PITTING CORROSION AND INTERGRANULAR CORROSION OF Al AND Al-Cu ALLOY SINGLE CRYSTALS AND BICRYSTALS

by

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ABSTRACT

Single crystals and bicrystals have been used to study pitting corrosion and intergranular corrosion of Al and Al-Cu alloys in 0.5M NaCl solution.

The critical pitting potential and pit density were examined as a function of a number of factors. These included crystallographic orientation; the bulk solution chemistry including Cl⁻ concentration, NO₃⁻ addition and pH; the effect of Cu alloying; and the effects of homogenizing and aging on the alloy crystals.

The susceptibility for pitting corrosion was found to depend on crystallographic orientation in pure Al with {111} showing maximum pitting and {011} and {001} exhibiting progressively less pitting. This crystallographic effect was not observed in the Al-3 wt% Cu alloy. The addition of Cu to pure Al was found to raise the Epit and produce a higher pit density on the surface. The increase of Cl⁻ concentration was found to enhance pitting corrosion, producing a higher pit density and lowering the Epit. Addition of NO₃⁻ to the solution decreases pitting corrosion, reduces the pit density and substantially shifts the Epit to a more noble potential.

A model of pitting corrosion is proposed, based on a local kinetic balance between the repassivation process and the dissolution process at the bare metal surface at the base of a preexisting oxide flaw on the crystal surface. The model successfully accounts for the observed effects of the Cu alloy addition, and the solution composition variations on pitting corrosion.

In the alloy bicrystals, it was observed that pitting corrosion in the grain boundary region was dependent on the composition and thermal history of the crystal. In most of the homogenized Al-Cu bicrystals, the presence of the grain boundary did not influence the pitting corrosion. In a 0.1 wt% Cu alloy with a tilt boundary of 28° about the <001> direction preferential pitting along the grain boundary was observed. The preferential pitting is attributed to nonequilibrium depletion of Cu at the high angle tilt boundary. Preferential attack is also observed at grain boundaries in as-grown and in aged bicrystals. This is attributed to Cu segregation in the crystals and the lower value of Epit associated with the Cu depleted regions.
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LIST OF SYMBOL AND ABBREVIATION

AES: Auger electron spectroscopy.
CW: Cell Wall of solidification substructure.
EDX: X-ray energy dispersive analysis.
EELS: Electron energy loss spectroscopy.
EPMA: Electron probe microanalysis.
Epit: Critical pitting potential.
Eprot: Protection potential.
GB: Grain boundary.
M23C6: M represents Fe or other solutes in the stainless steel.
PFZ: Precipitate free zone.
PPC: Potentiodynamic pitting corrosion test.
SCE: Saturated calomel reference electrode.
SIMS: Secondary ion mass spectrometry.
SEM: Scanning electron microscopy.
STEM: Scanning transmission electron microscopy.
TEM: Transmission electron microscopy.
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1. INTRODUCTION

Aluminium and its alloys are widely used engineering materials. The applications include structural, electrical, electronic, packaging, and transportation, particularly in the automotive and aerospace industries. The wide range of applications result from the favorable physical properties of aluminium, namely the low specific gravity, good strength and good general corrosion resistance. However, aluminium and its alloys, especially the high strength alloys, are highly susceptible to localized corrosion. These limit the application of the alloys in certain aqueous environments.

The general corrosion resistance of aluminium depends on the passivity of the surface oxide film. Pitting and intergranular corrosion occur under conditions where the film becomes locally unprotective. These conditions are often unexpected and can lead to failure of the component in service.

In the following sections, current mechanisms of pitting corrosion and intergranular corrosion will be discussed, referring specifically to aluminium and its alloys when possible.

1.1 Pitting Corrosion

Much research has been carried out related to corrosion and a number of mechanisms and theories have been proposed to account for pitting corrosion. However, none has been universally accepted. One reason for the differences among the mechanisms is that they often refer to different stages of the overall pitting process.

In many cases, pitting corrosion is attributed to local cell action in the presence of an electrolyte. The local anodic reaction is the dissolution of metal and the cathodic reaction is the evolution of hydrogen or reduction of oxygen. In an early paper, Mears and Brown suggested that local cell formation can be attributed to many possible factors, depending on the metal substrate, environment and cell arrangement.

Because many factors influence localized corrosion, the approach of various research groups is quite different. Some study structural dislocations that exist within the metal substrate, or flaws within the passive layer. Others concentrate on the thermodynamic and kinetic factors by using electrochemical techniques.
Recently, computer simulation\(^{(11)}\) has been applied to calculate the potential and electrolyte concentration at an electrode surface by using mass transport equations and assuming a simple geometry for the corrosion pit.

The major research areas on pitting corrosion, following Szklarska–Smialowska\(^{(4)}\), are listed below:

1. Determination of breakdown potential.
2. Studying the effect of alloying elements on pitting.
3. Studying the effect of electrolyte compositions.
4. Studying the effect of temperature, pH, cold working, heat treatment, etc.
5. Determination of the induction time for pit formation.
6. Determination of the metal sites most susceptible to pitting.
7. Observation of the shape of pits.
8. Kinetic studies of pit growth under potentiostatic and galvanostatic conditions.
9. Study of oxide films, i.e. structure, thickness, and conductivity.

1.1.1 General Theories of Pitting Corrosion

Pitting corrosion is a problem of particular concern with metals and alloys that rely upon a protective (passive) oxide film for corrosion resistance. It is manifested as a localized corrosion (pitting) on freely exposed metal surfaces in aqueous environments.

Pitting corrosion can usually be divided into two steps; pit nucleation and growth. Zaya\(^{(12)}\) has further divided pitting corrosion into four steps: (1) The occurrence of a localized break in the surface film. (2) The early development of a different solution chemistry within the restricted region of the break. (3) The widening of the pit to greater than atomic dimensions, and (4) the coarsening of the pit to macroscopic scale, e.g. millimeter dimensions.

In the following, theories of pitting corrosion will be reviewed. Many of the theories refer to different steps in the overall pitting corrosion process.
1.1.1.a Imperfection theory

The imperfection theory was proposed by Seligman and Williams\(^\text{13}\) in 1920. After immersing aluminium in hard water, these authors found that pitting corrosion only occurred if there were imperfections such as crevices, sub-surface cavities and surface cracks existing at the surface of the metal substrate.

Although the importance of surface imperfections as sites for pit initiation is well known, it is not a necessity for pitting corrosion to occur. The imperfection theory was discounted after the observations by Pearson et al.\(^\text{14}\) in an electron microscope study of pitting corrosion of aluminium. These authors found that pits in aluminium can form independent of surface irregularities. Therefore, other factors such as surface pretreatment\(^\text{15,16}\) have to be taken into account. Depending on pretreatment, aluminium may have a thin or a thick surface oxide film which varies from the thin air-formed film to the few micrometers thick film formed by anodizing. Pitting corrosion requires that a break occurs in this passive film which may result from surface imperfections in the matrix.

1.1.1.b Flaw Induced Breakdown of Oxide Film

Wood et al.\(^\text{17-20}\) have shown that exposure of aluminium to halide solutions causes a crack/heal type process to occur at the base of the flaws in the covering oxide film, transiently revealing bare substrate metal which can then either dissolve or repassivate. This occurs independent of the composition of the oxide film.

The sources of "flaws"\(^\text{17}\) can be "mechanical flaws" which occur at scratches and other surface irregularities and are thought to be predominant in air-formed films. The other source can be "residual flaws" which are produced during film growth and are associated with solute segregation and second phase precipitation, where the growth and integrity of the overlying film is effected. The "residual flaws" are believed to be predominant and persist even in thicker anodized films. According to Wood, the evidence for flaws and their role in breakdown of the passivity of aluminium induced by air-formed and anodic films are summarized as follows:

1. Flaws in oxide films stripped from aluminium have been observed by electron microscopy\(^\text{20}\).
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2. Flaws in air-formed and anodized films are exposed by copper decoration (20).
3. Evolution of hydrogen and oxygen at specific locations on the electrode surface.
4. Impedance changes could be best explained in terms of flaws developing into pits and undermining the surface (19).
5. The superimposed fluctuations on the steady drop of electrode potential in the active direction (becomes more negative) upon immersion of aluminium in chloride solution can only be realistically interpreted in terms of rapid exposure of bare metal at preexisting flaws.
6. No chlorine contamination of the film, either by an anion exchange process or by a field induced entrance mechanism, is detected by using the Secondary Ion Mass Spectrometry (SIMS) technique (21).

Wood et al. (17) in their model did not consider "pit initiation" as a separate and distinct process from the "pit propagation" process. Instead, the authors considered that the pit propagates rapidly from the instant of immersion in the solution and achieves the highest rate when the cathode/anode area ratio for the electrode is greatest. The authors also considered that pitting can occur during induction periods and below the pitting potential. The pitting potential only represents the stage at which the potentiostat has to support a sudden increase in current due to the change in anode/cathode area ratio on the specimen.

The flaw induced breakdown of the oxide film model provides a feasible pitting mechanism for the metals which exhibit active passive transitions. However, there has been criticism in the interpretation of the impedance results because of doubts concerning the analog methods used to calculate the solution resistant and the double layer corrections (22). In addition, de Wexler and Galvele (23) showed that neither the existence of preformed flaws, nor the mechanical breakdown of the passive film, could explain pitting nucleation in the electrochemical pitting processes. They found that no pit nucleation occurred at slip steps in an intentionally broken oxide film if the potential was lower than the pitting potential.
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1.1.1.c Ion Penetration Mechanism

The passive film in this model is considered to be an oxide layer of finite thickness and not an adsorbed oxygen film. Penetration of anions or cations through the oxide film is necessary for attack to occur.

Britton and Evans (24), in an early paper, suggested that the specific pitting tendency of the chlorine ion was due to its smaller diameter which permitted it to penetrate the oxide layer. By observing the current flow between two aluminium sheets in potassium dichromate solution containing various salts, Britton and Evans (25) found that the magnitude of the current flow decreased in the order:

\[ \text{KCl} > \text{KBr} > \text{KI} > \text{KF} > \text{K}_2\text{SO}_4 > \text{KN}03 > \text{Na}_3\text{PO}_4. \]

It was concluded that the current flow was a direct measure of the ability of the various anions to penetrate the oxide layer on the aluminium surface. However, it was found later that the order of current flow was not in complete accordance with the order of the ionic radii.

\[ \text{F}(1.36 \text{ Å}) < \text{Cl}(1.81 \text{ Å}) < \text{Br}(1.95 \text{ Å}) < \text{I}(2.16 \text{ Å}) (26) \]

Therefore, the penetration mechanism as proposed by Evans is questionable.

Rosenfeld and Danilov (27) suggested that the breakdown of the oxide film was caused by the exchange adsorption of oxygen by chloride ions at sites where the metal-oxygen bonding is weakest. Any anion which displaces oxygen from the oxide surface, penetrates into the passive film and concentrates at the metal-film interface is capable of causing pit initiation.

Hoar and Jacob (28) on the other hand, proposed a model involving anion penetration without oxygen exchange. They suggested that under the influence of the electrostatic field across the oxide-solution interface, the halide ion adsors on the oxide film surface and penetrates the oxide film without exchange with oxygen in the oxide lattice site. The authors also attributed the critical electrostatic field to be the pitting potential. Consequently, the smaller ions penetrate the lattice more readily.
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Conflicting experimental evidence regarding the ability of the aggressive ions to penetrate the oxide film was presented by Burwell and May(29). These authors measured the permeability characteristics of a stripped aluminum oxide film and showed that chloride and nitrate ions penetrated the oxide film at the same rate, even though their effect on pitting are quite different. Therefore, it could be concluded that the ability of ions to penetrate the oxide film is not responsible for the special aggressiveness of the halide ions.

Hoar and Jacob(30) in a final improvement of their theory, considered that three or four halide ions jointly adsorb on the oxide film surface around a lattice cation. The transitional complex thus formed will be of high energy and the probability of its formation at any instant will be very small. Once formed, however, the complex is ready to dissolve into the solution. Under the anodic field, another cation migrates through the film to replace the cation vacancy. The constant anodic field is stronger at the thinned sites where the replacement cations meet with more halide ions, complex with them and dissolve away. The process is repeated catalytically. Thus, once localized breakdown starts with the initial transitional complex, it accelerates "explosively".

One important factor that has not been considered by the above theories is the stoichiometry of the oxide film. The aluminum oxide film is stoichiometric in nature and may hinder diffusion of ions through the film. In this regard, Beck et al.(31) suggested that the oxide film consists of the stoichiometric $\gamma$-Al$_2$O$_3$ unit cells. Each cell contains 32 oxygen ions in an FCC lattice. At stoichiometry, there must be an average of 21 and 1/3 uncharged cation vacancies per unit cell.

Pryor(32) proposed a model based on the migration of aluminum ions through the stoichiometric $\gamma$-Al$_2$O$_3$ oxide film of poorly developed long ranged order. Aluminium ions dissolve in solution in order to preserve electrical neutrality after exchange of chloride ions in solution with oxygen in the oxygen lattice. In an immersion test in sodium chloride solution, Pryor found that no corrosion of the aluminum, thinning or other topographical modification of the aluminum oxide film was detected. Also, impedance measurements at low frequency dropped substantially while unchanged at high frequency. The results were interpreted by the author as showing that upon immersion in NaCl solution, a drop in ionic resistivity of the film occurred, but that there was no change in its electronic resistivity. This was attributed to the exchange of chloride ions from solution with oxygen ions from the oxide lattice, with electrical
neutrality being maintained by removal of 1 aluminium ion from the lattice into solution for each replacement of 3 oxygen ions by 3 chloride ions via equation 1.1:

$$\text{Al}_3^+(\text{L}) + 3\text{O}_2^-(\text{L}) + 3\text{Cl}^-\text{(S)} + 6\text{H}^+ = \text{Al}_3^+(\text{S}) + 3\text{Cl}^-\text{(L)} + 3\text{H}_2\text{O} \quad \ldots \ldots \ldots \ldots \quad (1.1)$$

In equation (1.1), (L) represents a lattice site and (S) the solution. As a consequence, chloride ions remain in the lattice of the oxide film, and additional uncharged cation vacancies are created, which permit enhanced rates of transport of aluminium ions through the $\gamma$-Al$_2$O$_3$ oxide film.

Substitution of chloride ions is expected to be most easy in the vicinity of preexisting anion vacancies or at locations in the oxide containing substantial quantities of substituted hydroxyl ions(33). These locations were hypothesized to be in the regions of high concentrations of impurity, at certain favorably oriented grain boundaries and, perhaps, at the emerging edge dislocations in the substrate metal surface. The nonuniform substitution of chloride ions will result in an equivalent nonuniform distribution of additional cation vacancies. This causes locally enhanced migration of aluminium ions and eventually leads to the initiation of pitting corrosion.

Questions(34) have been raised about the experimental technique of Pryor and the lack of a satisfactory explanation for the localized nature of pit initiation. Also, it is difficult to understand why the negatively charged oxygen ions could migrate in the oxide layer away from the metal, which is contrary to the electrostatic field(35).

One most important consequences of the penetration theories is the contamination of the oxide film by the chloride ions. Following the recent introduction of new surface analytical techniques, extensive surface composition studies have been carried out on aluminium which have given contradictory results. Many authors reported the incorporation of chloride in the passive film(36,37), while others reported no such contamination(38).
1.1.1.d Adsorption Mechanisms

1.1.1.d(1) Competitive Adsorption Mechanism

Kolotyrikin(39) considers passivity to be the adsorption of an oxygen layer on the metal surface. The author proposed that pit initiation was caused by a reversible competitive adsorption of chloride ions and oxygen for sites on a passive metal surface. Once in contact with the metal surface, chloride ions favour hydration of metal ions and enhance its dissolution into the electrolyte, resulting in pit formation. The author postulated that where the pit initiation occurs, an irregular current distribution exists in the metal surface due to the local heterogeneity. Therefore, more chloride ion adsorption occurs on the same locations and this in turn causes an increased metal dissolution and propagation of pits. The pitting potential, in this case, is considered as the minimum electrode potential at which aggressive anions are able to reversibly replace the passivating oxygen on the metal surface. This mechanism appears to be unlikely since, as mentioned previously, there is abundant evidence(40) that aluminium metal in a neutral solution is covered with a thin persistent air-formed film.

1.1.1.d(2) Adsorption - Mechanical Breakdown

Hoar(41) proposed that as anion adsorption on the oxide film proceeds, the interfacial tension, or interfacial free energy of the oxide/solution interface is progressively lowered by the mutually repulsive forces between the charged particles. Eventually, the interfacial tension is so far lowered that a kind of peptization by interfacial change occurs - the adsorbed anions push one another, and force apart the oxide to which they are strongly attached. Any crack or split so produced in the film immediately undergoes more anion adsorption on to its sites and the process is continued. Finally, direct attack of the exposed metal occurs, resulting in pit initiation.

The mechanism is theoretically possible. However, there is a lack of supporting experimental evidence.

1.1.1.d(3) Adsorption-Complexing-Oxide Thinning-Direct Metal Attack Mechanism

Other adsorption theories consider passivity as an oxide film covering the metal surface. Adsorption of chloride ions on this oxide film occurs upon immersion into the
The adsorbed ions complex with the metal ions on the oxide surface, leading to the thinning of the oxide film by dissolution of the chloride complex salt.

One of the theories belonging to this classification was proposed by Foroulis. By using the Engell-Stolica method for measuring pit initiation on pure Al in a neutral solution, Foroulis concluded that electrochemisorption of chloride ions occurs during passivity breakdown. The author suggested that chloride ions migrate through the double layer under the influence of the electrostatic field and partially replaced OH and water molecules which normally are adsorbed on the passive film surface. At the critical pitting potential, the adsorbed chloride ions combine with the ionized hydrated oxide surface to form a soluble basic aluminium chloride salt via the following reaction:

\[
\text{Ionization of the hydrated oxide surface:} \\
\text{Al(OH)}_3 = \text{Al(OH)}_2^+ + \text{OH}^- \quad (1.2)
\]

and complex salt formation

\[
\text{Al(OH)}_2^+ + \text{Cl}^- = \text{AlCl(OH)}_2 \quad (1.3)
\]

The basic aluminium chloride salt so formed goes directly in solution much more readily than the aluminium cations present in the hydrated oxide film. Consequently, thinning of the oxide film occurs.

This process of field assisted chloride ion adsorption, formation of a soluble aluminium chloride basic salt, and localized oxide dissolution will have a high probability of repeating itself at the same sites, because at constant anodic potential, the electrostatic field will be stronger at the thinned sites. Thus, the localized oxide thinning process is likely to continue until the oxide film is locally dissolved. Once this happens, direct dissolution of the substrate metal begins and a pit initiates. The author suggested

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1 In the Engell-Stolica method, the aluminium electrode is potentiostated in the passive range, a known concentration of an aggressive anion is injected into the solution, and the induction time for pitting is measured. A relationship between the induction time and the concentration of aggressive anion allows an estimation to be made of \( n \), the number of anions associated with a single surface site during the primary pitting process.
that oxide defects, such as scratches, voids, pores or other flaws where the oxide thickness is smaller will be the initial chloride adsorption sites.

In the same manner, Nguyen and Foley\(^{(44)}\) proposed a mechanism in which aluminium halide complex salt formation is considered to be the critical step. The authors reported that the stoichiometry of the aluminium complex is pH dependent. In a number of experiments, it was found that the pattern emerged of a high number of halides in the complex in acid solution, e.g., \(\text{AlX}_4^-\), a number of unity in neutral solutions, i.e. \(\text{AlX}^-\), and an intermediate number in the pH range of 3 to 5 where \(X\) represents the aggressive halide ions. The pH influences the intermediate complex formed during the pitting process.

Both groups assumed the critical pitting potential to be the minimum potential required for electrochemisorption of chloride ions on the oxide surface sites.

1.1.1.e Autocatalytic Mechanism

The autocatalytic theory of pitting was first proposed by Hoar\(^{(45)}\) in 1947. The author suggested that a pit propagates as a result of the decrease in pH that takes place locally at the anodic regions, which hinders the repassivation process.

During corrosive attack in an electrolyte containing aggressive ions, metal actively dissolves according to the following reaction:

\[
\text{Al} = \text{Al}^{3+} + 3\text{e}^- \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (1.4)
\]

followed by hydrolysis of the \(\text{Al}^{3+}\):

\[
\text{Al}^{3+} + 3\text{H}_2\text{O} = \text{Al(OH)}_3^+ + 3\text{H}^+ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad (1.5)
\]

Therefore, the pH of the solution at the pit site will decrease corresponding to reaction (1.5). This is accompanied by an increase in the \(\text{Cl}^-\) ion concentration inside the pit due to the electromigration of negative charge ions in order to maintain electrical neutrality within the electrolyte in the pit. Therefore, corrosion attack is accelerated and localized in the pit.

Although the autocatalytic theory has been applied successfully to elucidate pit propagation, it does not elucidate clearly the pit initiation process.
1.1.2 Effect of Crystallographic Orientation on Corrosion Behavior of Active-Passive Metals

1.1.2.a FCC Metals

Latanision and Oppenhauser(46) studied the steady state potentiostatic polarization of low index nickel single crystal surfaces in 1 M H$_2$SO$_4$ and found a strong anisotropy in passive current densities which was related to crystal growth direction. For crystal growth parallel to the $<110>$ axis, the degree of protection provided by the passive film on a $\{111\}$ surface was greater than that on either the $\{110\}$ or the $\{100\}$ faces, i.e., the passive current densities were in the order: $\{111\} < \{110\} < \{100\}$. On the other hand, the authors observed a reverse dependence in passivation current density when the growth direction of the single crystal was parallel to the $<100>$ axis. The results were explained by considering the dislocations in the crystal generated during growth. The density of active sites on a particular crystal face might depend on the distribution and character of dislocations intersecting that surface. Consistent with the former observation, Gwathmey and Lawless(47) reported that the relative rates of gaseous oxidation of the various crystal faces of nickel are in the order:

$$\{111\} < \{110\} < \{100\}.$$

By the application of dislocation etching techniques, Schatt and Worch(48) found that the etch pits produced by anodic potentiostatic polarization of nickel single crystals in chloride solutions might be assigned to emergent sites of dislocations on the surface. It was also found that the active sites were formed preferentially at sub-boundary branching and, to a lesser degree, within sub-grains. On the other hand, Yagupolskaya and Movchan(49) found that the $\{110\}$ face of nickel was more highly oxidized than the $\{100\}$ or $\{111\}$ faces. This ease of oxidation of $\{110\}$ was attributed to the greater number of dislocation intersections with the less densely packed plane and also to the ease of chemical sorption of oxygen on this plane.

Arora and Metzger(50) studied the anisotropic corrosion rate of annealed, coarse-grained polycrystalline sheet aluminium in 16% HCl solution. They found that the corrosion rate was greatest in grains with crystal planes orientated near $\{111\}$ planes, and least on surface planes near $\{100\}$. This orientation dependence was consistent with the results of Orem(51) who performed corrosion tests by immersing aluminium single
crystal spheres and disks in an aqua regia-hydrofluoric acid mixture (65 ml HCl, 35 ml HNO₃, and 5 ml 48% HF). The etch pits observed were bounded by \{001\} planes and the relative corrosion rates were in the order of \{111\} > \{110\} > \{100\}.

1.1.2.b BCC Metals

Kruger(52) immersed iron single crystals of low index planes in distilled water and observed that the \{110\} plane had the greatest number of pits per unit area. The order of decreasing pitting susceptibility was \{110\} > \{100\} > \{111\}. In a later paper(53), by using copper decoration and transmission electron microscopy techniques, Kruger was able to demonstrate the effect of crystallographic orientation on the number of sites of breakdown. He found that the closest packed \{110\} planes exhibited the largest number of pits, confirming his earlier finding(52). In addition, it was found with the Cu decoration technique that there was not a one-to-one correspondence with the cathodic sites observed on the same surface prepared under two different conditions (i) un-passivated and (ii) passivated prior to the decoration. Thus, the author concluded that the phenomena observed on passivated surfaces was dependent on the properties of the film which, in turn, was affected by the iron substrate. The author also found that the sites of breakdown in the passive film were not related to dislocations.

