function of deviation angles from exact $\Sigma$ values (x:corroded, o:non-corroded, Δ: partially corroded boundary).
In figures 4.26–4.28, the results shown in figures 4.23–4.25 were replotted but now with the angular deviation limit proposed by Palumbo and Aust, (1990). Since the Palumbo-Aust criterion is more restrictive than Brandon's criterion ($\Delta \theta = 15\Sigma^{-1/2}$), it is located below Brandon's criterion in these figures. It can be seen that most of the corroded boundaries lie below Brandon's criterion but not below Palumbo-Aust's criterion in particular with increasing acid concentration. Very few other low $\Sigma$ boundaries ($\Sigma 5 \sim \Sigma 29$) which satisfied Palumbo-Aust criterion were found in the 38 and 16% corrosion tests. Therefore, its applicability in determining the special property against high concentrations of HCl still needs to be verified. Nevertheless, it was clearly demonstrated in this study that a more restrictive criterion than Brandon's criterion was needed in order to predict the susceptibility of grain boundaries to intergranular attack in 38% and 16% HCl.

Experimental support for the applicability of the Palumbo-Aust criterion was recently presented in studies by Pan et al.(1996) and Palumbo et al.(1998). Pan et al. (1996) showed in a study of intergranular cracking in alloy X-750 that grain boundaries classified as CSL's using the Palumbo-Aust rather than Brandon's criterion were found to display 'special' cracking-resistant behavior. Moreover, Palumbo et al. (1998) have examined various intergranular degradation phenomena such as corrosion in alloy 800, cracking in alloy 600 and cavitation in commercially pure nickel. Negligible percentage ($\approx 3\%$) of grain boundaries showed susceptibility to these intergranular phenomena when the boundaries were classified using the Palumbo-Aust criterion while 12–16% of grain boundaries displayed attack when Brandon's criterion was used to classify the grain boundaries.
In summary, in the present study, it has been shown that Brandon's criterion can be useful in classifying 'special' low $\Sigma$ grain boundaries in 99.9999% aluminum subjected to intergranular corrosion in 8% HCl. However, a more stringent criterion such as the Palumbo-Aust criterion would be required in order to determine whether or not CSL boundaries display 'special' properties in higher concentrations of HCl (16% and 38%) i.e. at higher driving forces for the intergranular degradation process.
Figure 4.26 Replot of figure 4.23 showing the angular limit proposed by Palumbo and Aust (1990).

Figure 4.27 Replot of figure 4.24 showing the angular limit proposed by Palumbo and Aust (1990).
Figure 4.28  Replot of figure 4.25 showing the angular limit proposed by Palumbo and Aust (1990).
CHAPTER 5 - CONCLUSIONS

1. The GBCD in 99.9999%Al significantly depended on the texture associated with particular thermomechanical treatments, notably for $\Sigma 1$ and $\Sigma 3$ boundaries. The length fraction of $\Sigma 1$ boundaries decreased from 0.65 to 0.06 and that of $\Sigma 3$ boundaries increased from 0.01 to 0.08, as the texture changed from a sharp cube texture to a more random texture. The texture in the samples depended strongly on the processing parameters. Unidirectional rolling combined with slow heating favored the formation of the cube texture while cross-rolling and rapid heat treatment promoted a more random texture formation. Also, evidence of twinning even in the bulk aluminum was observed in this study.

2. Exposure of annealed aluminum to HF as a pretreatment to remove surface oxides prior to corrosion testing in HCl resulted in surface dissolution without localized attack with the dissolution rate being depended upon the crystallographic orientation of the grains. A higher dissolution rate was observed for grains having a surface orientation close to (111). Localized attack such as pitting initiated at some of the grain boundaries and inside the grains appeared only after the aluminum samples were immersed in HCl. The degree of facetting in the pit morphology was found to be dependent on the hydrochloric acid concentration.

3. The GBCD has been shown to have a great effect on intergranular corrosion susceptibility in HCl, especially for low angle ($\Sigma 1$) boundaries whose resistance against
intergranular corrosion was exhibited in all concentrations of HCl (8%, 16% and 38%) used in this study. A higher resistance of twin (Σ3) boundaries against corrosion in 16% and 8% HCl as compared to random and other low Σ boundaries (5 ≤ Σ ≤ 29) was also observed.

4. The corrosion susceptibilities of random and other low Σ boundaries (5 ≤ Σ ≤ 29) was observed to be the same at higher concentrations of HCl (38% and 16%). However, less corrosion susceptibility of other low Σ boundaries compared to random boundaries was found in 8% HCl solution.

5. Brandon's criterion which gives the angular deviation for special boundaries was found to be not restrictive enough in determining the susceptibility of grain boundaries to corrosion. A more restrictive criterion such as the Palumbo-Aust criterion would be more appropriate in particular for higher concentrations of HCl.
CHAPTER 6 - RECOMMENDATIONS FOR FUTURE WORK

Based on the results and conclusions of this research work, a number of recommendations for future work can be made.

- More data should be evaluated for the corrosion susceptibility of other low $\Sigma$ boundaries ($5 \leq \Sigma \leq 29$), which satisfy the restrictive Palumbo-Aust criterion, in various concentrations of HCl and other corrosive environments.

- The origin of the banded structure after unidirectional rolling combined with slow heating which exhibited distinct crystallographic texture and GBCD, needs a further investigation.

- More systematic thermomechanical processing should be studied in an attempt to increase the fraction of low $\Sigma$ boundaries and, at the same time, decrease the fraction of random boundaries in aluminum.

- The effect of impurities typically found in commercial alloys such as Fe, Si, etc. on intergranular corrosion should be examined by carefully adding controlled impurity levels.

- A more detailed study on the pit morphology as a function of acid concentration should be conducted.
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