On the other hand, Haruyama et al.(54) in an examination of the potentiostatic transient current on iron whiskers in a chloride-containing solution at low anodic potential, 200 mV, observed random current pulses. These were attributed to the breakdown and repassivation of the passive film on a substantially dislocation free whisker as pitting occurred on the twisted whisker. They concluded that the breakdown of a passive film could occur at physical or chemical inhomogeneities anywhere in the film, but pitting corrosion could occur only when the breakdown was located at the emergent dislocation sites in the substrate.

Fontana et al.(55) reported that the dissolution rate of the iron whisker with a \{110\} plane was greater than that of a \{100\} plane and that the dissolution kinetics followed a mechanistic analysis based on the "Terrace-Step-Kink" surface model.
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1.2 Intergranular Corrosion

1.2.1 Historical Background

Most heat treatable high strength aluminium alloys are susceptible to intergranular corrosion, depending upon the heat treatments that have been performed on the alloys. Intergranular corrosion is a type of localized attack producing rapid dissolution at the grain boundary.

The intergranular corrosion of Duralumin sheet used in aircraft was first reported by Rawdon et al. (56), and the intergranular corrosion of aluminium alloys was a matter of concern among aerospace engineers. The cause of the problem has been attributed to improper heat treatment, particularly the quality of quench following solution heat treatment. Several methods have been developed to improve the corrosion resistance of the alloys, including coating or cladding of pure aluminium to 2017-T4 sheet. However, the advantages of these sprayed or Alclad products can not be realized because parts are machined frequently from thick plate and extruded sections. Therefore, beginning in the 1950’s and continuing to date, special tempers (i.e. temper to the overaged condition) have been introduced to assure the corrosion resistance.

Changes in microcomposition and microstructure have been related to the improvement and have become a matter of research interest. The susceptibility to intergranular corrosion is considered to be a result of the chemical composition or microstructure variation near the grain boundary and in the grain boundary itself. Therefore, any added alloying or included impurity solute or heat treatment that influences the segregation and precipitation of the solute can influence the susceptibility to intergranular corrosion of the alloys.

In the following sections, we shall discuss the mechanisms of intergranular corrosion, the effect of segregation on it, and the factors that influence the solute segregation, especially the grain boundary misorientation.
1.2.2 Experimental Evidence of Intergranular Corrosion

Many engineering alloys (e.g., aluminium alloys and stainless steels) are susceptible to intergranular corrosion, whereas, metals of high purity usually do not suffer from this type of attack. A trace amount of impurity segregated at the grain boundary will be sufficient to allow local electrochemical differences to be established. Also, a grain boundary may be expected to be more reactive than that in the grain because the grain boundary is a relatively distorted region. Thus, the grain boundary may possibly be corroded even in the absence of segregated impurities, although usually the strain energy at the grain boundary does not contribute significantly to intergranular corrosion.

Lacombe and Yannaquis have shown that the attack of high purity aluminium by 10% HCl occurred at grain boundaries where there was a large misorientation. In contrast, Metzger and Intrater have shown that iron tends to segregate to the grain boundaries in aluminium inducing the intergranular corrosion problem. Moreover, Perryman has shown that 0.009% Fe in aluminium is enough to cause intergranular corrosion, the degree depending on the heat treatment of the alloys.

Aust and Iwao found that increasing the minor impurities (Cu, Sn and Ti up to 100 ppm) addition to aluminium increased the corrosion rate both at the grain boundaries and at the matrix surfaces for coarse grained and bicrystal specimens in 16% HCl solution. The corrosion rate was in the decreasing order Al-Cu > Al-Sn > Al-Ti. The authors attributed the corrosion of Al-Cu to an autocatalytic effect while the non-equilibrium solute segregation induced by vacancies in addition to the autocatalytic effect, was held responsible for the corrosion of the others.

The susceptibility to intergranular corrosion of aluminium alloys is also associated with the precipitation and segregation of phases at grain boundaries. It can be summarized as follows:

(a) In Al-Mg alloys (5000 series), the grain boundary precipitate is β phase, Mg5Al8. It tends to form a continuous layer and, being strongly anodic to the grain, can cause considerable intergranular corrosion.
(c) In Al-Cu (2000 series), the equilibrium grain boundary precipitate is θ phase, CuAl$_2$, which is accompanied by a solute depleted zone. The intergranular corrosion is heat treatment dependent and is usually observed in alloys aged before peak hardness.

(d) In Al-Zn-Mg (7000 series), the equilibrium grain boundary precipitate is η phase, MgZn$_2$ or τ phase, (AlZn)$_{49}$Mg$_{32}$\textsuperscript{6}. Possible segregation of Mg and Zn at the grain boundary also has a detrimental effect in intergranular corrosion resistance, the elements Cr, Zr or Mn accelerate the precipitation sequence in these alloys\textsuperscript{66}, because they precipitate during solution heat treatments and act as nuclei for the later heterogeneous precipitation within the grain, thereby increasing the intergranular corrosion resistance\textsuperscript{67}. Depletion of the minor alloying element Cu (included in η phase) from the grain boundary region is also considered as the reason for susceptibility to intergranular corrosion\textsuperscript{68}.

1.2.3 Theories of Intergranular Corrosion

There are several theories to account for the intergranular corrosion. These include:

1. Theories concerning the galvanic effects
   (a) Solute depletion theory.
   (b) Segregation of impurity at the grain boundaries
   (c) Precipitation of second phases.
   (d) Autocatalytic theory.

2. Theory concerning the Difference in pitting potentials between matrix and grain boundary regions.

3. Strain theory.
1.2.3.a Theories Concerning the Galvanic Effects

Galvanic corrosion is a type of accelerated corrosion by the electrical contact between two dissimilar metals in the presence of an electrolyte. Galvanic couples arise from several sources. These include:

(i) The use of dissimilar metals in structural components.
(ii) The application of noble or sacrificial coatings to a base alloy.
(iii) The re-deposition of noble metal ions which have been dissolved in the environment on part of a metal.
(iv) The segregation or depletion of impurity or alloying solute.
(v) The occurrence of precipitation of second phases.

In the following sections we shall review the theory of intergranular corrosion produced by solute re-deposition, segregation and precipitation of second phases only, as these are relevant to the present study.

1.2.3.a(1) Solute Depletion Theory

One of the earliest and most widely accepted theories for intergranular corrosion is the solute depletion theory. The susceptibility to intergranular corrosion of Al-Cu alloys was attributed by Mears et al.\(^\text{(69)}\) to the difference in corrosion potentials between the matrix and grain boundary regions.

This theory was based on two observations. First, it was found by Dix\(^\text{(70)}\) that precipitation at the grain boundaries was easier than within the grains, and the precipitates were found to be surrounded by narrow zones that etched smoothly in 1% NaOH solution. Secondly, the work of Edwards et al.\(^\text{(71)}\) showed that in chloride solutions pure aluminium was more reactive than many of its alloys, particularly Duralumin, whereas Brown et al.\(^\text{(72)}\) showed that the retention of 5% Cu in solid solution moved the electrode potential of aluminium about 200 mV in the cathodic direction.

Ageing the alloys at an elevated temperature causes the grain boundary precipitation of copper rich constituents from the supersaturated solid solution, altering the potential in the anodic direction. Initial precipitation of discrete particles occurs in
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the grain boundaries and copper depleted zones develop adjacent to the boundaries. In a corrosive electrolyte containing chloride ions, electrochemical attack occurs in the copper depleted grain boundary regions. The severity of the grain boundary attack is also accelerated by the large relative area of cathodic sites, (matrix) to anodic sites, (Cu depleted zone).

This theory has been confirmed by Garner and Tromans(73). They were able to observe directly by transmission electron microscopy the same areas of Al-4% Cu foils before and after corrosion in an oxidizing chloride solution. The under-aged samples underwent localized attack at the grain boundary regions and adjacent to the grain boundary precipitates. They concluded that the localized attack was responsible for the intergranular corrosion.

However, there had been no direct evidence of the solute depletion until the development of quantitative high spatial resolution microanalysis techniques. Also, the solute depletion theory can not explain the occurrence of intergranular corrosion of as-quenched high purity Al-Fe alloys(°T), which do not contain precipitates.

1.2.3.a(2) Segregation Theory

The effect of impurity on intergranular attack of Al-Fe alloys as a function of iron content up to 0.055% Fe has been investigated by Perryman(61). It was found that in the as-quenched material, the rate of intergranular attack in 0.3N NaOH and 10% HCl increased with increasing Fe content. The effect was attributed to the equilibrium segregation of Fe at the grain boundary. The ratios of width to depth of the corroded grooves were found greater than that in the case of Al-Cu for which the depletion theory is applicable. Such groove shapes are consistent with the grain boundaries being cathodic to the grains, and indeed, if the iron concentration at the grain boundaries is greater than that within the grains, the grain boundary would be expected to be cathodic to the grains. Consequently, as observed by Evans(74), the corrosion current density will decrease gradually under these conditions as one goes farther away from the cathodic grain boundary.
1.2.3.a(3) Precipitation of Second Phases

Kinzel(75) proposed that in austenitic stainless steel, the M23C6 precipitates are more noble than the matrix, thus setting up a potential difference at the carbide-matrix interface and encouraging electrochemical attack. Stickler and Stickler and Vinkier(76) found that the potential difference between M23C6 and austenite depended upon the electrolyte used. The carbide exhibited a much more positive value than austenite when tested in Strauss solution. The reverse situation, (the austenite being more noble than the carbide), existed when the test was conducted in Huey solution. These observations have been used to account for the effect of the different solutions on the intergranular corrosion of stainless steels.

The precipitation of CuAl2 in the Al-Cu system is cathodic to the α phase and hence considered to have a similar effect.

1.2.3.a(4) Autocatalytic Theory

Arora and Metzger(77,78) showed that aluminium containing 20 ppm Cu, when immersed in hydrochloric acid had an autocatalytic acceleration effect on the grain boundary corrosion. The effect was attributed to catalytic boundary corrosion. The effect was attributed to catalytic stimulation of the boundary corrosion rate by the deposition of copper from the Cu ions that were introduced into the acid by corrosion of the alloy. The deposition occurs as patches of elemental copper on the alloy surface and enhances the corrosion rate by providing cathodic areas with lower hydrogen overvoltage. The effect is "autocatalytic" because the copper deposit is a product of the corrosion reaction.

It was suggested that such an autocatalytic reaction is significant even with 1 ppm Cu in aluminium, since Mintariol(79) observed slower intergranular and general attack at 0.06 ppm Cu than at 2 or 4 ppm.

2 Strauss solution is a boiling copper sulfate sulfuric acid solution containing 100 g/l CuSO4 and 100 ml/l H2SO4.

3 Huey solution is a boiling nitric acid solution containing 5N HNO3 and 4 g/l Cr6+ as K2CrO4.
Metzger and Arora\(^{78}\) concluded that it is necessary to identify and separate any autocatalytic effects occurring in order to make a meaningful statement about intrinsic boundary corrosion rates. From the grain boundary penetration rate vs time curves, he pointed out that the autocatalytic effect would appear in the later stages in which the corrosion rate was accelerated.

However, in a later paper by Hendrickson and Metzger\(^{80}\), it was stated that one could not determine the intrinsic boundary corrosion from the early stages from the penetration-time curves because the corrosion state of the specimen is mixed in this period. Some boundaries still have entirely intrinsic corrosion while some have autocatalytic corrosion along part of their length. Therefore, caution is necessary in separating "intrinsic" boundary corrosion rates from autocatalytic effects. Also, there are still some questions about whether this theory is applicable to the intergranular corrosion of aluminium when the bulk impurity concentration is of the order of ppm.

1.2.3.b Difference in the Pitting Potential

Galvele et al.\(^{81,82}\), have shown that the behavior of intergranular corrosion of Al-Cu alloys could be related to the pitting potential of the individual constituents of the microstructure near the grain boundary. The pitting potential was increased by more than 100 mV in the noble direction by the addition of 4% Cu to aluminium. Furthermore, the pitting potential was reduced as compared to the as-quenched alloy upon ageing. At the peak hardness condition, the pitting potential found was equal to the value for the 0.5% Cu alloy. This concentration was the copper content of the Cu-depleted zone at the grain boundary\(^{83}\). These results led the authors to conclude that the change in pitting potential during ageing of Al-Cu alloy is due to changes in the composition of the solute depleted zone adjacent to the precipitates at the grain boundary. They also pointed out that a difference in pitting potentials between the grain boundaries and grains is a necessary condition for intergranular corrosion to occur.

This mechanism has also been applied to explain the intergranular corrosion behavior of 7075 alloy by Maitra et al.\(^{84}\). However, they assumed that the enrichment of detrimental alloying elements (Zn and Mg) at grain boundaries occurred as a result of the equilibrium segregation instead of solute depletion.
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### 1.2.3.c Strain Theory

Kinzel(75) observed that the intergranular corrosion of sensitized steels was accompanied by knife edge attack on one side of the carbide austenite interface. Based upon crystallographic consideration, this was attributed to the result of strains existing at the interface.

Streicher(85) and Coriou et al.(86) also suggested that the strain energy associated with grain boundaries provides the driving force for intergranular corrosion.

### 1.2.4 Effect of Heat Treatment on Intergranular Corrosion

Heat treatment has a pronounced effect on the susceptibility to intergranular corrosion of aluminium alloys through its influence on the microstructure. Al-Cu alloy will be discussed as a typical example.

The Al-Cu alloys are not found to be susceptible to intergranular corrosion in the as-quenched condition but are susceptible to attack in the under-aged condition, the degree of susceptibility is reduced upon further ageing to the over-aged condition. The effect of heat treatment can be explained either by the solute depletion theory or the mechanism based on the difference in pitting potential.

Brown et al.(69), using a masking technique, were able to measure the potential differences between the grain boundaries and the grains. They found that the maximum potential difference occurred for the under-aged condition.

This difference was reduced upon further ageing. By direct electron micrographic observation, Garner and Tromans(73), found that in the under-aged specimen, θ-phase equilibrium precipitates with accompanying copper depleted zones were formed on the grain boundaries but not in the grains. Thus, copper depleted anodic sites will be restricted to regions close to the grain boundary precipitates, resulting in intergranular corrosion. In the overaged condition, matrix precipitation will have progressed through a typical ageing sequence to a stage at which precipitates are widespread throughout the matrix. The matrix precipitates now have accompanying significant copper depleted zones. Therefore, anodic sites are distributed throughout the matrix, and attack is no
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longer confined to the grain boundary regions. In the over-aged condition, the alloys exhibits a two-phase structure. (CuAl₂ precipitates and Al-0.2% Cu solid solution). Accordingly, alloys with this structure should show strong pitting corrosion in both the grain boundaries and the grains at potentials higher than the pitting potential of Al-0.2% Cu solid solution.

### TABLE 1

Relation Between Pitting Potentials and Intergranular Corrosion in Solutions Other than NaCl

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>V(NHE)</th>
<th>Intergranular corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>4%-Cu</td>
</tr>
<tr>
<td>1 M NaCl</td>
<td>- 0.52</td>
<td>0.39</td>
</tr>
<tr>
<td>1 M KBr</td>
<td>- 0.42</td>
<td>- 0.28</td>
</tr>
<tr>
<td>1 M KI</td>
<td>- 0.26</td>
<td>- 0.13</td>
</tr>
<tr>
<td>1M NaClO₄</td>
<td>- 0.17</td>
<td>+ 0.03</td>
</tr>
<tr>
<td>1M NaNO₃</td>
<td>+ 1.80</td>
<td>+ 1.85</td>
</tr>
<tr>
<td>1M Na₂SO₄</td>
<td>&gt; + 3.00</td>
<td>&gt; + 3.00</td>
</tr>
<tr>
<td>1M H₂SO₄</td>
<td>&gt; + 3.00</td>
<td>&gt; + 3.00</td>
</tr>
<tr>
<td>0.1M NaIO₃</td>
<td>&gt; + 3.00</td>
<td>&gt; + 3.00</td>
</tr>
<tr>
<td>1M Ammonium</td>
<td>&gt; + 3.00</td>
<td>&gt; + 3.00</td>
</tr>
<tr>
<td>tartrate</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In parentheses, potentials at which the intergranular corrosion susceptibility was tested. After Galvele et al. (81).
1.2.5 Effect of Anions on Intergranular Corrosion

Localized corrosion of pure Al and as-quenched Al-4% Cu, which simulate the Cu-depleted zone at grain boundaries and the grains, respectively, have been studied in several solutions by Galvele et al. (81). As shown in Table 1, intergranular corrosion was observed only in solutions containing halide ion, e.g. Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), or ClO\(_4\)\(^{-}\) and when there was a difference in pitting potentials between the two phases.

The pronounced effect of halides on corrosion behavior was suggested to be due to the superior diffusiveness of halide ions in the oxide lattice and to their ability to promote breakdown of the oxide film.

1.2.6 Experimental Evidences of Grain Boundary Segregation

Several grain boundary segregation and depletion studies have been carried out on aluminium base alloys using various microanalytical techniques. (Al-7% Mg(87), Al-Cu(88,89), Al-Zn-Mg and Al-Cu-Si alloys(90)).

Solute depletion of copper near the grain boundary in Al-4.1% Cu has been studied by both electron energy loss spectroscopy (EELS) and X-ray analysis(89,91) of electron transparent film* with excellent agreement.

The amount of solute depletion and the width of depletion zone have been related to the stress corrosion properties.

In Al-Zn-Mg alloys, Doig and Edington(92-94) reported the Mg concentration profiles across the grain boundaries in as-quenched, under, peak, and over-aged conditions. By monitoring the energy loss spectra of the transmitted electrons, they were able to determine the spatial distribution of Mg as the electron beam was traversed across the grain boundaries. For as-quenched specimens, the authors found a concentration of Mg at the grain boundary approximately 1 wt% above that of the bulk. The segregation extended about 70 nm on both sides of the grain boundary. In contrast, an oil quenched specimen shown a depletion of Mg in the precipitate free zone (PFZ), the Mg content

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* This technique is conducted in the transmission electron microscope (TEM) using a very narrow electron beam. The X-rays generated may be analysed by wave length dispersive spectroscopy(WDS) or energy dispersive spectroscopy(EDS).
decreasing from the bulk value of 3.2% to about 1.5% at the grain boundary. The above results were interpreted by considering that in the slowly cooled or over-aged condition, a major portion of Mg at the grain boundary combines to form the MgZn2 precipitates, leaving the region between the precipitates depleted in Mg. In the rapidly quenched specimens, segregation occurs as a Mg solute enrichment without visible precipitation.

This localized Mg enrichment is similar to that reported by Cundy et al. (87), for Al-7wt% Mg water quenched from 540°C. The Mg enrichment around the grain boundary in water-quenched alloys cannot be explained by equilibrium segregation. However, it can be accounted for by a high vacancy flux to the grain boundary which acts as an efficient sink during the quench. This vacancy flux causes the slow moving solute atoms to move towards the boundary.

Similarly, Malis and Chaturvedi (95) showed the segregation of Mg atoms to a level 2 to 3 times higher than the alloy composition, uniformly distributed along the grain boundaries in the as-quenched state.

These results are in contrast with those obtained with Auger electron spectroscopy (AES) by Green and Montague (96). AES and argon ion sputtering were used to obtain the chemical depth profiles of grain boundary fractured surfaces of as-quenched, peak and over-aged samples. The AES measurement showed an accumulation of Mg at the grain boundary under all conditions.

The apparent controversy is resolved (97) when one realizes that the narrow electron beam EDS technique (95) provides near boundary composition, while AES provides the average composition of grain boundaries in specimens fractured in the intergranular mode. Figure 1 shows a schematic diagram illustrating the various contributions to the measured Mg depth profile of the over-aged samples in AES. The total Mg profile (Curve a) measured by the AES analysis would be the sum of the profile at the grain boundary (curve b), the profile between the precipitates (curve c), and the profile of the precipitate (curve d). Curve c would be that measured by Doig and Edington by the TEM-EELS between two grain boundary precipitates. However, Raghavan (98) by using STEM-EDS, showed that little or no depletion of Zn or Mg in an air cooled Al2.2At%Zn-4.7At%Mg was observed. Upon ageing, solutes (Mg and Zn) were depleted increasingly with ageing time.
Solute segregation of Zn, Mg, Cu and Si in 7075 Al alloys that were solution treated at different temperatures, followed by ageing to peak hardness, has been studied by Joshi et al. (99) using Auger analysis. The concentration of Cu, Zn, Mg, and Si at the grain boundary increased with solution heat treatment temperature above 800°F, suggesting that quenched-in vacancies and vacancy-solute interactions play an important role in the segregation process. The scanning Auger microprobe study of the intergranular fracture surfaces further revealed that Zn, Mg, and Si are present in the form of second phases. The concentration depth profile obtained from a Mg and Zn rich precipitate revealed that the precipitates are typically two dimensional with a thickness estimated in the 5 to 30 Å range.
1.2.7 Effect of Grain Boundary on Solute Segregation

Solute enrichment or depletion at grain boundaries, either by equilibrium or non-equilibrium segregation, should depend on grain boundary structure. There is evidence that relates the physical and chemical properties of the grain boundary (such as boundary surface energy, mobility, diffusion, precipitation, corrosion and stress corrosion cracking) to boundary misorientation. However, no direct experimental studies have been conducted on the relationship between segregation and boundary misorientation (including tilt and twist boundaries).

The grain boundary energy of Al depends on the degree of misorientation. It shows minima for certain special orientations of the boundary (Figure 2). If the equilibrium segregation is considered, segregation will show minimum values at the special orientations since the segregation energies will be at a minimum.

![Figure 2 Computed grain boundary energy at 0°K for symmetric tilt boundaries in aluminium: (a) [100] rotation axis; (b) [110] rotation axis. The energy shows minima at 70.5°, 129.5°, corresponding to Σ = 3,11, CSL boundaries. After Hansson and Goux.](image)

In an elegant in-situ high voltage electron microscope study of the nucleation and growth of precipitates on grain boundaries in Al-Zn-Mg alloys, Butler and Swann found that no precipitate nucleation was observed on boundaries close to a coincidence relationship. Nucleation was observed to be easiest on random high angle grain boundaries. They postulated that the amount of solute segregated at the boundaries plays an important role in both nucleation and in the initial stages of growth of precipitates.
1.2.8 Effect of Grain Boundary on Intergranular Corrosion

The earliest paper that relates intergranular corrosion to orientation of the grains may be that of Lacombe and Yannaquis(59). They found that grain boundary attack in high purity aluminum (99.999%) depended upon the relative orientation of the grains, large differences in orientation favoring rapid attack. Boundaries where the two neighboring grains were similarly oriented gave high resistance to attack, as did twin boundaries. Arora and Metzger(102) have studied the effects of orientation of the boundaries in special high purity aluminum bicrystals on corrosion in 16% HCl solution. They reported that <001> symmetrical tilt boundaries are attacked increasingly with increasing misorientation angle up to about 15°. The attack does not change substantially with misorientation more than 15°, except for 23° and 37° <001> tilt bicrystals which have about half the corrosion rate of other large angle boundaries. The 16°<010> twist boundary shows the lowest penetration rate (Figure 3).

![Figure 3](image)

**Figure 3** Depth of corrosion for bicrystal aluminum specimens with (001) nominal reference surface exposed 10 days in 16% HCl. After Arora and Metzger(102).

Examples of special high angle boundaries are shown in Figure 4. These boundaries, which had small corrosion rates, correspond to boundaries with coincident
site lattices (CSL) e.g. 23°<001> tilt, X = 13 CSL, 37°<001> tilt, Ξ = 5 CSL. However, as stated by Arora and Metzger, this coincident site lattice relationship can not explain successfully the lower penetrations in these boundaries in terms of grain boundary energy.

Figure 4 Appearance of surface and groove in some bicrystals with (001) nominal reference surface. All specimens had been initially electropolished and etched. (a) No. 27, 8° tilt; (b) No. 30, 23° tilt; (c) No 35, 44° tilt; (d) No. 61, 16° twist; (e) No. 60, 54° twist. X680. Reduced approximately 9 pct for reproduction. After Arora and Metzger(102).

The variation of calculated <001> symmetrical tilt boundary energy in Al with misorientation varies approximately 10% outside the small angle regime (Figure 2a). Although Figure 2a shows a similar trend to the experimental penetration curve (Figure 3), but the extent of variation in both curves is not coincident. (50% of the maximum penetration rate at Ξ = 5CSL, as compared to 10% variation in grain boundary energies).

Intergranular corrosion of high purity Al <011> tilt bicrystals in hot water at 150°C (which simulates the environment in the heat exchange system of water cooled reactors) has been studied by Boos and Goux(103). The depth of the intergranular
corrosion grooves was measured as a function of the misorientation of the bicrystal as shown in Figure 5. The curve shows two cusps for \( X = 70.5^\circ \) and 129.5\(^{\circ} \), corresponding to \{111\} and \{311\} twins, respectively. This is consistent with the computed boundary energies for \(<011>\) symmetrical tilt boundaries in Al (Figure 2b)(103). However, the curve in Figure 5 does not show cusps for any other values of misorientation. For example, there is no cusp for \( \Xi = 109.5^\circ \) which corresponds to the \{211\} twin. (Compare Figure 2b and Figure 5). From the above discussion, the grain boundary structure (in terms of the coincident lattice site model and corresponding boundary energy) can not be considered as the only factor that controls intergranular corrosion.

![Depth of boundary groove in Al<110> symmetric tilt boundaries exposed to water at 150°. From Boos and Goux(103).](image)

Figure 5 Depth of boundary groove in Al<110> symmetric tilt boundaries exposed to water at 150°. From Boos and Goux(103).

Arora and Metzger(102) consider that a preferentially corroding boundary is an anode and that the corrosion susceptibility arises not in the driving force (thermodynamics), but in the polarization (kinetic)characteristic. The grain boundary energy would be several hundred ergs per square centimeter. The grain boundary material would then have a hypothetical reversible potential of 10 to 20 mV anodic to the grain body, which is considered small when compared to the total driving force. The type of anodic polarization which can produce a structural dependence is one involving the formation of a passive film. It was suggested that a high angle grain boundary suffers more attack than a \{001\} surface in the \(<001>\) tilt bicrystals of Al because of the less perfect film formed over the boundary zone.
The strength of the passive film may depend not only upon the substrate structure but also upon the chemical composition of the substrate, i.e. the segregated grain boundary region. Vermilyea and Tedmon(104) suggested that impurities segregated at grain boundaries might locally increase the electronic conductivity of the oxide, thereby facilitating corrosion at grain boundaries.

Arora and Metzger(102) also pointed out that for a symmetrical tilt <111> bicrystal, the {111} surface corroded as fast as the boundaries and that either none or only very shallow boundary grooves were observed. Corrosion on the {111} surface was faster than that of the {001} surface. The authors suggested that a part of the anodic polarization of Al in the acid involves the tendency to form a thin coherent film which is more perfect on {001} surfaces because of the particular atomic arrangement on this surface. A less perfect film was formed on surfaces with different atomic arrangement, such as on the {111} surface.

It is clear that further experiments are required to evaluate the effect of grain boundaries in terms of those parameters mentioned above.
Chapter 1: Introduction

1.3 Summary

Several mechanisms for the effect of chloride ions on pitting corrosion have been proposed in the literature. None of these are generally accepted partly due to the complexity of the pitting corrosion process, and partly due to the metal substrates having microstructural characteristics such as voids, dislocations, and grain boundaries, that influence the pitting corrosion process in an uncertain manner. In spite of the importance of the metal substrate characteristics to pitting corrosion, and in particular the crystallography of the corrosion surface, little work has been reported in this area.

Considering grain boundary corrosion, the literature survey indicates the following:

(1) There is little direct experimental evidence that relates segregation at grain boundaries to the type of boundary.

(2) The quantitative measure of grain boundary segregation, as a function of the grain boundary orientation and type is unclear.

Accordingly, the dependence of intergranular corrosion on grain boundary segregation and grain boundary orientation is not established.

1.4 Present Objectives

The present study was undertaken to examine pitting corrosion and intergranular corrosion as it relates to the substrate. To this end, single crystal surfaces of known orientation and bicrystals of controlled orientation differences are used as substrates for the corrosion studies. The substrate material is Al and Al-Cu alloys. The corrosion environment is chloride solutions, with nitrate inhibitors in some cases.

As part of the study, grain boundary segregation and precipitation of Cu in bicrystals are examined in as-grown bicrystals, after full homogenizing and ageing.
2. EXPERIMENTAL PROCEDURE

2.1 Preparation of Aluminium and Al-Cu Single Crystals and Bicrystals

2.1.1 Material Preparation

The starting materials for the samples examined in this investigation were Al and Cu of 99.99 wt% purity. A master alloy of Al 33.2 wt% Cu was produced by melting the constituents in a graphite covered cylindrical mold, under an argon atmosphere, using induction heating. The alloy composition was verified by electron probe microanalysis (EPMA). Alloys of the required composition were prepared from pure Al and weighed amounts of the eutectic by induction melting under an argon atmosphere, mixed thoroughly, then allowing to solidify in a graphite crucible.

After the alloys had cooled they were removed from the graphite crucibles. They were reheated to 400°C and rolled to plate of 10 mm thickness.

After rolling the plate was heated at 550°C for \(6 \times 10^5\) sec in air to homogenize the Cu distribution in the alloy. For pure Al samples, blocks of pure Al were cut from the material supplied, heated and rolled to give plates similar to the alloy material.

2.1.2 Growth of Single Crystals

Single crystals were grown by the horizontal Bridgman technique\(^{(105)}\). This consisted of growing the crystals from an oriented seed crystal (50 x 10 x 6 mm) in a horizontal graphite boat by progressive solidification. The graphite mould configuration is shown in Figure 6. The seed was placed in the right side of the mold and the crystal grown on the left. A weighted cover sat on the mould which was required to obtain a crystal of uniform thickness with a flat upper surface. The crystals were grown in an argon atmosphere.
To grow a crystal, a strip of Al or AlCu alloy charge material was cut from the rolled and annealed slabs to fit into the crystal section of the boat. The charge material and the seed crystal were then cleaned in a 10% NaOH solution at 70°C, 50% HNO₃ and distilled water at room temperature, dried, and placed in the mold. The mold was then placed in the growing furnace shown in Figure 7. The furnace was resistance heated and had the axial temperature distribution shown in Figure 8. The furnace was mounted on wheels and could be moved smoothly along horizontal tracks at controlled slow rates with a motor.
The crystal was grown by positioning the furnace around the charge, melting it and approximately 10mm of the seed crystal adjacent to the charge. This was done in a quartz tube in a flowing argon atmosphere. The interface between the melted charge and the partially melted seed was removed with a quartz pointed rod coated with graphite which was inserted into the melt in the junction region. When steady state was reached the furnace was moved uniformly away from the seed crystal at a rate between 6.7 x 10^{-4} and 1.1 x 10^{-3} cm/s, until the metal had completely solidified.

Figure 7 Arrangement of the crystal growing apparatus

Distance along the longitudinal direction(cm)

A: High purity graphite
B: Seed crystal
split mold
C: Charge material
D: Electrical resistive Furnace
E & F: Argon gas inlet & outlet
G: Rail
H: Quartz tube
I: Solidification front
After solidification the material was carefully removed from the boat and etched in 10% NaOH to determine whether the resultant material was a single crystal. This could be readily established visually. The orientation of the crystal was then subsequently determined by back reflection X-ray Laue procedures. 

All of the single crystals examined had an orientation in which the growth direction was nearly parallel to the [100] direction and the top surface close to the {100} plane. The alloy crystals were grown from pure Al seeds. This resulted in the dilution of the alloy content in the vicinity of the seeds since there was some mixing of the melt from the pure Al seed and the alloy melt.
CHAPTER 2: Experimental procedure

The dimensions of the as-grown crystals were 235 mm long, 10 mm wide and 8 mm thick. Samples for electrodes having (001) (011) and (111) faces were prepared from the crystal by spark machining to expose the required plane followed by careful mechanical polishing, finishing with 5μm alumina slurries. The orientation of the crystal surface was determined by X-ray Back reflection Laue methods. The final surface area of an electrode of defined surface orientation was approximately 1cm by 1cm. The orientation of the surface orientations were coincident with the specified orientation to ±5°.

2.1.3 Growth of Bicrystals

Bicrystals were grown in a manner similar to that used for single crystals with two seed crystals of predetermined orientation, separated by a graphite spacer, replacing the single seed crystal.

The two seed crystals were placed in a graphite mold (Figure 9) and oriented such that both crystals had their surfaces parallel to the (001) plane and their [001] directions were inclined to the growth direction, produced by a rotation about a vertical axis. This produced a symmetrical tilt boundary of angle θ with the tilt axis perpendicular to the top surface and (001) plane of the bicrystal. Growth rates of 6.7x10^4 and 1.05x10^-3 cm/s were used.

After growth the bicrystals were etched in 10% NaOH, which clearly delineated the boundary. In general, the trace of the boundary plane on the top surface was reasonably straight and parallel to the growth direction. The boundary plane was approximately perpendicular to the top surface.

X Ray back reflection Laue photographs were obtained for several positions along each of the crystals in the bicrystal to establish that the orientations were maintained along the length of the crystals. This was found to be the case. The specific orientations of each of the crystals in the bicrystal and their precise misorientation was determined from the Laue photographs with a graphical stereographic projection technique(107).
Figure 9  Mold for growing bicrystals

The graphical method is described below, along with an example for an Al-4\% Cu bicrystal. The bicrystal was positioned as shown in Figure 10 with the Z axis parallel to the crystal growth direction and X axis perpendicular to its surface for projection.
The stereographic projections of the X-ray pattern of the right (R) side crystal is shown in Figure 11a. The projected points from the X-ray pattern are indicated as dots in the projections. The great circles and the poles of the major low index planes are indicated, based on the pattern solution. The projection clearly shows the pole of the top surface of the crystal is close to [001] and the Z axis is close to the [100] direction.

The corresponding stereographic projection for the crystal on the left (L) hand side of the bicrystal is shown in Figure 11b.

From Figures 11a and 11b, the poles of two pairs of low index planes (in this case, [(011)R, (011)L]*5 and [(101)R, (101)L]) were replotted on a stereograph shown in Figure 12.

A great circle was drawn through the (011)R and (011)L poles, and the pole of the bisection (pole 1) of the arc between these two (011) poles was located. The pole 1

\[ (hkl)_R \] indicates the pole of (hkl) plane of the crystal on the right hand side of the bicrystal and \( (hkl)_L \) for the corresponding pole of the left hand side.
was linked to the pole $P_{011}$ of the great circle through the two $(011)$ poles. Since each point on this great circle is at an equal angle from $(011)_R$ and $(011)_L$, it is clear that the axis of misorientation lies on this great circle.

Similarly, the axis of misorientation should lie on the second great circle linking pole $P_{011}$ and pole 2 that bisects the $(101)_R$ and $(101)_L$. The intersection of these two great circles gave the axis of rotation ($P_r$) of the bicrystal. The deviation of $P_r$ from the X axis was measured as $\delta = -3^\circ$ and $\gamma = -1^\circ$. In order to determine the angle of misorientation ($\theta$), the pole $P_r$ was rotated to coincide with the center of projection and the corresponding poles $(011)^*_R$ and $(011)^*_L$ of poles $(011)_R$ and $(011)_L$, respectively, were determined. The angle between poles $(011)^*_R$ and $(011)^*_L$ gave the angle of misorientation. This angle of misorientation was measured as $\theta = 10^\circ$. Using the same method, the misorientation axes and angles of the other bicrystals used in the present study were determined and listed in Table 2.

The orientation of the grain boundary plane, which was determined from the traces on the top surface and on the cross-section perpendicular to the growth direction, after polishing and etching, is also indicated as $P_{gb}$ on Figure 12. ($P_{gb}$ is coincident with Y axis in this Figure).

The boundary trace on the top surface was most clearly delineated in homogenized bicrystal samples. An example of the appearance of the boundary trace on the top surface and on a cross-section perpendicular to the growth direction for the Al$_4$Cu-2 bicrystal is shown in Figures 13(a),(b). The corresponding appearance of Al 2% Cu and pure aluminum bicrystals are shown in Figures 14 and 15.
Figure 11 Stereographic projection of the Laue patterns obtained from the bicrystal Al4Cu2. (a) Right, and (b) left component single crystal. N pole and the center of the projection are coincident with the crystal growing direction (Z), and the top surface (X) of the bicrystal.
Figure 12 Graphical method for determination of the misorientation axis and angle for the bicrystal Al4Cu-2.
TABLE 2. Orientation of Bicrystals Used in the Present Study

<table>
<thead>
<tr>
<th>Bicrystal</th>
<th>Nominal Cu (wt%)</th>
<th>Pole of Axis of Rotation</th>
<th>Tilt Angle</th>
<th>Growth Speed (cm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1B-3</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>A1B-4</td>
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</tr>
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<td>-8</td>
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</tr>
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</tr>
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</tr>
<tr>
<td>Al4Cu-4</td>
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<td>-6</td>
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</tr>
</tbody>
</table>

*Deviation from the normal of the bicrystal surface, close to the <001> direction of two component single crystals.
Figure 13 Top and side views of the homogenized Al4Cu-2 bicrystal.
Figure 14 Top and side views of the homogenized Al2Cu-1 bicrystal.
Figure 15  Top and side views of the AlB-3 bicrystal.
In all three cases the boundary traces are straight and the boundary planes are observed to be nearly perpendicular to the top surface.

In examining the configuration of the boundary plane as a function of growth rate it was observed that planer boundaries parallel to the growth direction could only be obtained at low growth rates, particularly for the alloy crystals. Growth rates of $1.06 \times 10^{-3}$ cm/sec were adopted for the pure Al bicrystals which resulted in satisfactory bicrystals, and $6.7 \times 10^{-4}$ cm/sec for the alloy crystals, as listed in the table. For the bicrystals with a large orientation difference only pure Al and Al 0.1% Cu could be grown to give suitable test samples.

### 2.2 Alloy Composition Determination

Composition of the AlCu alloy electrodes cut from the single crystals and bicrystals were determined using a JEOLCO JXA-3A electron probe microanalyser (EPMA). The measurements were made using an accelerating voltage of 25KV with a 20° X-ray take-off angle and 1 μs dead-time. Counts of the AlKα and CuKα radiation were obtained at 5 different locations on the test sample for 10 second intervals. The counts were then compared to the corresponding counts from pure Al and Cu, and the results converted to weight percent using the MAGIC programme. (108)

### 2.3 Solute Segregation Determination

#### 2.3.1 EPMA Measurement

All of the alloy samples exhibited a cell structure in the as grown condition (109). The appearance of the cells will be described in the observations following. Solute was segregated at the cell boundaries. Composition variations in the as-grown alloy bicrystal test samples were determined by EPMA scan analysis across the sample surface.
Chapter 2: *Experimental procedure*

X-ray line scan analyses were conducted over distances of approximately 3mm at six locations on the surface of the samples, and the generated CuKα radiation count rates were recorded. The scans were carried out by the lateral translation of the specimen with respect to the electron beam.

The maxima and minima of the copper concentration were quantitatively determined by stopping the specimen to allow the electron beam to situate at the maxima or minima of the CuKα counts rate profile during the reversed scan on the same location, then the X-ray counts were determined and converted to copper concentration as described earlier.

2.3.2 STEM-EDX Measurement

Microcomposition of the samples was determined using a scanning transmission electron microscope (STEM), Hitachi Model H-800, which is equipped with an X-ray energy dispersive system (EDX) for chemical analysis.

The samples for the STEM-EDX analyses were prepared as follows:

Cylinders of 3 mm diameter were spark machined from the grain boundary region so that the axis of the cylinder was parallel to the grain boundary plane and perpendicular to the crystal growth direction. Some samples were from the component single crystals on either side of the grain boundary plane of the bicrystal. The cylinders were cut with a jeweller’s saw to slices of about 0.5mm thick, followed by mechanical polishing on both sides with wetted 4/0 SiC paper to about 200μm thick. Then, the specimen was jet polished on both surfaces simultaneously in a TENUPOL-2 double jet polisher, using a perchloric acid base solution. (Perchloric acid 70%, 67 ml, denatured Ethanol, 700 ml, Butylcellosolve, 100 ml, and distilled water, 120 ml). An ion beam milling machine was used to remove any surface contaminants, if necessary.

Quantitative EDX analyses were carried out at a series of points located across (transverse to) the grain boundary of the bicrystal sample or across (transverse to) the cellular walls of the single crystal. X-ray AlKα and CuKα pulses were counted and converted to the wt% concentration by using the "standardless procedure" of the ZAPTEM(110) programme for thin film specimen.
It is desirable to have longer counting periods (i.e. higher total X-ray counts) in order to reduce the statistical counting error. However, this requirement causes problems with contamination and drift of the specimen. In the present study, the preset analysis count from the integral area under the peak of the minor component (CuKα) of the X-ray spectrum was set at 1000 X-ray counts. This preset required a counting time of 1 to 3 minutes, depending on the copper concentration at the analyzed locations of the sample. No specimen drifting was observed in these time intervals.

The grain boundary plane of the bicrystal samples in the present study was parallel to the electron beam within a tilt angle of 0° to 5°. An electron beam spot size of 5nm and 200 KeV beam acceleration voltage was used for the analyses. The higher KeV minimizes the beam spreading effect. Any analysed data that did not meet the thin film criterion*(111,112) was discarded.

* The thin film criterion requires that each element measured meets the condition χρt < 0.1, where ρ is the density of the specimen, t is the thickness of the specimen and χ is μ/ρ*sinε*cscψ.(μ/ρ is the mass absorption coefficient for the Kα radiation of the element, ε is the incident angle of the electron beam and ψ is the X-ray take off angle.)
Chapter 2: Experimental procedure

2.4 Heat Treatment

Part of the objective of this programme was to examine the corrosion which occurred at grain boundaries under different solute distribution conditions. This was accomplished by heat treatment. The pure aluminum single crystals and bicrystals, after growing, were subjected to annealing at 540°C for $1.4 \times 10^4$ s and furnace cooled in order to reduce the possible grown in dislocation density, whereas the alloy samples were subjected to homogenizing. Ageing heat treatment was done at 200°C for 4 hours in the same environment.

Homogenization treatments were conducted at 540°C for 30 days. the time was considered to be more than sufficient to produce a fully homogenized alloy because it was at least one order of magnitude larger than the approximately estimated time required for homogenization based on diffusion theory. The procedure for estimating the homogenization period is shown below.

From the EPMA line scan and etching studies, which will be described later, it was found that a cellular structure and solute segregation developed in the as-grown bicrystals used in the present studies. The average cell spacing of these cellular structures ranged from 185 µm to 400 µm. From the Cu concentration profiles, the initial stage for diffusion can be approximated to a sine function source with a wave length of 400 µm as sketched in Figure 16a. There is no exact solution to this diffusion problem. However, it can be simplified to a problem of diffusion to a slab of thickness $h$ with the concentrations of it's boundary being kept at $C = C_0$ for $t > 0$, as depicted in Figure 16b. The relative change in concentration is given by:  

$$\frac{(C_0 - C)}{C_0} = 4/\pi \sin(\pi x/h) \exp(-\pi^2Dt/h^2) \quad \quad \quad \quad (2.1)$$

If at the end of homogenizing heat treatment, the relative change in concentration at the center of the slab is reduced to 1% then:

$$\frac{(C_0 - C)}{C_0} = 4/\pi \exp(-\pi^2 Dt/h^2) = 0.01 \quad \quad \quad \quad (2.2)$$

for $D = 14.2 \times 10^{-10} \text{ (cm}^2/\text{sec)}$, $h = 400 \mu\text{m}$, The required minimum time for homogenization is $36.5 \text{ hr}$.

![Diagram](image)

**Figure 16a** Initial Cu concentration profile in the as-grown bicrystals.

![Diagram](image)

**Figure 16b** Simplified initial stage for homogenization heat treatment.
2.5 Potentiodynamic Pitting Corrosion Studies

2.5.1 Sample Preparation

Single crystal electrode samples were prepared from sections cut from the annealed or homogenized crystals. The samples were mounted in epoxy resin for electrochemical studies. The electrode surface was abraded on 4/0 SiC paper, then polished successively on 5, 1 and 0.06 μm alumina slurries. The orientation of each sample was determined using X-ray analysis and the composition by EPMA or STEM-EDX analysis. Prior to each corrosion test, the electrodes were electropolished in 10% perchloric acid, 20% glycerine and 70% ethanol to remove the mechanically deformed layer. The samples were then rinsed in ethanol and distilled water, dried, and covered by lacquer to expose an area of approximately 1 cm². Freshly prepared surfaces were used for each test.

Bicrystal electrodes having areas of 2cm x 2cm and containing the grain boundary at its center were cut from the bicrystal samples. The electrode samples were mounted in epoxy-resin and polished by the same procedure as used for the single crystal electrodes. The electrode surface, after preparation, was partially masked by lacquer exposing either the grain boundary region, or a single crystal grain surface, prior to electrochemical testing. When the grain boundary was exposed a region of 2 mm x 15 mm containing the grain boundary trace was left uncovered by the lacquer.

2.5.2 Electrolytes

The solutions used for the corrosion studies were prepared from distilled water and reagent grade chemicals. Solutions of NaCl, AlCl₃ of different concentrations and nitrate inhibited solutions were used. Solution compositions included those simulating sea water (0.5M NaCl) and the concentrated solution formed in pits. The pH value was adjusted by using 0.1N HCl.

The solutions were deaerated by bubbling argon gas through them in a deaeration container for at least 24 h. They were then transferred into the electrolytic test cell without allowing exposure to the air environment.
Chapter 2: *Experimental procedure* -51-

The electrolytic cell, containing the test (working) electrode, was purged with argon gas for 30 minutes before and after the solution was introduced. The end of the purging tube was placed above the level of solution and argon gas was kept continuously flowing into the cell during the test.

Deaeration was necessary in order to depress the corrosion potential of the electrode below the pitting potential, otherwise pitting potential determinations could not be made.
2.5.3 Electrolytic Cell and Equipment

Electrochemical studies were conducted in a single compartment cell. The main cell was an air tight glass vessel (EG&G C, K47 cell) containing five ports, as shown in Figure 17. The specimen enters the cell through the central port.

Figure 17 Electrolytic cell
The external saturated calomel reference electrode (SCE) was connected to the working electrode via a salt bridge containing the same test solution and a Luggin capillary that terminated about 1mm from the surface of the specimen.

The counter electrode (i.e. the auxiliary electrode) consisted of a platinum coil and was placed in a separate glass tube compartment containing a fine porosity glass frit. The counter electrode compartment was immersed in the main compartment through one of the five ports. (see Figure 17)

A microprocessor-based corrosion measurement system, (EG&G Model 350A) was used for the potentiodynamic pitting scan test. The applied potential range of the system is ±4 V, with an accuracy of 2 mV in this potential range, and current range of 10 nA to 1 A, with accuracy of 0.5% of the maximum current decade in use. The potential scan rate was controlled by varying the potential with a staircase waveform. e.g. in order to generate a scan rate of 0.5 mV/sec, the potential of the electrode is stepped 2 mV every 4 sec. The corresponding current is measured for 16.7 ms immediately prior to each step.

2.5.4 Selection of Potential Scanning Rate

The value of the critical pitting potential, as determined by electrochemical techniques, is a function of the potential scan rate(113,114). The slower scan rates are thought to yield values closer to the true value. Nisancioglu and Holtan(113) used various techniques, i.e. potentiostatic, potentiodynamic, galvanostatic and galvanodynamic to measure the critical pitting potential of aluminum and pointed out that the potentiostatic method was probably the most reliable method and that the scan rate should not exceed a few mV/min in order to obtain reasonably accurate values. However, a major problem associated with either the long term potentiostatic or slow scan rate polarization method is the interference of corrosion that occurs between the surface of the working electrode and the lacquer coating. This increases the anodic currents and makes detection of pitting potential difficult. Another disadvantage of the potentiostatic and slow scan rate techniques is the requirement of lengthy experimental test periods for applied potentials in the vicinity of the critical pitting potential. Therefore, it can not be regarded as an accelerated test method. In their potentiostatic measurement, Holtan et al. concluded that a sample did not show a tendency for pitting at the applied potential when there was no current increase after 1000 min. However, the length of this time also needs justification. (i.e. It is not assured that the specimen will not pit if it is held for a longer time.)
In the present study, preliminary experiments showed that there was no significant difference in the values of the pitting potential determined by potentiodynamic methods at scan rates of 0.1 mV/sec and 0.5 mV/sec. Therefore, the potentiodynamic method was adopted in all experiments, using a scan rate of 0.5 mV/sec. This scan rate allowed the test to be concluded in a reasonable period of time and avoid crevice corrosion at the metal-lacquer interface.

The steps in the potentiodynamic pitting scan test are summarized below:
1. Insert specimen into the air tight cell.
2. Purge air from the cell with argon gas for 30 min.
3. Introduce the deaerated electrolyte into the cell without contact with air.
4. Purge the electrolyte with argon gas for 30 min., then place the end of the purging glass tube above the electrolyte level and keep argon gas flowing into the cell during the test.
5. Begin anodic polarization at the corrosion potential and scan in the positive (noble) potential direction at a scan rate of 0.5 mV/sec.
6. Scan is reversed towards the active directions when the anodic current density reaches $5 \times 10^6$ nA/cm$^2$. (In some experiments, the scan was reversed when the potential reached a preset value, i.e. -400 mV (SCE)).
7. Continue reverse scan until corrosion potential is reached.

2.6 Dependence of Protection Potential and Repassivation Current Density on Pit Propagation

In these experiments, the pure aluminium single crystal electrodes of {001}, {011} and {111} planes were galvanostatically pitted at different anodic current densities using an ECO Model 549 Potentiogalvanostat. After the desired amount of anodic charge was passed, the potential of the electrode was potentiodynamically scanned* towards the active direction at a scan rate of 0.5 mV/sec until the protection potential was reached.

* The EG&G 350A system was used for the reverse potentiodynamic scan.
2.7 Pit Area Ratio and Pit Density

Pit nucleation and the lateral growth rate of the pitted specimens were measured in terms of pit density and pit area ratio.

Single crystal electrodes were pitted galvanostatically at a current density of 5 mA/cm² for 1000 seconds. The number and area of pits formed on each electrode surface were measured by using the "LEITZ TAS PLUS" automatic image analyser. The "LEITZ TAS PLUS" is an image analyzing computer in conjunction with a metallographic microscope. The live image of the sample that contains the features (pits) to be counted and the featureless (unpitted) area was translated to a binary bitplane image. This process is called detection. Detection compared the intensity (grey level) of each picture point (pixel) with a selected threshold and then used this as the criterion for the binary decision (on or off). The dark area of the binary bitplane image was counted by the "Image Analyser" and the area measured.

The total number of pits and their summat projection area in each frame were measured and then converted to pit density and pit area fraction by dividing by the frame area. Since pits occur randomly and frequently touched each other to form pit clusters, no attempt was made to measure the pit size distribution. In addition, each cluster was counted as a single pit. For this reason, the measured pit density should be treated as a relative value showing the tendency of pit nucleation.

Because of the randomness of the pit distributions, the size of the frame was chosen as large as possible to give a representative area of the sample. The chosen frame length was 750 µm and the width was 649.5 µm. Therefore, the area within which pits were counted was 487,125 square micrometers.

When the counting on a single frame of the binary bitplane image was finished, the specimen was moved to the next frame automatically and the counting repeated. Thirty frames were analysed in each test, unless otherwise mentioned. The data were treated statistically, i.e. histograms were obtained for pit area ratio and pit density.
2.8 Morphology of Pits

Pit morphology was studied by means of scanning electron microscopy (SEM). The specimens were coated with carbon to increase electrical conductivity of the oxide film that covered the corroded surface. The coating prevented electrostatic charging and gave better SEM resolution.
3 RESULTS

3.1 Pitting Corrosion of Aluminium and Aluminium-Copper Single Crystals

A typical potentiodynamic pitting (PPC) diagram is shown in Figure 18 commencing at the corrosion potential. The anodic current density increases rapidly and then reaches a limiting value (passive current density) when the electrode potential is scanned in the noble (positive) direction. Upon reaching the critical pitting potential ($E_{pit}$), the anodic current density starts to rise rapidly due to the localized breakdown of the passive film. The increased current can be a result of pit nucleation and pit growth. When the current density reaches the point $H_2$ hydrogen bubbles evolve vigorously and locally from the electrode surface, and the current jumps directly to the diffusion limiting current density. After the pre-programmed maximum noble potential ($-400$ mV SCE) is reached, the scan is reversed towards the active (negative) direction. The current density decreases* in the reverse scan until it reaches the protection potential ($E_{prot}$), as shown on Figure 18.

The pitting scan diagram, which exhibits hysteresis, can be divided into 3 regions characterized by two values, the $E_{pit}$ and the $E_{prot}$:

1. At potentials above the $E_{pit}$, pit nucleation and growth occurs. (region I in Figure 18).
2. At potentials between the $E_{pit}$ and $E_{prot}$, the existing pits will grow while no new pits are formed. (region II in Figure 18).
3. Below the $E_{prot}$, no new pits are formed and existing pits stop growing. i.e., repassivation occurs. (region III in Figure 18).

---

8 For a potential scan that is programmed to reverse when the rising current density reaches $5 \times 10^6$ mA/cm$^2$, the current continues to increase in the reverse scan for a certain potential range before it begins to decrease.
3.1.1 Effect of Crystallographic Orientation on Epit and Eprot of Al Single Crystals

PPC scan test were performed on a number of low index crystallographic surfaces of pure aluminum single crystals. The orientations of these surfaces which were determined by X-ray diffraction are listed in Table 3. Figure 19 shows the representative PPC scan diagrams of {001}, {011}, and {111} planes in a deaerated 0.5 M NaCl solution of pH 6.5.

The results show that the value of the Epit is a function of the crystallographic orientation of the surface. The potential decreases in the order Epit(001) : Epit(011) : Epit(111) on the {001}, {011} and {111} planes respectively. On the other hand, the Eprot is observed to be independent of the crystallographic orientation. The values of Epit and Eprot are summarized in Table 4 and plotted in Figure 20.

The difference in Epit between the {001} and {111} planes is measured as high as 39 mV as shown in Table 4.
CHAPTER 3: RESULTS

TABLE 3
Orientations of Pure Aluminium
Single Crystal Electrodes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Orientation plane</th>
<th>( \sigma )</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>{001}</td>
<td>-3°</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>{011}</td>
<td>-4°</td>
<td>-30</td>
</tr>
<tr>
<td>3</td>
<td>{111}</td>
<td>4°</td>
<td>0°</td>
</tr>
</tbody>
</table>

Figure 19 Representative PPC scan diagrams of pure aluminium {001}, {011}, and {111} single crystals in 0.5M NaCl solution of pH 6.5
CHAPTER 3: \textit{RESULTS}

TABLE 4
Epit and Eprot of Pure Al Single Crystals in various Chloride Salt solutions.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Salt</th>
<th>Concentration (M)</th>
<th>pH</th>
<th>Epit(mV)* Average</th>
<th>Eprot(mV)* Average</th>
<th>σ</th>
<th>No of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>{001}</td>
<td>NaCl</td>
<td>0.5</td>
<td>6.5</td>
<td>-700</td>
<td>-799</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>{001}</td>
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<td>6.5</td>
<td>-724</td>
<td>-800</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>{111}</td>
<td>NaCl</td>
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<td>6.5</td>
<td>-739</td>
<td>-800</td>
<td>15</td>
<td>3</td>
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<tr>
<td>{001}</td>
<td>NaCl</td>
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<td>2.5</td>
<td>-721</td>
<td>-797</td>
<td>8</td>
<td>5</td>
</tr>
<tr>
<td>{001}</td>
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<td>6.5</td>
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<td>-812</td>
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<td>2</td>
</tr>
<tr>
<td>{001}</td>
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<td>5.5</td>
<td>-787</td>
<td>-836</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>{001}</td>
<td>NaCl</td>
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<td>-872</td>
<td>6</td>
<td>3</td>
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<tr>
<td>{001}</td>
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<td>2.0</td>
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<td>-842</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>{001}</td>
<td>AlCl₃</td>
<td>2.0</td>
<td>1.5</td>
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<td>-875</td>
<td>4</td>
<td>1</td>
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<td>-876</td>
<td>-890</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

* The electrode potential is reported with respect to the Saturated Calomel Electrode (SCE).
Figure 20  Effect of crystal orientation on $E_{\text{pit}}$ and $E_{\text{prot}}$ of pure aluminium single crystal.
3.1.2 Effect of pH on $E_{\text{pit}}$ and $E_{\text{prot}}$ of Al Crystals

PPC scans were made on (001) aluminium single crystal surfaces in the deaerated 0.5M NaCl solutions having pH values between 2.5 and 6.5. Representative pitting scan diagrams are shown in Figure 21. The results show that the $E_{\text{pit}}$ is depressed to more active values as the pH of solution is lowered. The pH does not affect the $E_{\text{prot}}$ of the pure aluminium (001) single crystal. The values of $E_{\text{pit}}$ and $E_{\text{prot}}$ are summarized in Table 4 and plotted against the pH values in Figure 22. The $E_{\text{pit}}$ decreases from -700 mV to -720.5 mV as the pH of solution decreased from 6.5 to 2.5. The average effect of pH was determined to be 5.1 mV/pH unit. Hence, the pitting potential increases 5.1 mV for every 10 fold increase in OH$^-$ concentration.

Figure 21 Representative PPC scan diagrams of Al(001) single crystals in 0.5M NaCl solution of pH 2.5 and pH 6.5.
3.1.3 Effect of Chloride Concentration on Epit and Eprot of Al-Single Crystals

PPC scan tests were carried out as a function of the concentration of NaCl solutions up to 5.42M, the room temperature saturation value, on {001} surfaces. The resultant pitting scan diagrams are shown in Figure 23. The results show that both the Epit and the Eprot decrease with increasing chloride concentration.

Values for the Epit and Eprot are listed in the foregoing Table 4. The hysteresis (Epit-Eprot), shown in Figure 23, was also diminished with increasing chloride concentration. The values of the Epit and Eprot are plotted against the logarithm of chloride concentration in Figure 24. Both potentials decrease linearly with log(Cl⁻) and converge at a point corresponding to a chloride concentration of 12M and a potential of -898 mV. These linear relationships are:

\[
\text{Epit} = -744 - 140 \times \log(\text{Cl}^-) \text{, mV}_{\text{SCE}} \quad (3.1)
\]

\[
\text{Eprot} = -817 - 72 \times \log(\text{Cl}^-) \text{, mV}_{\text{SCE}} \quad (3.2)
\]
Figure 23 PPC scan diagrams of Al(001) single crystals in NaCl solution of various chloride concentration.
PPC scan tests were also done in AlCl₃ solutions up to the room temperature saturation value of 3.18M AlCl₃. The resultant pitting scan diagrams are shown in Figure 25 and the potential values listed in Table 4. The potentials are observed to decrease with increasing AlCl₃ concentration, as for NaCl solutions. The values of Epit and Eprot are plotted against log (Cl⁻) in Figure 24, giving linear plots similar to NaCl.

The overall effect of Cl⁻ on pitting, independently of whether it was added as NaCl or AlCl₃, is to decrease the Epit by 140 mV/decade and the Eprot by 72 mV/decade, as evident from equations 3.1 and 3.2.

Figure 24 Effect of Cl⁻ concentration on Epit and Eprot of pure aluminium (001) single crystal.
3.1.4 Dependence of $E_{prot}$ and Repassivation Current Density on Pit propagation

Aluminium single crystal electrodes of (001), (011) and (111) planes were galvanostatically pitted at the arbitrary anodic current densities of $1 \times 10^6$, $5 \times 10^6$ and $50 \times 10^6$ (nA/cm$^2$) for 1000 sec in the 0.5M NaCl solution. $E_{prot}$ and the corresponding repassivation current density, determined during the reverse potentiodynamic scan, were recorded. The values are listed in Table 5. The results show that the $E_{prot}$ is constant, to within a few mV, with the amount of charge passed. The repassivation current density increases approximately from 3 to 10 times in magnitude when the amount of charge passed was increased from 5 to 50 C/cm$^2$ as shown in Table 5.

Figure 25 PPC scan diagrams of pure aluminium (001) single crystals in AlCl$_3$ solution of various concentration.
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TABLE 5
Effect of Charge Passed During Pit Propagation on \( E_{\text{prot}} \) in 0.5M NaCl solution

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Current Density (nA/cm(^2))</th>
<th>Charge Passed (C/cm(^2))</th>
<th>( E_{\text{prot}} ) (mV)</th>
<th>Re-Passivation C/D (nA/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>{001}</td>
<td>( 1 \times 10^6 )</td>
<td>1</td>
<td>-793</td>
<td>1.1 \times 10^6</td>
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<tr>
<td></td>
<td>( 5 \times 10^6 )</td>
<td>5</td>
<td>-797</td>
<td>2.5 \times 10^6</td>
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<td></td>
<td>( 50 \times 10^6 )</td>
<td>50</td>
<td>-794</td>
<td>8.2 \times 10^6</td>
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<tr>
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<td>-800</td>
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<td>( 50 \times 10^6 )</td>
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<td>-794</td>
<td>2.9 \times 10^6</td>
</tr>
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</table>

3.1.5 Effect of Cu Content on \( E_{\text{pit}} \) and \( E_{\text{prot}} \)

PPC scan tests were carried out on homogenized Al-Cu single crystals in 0.5M NaCl solutions. The surfaces studied were close to the {001}, {011} and {111} planes. The compositions and orientation of these electrodes were determined by EPMA and X-ray diffraction and are shown in Table 6. A representative PPC scan diagram for the {001} surface is shown in Figure 26.

TABLE 6
Composition and orientation of Al-Cu single crystals

<table>
<thead>
<tr>
<th>Plane</th>
<th>Orientation</th>
<th>( \delta )</th>
<th>( \gamma )</th>
<th>wt%</th>
<th>Stdev</th>
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<tr>
<td>{001}</td>
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<td>0°</td>
<td>0°</td>
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<td>0.05</td>
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</tbody>
</table>
In this figure, a diagram from pure aluminium of the same orientation is shown for comparison. It is observed that both Epit and Eprot are raised to more noble (positive) values with the addition of Cu. A similar behavior is observed for pitting on the {011} and {111} surfaces. The Epit and Eprot are summarized in Table 7. In contrast with pure aluminium, crystallographic orientation has no effect on the Epit of Al-Cu single crystal as seen in Figure 27. (Compare with Figure 20 for the pure Al crystal).

**TABLE 7**

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Cu (Wt%)</th>
<th>Epit (mV) Average</th>
<th>σ</th>
<th>Eprot (mV) Average</th>
<th>σ</th>
<th>No. of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>{001}</td>
<td>2.95</td>
<td>-555</td>
<td>15</td>
<td>-637</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>{011}</td>
<td>3.05</td>
<td>-559</td>
<td>9</td>
<td>-647</td>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>{111}</td>
<td>3.08</td>
<td>-550</td>
<td>12</td>
<td>-648</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 26 PPC scan diagrams on the Al-2.95%Cu {001} single crystals in 0.5M NaCl solution.
3.1.6 Pit Area Ratio and Pit Density on Al Crystal

3.1.6.a Effect of Crystallographic Orientation

Pure aluminium single crystal surfaces of {001}, {011} and {111} were subjected to galvanostatic pitting corrosion at 5mA/cm² for 1000 sec. in 0.5M NaCl solution. Pits were obtained as shown in the SEM micrographs in Figure 28a, 28b, and 28c. The micrographs were transformed to the binary bitplane images shown in Figure 29a, 29b, and 29c.

The dark area in these binary bitplane images were the images of the pits or pit clusters for which the pit area and pit density were measured. Thirty frames were measured in each run unless otherwise mentioned.

It is observed from Figures 28 and 29 that more small pits and pit clusters developed on the {111} plane than on the {001} and {011} planes.
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a. \{001\} in 0.5M NaCl  
b. \{011\} in 0.5M NaCl  
c. \{111\} in 0.5M NaCl

Figure 28 SEM micrographs of pits developed on the \{001\}, \{011\} and \{111\} planes of aluminum single crystal after galvanostatic pitting tests at 5 mA/cm² for 1000 sec.
Figure 29 Binary bitplane images of pit developed on the \( \{001\} \), \( \{011\} \) and \( \{111\} \) planes of Al single crystal after the galvanostatic test in 0.5M NaCl solution at 5 mA/cm\(^2\) for 1000sec.
The results of pit area ratio and pit density on \{001\}, \{011\}, and \{111\} planes are plotted in the form of frequency histogram as shown in Figure 30, and the averages are summarized in Table 8.

### Table 8

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Cu wt%</th>
<th>Solution</th>
<th>Pit Area (%)</th>
<th>Pit (pits/mm(^2))</th>
<th>No. of Test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average*</td>
<td>Average*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\sigma)</td>
<td>(\sigma)</td>
<td></td>
</tr>
<tr>
<td>{001}</td>
<td>0</td>
<td>0.5M NaCl</td>
<td>1.89</td>
<td>14.0</td>
<td>13</td>
</tr>
<tr>
<td>{011}</td>
<td>0</td>
<td>0.5M NaCl</td>
<td>1.60</td>
<td>21.9</td>
<td>9</td>
</tr>
<tr>
<td>{111}</td>
<td>0</td>
<td>0.5M NaCl</td>
<td>2.48</td>
<td>42.7</td>
<td>5</td>
</tr>
<tr>
<td>{001}</td>
<td>0</td>
<td>2.0M NaCl</td>
<td>10.20</td>
<td>30.4</td>
<td>6</td>
</tr>
<tr>
<td>{001}</td>
<td>0.54</td>
<td>0.5M NaCl</td>
<td>2.80</td>
<td>263</td>
<td>66</td>
</tr>
<tr>
<td>{001}</td>
<td>0</td>
<td>0.5M NaCl +0.5M NaN(_3)</td>
<td>1.05</td>
<td>6.1</td>
<td>4</td>
</tr>
</tbody>
</table>

*Galvanostatic pitting tests were done at 5 mA/cm\(^2\) for 1000 sec.

To compare the histograms, the pit area results were normalized by dividing the number of frames having the same pit area ratio by the total number of frames examined, giving the results shown in Figure 31a. The corresponding normalized histograms for pit density are shown in Figure 31b.

From Table 8 and Figure 31, pit area ratio and pit density are observed to be strongly dependent on crystallographic orientation. The \{111\} plane shows the highest pit density and largest pit area ratio.

\[
\begin{array}{ccc}
\{111\} & \{011\} & \{111\} \\
\text{Pit area ratio(%) } & 2.48 & > 1.60 & < 1.89 \\
\text{Pit density(pits/mm) } & 42.7 & > 21.9 & > 14.0 \\
\end{array}
\]
Figure 30 Frequency histograms of pit area ratio and pit density on {001}, {011} and {111} planes of aluminium single crystal. The samples were galvanostatically pitted at 5 mA/cm² for 1000 sec in 0.5 M NaCl. (a), (b) and (c) are the histograms showing the number of frames having a specific pit area ratio, (d), (e), and (f) are the corresponding histograms of frames having a specific pit density.
Figure 31 Normalized frequency histograms showing the effect of crystallographic orientation on pit area ratio (a) and pit density (b).
3.1.6.b Effect of Cl⁻ Concentration on Pit Density and Pit Area Ratio

The SEM micrograph of the (001) plane of aluminium after galvanostatically pitted at 5 mA/cm² for 1000 sec. in 2M NaCl solution is shown in Figure 32(a). The corresponding binary bitplane images are shown in Figure 33(a). Comparing these figures to those of Figures 28(a) and 29(a) for a 0.5M NaCl solution, it is seen that larger pits and a higher density of pits are obtained with the more concentrated solution.

The normalized histograms are shown in Figure 34 which includes the 0.5M NaCl solution results for comparison. The average values of pit area ratio and pit density are listed in the foregoing Table 8.

From Figure 34 it is evident that the pit area ratio and pit density increases significantly with increases in solution concentration of 0.5 to 2M NaCl. Quantitatively, from Table 8, the pit area ratio is increased from 1.89 to 10.20% and the pit density increased from 14.0 to 30.4 pits/mm².
Figure 32 SEM micrographs of pits developed on Al{001} face in (a) 2M and (b) 0.5M NaCl solution after galvanostatic pitting test at 5mA/cm² for 1000s (5 C/cm²).
Figure 33 Binary bitplane images of pits developed on the {001} plane of aluminium single crystal after galvanostatic pitting test at 5 mA/cm² for 1000 sec (a) in 2 M NaCl and (b) in 0.5 M NaCl solutions.
Figure 34 Normalized frequency histograms showing the effect of chloride concentrations on pit area ratio (a) and pit density (b) on the {001} plane of aluminium single crystal.
3.1.6.c Effect of Cu

The SEM photograph and the corresponding binary bitplane images of the (001) plane of a Al-0.54%Cu crystal, after galvanostatically pitted at 5 mA/cm² for 1000 sec in a 0.5M NaCl solution are shown in Figures 35a and 36a respectively. By comparing with those for the pure aluminium shown in Figure 35b and 36b, it is seen that more pits were formed on the alloy crystal surface.

The pit area ratio and pit density of the alloy crystal were measured and the corresponding normalized frequency histograms are shown in Figure 37.

The average values of pit area ratio and pit density are summarized in Table 8 listed previously. From the normalized frequency histograms Figure 37, a small increase in pit area ratio from 1.89 to 2.80%, and a drastic increase in pit density from 14.0 to 263 pits/mm² are observed with 0.54% Cu addition to aluminium.
Figure 35 SEM micrographs of pits developed on (001) faces of Al and Al-0.54%Cu after galvanostatic pitting test at 5mA/cm² for 1000sec (5 C/cm²) in 0.5M NaCl solution.
Figure 36 Binary bitplane images of pits developed on the {001} plane of Al and Al-0.54%Cu single crystals after galvanostatic pitting test at 5 mA/cm² for 1000 sec (5 C/cm²) in 0.5 M NaCl solution. (a) Al-0.54%Cu and (b) pure aluminium.
Figure 37 Normalized frequency histograms showing the effect of Cu addition on (a) pit area ratio and (b) pit density, for \{001\} plane.
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3.1.7 Morphology of Pits

3.1.7.a Crystallographic Effect

Corrosion pits having crystallographic faceted surfaces were observed on all of the samples examined.

Figure 38 shows the shapes of pits formed on the \{111\} plane of an aluminium single crystal after a galvanostatic pitting test at 50 mA/cm\(^2\) for 1000 sec. in 0.5M NaCl solution. The electrode was polarized to above the Epit in region I of the pitting diagram shown in Figure 18. In this region pit nucleation and growth occurs simultaneously, resulting in pits which have a range of sizes. Some pits have grown appreciably as others are just nucleating.

A pin hole micropit of approximately 0.5\(\mu\)m in diameter, which is indicated as "1" in photograph 38(a), could probably correspond to the early stage of pit nucleation. Crystallographic features are observed at the grown pit "2". The projection of this pit on the \{111\} plane are bounded by three <011> directions. Pits which had grown further, to a size of about 3 and 10\(\mu\)m are shown at "3" in photograph 38(b) and "4" in photograph 38(a). The projections of three <001> axes, which are the intersection of two of three \{001\} planes that bound the pit, are exposed in these pits. From a fully developed pit ("5" in photograph 38(c)) it is evident that dissolution started at the corner of the three bounding \{001\} planes and propagated into these planes in the manner of layer by layer, producing the step like \{001\} faceting. Figure 38(d) shows a fully developed pit cluster; pronounced tunnel-like undermining and side branching (at "6" in the photograph) are observed. The pits are bounded by \{001\} planes and have triangular or hexagonal projections.
Figure 38 Morphology of pits at various stages of growth on the \{111\} plane of aluminium single crystal after the galvanostatic pitting test at 50 mA/cm² for 1000 sec in 0.5 M NaCl solution.
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Pits that developed on the \{011\} plane of aluminium single crystal after galvanostatically pitting at 50 mA/cm\(^2\) for 1000 sec. in 0.5M NaCl solution are shown in Figure 40. The size of the pits varied from less than 0.5 \(\mu\)m in diameter to very large pit clusters, similar to the \{111\} situation. A micro pit of rectangular shape, which may be in the early stage of development is indicated as "1" in Figure 40(a). A developed pit of about 5\(\mu\)m in size is indicated at "2" in the same photograph. The projection of these pits on the \{011\} plane is bounded by two parallel \(<001>\) and two parallel \(<011>\) directions. The line along the \(<001>\) direction at the center of pit "2", which is the intersection of two bounding \{001\} planes of the pit, is also seen. Figure 40(b) shows the undermined tunnel-like pits. Figure 40(c) shows the evidence that dissolution started at certain locations along the intersection of the two pit bounding \{001\} planes, and developed into these two planes layer by layer, resulting in the stepped \{001\} faceting at the bottom of the pit.

Figures 41 show the morphology of pits developed on the Al\{001\} surface after the galvanostatic pitting test at 50 mA/cm\(^2\) for 1000 sec. Crystallographic and undermining tunnel-like attack was observed in the micrographs. The projection of pits on the \{001\} surface is bounded by four \(<001>\) directions. Faceting is observed on \{001\} planes at the bottom of the pits.

Details of the bottom of pits on the \{001\}, \{011\} and \{111\} planes are compared in Figure 42. It is apparent that in spite of the difference in the initial crystallographic orientation of the sample surfaces, \{001\} faceting occurs during pitting corrosion in all situations.

3.1.7.b Effect of Chloride Concentration

SEM micrographs of a \{001\} plane of an aluminium crystal after galvanostatic pitting at 5 mA/cm\(^2\) for 1000 sec. in 2M NaCl solution are shown in Figure 43. Similar to those for the 0.5M NaCl solutions, crystallographic and tunnel-like attack is observed in these photographs, although finer \{001\} stepped faceting is produced in the concentrated solution as shown in Figure 43(b). (Compare with Figure 42a for 0.5M NaCl).
Figure 40 Pit morphologies developed on the \{011\} plane of Al single crystal after galvanostatic pitted at 50 mA/cm$^2$ for 1000 sec in 0.5 M NaCl solution.
Figure 41  Pit morphology on the \{001\} plane of aluminium single crystal after galvanostatically pitted at 50 mA/cm² for 1000 sec in 0.5 M NaCl solution.
Figure 42 Details of the bottom of pit developed on the (001), (011) and (111) surfaces after galvanostatic pitting test at 5 mA/cm² for 1000 sec.
Figure 43  Pit morphology on \{001\} surface of aluminium single crystal after galvanostatic pitting test at 5 mA/cm$^2$ for 1000 sec in 2 M NaCl solutions.
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3.1.7.c Effect of Copper

The morphological feature of corrosion pits that formed on the \{001\}, \{011\} and \{111\} surfaces of a Al-3\% Cu single crystal are shown in Figure 44. The pits show no faceting, in contrast to a pure aluminium crystal. An irregular spongy morphology developed inside the pits in all three faces.

It is also observed that there are no differences in morphology on the three differently oriented surfaces.
Figure 44 Pit morphology on the \{001\}, \{011\} and \{111\} surfaces of the Al-3\%Cu single crystal after PPC test in 0.5M NaCl solution.
Figure 45  Optical micrograph of the etched surface of the as-grown 9°<001> tilt bicrystal of 4.2%Cu.(Sample No 23,Al4Cu-2). The average cell spacing is 210μm.

Figure 46  SEM micrograph of the etched surface of the as-grown 9°<001> tilt bicrystal of 0.52%Cu.(Sample No13,Al1Cu-9). The cell spacing is 185 μm.
3.2 Grain Boundary Segregation and Intergranular Corrosion of Bicrystals

3.2.1 Solute Segregation

3.2.1.a As-Grown Bicrystal

Surfaces of the as-grown bicrystal specimens were subjected to etching* in order to reveal their substructure. The micrographs of the etched surfaces of sample #23 (Al4Cu-2) and #13 (Al1Cu-9) bicrystals are shown in Figures 45 and 46 respectively. From these micrographs, it was observed that a cellular structure had developed in each component single crystal of the alloy bicrystals. The cellular structure was due to solute re-distribution and transverse solute concentration periodicity occurring during the solidification process. The average cell spacing of the specimens was measured as 210 \( \mu \text{m} \) for sample #23 (Al4Cu-2) and 185 \( \mu \text{m} \) for sample #13 (Al1Cu-9).

EPMA Studies

The same specimens, after re-polishing, were analyzed with the EPMA. Line scan analyses were performed at six locations on the specimen surface. Figure 47 shows a representative line scan analysis of the Al4Cu-2 (sample #23) bicrystal. The X-ray intensity of CuK\( \alpha \) is plotted on the vertical axis and distance along the line is plotted on the horizontal axis. Line analyses were conducted perpendicular to the crystal growth direction. The CuK\( \alpha \) intensity (i.e. Cu concentration) varied with scan distance, showing maxima and minima which correspond to the Cu concentration at the cellular nodes (or walls) and cell centers respectively. The average maximum and minimum Cu concentration are presented in Table 9 for six different line analyses. The average cell spacings, measured from the Cu concentration profile are also listed. The cell spacing values are reasonably consistent with that measured from the micrograph of the etched surface. (210 \( \mu \text{m} \))

Similarly, the representative Cu concentration profile of the as-grown Al1Cu-9 bicrystal (sample No. 13) is shown in Figure 48. The average maximum and minimum

---

9 Etching was carried out in 10% NaOH solution at 70 °C
of Cu concentration and cell spacing for five different line analyses are presented in Table 10. The overall average difference of the Cu concentration between the maximum and minimum values was found greater for the sample #23 (Al4Cu-2) bicrystal than for the sample #13 (Al1Cu-9) bicrystal, i.e. $\Delta C_m = 1.65\%$ Cu for the sample #23 (Al4Cu-2) bicrystal and $0.36\%$ Cu for the sample #13 (Al1Cu-9) bicrystal.

Figure 47 Representative EPMA line scan analysis of the as-grown $9^\circ<001>$ tilt bicrystal of 4.2$\%$Cu. (Al2Cu-4, sample No. 23)
Figure 48 Representative EPMA line scan analysis of the as-grown 90°<001> tilt bicrystal of 0.54%Cu. (Al1Cu-9, sample No. 13)
## TABLE 9

Average Cell Spacing and Average Maximum and Minimum Cu Concentration of the As-Grown 9°<001> tilt Bicrystal of 4.2%Cu*1(Al4Cu-2, sample No. 23)

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Avg Cell Spacing</th>
<th>Avg Cu Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μm</td>
<td>Max (%)</td>
</tr>
<tr>
<td>23-1</td>
<td>183</td>
<td>3.14</td>
</tr>
<tr>
<td>23-2</td>
<td>241</td>
<td>3.27</td>
</tr>
<tr>
<td>23-3</td>
<td>275</td>
<td>3.07</td>
</tr>
<tr>
<td>23-4</td>
<td>259</td>
<td>3.24</td>
</tr>
<tr>
<td>23-5</td>
<td>293</td>
<td>3.56</td>
</tr>
<tr>
<td>23-6</td>
<td>199</td>
<td>3.28</td>
</tr>
<tr>
<td>Overall Avg</td>
<td>= 210 μm</td>
<td>Overall Avg ΔC_m *3 = 1.65% Cu</td>
</tr>
</tbody>
</table>

*1 Cu concentration indicated here is the Cu concentration of an adjacent homogenized sample cut out from the same bicrystal.

*2 Average cell spacing measured from the photograph of the etched surface.(Figure 45)

*3 ΔC_m is the overall average of ΔC.

## TABLE 10

Average Cell Spacing and Average Maximum and Minimum Cu Concentration of the As-Grown 9°<001> tilt bicrystal of an 0.54%Cu*1(Al1Cu-9, sample No.13)

<table>
<thead>
<tr>
<th>Specimen No</th>
<th>Avg Cell Spacing</th>
<th>Average Cu Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μm</td>
<td>Max</td>
</tr>
<tr>
<td>13-1</td>
<td>157</td>
<td>0.93</td>
</tr>
<tr>
<td>13-2</td>
<td>164</td>
<td>0.79</td>
</tr>
<tr>
<td>13-3</td>
<td>165</td>
<td>0.72</td>
</tr>
<tr>
<td>13-4</td>
<td>198</td>
<td>0.80</td>
</tr>
<tr>
<td>13-5</td>
<td>164</td>
<td>0.83</td>
</tr>
<tr>
<td>Overall Avg</td>
<td>= 185 μm</td>
<td>Overall Avg ΔC_m *3 = 0.36 %Cu</td>
</tr>
</tbody>
</table>

*1 Cu concentration indicated here is the Cu concentration of an adjacent homogenized sample cut out from the same bicrystal.

*2 Average cell spacing measured from the photograph of the etched surface.(Figure 46)

*3 ΔC_m is the overall average of ΔC.
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STEM-EDX Studies: Grain Boundary

Electron transparent specimens prepared from the as-grown bicrystal (Al4Cu-2) were analysed using the STEM-EDX.

The transparent area of the thin samples was about 100 μm². Since the average cell spacing is generally larger than 100 μm, the electron transparent area may therefore not contain any grain boundary or substructure boundary or at most, one boundary.

A STEM Micrograph of the sample prepared from the grain boundary region of the as-grown bicrystal of 4.20%Cu(Al4Cu-2, samples No. 23) is shown in Figure 49a.

It is clear from this micrograph that a second phase precipitates along the grain boundary. The average width of the precipitates ranged from 0.12 to 0.18 μm and the average length was 2 μm. The separation between precipitates was approximately 1 μm. Details of a typical grain boundary precipitate are shown in Figure 50. No lamellar structure corresponding to the eutectic was found. The precipitate in Figure 50 appears to be a single grain of second phase. The interfacial boundary is inclined with respect to the electron beam and their fringes are observed. Since the precipitated second phase was not the eutectic resulting from the solidification process, it could only be formed by precipitation from the supersaturated solid solution during the cooling process after the bicrystal was grown. Therefore, although the large precipitates were not identified in this case, they are undoubtedly the θ phase. No matrix precipitates were found, as confirmed by both Figure 49a and Figure 50.
Figure 49 STEM micrograph (a) and Cu concentration profiles across the grain boundary of the as-grown $9^\circ<001>$ tilt bicrystal of 4.2%Cu (Al4Cu-2, Sample No.23). (b) Analysed at points across the grain boundary between precipitates. (c) Analysed at points across the grain boundary with precipitates.
Figure 50  TEM micrograph showing detail of the grain boundary precipitate of the as-grown 9°<001> tilt bicrystal of 4.20%Cu (Al4Cu-2, sample No. 23)
Quantitative X-ray microanalysis was carried out at eight or more different point locations that were arranged along a line (trace) that traversed the grain boundary at approximately 90°, as indicated by the contamination spots in Figure 49a. The results are shown in Table 11. The corresponding Cu concentration profiles of the trace across the grain boundary between two precipitates and that for the trace crossing the grain boundary at a precipitate are shown in Figure 49b and 49c respectively. From Figure 49b, it can be seen that the Cu concentration drops from 4.2% Cu in both grains to 1.34% Cu at the grain boundary when free of precipitate. On the other hand, the Cu concentration profile corresponding to the trace with precipitate (Figure 49c) shows a sharp rise to 36% Cu at the grain boundary precipitate, decreasing in both grains in the immediate vicinity of the precipitate, and then increasing to the bulk concentration at more remote distances from the grain boundary. In both cases, solute-depleted zones were found adjacent to the grain boundary or grain boundary precipitate. Note that the measured concentration (36% Cu) of precipitate is considerably less than the composition of the possible θ phase (54% Cu), which suggests that the small volume of specimen analysed must have included both the precipitate and the matrix.

STEM-EDX Studies: Grain Interior

A TEM micrograph from a component single crystal area which was not located at the grain boundary of the Al4Cu-2 bicrystal (sample #23) is shown in Figure 51a. A boundary dividing the field of view into two parts is seen in this Figure. Features which are believed to be the second phase precipitates, probably the θ' phase, are observed along the boundary with the boundary fringes.

Selected-area electron diffraction patterns from areas located on the boundary and from each side were obtained to check the crystallographic orientation. Figure 51b is a diffraction pattern from a (100) zone that corresponds to area (B). It indicates that the crystal in this area has the (100) plane normal to the electron beam. Similarly, the (100)
CHAPTER 3: RESULTS

TABLE 11
EDX Analysis On Grain Boundary of the As-grown 9°<001> Tilt Bicrystal of 4.2% Cu*1 (Al4Cu-2, sample No. 23)

<table>
<thead>
<tr>
<th>Trace between ppts</th>
<th>Trace with ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dist. from GB(µm)</td>
<td>%Cu</td>
</tr>
<tr>
<td>2.50</td>
<td>4.22</td>
</tr>
<tr>
<td>1.60</td>
<td>3.88</td>
</tr>
<tr>
<td>0.47</td>
<td>3.0</td>
</tr>
<tr>
<td>0.00</td>
<td>1.34</td>
</tr>
<tr>
<td>0.50</td>
<td>4.21</td>
</tr>
<tr>
<td>1.30</td>
<td>4.60</td>
</tr>
<tr>
<td>2.20</td>
<td>4.50</td>
</tr>
<tr>
<td>3.40</td>
<td>4.23</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 Cu concentration indicated here is the Cu concentration of an adjacent homogenized sample cut from the same bicrystal

plane of the lower part of the crystal (D) is normal to the beam as demonstrated by the {100} zone diffraction pattern from this region (Figure 51d). No significant orientation difference between the two parts of the crystal was detected by observing the selected area electron diffraction pattern (Figure 51c) obtained from region (C), which comprised both parts of the crystal adjacent to the boundary. The diffraction spots appear to correspond to a single crystal. However, small orientation differences can still exist between the two parts of the crystal that are too small to be easily detected by the electron diffraction analysis. The presence of Kikuchi lines in Figure 51d (area D) and their absence in Figure 51b (area B) suggest very small angular difference in orientation in these two areas.
Figure 51 TEM micrograph and electron diffraction patterns from grain interior of the as grown $9^\circ<001>$ tilt bicrystal of 4.20%Cu. (Al4Cu-2, sample No. 23) The diffraction patterns were obtained from the corresponding selected areas in Figure 51a.
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The most common boundary in the as grown alloy single crystal is the cellular wall with composition variation. Therefore, the boundary observed here could be the solidification cellular wall, as expected.

Details of a typical precipitate that formed at the cell wall is shown in Figure 52. (indicated by the arrow). The selected area diffraction pattern obtained from the boundary area is superimposed on the figure.

From this figure it is observed that the precipitate is parallel to the <001> direction or (001) plane of the matrix. (See also precipitates in Figure 51a, region C). A segment of cell wall is aligned parallel to the precipitate and, therefore, parallel to the (001) plane of the matrix on which the precipitate has formed.

The results of several point analyses conducted at different locations aligned normal to the cell wall, as illustrated by the contamination spots in Figure 53c, are summarized in Table 12.

A Cu depleted zone was found at the cell wall for the trace between precipitates (Figure 53a). For the trace with precipitate, the Cu concentration profile shows a gradual decrease as the cell wall is approached and 15.4% Cu at the precipitate. (Figure 53b). However, the extent of solute depletion was not as significant as for the grain boundary. (Compare Figures 49c and 53b). Again, the volume of specimen analysed may have contained a region of matrix, in addition to the precipitate, and this could be responsible for the low Cu concentration of the precipitate as compared with the composition of the θ' phase.
Figure 52 TEM micrograph showing detail of the precipitate at the cell wall shown in Figure 51. The \{001\} diffraction pattern is superimposed in the figure.
Figure 53 Grain interior containing a cell wall of the $9^\circ<001>$ tilt bicrystal sample (Al4Cu-2, Sample No. 23). (a) Cu concentration profile of analytical trace between ppts. (b) Cu concentration profile of analytical trace with ppt. and (c) STEM micrograph
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TABLE 12

EDX Analysis on the Cell Wall of the Component Single Crystal of the As-grown 9°<001> Tilt Bicrystal of 4.2%Cu*1 (Al4Cu-2, Sample No. 23).

<table>
<thead>
<tr>
<th>Trace between ppts</th>
<th>Trace with ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dist. from C.W.(µm)</td>
<td>%Cu</td>
</tr>
<tr>
<td>1.76</td>
<td>3.86</td>
</tr>
<tr>
<td>1.42</td>
<td>3.29</td>
</tr>
<tr>
<td>0.88</td>
<td>3.60</td>
</tr>
<tr>
<td>0.59</td>
<td>3.23</td>
</tr>
<tr>
<td>0.27</td>
<td>3.39</td>
</tr>
<tr>
<td>0.00</td>
<td>2.18</td>
</tr>
<tr>
<td>0.36</td>
<td>3.13</td>
</tr>
<tr>
<td>0.64</td>
<td>3.21</td>
</tr>
<tr>
<td>0.84</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 Cu concentration indicated here is the Cu concentration of an adjacent homogenized sample cut from the same bicrystal.

TABLE 13

EDX Analysis Along a Cell Wall of the Component Single Crystal of the 9°<001> Tilt As-grown Bicrystal of 4.2%Cu*1 (Al4Cu-2, Sample #23).

<table>
<thead>
<tr>
<th>Dist. Along the Cell Wall (µm)</th>
<th>%Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (arbitrary)</td>
<td>2.71</td>
</tr>
<tr>
<td>0.5</td>
<td>2.91</td>
</tr>
<tr>
<td>1.0</td>
<td>2.91</td>
</tr>
<tr>
<td>1.4</td>
<td>2.59</td>
</tr>
<tr>
<td>1.85</td>
<td>2.18</td>
</tr>
<tr>
<td>(on ppt)</td>
<td>30.9</td>
</tr>
</tbody>
</table>

*1 Cu concentration indicated here is the Cu concentration of an adjacent homogenized sample cut from the same bicrystal.
Spot analyses were done along the cell wall where it was free of precipitate, as shown in Figure 54a. The results are summarized in Table 13. Clearly, Cu was depleted along the cell wall. (Compare with the bulk concentration listed in Table 12). It was also observed that the solute concentration decreased gradually with decreasing distance from the large precipitate, as seen in Figure 54b.
Figure 54  Cell wall in a grain interior of the as grown bicrystal sample (Al4Cu-2, Sample No. 23, grain interior). (a) SEM micrograph (b) Cu concentration profile along the cell wall.
In summary, the results of the EPMA and STEM-EDX studies on the as-grown bicrystal showed that:

(1) A cellular structure was formed in the component single crystal of the as-grown alloy bicrystal, with solute segregation occurring at the grain boundary and the cell walls.

(2) Second phase precipitation, associated with a Cu depleted zone, occurred along the grain boundary and the cell walls.

3.2.1.b Homogenized Bicrystal

EPMA Studies

Figure 55 shows the EPMA line scan analysis of the 4.2% Cu bicrystal (Al4Cu-2, Sample No. 24) before and after the solution heat treatment. The uniform distribution of Cu, with no periodicity, in the homogenized specimen shows that the solidification cellular segregation was completely homogenized after the heat treatment.

The Cu concentration of the different homogenized bicrystal samples used in the present studies were determined by the EPMA method and the analysis results are listed in Table 14.
TABLE 14

EPMA Analysis of Copper Concentration of the Homogenized <001> Tilt Bicrystal Samples

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Sample #</th>
<th>wt %Cu</th>
<th>Crystal</th>
<th>Sample #</th>
<th>wt %Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al1Cu-9</td>
<td>14-1</td>
<td>0.55</td>
<td>Al1Cu-10</td>
<td>35-1</td>
<td>0.50</td>
</tr>
<tr>
<td>(nominal</td>
<td>14-2</td>
<td>0.50</td>
<td>(nominal</td>
<td>35-2</td>
<td>0.48</td>
</tr>
<tr>
<td>9° tilt</td>
<td>14-3</td>
<td>0.56</td>
<td>14° tilt</td>
<td>35-3</td>
<td>0.49</td>
</tr>
<tr>
<td>1% Cu)</td>
<td>14-4</td>
<td>0.55</td>
<td>1% Cu)</td>
<td>35-4</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>14-5</td>
<td>0.54</td>
<td></td>
<td>35-5</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>14-6</td>
<td>0.54</td>
<td></td>
<td>35-6</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.54</td>
<td>Average σ</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>Average σ</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Al2Cu-1</td>
<td>20-1</td>
<td>1.40</td>
<td>Al2Cu-3</td>
<td>41-1</td>
<td>1.43</td>
</tr>
<tr>
<td>(nominal</td>
<td>20-2</td>
<td>1.39</td>
<td>(nominal</td>
<td>41-2</td>
<td>1.45</td>
</tr>
<tr>
<td>9° tilt</td>
<td>20-3</td>
<td>1.42</td>
<td>14° tilt</td>
<td>41-3</td>
<td>1.40</td>
</tr>
<tr>
<td>2% Cu)</td>
<td>20-4</td>
<td>1.40</td>
<td>2% Cu)</td>
<td>41-4</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td>20-5</td>
<td>1.36</td>
<td></td>
<td>41-5</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>20-6</td>
<td>1.40</td>
<td></td>
<td>41-6</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.40</td>
<td>Average σ</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.02</td>
<td>Average σ</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Al4Cu-2</td>
<td>24-1</td>
<td>3.81</td>
<td>Al4Cu-4</td>
<td>45-1</td>
<td>2.81</td>
</tr>
<tr>
<td>(nominal</td>
<td>24-2</td>
<td>4.00</td>
<td>(nominal</td>
<td>45-2</td>
<td>2.90</td>
</tr>
<tr>
<td>9° tilt</td>
<td>24-3</td>
<td>3.90</td>
<td>14° tilt</td>
<td>45-3</td>
<td>2.78</td>
</tr>
<tr>
<td>4% Cu)</td>
<td>24-4</td>
<td>4.32</td>
<td>4% Cu)</td>
<td>45-4</td>
<td>3.55</td>
</tr>
<tr>
<td></td>
<td>24-5</td>
<td>4.51</td>
<td></td>
<td>45-5</td>
<td>3.60</td>
</tr>
<tr>
<td></td>
<td>24-6</td>
<td>4.43</td>
<td></td>
<td>45-6</td>
<td>3.57</td>
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<tr>
<td></td>
<td></td>
<td>4.16</td>
<td>4% Cu</td>
<td></td>
<td>3.20</td>
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<tr>
<td></td>
<td></td>
<td>0.27</td>
<td>Average σ</td>
<td>0.37</td>
<td></td>
</tr>
</tbody>
</table>
Figure 55 EPMA line scan analyses of the homogenized 9°<001> tilt bicrystal of 4.2%Cu (sample No 24, Al4Cu-2). (a) Before and (b) After the homogenizing heat treatment (540° for 30 days)
STEM-EDX Studies

A thin film of the homogenized 9° <001> tilt bicrystal (sample #24, Al4Cu-2) was examined by STEM-EDX with the grain boundary plane paralleled to the electron beam. The boundary appeared as a sharp straight line when viewed in the TEM, as shown in Figure 56. No grain boundary or matrix precipitates were observed. Composition point analyses were obtained by EDX techniques along traces normal to the grain boundary, at locations depicted by the contamination spots in Figure 56. The results are summarized in Table 15 and the Cu concentration was plotted as a function of distance from the grain boundary in Figure 57. The Cu concentration profiles showed no evidence of microsegregation at the grain boundary. The EDX results shown in Table 15 are consistent with those measured from the same sample by the EPMA technique (see Table 14, Sample No. 24.).

Figure 56 TEM micrograph of the homogenized, 9°<001> tilt bicrystal. (Sample #24, Al4Cu-2).
TABLE 15

EDX Analysis On Grain Boundary of the Homogenized 9°<001> Tilt Bicrystal (Al4Cu-2, sample No. 24)

<table>
<thead>
<tr>
<th>Dist. from GB(μm)</th>
<th>%Cu</th>
<th>Dist. from GB(μm)</th>
<th>%Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.75</td>
<td>4.37</td>
<td>2.80</td>
<td>4.15</td>
</tr>
<tr>
<td>1.20</td>
<td>4.30</td>
<td>1.69</td>
<td>4.05</td>
</tr>
<tr>
<td>0.55</td>
<td>4.63</td>
<td>0.63</td>
<td>4.15</td>
</tr>
<tr>
<td>0.00</td>
<td>4.50</td>
<td>0.00</td>
<td>4.10</td>
</tr>
<tr>
<td>0.60</td>
<td>4.32</td>
<td>0.50</td>
<td>3.96</td>
</tr>
<tr>
<td>1.25</td>
<td>4.14</td>
<td>1.48</td>
<td>4.20</td>
</tr>
<tr>
<td>1.95</td>
<td>3.03</td>
<td>2.50</td>
<td>3.89</td>
</tr>
<tr>
<td>2.80</td>
<td>4.46</td>
<td>3.50</td>
<td>4.26</td>
</tr>
</tbody>
</table>

Average 4.32  
Stdev 0.23

Average 4.10
Stdev 0.12

In summary, the EPMA and the STEM-EDX analysis showed that the homogenized alloy bicrystal samples exhibited no segregation (i.e. no cellular segregation, no solute segregation or solute depletion at the grain boundary and no precipitation of second phase).
Figure 57 Cu concentration profiles across the grain boundary of the homogenized 9°<001> bicrystal (Al4Cu-2, Sample No. 24).
3.2.1.c Aged Bicrystal

A TEM micrograph of the aged 9°<001> tilt bicrystal sample (Al4Cu-2, Sample #25) is shown in Figure 58. Irregularly shaped θ precipitates at the grain boundary and plate shape θ' precipitate in the matrix were observed.

A selected area diffraction pattern from the grain boundary region is superimposed on the TEM micrograph in Figure 59. The composite pattern contains the two (001) diffraction patterns from the adjacent crystals and shows that the tilt angle was 10°, which confirmed the result obtained by X-ray diffraction techniques. (See Table 2, Al4Cu-2 bicrystal). It is also seen from Figure 59 that the platelet θ' precipitates lie parallel to the {001} planes of their matrix crystals.
Figure 59 TEM micrograph of the aged $9^\circ<001>$ tilt bicrystal sample (Al$_4$Cu-2, Sample No. 25) and the superimposed selected area electron diffraction pattern from the grain boundary region. The diffraction pattern contains two (001) diffraction patterns from the two adjacent single crystals of the bicrystal.
Composition point analyses were obtained along traces normal to the grain boundary. The results of two traces, one intersecting a grain boundary precipitate and one passing between grain boundary precipitates are summarized in Table 16 and the Cu concentration profiles are plotted in Figure 60. From these profiles, it is obvious that a Cu solute depleted zone was developed at the grain boundary and adjacent to the grain boundary precipitates.

**TABLE 16**

EDX Analysis On Grain Boundary of the Aged 9°<001> Tilt Bicrystal of 4.2%Cu*1(Al4Cu-2, sample No. 23)

<table>
<thead>
<tr>
<th>Trace between ppts</th>
<th>Trace with ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dist. from GB(µm)</td>
<td>%Cu</td>
</tr>
<tr>
<td>0.58</td>
<td>4.10</td>
</tr>
<tr>
<td>0.40</td>
<td>4.05</td>
</tr>
<tr>
<td>0.16</td>
<td>3.32</td>
</tr>
<tr>
<td>0.05</td>
<td>2.26</td>
</tr>
<tr>
<td>0.00</td>
<td>2.18</td>
</tr>
<tr>
<td>0.20</td>
<td>2.92</td>
</tr>
<tr>
<td>0.40</td>
<td>4.12</td>
</tr>
<tr>
<td>0.60</td>
<td>4.22</td>
</tr>
</tbody>
</table>

*1 Cu concentration indicated here is the Cu concentration of an adjacent homogenized sample cut from the same bicrystal.
Figure 60 Cu concentration profiles across the grain boundary of the aged 9°<001> tilt bicrystal sample (Al4Cu-2, Sample No. 25). (a) Trace between precipitates (b) Trace with precipitate
3.2.2. Potentiodynamic Pitting Corrosion Test

3.2.2.a Homogenized Bicrystal

PPC tests were conducted on the 9°<001> tilt bicrystals of annealed aluminum and homogenized Al-Cu alloys, with the grain boundary region and component single crystal faces exposed alternately to a 0.5M NaCl solution. The Epit and Eprot were obtained from the PPC diagrams. They are summarized in Table 17 and plotted as a function of Cu content in Figure 61.

The Epit was found to increase with increasing Cu content of the bicrystals within the range of composition studied. An increase of ~180 mV in Epit was observed with the addition of 4.2 wt% Cu. However, Eprot behaved in a different manner. It increased initially with Cu content up to 1.4 wt% Cu, then became constant at higher Cu concentrations.

<table>
<thead>
<tr>
<th>Tilt Angle</th>
<th>Cu* (wt%)</th>
<th>Epit(mV)</th>
<th>Eprot(mV)</th>
<th>Epit(mV)</th>
<th>Eprot(mV)</th>
<th>No.of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>9°</td>
<td>0.00</td>
<td>-693</td>
<td>-794</td>
<td>-705</td>
<td>-795</td>
<td>5</td>
</tr>
<tr>
<td>9°</td>
<td>0.54</td>
<td>-654</td>
<td>-715</td>
<td>-649</td>
<td>-713</td>
<td>5</td>
</tr>
<tr>
<td>9°</td>
<td>1.40</td>
<td>-617</td>
<td>-654</td>
<td>-616</td>
<td>-655</td>
<td>8</td>
</tr>
<tr>
<td>9°</td>
<td>4.20</td>
<td>-510</td>
<td>-658</td>
<td>-532</td>
<td>-653</td>
<td>3</td>
</tr>
<tr>
<td>14°</td>
<td>0.00</td>
<td>-694</td>
<td>-799</td>
<td>-669</td>
<td>-795</td>
<td>6</td>
</tr>
<tr>
<td>14°</td>
<td>0.10</td>
<td>~</td>
<td>~</td>
<td>-696</td>
<td>-752</td>
<td>4</td>
</tr>
<tr>
<td>14°</td>
<td>0.49</td>
<td>-660</td>
<td>-724</td>
<td>-670</td>
<td>-721</td>
<td>1</td>
</tr>
<tr>
<td>14°</td>
<td>1.52</td>
<td>-604</td>
<td>-671</td>
<td>-618</td>
<td>-670</td>
<td>8</td>
</tr>
<tr>
<td>14°</td>
<td>3.20</td>
<td>-550</td>
<td>-699</td>
<td>-554</td>
<td>-663</td>
<td>3</td>
</tr>
<tr>
<td>28°</td>
<td>0.00</td>
<td>-704</td>
<td>-806</td>
<td>-715</td>
<td>-798</td>
<td>~</td>
</tr>
<tr>
<td>28°</td>
<td>0.10</td>
<td>-708</td>
<td>-798</td>
<td>-716</td>
<td>-797</td>
<td>~</td>
</tr>
</tbody>
</table>

* Data were measured by EPMA.
CHAPTER 3: **RESULTS**

No significant difference in \( E_{\text{pit}} \) and \( E_{\text{prot}} \) was detected between the grain boundary and its adjacent single crystal surfaces.

Similar PPC tests were conducted on the homogenized \( 140^\circ<001> \) tilt bicrystals of different Cu contents. The values of \( E_{\text{pit}} \) and \( E_{\text{prot}} \) are listed in Table 17 and plotted in Figure 62. Comparisons of Figure 62 and 61 shows that Cu affected the \( E_{\text{pit}} \) and \( E_{\text{prot}} \) in the same way as for the \( 9^\circ<001> \) tilt bicrystals. Also, there was no significant influence of the grain boundary on either the \( E_{\text{pit}} \) or \( E_{\text{prot}} \) for the \( 140^\circ<001> \) tilt bicrystals.

The values of \( E_{\text{pit}} \) and \( E_{\text{prot}} \) at the grain boundary region of the bicrystals of different tilt angles are plotted in Figure 63. The increase of tilt angle of the bicrystals from \( 9^\circ \) to \( 14^\circ \) did not produce any noticeable effect on the \( E_{\text{pit}} \) and \( E_{\text{prot}} \). Within experimental reproducibility, increasing the tilt angle up to \( 28^\circ \) for pure Al and Al-0.1\%Cu bicrystals had no significant effect on \( E_{\text{pit}} \) and \( E_{\text{prot}} \).
Figure 61 Effect of Cu content on the Epit and Eprot of the homogenized 9°<001> tilt bicrystal.
CHAPTER 3: RESULTS

Figure 62 Effect of Cu content on the Epit and Eprot of the homogenized 14°<001> tilt bicrystal.

Figure 63 Effect of tilt angle on the Epit and Eprot of the homogenized Al-Cu alloy bicrystal.
3.2.2.2 As-Grown Bicrystal

PPC tests in 0.5M NaCl solution were carried out on the as-grown 9°<001> tilt bicrystals of Al-0.54%Cu and Al-4.2%Cu. Values of Epit and Eprot are summarized in Table 18 and plotted against Cu content in Figure 64. In this figure, the corresponding curves of Epit and Eprot for the homogenized bicrystals from Figure 61 are also shown for comparison.

It was observed from Figure 64 that both the Epit and Eprot of the as grown bicrystals of both 0.54%Cu and 4.2%Cu Al-Cu alloys were shifted in the active direction as compared to the corresponding homogenized bicrystals. The shift increased with Cu content and was most pronounced for Epit. For example, potential differences between Epit for the 0.54%Cu and 4.2%Cu alloys were 16mV and 78mV, respectively.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Cu*1 (wt%)</th>
<th>Grain Interior</th>
<th>Grain Boundary</th>
<th>No. of Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Epit(mV) Avg</td>
<td>Eprot(mV) Avg</td>
<td>Epit(mV) Avg</td>
</tr>
<tr>
<td>As-grown 4.20*2</td>
<td>4.20*2</td>
<td>-608 2</td>
<td>-680 15</td>
<td>-610 7</td>
</tr>
<tr>
<td>As-grown 0.54*2</td>
<td>0.54*2</td>
<td>~ ~ ~ ~</td>
<td>~ ~    ~ ~</td>
<td>-665 ~</td>
</tr>
<tr>
<td>Aged 4.20*2</td>
<td>4.20*2</td>
<td>-586 5</td>
<td>-702 6</td>
<td>-595 3</td>
</tr>
</tbody>
</table>

*1 Data were measured by EPMA.
*2 The Cu % indicated here is the concentration of an adjacent homogenized sample cut from the same bicrystal of the test piece.
3.2.2.2 Aged Bicrystal

The $\text{E}_{\text{pit}}$ and $\text{E}_{\text{prot}}$ potentials of the aged $9^\circ<001>$ tilt bicrystals of Al-4.2%Cu alloy, are listed in Table 18.

Similar to the as grown bicrystals, both the $\text{E}_{\text{pit}}$ and $\text{E}_{\text{prot}}$ of the aged sample are moved to the active potential with respect to the homogenized bicrystal as shown in Figure 65. The shift is most pronounced for $\text{E}_{\text{pit}}$, where the difference between the homogenized and aged 4.2%Cu alloy is 63 mV.
Figure 65 $E_{\text{pit}}$ and $E_{\text{prot}}$ of the aged $9^\circ<001>$ tilt bicrystal of 4.20% Cu alloy. The dashed curves are (a) $E_{\text{pit}}$ and (b) $E_{\text{prot}}$ of the corresponding homogenized bicrystals.

3.2.3 Morphology of Corrosion Pits

3.2.3.a Homogenized Bicrystal

Corrosion pits were observed on all homogenized bicrystals after PPC tests. The pits were of different sizes and were distributed over the entire specimen surface. Many of the pits overlapped, forming pit clusters. No preferential attack on the grain boundary was observed for low angle bicrystals. For example, Figure 66a and 66b are two typical SEM photographs showing uniform pit distribution on the $9^\circ<001>$ tilt bicrystals of Al and homogenized 1.42% Cu alloy which contain a grain boundary within the area of view.
Figure 66 Typical SEM micrographs showing the corrosion pit distribution on the 9°<001> tilt bicrystal samples containing grain boundary area.
(a) Pure Al
(b) Homogenized Al-1.4 %Cu alloy
Figure 67 Typical SEM micrographs showing the corrosion pit distribution on the $28^\circ<001>$ tilt bicrystal samples containing grain boundary area.
(a) Pure Al
(b) Homogenized Al-0.1%Cu alloy
At higher tilt angles, corresponding to $28^\circ<001>$, the pits were uniformly distributed on pure Al bicrystals (Figure 67a), but showed evidence of preferential grain boundary pitting in the 0.1%Cu bicrystal (Figure 67b).

The effects of Cu content on the morphology of pits on the individual component crystal surfaces of $9^\circ<001>$ tilt bicrystals are illustrated in Figure 68. Crystallographic {001} facets developed at the bottom of the pits in pure Al, as shown in Figure 68(a). The addition of 0.1%Cu did not change this morphology (Figure 68b). However, a dramatic transformation from {001} faceting to an irregular spongy morphology occurred at 0.54%Cu (e.g. Figure 68c). A similar irregular pit morphology was found for higher Cu content (1.42%Cu in Figure 68d).
Figure 68 Details of corrosion pit morphologies developed on the homogenized tilt bicrystal samples
(a) Pure Al,9°<001>, (b) 9°<001>, Al-0.1%Cu alloy, (c) 9°<001>, Al-0.54%Cu and (d) 9°<001>, Al-1.4%Cu.
3.2.3.b Aged Bicrystal

Figure 69 shows an SEM micrograph of the surface of an aged, 9°<001> tilt bicrystal of 4.2%Cu after a PPC test in 0.5M NaCl solution. A sharp straight corrosion groove is evident along the location of the grain boundary as the result of preferential grain boundary attack. Corrosion attack also occurred as straight grooves on the surface of the component single crystals. Some of the grooves on the same component single crystal were closely parallel. Others were normal to each other, and formed angles of approximately 40° or 50° with respect to the grain boundary, as indicated in Figure 69.

Since the specimen in Figure 69 was a symmetrical 9°<001> tilt bicrystal having the {001} plane of both the component single crystals parallel to the plane of the micrograph, the crystallographic orientations of the bicrystal could be analyzed and sketched, as shown in Figure 70. By comparing Figure 69 with Figure 70, it was found that corrosion grooves on the surface of the component single crystals were consistent with the traces of {111} slip planes on {001} surfaces.

Figure 71 contains SEM micrographs of the same aged sample after re-polishing and subjecting to another PPC test. As clearly shown in the photograph, preferential corrosion occurred again along the grain boundary and traces of slip planes. This confirmed that aged crystals were subject to preferential attack. The severely attacked locations marked as A in Figure 71b were attributed to precipitates falling out of the grain boundary after dissolution of their surrounding matrix.
Figure 69  SEM photograph of the aged 9°<001> tilt bicrystal of Al-4.2%Cu alloy after a PPC test in 0.5M NaCl solution.
Figure 70 Corresponding sketch of crystallographic orientation of the aged 9°<001> tilt bicrystal of 4.2% Cu alloy, shown in Figure 69.
Figure 71 Corrosion morphologies developed on the aged $9^\circ<001>$ tilt bicrystal of 4.2% Cu alloy after a PPC scan.
3.2.3.3 As-Grown Bicrystal

The corrosion morphology of the as-grown 9°<001> tilt bicrystal of a high copper 4.2% Cu alloy is shown in Figure 72 after being subjected to a PPC test in 0.5M NaCl solution. Figure 72a illustrates several features of the corrosion attack; (i) preferential corrosion occurred along the grain boundary and produced a sharp straight groove, (ii) pit clusters were distributed in wide bands that were aligned along the solidification cell directions and (iii) narrow zones of attack occurred along the solidification cell direction.

Severe grain boundary corrosion can be observed in the detailed micrograph in Figure 72b. Some grain boundary precipitates (indicated as A in this figure) were left behind when the surrounding matrix was dissolved away, resulting in a deep grain boundary groove with precipitate islands. In addition, some small particles, appearing as white spots (marked as B in Figure 72b), were observed near to the grain boundary region. These small particles were subsequently identified as Cu enriched particles.

In contrast, as-grown 9°<001> tilt bicrystals of a more dilute Cu concentration (0.54% Cu) showed that pitting corrosion occurred more uniformly over the surface, with no preferential attack along the grain boundary and no attack associated with the cellular solidification substructure, as confirmed by Figure 73.
Figure 72 SEM micrographs of corrosion morphologies developed on the as-grown $9^\circ<001>$ tilt bicrystal of 4.2 %Cu alloy after a PPC test in 0.5 M NaCl solution.
Figure 73  Morphology of the corrosion pits developed on an as grown 9°<001> tilt bicrystal of Al-0.54%Cu alloy after a PPC test in 0.5 M NaCl solution.
3.2.4 Location Of Corrosion Attack on the As-Grown Bicrystal Of Al-4.2%Cu

Efforts were made to locate the preferential sites of attack on the component crystals of the as-grown bicrystal of 4.2%Cu. The specimen was first polished and two reference micro indentation marks, approximately 1mm apart, were made on a line that was normal to the longitudinal direction of the cellular solidification structure, as shown in Figure 74. Subsequently, an EPMA line scan analysis for Cu distribution was conducted between the indentations. Afterwards, the indentation marks and the analyzed area were masked by lacquer, to protect subsequent corrosion of these regions, and the specimen was subjected to a PPC test. The appearance of corroded surface was correlated to the EPMA Cu concentration profile, as shown in Figure 74. Two important correlations were evident; (i) wide bands of pit clusters were located at the places where there was a low Cu concentration (i.e., at cell centers) and (ii) sharp narrow corrosion grooves were located where there was a higher Cu concentration, (i.e., at the cellular walls or nodes).

Figure 75 shows the details of some of the sharp narrow corrosion grooves. At occasional locations along the grooves, corrosion was more pronounced (e.g. area marked A in Figure 75b) and is attributed to the presence of a precipitate of CuAl2 in the cell wall. The precipitate was believed to having fallen out of the specimen after the surrounding matrix was dissolved.
Figure 74  EPMA line scan analysis and the corroded surface of the as grown 9°<001> tilt bicrystal of Al-4.2%Cu alloy
Figure 75 Details of the sharp narrow corrosion grooves (arrows) on the surface of the as-grown 9°<001> tilt bicrystal of 4.2 %Cu alloy shown in Figure 74.
3.3 Extraction Replica

Extraction replicas were obtained from the grain boundary regions of the as-grown 9°<001> tilt bicrystal of 4.2%Cu after being subjected to a PPC test in 0.5 M NaCl. An example of a grain boundary particle, labelled C, is shown in Figure 76. It was extracted from the grain boundary because its surrounding matrix had been dissolved preferentially during the PPC test. A quantitative EDX analysis of the particle C was 43.63 %Wt Cu. This value is much closer to the composition of θ phase (CuAl2) than the value obtained directly from the surface of the corroded specimen (see Table 19), because the replica technique eliminated the alloy matrix contribution to the X-ray signal.

Figure 77 shows another extraction replica from the grain boundary region (Figure 77a) and the corresponding CuKα X-ray image. (Figure 77b) The particle labelled "D" in Figure 77a is obviously enriched in Cu and corresponds to one of the white spots (particle) shown in Figure 72b. An EDX spectrum of the particle is shown in Figure 77. A quantitative EDX analysis of the extracted particle gave a composition of 83.4%Wt Cu. This value approached the value of pure Cu. The Cu particle may arise from dealloying of the less noble Al and surface diffusion of Cu to form aggregates.
CHAPTER 3: RESULTS

Table 19

EDX quantitative analysis of a grain boundary precipitate and particle.

<table>
<thead>
<tr>
<th></th>
<th>Direct measurement on corroded surface</th>
<th>On extraction replica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain boundary ppt</td>
<td>16.3wt% Cu 83.7wt% Al</td>
<td>43.6wt% Cu 56.4wt% Al</td>
</tr>
<tr>
<td>Small particle (white spot)</td>
<td>4.4wt% Cu 95.6wt% Al</td>
<td>83.4wt% Cu 16.6wt% Al</td>
</tr>
</tbody>
</table>

Figure 76 SEM micrograph of an extraction replica of a grain boundary ppt from the as grown 9°<001> tilt bicrystal of 4.2%Cu alloy.
Figure 77  Extraction replica from the region adjacent to the grain boundary of the as-grown 9°<001> tilt bicrystal of 4.2% Cu alloy. (a) SEM micrograph, (b) CuKα, and (c) EDX spectrum from particle D indicated in (a).
3.4 Pitting Corrosion of Al Single Crystals in Nitrate Inhibited Solutions

3.4.1. Effect of Nitrate on $E_{\text{pit}}$ and $E_{\text{prot}}$

PPC tests were performed on the {001}, {011} and {111} faces of Al single crystals in a chloride solution, containing nitrate ions. (0.5 M NaCl + 0.5 M NaNO₃).

A representative pitting scan diagram of the {001} face is shown in Figure 78. The corresponding diagram for the nitrate-free 0.5 M NaCl solution (Figure 73) is reproduced in Figure 78. From these diagrams, it is evident that both the $E_{\text{pit}}$ and $E_{\text{prot}}$ were shifted very significantly to more noble potentials by the presence of NO₃⁻. Therefore pitting corrosion was inhibited in the nitrate-containing solution.

The same effect of nitrate was found for the {011} and {111} faces and their behavior is summarized in Table 20.

For simplicity, the inhibition index in Table 20 is defined here as

$$\Delta E = E_{\text{pit(NO}_3^-)} - E_{\text{pit(Cl}^-)}$$

where $E_{\text{pit(NO}_3^-)}$ and $E_{\text{pit(Cl}^-)}$ are the $E_{\text{pit}}$ in 0.5M NaCl + 0.5M NaNO₃ and 0.5M NaCl solutions, respectively. The index is a measure of the ability of the inhibitor to shift $E_{\text{pit}}$ to more noble values.

Table 20 shows that the pitting potential progressively decreases as the crystal face changes from {001} to {011} to {111}. The inhibition indices are in the same order, i.e., $\Delta E(001) > \Delta E(011) > \Delta E(111)$. 
Table 20

Epit and Eprot of the Al single crystals in 0.5 M NaCl and 0.5M NaCl+0.5M NaNO₃ solutions.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Solution</th>
<th>Epit (mV)</th>
<th>σ</th>
<th>Eprot (mV)</th>
<th>σ</th>
<th>No.of Data</th>
<th>ΔE (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>{001}</td>
<td>0.5M NaNO₃+0.5m NaCl</td>
<td>-282</td>
<td>46</td>
<td>-616</td>
<td>13</td>
<td>5</td>
<td>418</td>
</tr>
<tr>
<td></td>
<td>0.5M NaCl</td>
<td>-700</td>
<td>16</td>
<td>-799</td>
<td>5</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>{011}</td>
<td>0.5M NaNO₃+0.5m NaCl</td>
<td>-337</td>
<td>57</td>
<td>-591</td>
<td>36</td>
<td>5</td>
<td>387</td>
</tr>
<tr>
<td></td>
<td>0.5M NaCl</td>
<td>-724</td>
<td>6</td>
<td>-800</td>
<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>{111}</td>
<td>0.5M NaNO₃+0.5m NaCl</td>
<td>-397</td>
<td>39</td>
<td>-556</td>
<td>9</td>
<td>5</td>
<td>342</td>
</tr>
<tr>
<td></td>
<td>0.5M NaCl</td>
<td>-739</td>
<td>15</td>
<td>-800</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

Figure 78  Representative PPC scan diagrams performed on a {001} face of Al single crystal (a) in a 0.5M NaCl+0.5M NaNO₃, and (b) in a 0.5M NaCl solutions
3.4.2 Effect of Nitrate Addition On Pit Growth

The ability of NaNO3 to prevent pit growth was examined by an interruption method, whereby NaNO3 was added to an initially un-inhibited solution after pits had initiated and propagated during a PPC scan.

Figure 79 a,b,c and d show the effect of NaNO3 on pit propagation on a {001} Al single crystal face.

(a) As shown in Figure 79a, the specimen was subjected to a PPC scan in a 0.5 M NaCl solution up to a potential E, in the anodic scan direction, where:

$$E_{\text{prot}(\text{NO}_3^-)} = -616 \text{ mV} > E = -620 \text{ mV} > E_{\text{pit}(\text{Cl}^-)} = -700 \text{ mV}.$$

The subscripts Cl$^-$ and NO$_3^-$ indicate the environment of 0.5 M NaCl and 0.5 M NaCl + 0.5 M NaNO3 respectively. Upon reaching $E = -620 \text{ mV}$ in the anodic scan direction, where pit growth was in its early stage, NaNO3 was added to produced a solution of 0.5M NaCl + 0.5M NaNO3.

After the addition of NaNO3, it was observed that current density decreased, indicating retardation of pit growth. The current decreased to the passive current density and remained at this value until the potential reached $E_1$, where $E_{\text{pit}(\text{NO}_3^-)} > E_1 \approx -450 \text{ mV}$. Further increases in potential produced pitting corrosion, as confirmed by the increasing current density.

(b) In Figure 79b, the potential was scanned anodically to $E = -660 \text{ mV}$ (i.e., close to the value of -620 mV in Figure 79a) and held at this potential for a passage of 67 c/cm$^2$. After passage of this charge, during which the pit propagated extensively, the NaNO3 was added to the solution. Again, the current density decreased, consistent with retardation of pit growth. However, the minimum current density ($\sim 3 \times 10^5 \text{nA}$) was higher than in Figure 79a ($5 \times 10^3 \text{nA}$) and was close to the apparent passive current density observed on the reverse scan ($\sim 1.5 \times 10^5 \text{nA/cm}^2$). Also, the reverse scan apparent current density in Figure 79b was higher than the reverse scan apparent current density ($\sim 1 \times 10^4 \text{nA/cm}^2$) in Figure 79a. These differences were attributed to the extensive propagation of pits that was allowed to occur prior to the addition of NaNO3 in Figure 79b.
(c) In Figure 79C, the addition of NaNO₃ was made during the anodic scan after the potential reached \( E \) where, \( E_{\text{pit(NO₃)}} > E \) = -500 mV > \( E_{\text{prot(NO₃)}} > E_{\text{pit(Cl⁻)}} \) and held at this value for a passage of 655 C/cm². Clearly, the NaNO₃ addition did not stop pit propagation in this potential range. However, the current density dropped to the reversed scan level, which could be due to the reduction of number of active pit dissolution sites by the NaNO₃ addition.

(d) Similar behavior to Figure 79c was observed when the NaNO₃ addition was made during the anodic scan near to the same potential as in (c) (i.e. \( E = -470 \) mV) and held at \( E \) for the passage of a smaller charge of 24C/cm².
Figure 79 PPC scan diagrams showing the effect of NaNO₃ addition at potential E where, (E_{pit}NO₃ > E > (E_{prot}NO₃ > (E_{pit}Cl. (a) NaNO₃ added immediately reaching E=-620mV. (b) NaNO₃ added after reaching E=-660mV and held at E for a passage of 67C/cm². (c) NaNO₃ added after reaching E=-500mV and held at E for a passage of 655C/cm². (d) NaNO₃ added after reaching E=-470mV and held at E for a passage of 24C/cm².
3.4.3 Pit Area Ratio And Pit Density in Nitrate Inhibited Solution

Figure 80 shows representative binary bitplane images of the \{001\} face of Al single crystal after galvanostatic pitting at a current density of 5 mA/cm\(^2\) for 1000 sec in 0.5 M NaCl + 0.5 M NaNO\(_3\) and 0.5 M NaCl solution.

As shown in the figures, the number of pits were reduced in the nitrate-containing solution, but the pits were larger.

The results of pit area ratio and pit density measured by the Image analyser are summarized in Table 21 for nitrate-containing and nitrate-free solutions. It was found that the pit area ratio was reduced from 1.89\% to 1.05\% and the pit density from 14.0 to 6.1 (number of pits/mm\(^2\)) by the presence of nitrate in the solution.
Table 21

<table>
<thead>
<tr>
<th>Solution</th>
<th>Pit Area Ratio (%)</th>
<th>Pit Density (Pits/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average</td>
<td>σ</td>
</tr>
<tr>
<td>0.5M NaNO₃ + 0.5M NaCl</td>
<td>1.05</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>6.1</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>0.5M NaCl</td>
<td>1.89</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>14.0</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>416</td>
<td></td>
</tr>
</tbody>
</table>

3.4.4. Pit Morphology of Al Single Crystal in Nitrate Inhibited Solution

Figures 81a and b show the pit morphology that occurred on the \( \{001\} \) face of an Al single crystal after a PPC test in the 0.5 M NaCl + 0.5 M NaNO₃ solution.

The same \( \{001\} \) faceting was observed at the bottom of pits (i.e. Figure 81) as in the un-inhibited 0.5 M NaCl solution (see Figure 43a). However, at some locations where the pit surfaces were near to the external surface of the crystal, and more easily accessible to the bulk electrolyte, the \( \{001\} \) facets was hindered (e.g. Figure 81c). This was attributed to easy transport of NO₃⁻ from the bulk solution to the pit surfaces at these locations.

The same pit morphology was found for the \( \{011\} \) and \( \{111\} \) orientations in Figure 82 and 83 respectively. The \( \{001\} \) faceting was hindered on pits surface near to the external crystal surface (Figure 82a and 83a), but was unhindered at the bottom of the pits (Figure 82b and 83b).
Figure 81. Morphologies of pits developed on a (001) face of an Al single crystal after a PPC test in a 0.5M NaCl+0.5M NaNO₃ solution. (a) and (b) near the bottom of pit, (c) appearance of pit close to the surface of the sample.
Figure 82  Morphologies of pits developed on a \{011\} face of an Al single crystal after a PPC test in a 0.5M NaCl+0.5M NaNO₃ solution. (a) Details of a pit cluster, and (b) Details of bottom of pit.
Figure 83  Morphologies of pits developed on a {111} face of an Al single crystal after a PPC test in a 0.5M NaCl+0.5M NaNO3 solution. (a) Morphologies of pit near the crystal surface, and (b) Morphologies of pit bottom.
3.5 Pitting Corrosion and Intergranular Corrosion of Al-Cu Bicrystals in Nitrate Inhibited Solution

3.5.1 PPC Tests

The effect of nitrates on pitting corrosion of the as-grown, homogenized and aged Al-Cu bicrystals were examined by a PPC test in 0.5M NaCl + 0.5M NaNO₃ and 0.5M NaCl with only the grain boundary region exposed to the solution.

The Epit values obtained are listed in Table 22 and plotted versus Cu content in Figure 84. The Epit values were shifted to more noble potentials by the nitrate, relative to those for the un-inhibited 0.5 M NaCl solution. The Epit also increased with an increase in Cu content as shown in Figure 84.

For the as-grown and aged bicrystals, the Epit at the grain boundary region showed a 178 mV and 172 mV difference relative to the homogenized bicrystal of the same Cu content.

Table 22
Epit of 9 <001> tilt bicrystals of Al-Cu alloys in 0.5M NaCl+0.5M NaNO₃ solution.

<table>
<thead>
<tr>
<th>wt%Cu</th>
<th>Heat treatment</th>
<th>0.5M NaCl*¹</th>
<th>0.5M NaCl+0.5M NaNO₃*³</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00*²</td>
<td>Homogenized</td>
<td>-705</td>
<td>-338</td>
</tr>
<tr>
<td>0.10*²</td>
<td>Homogenized</td>
<td>-696</td>
<td>-340</td>
</tr>
<tr>
<td>0.54</td>
<td>Homogenized</td>
<td>-649</td>
<td>-324</td>
</tr>
<tr>
<td>4.20</td>
<td>Homogenized</td>
<td>-532</td>
<td>-252</td>
</tr>
<tr>
<td>4.20</td>
<td>As-grown</td>
<td>-610</td>
<td>-430</td>
</tr>
<tr>
<td>4.20</td>
<td>Aged</td>
<td>-595</td>
<td>-424</td>
</tr>
</tbody>
</table>

*¹ From Table 17.
*² 14°<001> tilt bicrystal.
*³ Number of data is one for each test condition.
Figure 84 Epit on a grain boundary area of an Al-Cu bicrystal in a 0.5M NaCl+0.5M NaNO₃ solution. (O) 9°<001>, (■) 14°<001>, (▲) aged 9°<001> and, (△) as grown 9°<001>
3.5.2 Pit Morphology of the Al-Cu Bicrystals in Inhibited Solution

The pit morphologies developed in the grain boundary region of a $9^\circ$<001> tilt bicrystal of Al after a PPC test in 0.5 M NaCl + 0.5 M NaNO$_3$ are shown in Figures 85a and 85b.

No preferential grain boundary attack was observed as shown in Figure 85a. Pits appeared as large clusters. The details of pit morphologies were found to be similar to those for the Al single crystal in nitrate-inhibited solution i.e. {001} faceting at the bottom of pits and irregular shapes at some locations near the surface where the access of the solution was easy. (Figure 85b).

Similar behavior to pure Al was observed in the 0.1% Cu alloy bicrystals. No preferential grain boundary corrosion occurred and pits formed in random clusters (Figure 86a). Details of a pit cluster are shown in Figure 86b and details of the bottom of pits are shown in Figure 86c. The bottom of the pits were observed to have ridge lines steps superimposed on the {001} facets. In Figure 86d, a spiral pit is shown which is probably located on an emergent screw dislocation.

Increasing the Cu content of the bicrystal to 0.5 and 4.2% Cu did not change the pitting situation, e.g. pit clusters occurred randomly over all of the surface of the bicrystals (see Figures 87a and 88a). However, the morphology of the pits was changed.

Increasing the Cu content to 0.54% Cu, caused the {001} faceting to diminish. The pits surfaces appeared relatively smooth and concave. (Figure 87b).

Hemispherical pits were formed on the bicrystal of 4.2% Cu alloy. The internal walls of the pits consisted of some irregular depression, and the bottom appeared to be covered with some corrosion products. (Figure 88b).

Grain boundary corrosion was found on the as-grown bicrystal of 4.2% Cu as shown in Figure 89a. Pits developed along the grain boundary and within the component grains. The pits exhibited an hemispherical shape with irregular internal walls.
Preferential grain boundary attack was also observed on the aged bicrystal of 4.2\% Cu, as shown in Figures 90a and 90b. Pitting corrosion also occurred on the traces of \{111\} planes within the grains. (Figure 90c).
Figure 85  Morphologies of pit developed on a $9^\circ<001>$ tilt bicrystal of Al after a PPC test in a 0.5M NaCl + 0.5M NaNO$_3$ solution
Figure 86 Morphologies of pit developed on a homogenized 14°<001> tilt bicrystal of Al-0.1%Cu alloy after a PPC test in a 0.5M NaCl + 0.5M NaNO₃ solution.
* GB indicates the exposed grain boundary region.
Figure 87 Morphologies of pit developed on a homogenized 9°<001> tilt bicrystal of Al-0.54%Cu alloy after a PPC test in a 0.5M NaCl + 0.5M NaNO3 solution.

Figure 88 Morphologies of pit developed on a homogenized 9°<001> tilt bicrystal of Al-4.2%Cu alloy after a PPC test in a 0.5M NaCl + 0.5M NaNO3 solution.
Figure 89 Morphologies of pitting and intergranular corrosion on an as grown 9°<001> tilt bicrystal of Al-4.2%Cu alloy after a PPC test in 0.5M NaCl +0.5M NaNO₃ solution.
Figure 90 Morphologies of pitting and intergranular corrosion on an aged $9^\circ<001>$ tilt bicrystal of Al-4.2%Cu alloy after a PPC test in 0.5M NaCl +0.5M NaNO$_3$ solution.
4. DISCUSSION

4.1 Anisotropic Pitting Corrosion of Al Single Crystals.

4.1.1 General Behavior

Anisotropic pitting corrosion of Al single crystals was observed in 0.5 M NaCl. The critical pitting potential for the three low index planes were in the order \((E_{\text{pit}})^{\{111\}} < (E_{\text{pit}})^{\{011\}} < (E_{\text{pit}})^{\{001\}}\), as can be seen in Figure 20. Also, the low value of \((E_{\text{pit}})^{\{111\}}\) was accompanied by a higher density of pits, as evidenced in Table 8 where pit densities on \{111\}, \{011\} and \{001\} planes were 42.7, 21.9 and 14.0 pits/mm\(^2\) respectively. Furthermore, pitting attack in all cases resulted in pit morphologies where the sides of the pit were composed of \{001\} facets. Thus, all results showed that \{001\} planes were the least susceptible and \{111\} planes were the most susceptible to pitting.

The anisotropic effects observed in the present study were consistent with the corrosion behavior of Al reported by other workers. For example, Wood et al.(20) conducted natural immersion tests on polycrystalline zone refined Al exposed to 1M KCl and showed that the micropit density and size on differently oriented grains lay in the same order as those observed in the present work. Galvanostatic pitting studies by Feller et al. (115) on polycrystalline Al in 0.01M NaCl also showed higher pitting densities on \{111\}. Dissolution studies by Arora and Metzger (50), using coarse grained Al sheet, showed that dissolution rates were dependent on orientation with rates in the approximate ratio \{111\}::\{011\}::\{001\}::(1.71):(1.41):(1.0). Similar dissolution behavior has been observed in mixtures of aqua regia and hydrofluoric acid (51).

The studies in acid solutions (50,51) are particularly relevant to understanding the formation of pits with \{001\} facets. It is well established that pitting in chloride solutions leads to a local pit solution chemistry with a low pH (148,149,160) and high Cl\(^-\) concentration (150,151,157). Oxide films are not stable under these conditions (152). Therefore, development of \{001\} facets must be due to lower bare metal dissolution rates on \{001\} surfaces. The corrosion studies in acid solution (50,51) support this conclusion.

The results of the present study have definite implications relating to the pitting potential of polycrystalline Al. Several previously reported values of \(E_{\text{pit}}\) for this material in chloride solutions (e.g. 0.5 M NaCl, 3% NaCl) are scattered over a wide range
of potentials from -618 mV\textsubscript{SCE} to -765 mV\textsubscript{SCE} \(^{113,114,117,118}\). It is now clear that some of this scatter may be attributed to the variation of \(E_{\text{pit}}\) with crystal orientation. In general, it is expected that the measured pitting potential of polycrystalline specimens will lie somewhere between \(E_{\text{pit}}\) for the exposed grain surfaces having the lowest pitting potential and \(E_{\text{pit}}\) for the most frequently occurring grain orientation.

4.1.2 Influence of the Oxide Film

It is well established that Al is covered with a thin oxide film when exposed to air \(^{40}\) and that electrochemical processes maintain this film in near neutral aqueous solutions \(^{152}\). The film may influence pitting behavior in two ways. First, it may contain orientation dependent features that are imparted by the substrate crystallography. These features may then promote orientation dependent breakdown (pitting) of the film. Second, it may serve simply to locate pit initiation at defects (flaws) in the film that expose the substrate to the electrolyte. This situation implies that orientation dependent pitting dissolution (\(E_{\text{pit}}\)) is determined by the anisotropic dissolution behavior of the unfilmed substrate.

Hart\(^{119}\) examined the room temperature oxidation of electropolished Al single crystals in dry oxygen and humid (80%) oxygen. He used electron diffraction techniques and capacitance measurements to study the behavior of the three major low index planes. Hart found that the films were amorphous and that there were no significant differences between the oxidation rates on the different crystal planes. The film thickness after 7 days exposure was 35 Å in dry oxygen and 50 Å in humid oxygen. Consequently, Hart's results show that pitting anisotropy is not associated with the effect of substrate orientation on either the oxide film orientation or its thickness.

The very early stages of Al oxidation were studied by Martinson and Flodstrom\(^{120}\), using the techniques of Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). They found that the rates of uptake of oxygen during monolayer coverage of the low index planes were in the order \(\{001\} < \{111\} < \{011\}\). The appearance of the LEED patterns led to the proposal that initial oxidation of \(\{111\}\) was a two stage process involving ordered chemisorption at threefold sites followed by transformation to a bulk-like amorphous oxide. A similar proposal was made for \(\{011\}\), except that chemisorption produced a disordered first stage. The \(\{001\}\) surface was considered to
behave differently and that oxidation involved nucleation and growth of islands of amorphous oxide.

The relevance of the results of Martinson and Flodstrom(120) to pitting corrosion is that they show that the structural characteristics of the substrate/oxide interface depend on substrate orientation. These characteristics may influence the formation and number of flaws (imperfections) in the oxide film. For example, their results indicated that the degree of atomic order at the interface follows the pattern \{111\} > \{011\} > \{001\}. In order to maintain interfacial order, elastic strains may be generated in the film leading to formation of flaws. In this case, the ranking of flaw formation should follow the pattern \{111\} > \{011\} > \{001\}, which is the ranking of pitting susceptibility observed in the present work. It has been recognized for some time that the amorphous oxide film contains flaws (20) and that substrate attack may occur at these flaws to produce pits.

4.1.3 Influence of Dislocations

In principle, the presence of dislocations that terminate at the substrate/film interface may impart structural inhomogeneities to the interface that, in turn, promote flaws in the oxide film and influence the pitting behavior. Two situations need to be considered; (i) dislocations having Burgers vector $b$ parallel to the surface and (ii) dislocations that have a component of $b$ normal to the surface.

<table>
<thead>
<tr>
<th>Table 23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probability of step generation on different crystal surfaces by dislocations</td>
</tr>
</tbody>
</table>

| Dislocation | Surface Orientation |
| --- | --- | --- |
| $b$ | $g = [001]$ | $g = [011]$ | $g = [111]$ |
| $a/2[110]$ | $g.b = 0$ | $g.b \neq 0$ | $g.b = 0$ |
| $a/2[110]$ | $g.b = 0$ | $g.b \neq 0$ | $g.b \neq 0$ |
| $a/2[110]$ | $g.b = 0$ | $g.b \neq 0$ | $g.b \neq 0$ |
| $a/2[110]$ | $g.b = 0$ | $g.b = 0$ | $g.i = 0$ |
| $a/2[011]$ | $g.b \neq 0$ | $g.b = 0$ | $g.b \neq 0$ |
| $a/2[011]$ | $g.b \neq 0$ | $g.b = 0$ | $g.b = 0$ |
| Probability | 4/6 | 5/6 | 3/6 |
In the present study, situation (i) was represented by the low angle tilt boundaries in the Al bicrystals. Such boundaries may be considered to be represented by a wall of dislocations with \( \mathbf{b} \) parallel to the bicrystal surface. The pitting corrosion tests showed no preferential attack at these boundaries. Therefore, it may be concluded that dislocations with \( \mathbf{b} \) parallel to the surface have no influence on pitting behavior.

In situation (ii), the presence (motion) of a dislocation with a component \( \mathbf{b} \) normal to the surface will produce a step at the substrate film interface. If the normal to the surface plane is represented by the vector \( \mathbf{g} \), then the condition for formation of a step is \( \mathbf{g} \cdot \mathbf{b} \neq 0 \). The slip systems in Al are \{111\} \langle110\rangle and \( \mathbf{b} \) has the value \( a/2 \langle110\rangle \), where \( a \) is the lattice parameter. Table 23 lists the condition for which \( \mathbf{g} \cdot \mathbf{b} \neq 0 \) for all possible interactions of \( \mathbf{b} \) with the surface planes (001), (011) and (111). The listed probabilities represent the relative number of predicted steps, based on the number of conditions for which \( \mathbf{g} \cdot \mathbf{b} \neq 0 \).

From Table 23, the probability of step generation is in the order \{111\} < \{001\} < \{011\}, indicating that pitting susceptibility should be least on \{111\} planes. This is in disagreement with the observed pitting behavior in terms of both Epit potentials and pit density. Therefore it must be concluded that dislocations have no influence on the anisotropy of pitting. This conclusion is supported by the results of Edeleanu et al. (121,161), who found little correlation between pitting sites and dislocations in strained Al, and by the electron microscope studies of Pearson et al (14), who found that pits formed on Al independently of surface irregularities.

### 4.1.4 Surface Energy Considerations

Shemenski et al. (55), based on Volmer's (124) classical concepts of two-dimensional nucleation of vacancy disks on a perfect surface, indicated that the dissolution rate on a perfect crystal surface was proportional to the square of the surface energy(\( \gamma \)). Relative values of \( \gamma \) for fcc crystal surfaces have been calculated by Mackenzie et al. (125), using geometrical concepts based on the summation of the number of broken bonds of the 1st and 2nd nearest neighbors of atoms in the surface. They showed that:

\[
\frac{(\gamma)_{\text{hkl}}}{(\gamma)_{0_{h,k,l}}} = \cos \theta_{(hkl-h,k,l)} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4.1)
\]
The miller indices $h_0k_0l_0$ represent the reference plane having maximum $\gamma$, where $h_0,k_0,l_0: (2+2p):(1+2p):2p$ and $p$ is the ratio of the 2nd nearest neighbor bond energy to that of the 1st nearest neighbor bond energy. The angle $\theta(hkl-hokolo)$ represents the angle between the $(hkl)$ and $(hokolo)$ planes.

The Mackenzie et al. (125) calculation predicted $\gamma(011) > \gamma(001) > \gamma(111)$ for $p = 0$, $\gamma(011) > \gamma(001) = \gamma(111)$ at $p = 0.183$ and $\gamma(011) = \gamma(111) > \gamma(001)$ at $p = 0.612$. These results lead to the prediction that dissolution rates should be the highest on $\{011\}$, which is not in accord with the observed pitting anisotropy.

Sundquist (153) employed electron microscopical techniques to test the geometrical model of Mackenzie et al. (125) by observing the equilibrium shape of very small particles after thermal treatment in vacuum. He found that for fcc metals a value of $p = 0.1$ gave the best agreement, showing that $\gamma(011) > \gamma(001) > \gamma(111)$. Again, the predicted dissolution rates based on these $\gamma$ ratios and the model of Volmer (124) do not correlate with the pitting anisotropy of Al. Thus, pitting behavior is not readily interpretable in terms of surface energy related phenomena.

4.1.5 Protection Potential and Pit Morphology

In contrast with $E_{pit}$, the value of $E_{prot}$ in 0.5 M NaCl was found to be independent of the crystallographic orientations of the initial electrode surface (See Table 4 and Figure 20) and independent of the amount of pit propagation, as can be seen in Table 5. The only effect of increasing the anodic charge during propagation was to increase the apparent repassivation current density. This increase was probably due to the increasing number of active dissolution sites (pit area) and chemical changes in the local pit environment.

All three initial electrode surfaces, $\{001\}$, $\{011\}$ and $\{111\}$, developed pits with $\{001\}$ facets. The facet crystallography was unaffected by the amount of pit propagation (i.e. charge passed) over the range $5C/cm^2$ to $50C/cm^2$, as evidenced by the SEM micrographs shown in Figures 38, 40, 41 and 42. Therefore in all situations, $E_{prot}$ was determined by the behavior of $\{001\}$ facets in the local pit environment. The details of faceting at the bottom of pits, as shown in Figures 42a,b,c, consisted of $\{001\}$ terraces, steps in $<001>$ directions and kinks on the steps. This configuration is characteristic of
the TSK surface model, in terms of terraces, steps and kinks, described by Kossel (126) and Stranski (127) for crystal condensation and evaporation from or to the vapor phase.

On the atomic scale, imperfections such as vacancies and self-adsorbed atoms (ad-atoms) are considered to be present on the terraces, steps and kinks. With reference to Figure 91, removal (dissolution) of atoms from the crystal surface will occur preferentially at (a) adatoms on terraces, (path 1), (b) adatoms on steps (Path 2), (c) atoms at the kink sites (path 3), (d) removal anywhere on the edge of steps (path 4) and (e) removal anywhere on the terraces (path 5). These dissolution paths may involve surface diffusion along steps and on terraces (path 6, 7 and 8) to form the intermediate adatoms on the step or terraces, depending on which path(s) involve the lowest activation energy. Furthermore contact adsorption of ions may occur at the surface, particularly ions having a large ionic radius (e.g. Cl\(^-\))(154), and affect the removal (dissolution) of metal ions from the surface.

Figure 91 Surface showing terraces, steps, kinks and other surface imperfections.
4.2 Mechanism of Pitting of Al

Pitting is a process determined by local kinetic considerations rather than a predictable criterion of thermodynamic stability or instability. The discussions presented in the previous sections suggest that pit initiation sites are related to pre-existing defects (flaws) in the passive films, as suggested by Richardson, Wood and co-worker (17-20). In the absence of pitting, the maintenance of the oxide film may be viewed as a dynamic process, where the metal interface at the base of the flaws is constantly being subjected to repassivation (film healing) and dissolution processes. In deaerated neutral solutions, the main passivating (film forming) species are OH\(^{-}\) ions. These adsorb on the metal surface and promote repassivation via equations 4.2a and 4.2b.

\[ \text{Al} + \text{OH}^{-} = \text{Al(OH)}^{-\text{ads}} \] \hspace{1cm} (4.2a)
\[ 2\text{Al(OH)}^{-\text{ads}} + \text{H}_2\text{O} = \text{Al}_2\text{O}_3 + 4\text{H}^{+} + 6\text{e}^{-} \] \hspace{1cm} (4.2b)

where 4.2b is the charge transfer reaction.

In the presence of \(\text{Cl}^{-}\) ions, there is competition between \(\text{OH}^{-}\) and \(\text{Cl}^{-}\) for adsorption sites on the metal surface, consistent with Kruger’s (155) adsorbed anion displacement model of passivity breakdown on iron-based alloys. The adsorption of \(\text{Cl}^{-}\) leads to local dissolution, as shown in the idealized equations of 4.3a and 4.3b.

\[ \text{Al} + \text{Cl}^{-} = \text{AlCl}^{-\text{ads}} \] \hspace{1cm} (4.3a)
\[ \text{AlCl}^{-\text{ads}} + n\text{H}_2\text{O} = \text{Al(H}_2\text{O)}_n^{3+} + \text{Cl}^{-} + 3\text{e}^{-} \] \hspace{1cm} (4.3b)

where \(\text{Al(H}_2\text{O)}_n^{3+}\) represents the solvated \(\text{Al}^{3+}\) ion.

If the local rates of the reactions represented by equations 4.2a and 4.2b are faster than those of 4.3a and 4.3b, then film healing processes are dominant. On the other hand, if the rates of equations 4.3a and 4.3b are faster then local dissolution (pitting) will be dominant. The relative rates of reactions 4.3a and 4.3b will increase with increasing \(\text{Cl}^{-}\) concentration and increasing potential. Furthermore, based on the present work, it is
proposed that these rates (R) are dependent on the substrate orientation such that they are in the order R{111} > R{011} > R{001} for a given potential and Cl\(^-\) activity at the metal-solution interface. Thus, the metal has to be raised to higher potentials before dissolution reactions on {001} surfaces dominate over film forming reactions (i.e. (Epit)001 > (Epit)011 > (Epit)111).

The onset of pitting (pitting potential) is now seen to arise as a simple consequence of the dissolution reactions (4.3a and 4.3b) dominating over the film forming reactions (4.2a and 4.2b) at the base of the flaw. This leads to a local increase in concentration of solvated aluminum cations at the metal-solution interface because, following Galvele(156), electrochemical processes in the flaw will be under mass transport control. The increased concentration of cations inside the occluded cells (flaws) leads to two effects. First, hydrolysis of the cations occurs and produces a local lowering of pH (increased H\(^+\)). This is a well established phenomenon (e.g. Galvele) (156) and is represented in a general form by equation 4.4.

\[
\text{Al(H}_2\text{O)}_n\text{H}^{3+} = \text{Al(OH)}_x\text{(3-x)}^+ + (n-x)\text{H}_2\text{O} + x\text{H}^+ \quad \ldots \ldots \ldots \ldots \ldots \quad (4.4)
\]

where \(x = 1\) in the resulting acid solution.

The second effect arises from the well recognized requirement that electrical neutrality must be maintained throughout the electrolyte and, therefore, anions must migrate into the occluded cell to compensate for the local increase in cation concentration, as shown by the theoretical analysis of Ateya and Pickering (157). This leads to an increase in the Cl\(^-\) concentration in the flaw, because in neutral 0.5M NaCl solutions the concentration of Cl\(^-\) (0.5M) in the bulk electrolyte far exceeds that of OH\(^-\) (1x10\(^{-7}\) M) and Cl\(^-\) will be the dominant migrating species.

The overall effect of the pit initiation processes is to produce a micropit at the base of the flaw with a local solution chemistry that is different from that of the bulk solution. In particular, it has a lower pH and higher Cl\(^-\) concentration so that an even greater imbalance between the rate of the film forming reactions (equation 4.2a and 4.2b) and the dissolution reactions (equation 4.3a and 4.3b) occurs. Thus, the pit once initiated continues to propagate and enlarge.
The changes in solution chemistry within an active pit satisfactorily account for the fact that the observed repassivation potential of the pit (i.e. E_{prot}) was lower than the initial pitting potential (E_{pit}). For example, the proposed kinetic model of pitting predicts that E_{prot} must be equivalent to E_{pit} in a bulk solution of the same composition as the local chloride-enriched pit solution. This implies that under situations where the concentrations of Cl^{-} ions in the bulk solution are increased to produce a highly concentrated solution approaching that of the pit solution, the difference between E_{pit} and E_{prot} should become vanishingly small. The experimental results of Figure 24 confirmed this conclusion.

The observed constancy of E_{prot} of Al with respect to the initial crystal surface orientation (see Figure 20) was due simply to the fact that the sides of the pits were composed entirely of \{001\} facets. Thus, E_{prot} was, in effect, E_{pit} for the \{001\} surface in a solution of the same composition as the pit solution. The formation of \{001\} facets occurred because the overall dissolution process, represented by equations 4.3a and 4.3b, occurred most slowly on the \{001\} surface. The precise reason for this remains unknown and was beyond the scope of this study. It may be related to the effect of surface orientation on the density of step and kink sites and the effect of orientation on the activation energies of adsorption and dissolution processes at these sites.

4.3 Effect of Compositional Changes on Pitting Behavior

Changes to the bulk solution chemistry and metal alloy chemistry were found to influence pitting behavior. All of these changes may be rationalized in terms of the proposed kinetic model of pitting.

4.3.1 Effect of Cl^{-} Concentration on Al

Raising the Cl^{-} concentration of the bulk solution will increase its concentration at the metal-solution interface at the base of the flaws in the oxide film. This will increase the competition between OH^{-} and Cl^{-} ions for adsorption sites on the metal surface in favour of Cl^{-}. Thus, an imbalance will occur between film forming and dissolution reactions at a lower potential, causing E_{pit} to decrease, as shown in Table 4 and Figure 24 for the \{001\} surface.
CHAPTER 4: DISCUSSION

The results showed a linear relationship between \( E_{\text{pit}} \) and \( \log([\text{Cl}^-]) \) on \( \{001\} \) in Figure 24 and that \( E_{\text{pit}} \) decreased by 140 mV/decade. Similar studies were not conducted on \( \{001\} \) and \( \{111\} \) surfaces and were not considered necessary. At high \( \text{Cl}^- \) concentrations \( E_{\text{pit}} \) became virtually indistinguishable from \( E_{\text{prot}} \) (Figure 24) and the results showed that \( E_{\text{prot}} \) was the same for all three low index planes in the same bulk solution. Therefore, by using \( E_{\text{pit}} \) values for \( \{011\} \) and \( \{111\} \) obtained in 0.5 M NaCl (Table 4) and the \( E_{\text{pit}} = E_{\text{prot}} \) value at the very high \( \text{Cl}^- \) concentration in Figure 24 it is readily seen that the average change in \( E_{\text{pit}} \) was \( \sim 122 \) mV/decade for \( \{011\} \) and \( \sim 110 \) mV/decade for \( \{111\} \). The variations of \( E_{\text{pit}} \) with \([\text{Cl}^-]\) for the different crystal planes were comparable with both the magnitude and range of values reported in the literature on polycrystalline Al, e.g. 124 mV/decade by Kaesche (128), 90 mV by Hunkeler and Bohni (129) and 100 mV/decade by Stirrup et al. (130).

At low \( \text{Cl}^- \) concentrations, it is reasonable to expect \( \text{Cl}^- \) adsorption to occur primarily at the most favorable surface sites (e.g. kink sites). Increasing the \( \text{Cl}^- \) concentration promotes adsorption at the less favorable sites (e.g. edge of steps and terraces). Simple statistical reasoning suggests that in a given population of flaws in the oxide film, the base of every flaw will not expose the same type of surface site. Hence, as the \( \text{Cl}^- \) concentration is increased, increasing number of flaws should become possible sites for pit initiation. Thus, the density of pits during pitting corrosion should increase with \( \text{Cl}^- \) concentration. This was confirmed by the observations on the \( \{001\} \) surface of Al (see Table 8), where the pit density increased from 14 to 30.4 pits/mm\(^2\) as the \([\text{Cl}^-]\) increased from 0.5 to 2M.

Increasing the \( \text{Cl}^- \) concentration of the bulk solution should increase the concentration of the solution within an active pit, due to the enhanced migration of \( \text{Cl}^- \) resulting from a larger source of migrating ions. The observations showed that, within a few mV, \( E_{\text{prot}} \) was invariable with the amount of charge passed during galvanostatic pitting studies in 0.5 M NaCl, as shown in Table 5. This implied that a steady state condition, in terms of solution chemistry, was achieved within actively growing pits. In the case of \( \{001\} \) crystals, analysis of the data in Figure 24 allowed good estimates to be made of the pit solution concentrations. These data show the measured value of \( E_{\text{pit}} \) and \( E_{\text{prot}} \) for a wide variation in the bulk \([\text{Cl}^-]\). Consequently, recognizing that \( E_{\text{prot}} \) is equivalent to \( E_{\text{pit}} \) in a solution of the same composition as the pit environment, the equivalent value of bulk \([\text{Cl}^-]\) for the condition \( E_{\text{prot}} = E_{\text{pit}} \) was obtained from Figure 24 graphically (or from equations 3.1 and 3.2 that represent the same data). For
example, when the bulk \([\text{Cl}^-]\) was 0.5 M, \(E_{\text{prot}} = -795 \text{ mV}_{\text{SCE}}\) and the condition \(E_{\text{pit}} = -795 \text{ mV}_{\text{SCE}}\) corresponded to a bulk \([\text{Cl}^-]\) of 2.5 M. Therefore, a bulk solution containing 0.5 M \([\text{Cl}^-]\) produced an active pit solution containing 2.5 M \([\text{Cl}^-]\).

Pitting studies on \(\{001\}\) surfaces showed that increasing the \(\text{Cl}^-\) concentration of the test solution from 0.5 M to 2 M produced a larger number of finely faceted \(\{001\}\) steps on the sides of the active pit. This may be seen by comparing the SEM micrographs of Figure 42a with Figure 43b. Analysis of the data in Figure 24 showed that increasing the concentration of the test solution raised the \([\text{Cl}^-]\) in the active pit solution from 2.5 M to 4.7 M. The increased concentration of \(\text{Cl}^-\) will enhance the competitive adsorption of these species in the pit so that an increasing amount of adsorption will occur on the less favorable terrace sites. The resulting removal (dissolution) of an atom from a terrace creates a surface vacancy bounded by edge sites. This leads to the creation of new steps and promotes the development of a large number of finer facets during dissolution, as observed.

4.3.2 Effect of pH on Al

Decreasing the test solution pH at constant \(\text{Cl}^-\) concentration produces a decrease in \([\text{OH}^-]\) and a corresponding decrease in the rate of adsorption of these species on Al at the base of oxide film flaws. This should lead to an imbalance between the film forming reactions (equation 4.2a and 4.2b) and dissolution reactions (equations 4.3a and 4.3b) in favour of the dissolution process. Thus, localized dissolution (pitting) will occur at lower potentials. The limited studies on \(\{001\}\) surfaces, shown in Figure 22, confirmed that \(E_{\text{pit}}\) in 0.5 M NaCl was lowered by 5.1 mV/pH unit as the pH was decreased from 6.5 to 2.5 (i.e., a decrease in \([\text{OH}^-]\) from \(10^{-7.5}\) M to \(10^{-11.5}\) M). The data of De-Micheli (137) on polycrystalline Al were re-analyzed and found to give results comparable to the present study. Their data showed \(E_{\text{pit}}\) was lowered by 6 mV/pH unit in 5M NaCl and 5.8 mV/pH unit in 1M NaCl.

Changes in test solution pH from 6.5 to 2.5 were expected to have no effect on \(E_{\text{prot}}\) for two reasons; (i) the pH in the pit is controlled by hydrolysis of soluble Al species (equation 4.4) and (ii) migration of \(\text{OH}^-\) ions into the pit to maintain electrical neutrality will be negligible in relation to \(\text{Cl}^-\) migration because of the overwhelmingly larger concentration of \(\text{Cl}^-\) (e.g. \([\text{Cl}^-]/[\text{OH}^-] = 1.58 \times 10^7\) at pH 6.5 and 0.5 M NaCl). Figure 22 confirmed the insensitivity of \(E_{\text{prot}}\) to pH changes.
4.3.3 Effect of NO$_3^-$ Additions on Al

Addition of 0.5 M [NO$_3^-$] to the 0.5 M NaCl solution inhibited pitting corrosion on all three low index crystal surfaces by dramatically shifting both Epit and Eprot to more noble potentials. The anisotropic behavior of Epit that was observed in the uninhibited solution was preserved in the presence of NO$_3^-$ ions i.e. Epit(001) > Epit(011) > Epit(111), as shown in Table 20. The Table shows that the magnitude of the inhibitor index, \( \Delta E \), decreased in the same order. Hence, NO$_3^-$ species inhibited most effectively on {001} and least effectively on {111}.

The increase of Eprot showed that NO$_3^-$ ions were entering the pit solution in sufficient concentrations to raise the potential at which film forming reactions predominated over dissolution reactions. Thus, NO$_3^-$ ions must have responded to the requirement to maintain electrical neutrality in the pit by migrating in competition with Cl$^-$. The relative ease of migration of NO$_3^-$ ions was confirmed by the interrupted pitting test, where NO$_3^-$ ions were added to 0.5 M NaCl solution after pitting had commenced (e.g. Figure 79,a,b,c,and d). Initially, the only anion migrating into the pit was Cl$^-$, leading to a chloride-enriched pit solution. Within less than 1200 s after the addition of NO$_3^-$, E$_{prot}$ was the same as when NO$_3^-$ was present at the commencement of the test. Thus, within this time period competitive migration of NO$_3^-$ had change the pit solution composition to the [NO$_3^-$]/[Cl$^-$] proportions associated with the more noble Eprot.

In solutions containing both Cl$^-$ and NO$_3^-$ species, the pit morphology near the free surface was irregular, whereas at the base of the pit it exhibited more well developed {001} facets (e.g. Figure 81 through 84). Consistent with the kinetic model of pitting, these changes are believed to arise from the migration of Cl$^-$ and NO$_3^-$ species leading to a continuum of differences in the concentrations and proportions of these species between the bulk solution and that at the base of the pit.

The actual mechanism by which NO$_3^-$ species inhibit pitting in chloride solutions must have its origins in the competition between Cl$^-$ and NO$_3^-$ for adsorption sites at the metal-solution interface (i.e. at the base of oxide film flaws on the free surface and on the actively dissolving surfaces within the pit. Such competitive adsorption is expected to retard the effect of Cl$^-$ on dissolution processes. However, it appears
inconsistent to assume that simple adsorption of $\text{NO}_3^-$ promotes film healing whereas adsorption of $\text{Cl}^-$ does not. Therefore, other processes must be involved.

Aqueous thermodynamic data for the $\text{N}_2$-$\text{H}_2\text{O}$ system (158) show that $\text{NO}_3^-$ species are not thermodynamically stable under the conditions of potential and pH that prevailed during the pitting studies. In particular, $\text{NO}_3^-$ may be reduced electrochemically and two possible sequential reactions are shown in equations 4.5 and 4.6,

\[
\text{NO}_3^- + \text{H}_2\text{O} + 2e^- = \text{NO}_2^- + 2\text{OH}^- \quad \text{(4.5)}
\]

\[
\text{NO}_2^- + 6\text{H}_2\text{O} + 6e^- = \text{NH}_4^+ + 8\text{OH}^- \quad \text{(4.6)}
\]

Both reduction reactions lead to the formation of $\text{OH}^-$ ions and these are the film-forming species (equations 4.2a and 4.2b). Thus, it is believed that adsorption of $\text{NO}_3^-$ is followed by electrochemical reduction to produce adsorbed $\text{OH}^-$ species that promote film formation. This sequence of events accounts for the inhibitive properties of $\text{NO}_3^-$.

Adams et al. (142) have detected $\text{NH}_4^+$ after immersing Al in a $\text{Cl}^- + \text{NO}_3^-$ solution, confirming that reduction of $\text{NO}_3^-$ occurs. Also, Wexler and Galvele (141) detected $\text{N}_2$ gas by chromatographic techniques during pitting of Al in solutions containing $\text{NO}_3^-$. Again, this confirmed the reduction of $\text{NO}_3^-$, the corresponding reaction being given by equation 4.7.

\[
2\text{NO}_3^- + 6\text{H}_2\text{O} + 10e^- = \text{N}_2 + 12\text{OH}^- \quad \text{(4.7)}
\]

4.3.4 Effect of Alloying with Cu

The studies showed that Cu additions raised both the $\text{E}_{\text{pit}}$ and $\text{E}_{\text{prot}}$ of homogenized single crystals in 0.5M NaCl. However, the detailed responses of the two potentials to composition changes were different. The $\text{E}_{\text{pit}}$ increased continuously with increasing Cu over the whole range investigated (up to 4.2 wt% Cu), whereas $\text{E}_{\text{prot}}$ increased with Cu additions up to 1.4 wt% Cu and then became independent of composition. These effects are clearly shown in Figure 92, where the data on single
crystals in Table 7, together with data for the \{001\} faces of bicrystals ("grain interior" in Table 17), are plotted as a function of alloy composition.

The surface orientation anisotropy of Epit disappeared at the higher Cu concentration. Consequently, Epit of homogenized polycrystals (multiple orientations) and single crystals should be indistinguishable at higher alloy contents. This was confirmed by determining Epit of polycrystals as a function of Cu content and placing the data on Figure 92 for comparison purposes.

![Figure 92: Effect of Cu on Epit and Eprot of \{001\}, \{011\} and \{111\} single crystal surfaces. The dashed Curve is the Epit of polycrystalline samples.](image)

Changes in pitting potential behavior were accompanied by changes in pitting morphology. At Cu contents equal to, or higher than 0.54 wt\%, the pit sides were no longer composed of \{001\} facets. Instead they exhibited a spongy morphology (e.g., Figures 44 and 68). All of these effects, including improved pitting resistance and morphological changes, may be accounted for by incorporating the noble metal characteristics of Cu into the kinetic model of pitting.

The aqueous thermodynamic behavior of Cu (159) is such that it should behave in a completely inert (noble) manner under all conditions encountered during the pitting
studies. Any localized dissolution process will preferentially dissolve Al and leave the surface region enriched in Cu. This was readily confirmed by supplementary energy dispersive X-ray (EDX) analyses that were conducted on the homogenized 1.28 wt% Cu alloy after potentiostatic corrosion at -400 mVSCE in a saturated AlCl₃ solution. The potential corresponded to the highest value employed during the pitting studies and the EDX analyses gave an average concentration of 5.13 wt% Cu. Also, the surface exhibited a spongy appearance, consistent with selective leaching in other noble metal alloy systems (e.g. Cu-Zn and Au-Cu (138-140)).

The influence of Cu on pitting potentials will now be examined. Consider the situation where the potential of the alloy, E, is raised to the condition,

\[(E_{pit})_{Al} < E < (E_{pit})_{Alloy}\]  \hspace{1cm} (4.8)

Dissolution of Al atoms will occur at the metal-solution interface at the base of flaws in the oxide film, similar to the early stages of pitting in pure Al. The most favorable sites for dissolution are kink sites. As Al atoms are successively removed from these sites, causing the kinks to move along the edges of steps, unreactive Cu atoms eventually become exposed at the edge of many kink sites. At this stage, dissolution is retarded and pitting ceases (i.e. the kinetic imbalance between dissolution and film healing processes is restored in favour of film formation). In order for pitting to recommence, the potential must be raised even higher (to \((E_{pit})_{Alloy}\)) to activate dissolution at the less favorable sites, such as the edge of steps and the surface of terraces, as shown in Figure 93.

As the copper content is increased, copper atoms will appear with a higher frequency at kink sites. Therefore, dissolution processes will be retarded until even higher potentials are reached and \((E_{pit})_{Alloy}\) must increase with copper content, as observed. Furthermore, as the overpotential (difference) between \((E_{pit})_{Alloy}\) and \((E_{pit})_{Al}\) increases with composition, the rates of dissolution on the edges of steps and on the terraces of differently oriented crystal surfaces will become very similar, leading to the observed isotropic behavior of \((E_{pit})_{Alloy}\).

Within active pits, continuous dissolution of Al leads to enhanced surface enrichment of Cu, causing several effects. Copper atoms are now available for local surface diffusion and adsorption at kink sites and steps, forcing dissolution to occur
randomly on terraces. Consequently, faceted pits cannot develop and the pit sides become composed of randomly oriented, spongy surfaces. The retarding effect of Cu on dissolution will raise the repassivation potential so that (E_{prot}\text{alloy}) > (E_{prot}\text{Al}). Furthermore, above a certain alloy composition, preferential leaching of Al will always provide sufficient surface concentrations of diffusing and adsorbing copper atoms to have a saturating effect on surface behavior i.e., E_{prot} will become independent of composition, as observed.

Figure 93 Al dissolution from an Al-Cu alloy "Kink-Step-Terrace" surface.

The larger pit density on (001) surface of Al-0.54 wt% Cu (263 pits/mm²), relative to Al (14 pits/mm²) as listed in Table 8, may be attributed to two effects. First, the increase in potential, (E_{pit}\text{alloy}), due to the effect of Cu on dissolution at kink sites at the base of flaws in the oxide film, will activate local dissolution at the base of less reactive flaws where there are only terraces at steps at the metal/solution interface. Second, the presence of Cu atoms at the metal surface will inhibit the formation of an oxide film of aluminium in their immediate vicinity and this may increase the density of flaws in the original film.
4.4 Effect of Grain Boundaries

The influence of the grain boundary upon the pitting corrosion behavior of bicrystals in 0.5 M NaCl was dependent upon alloy composition and thermal history.

4.4.1 Homogenized Bicrystals

The only grain boundaries studied were <001> tilt boundaries, as summarized in Table 17. Within the limits of experimental error, tilt boundaries up to 28° had no significant effect on either Epit or Eprot of annealed Al. These potentials were very similar to those observed on {001} surfaces of single crystals of Al. Also, no preferential pitting of the tilt boundaries was observed. Therefore, the results show that grain boundaries, at least tilt boundaries, are not a preferential sources of flaws in the oxide film.

Homogenized Al-Cu bicrystals showed no difference in pitting behavior, relative to the {001} surfaces of alloy crystals, at copper concentrations up to 3.2 wt% and tilt angles of 14°. However, the combination of 0.1 wt% Cu and a higher angle tilt boundary of 28° was sufficient to produce a tendency towards preferential pitting along the boundary, as shown in Figure 67b. This was attributed to a lower Cu concentration in the boundary that promoted local dissolution of the alloy.

No direct evidence was obtained to support a negative Cu segregation at the 28° boundary. Such a non-equilibrium situation could arise by reverse atom flow via the solute-vacancy interaction model proposed by Aust and Westbrook(146). The Cu diffuses away from the boundary in reverse direction to the flow of vacancies.

4.4.2 As-Grown Bicrystal

As-grown bicrystals of 4.2 wt%Cu, containing a 9°<001> tilt boundary, exhibited preferential pitting corrosion along the boundary. A narrow corrosion groove containing undissolved particles of CuAl2 (θ-phase) was formed (see Figures 72 and 76). Furthermore, the Epit of the as-grown boundary (-610 mVSCe, Table 18) was lower than Epit of the boundary in the comparable homogenized bicrystal (-532 mVSCe, Table 17). The studies on the homogenized alloys clearly showed that Epit rises with increasing
concentration of Cu in solid solution. Therefore, the preferential attack of the as-grown boundary, and its lower Epit, must be due to local impoverishment of Cu. This occurred because local diffusion of solute had produced precipitates of CuAl₂ along the boundary. The data in Table 11 confirmed a lower copper content of ~1.34% between the boundary precipitates. Hence, Epit of the boundary should be determined by the lowest Cu content in the boundary (1.34%). Comparison with Figure 61 for the homogenized alloy indicates this should be near -620mV_SCE, close to the observed value of -610mV_SCE. In this regard, it is worth noting that Galvele et al. (81,82) has proposed a mechanism of intergranular corrosion based on local differences in pitting potential.

Consistent with the effect of an inhomogeneous distribution of Cu on the pitting of the tilt grain boundary, the as-grown bicrystals of the 4.2wt% Cu alloy showed preferential attack associated with the solidification cell structure (e.g. Figures 72, 74 and 75). Wide bands of pits are located in regions of lower average Cu content (cell centers) and narrow grooves of pits are associated with regions of higher average Cu content (cell walls). The Cu content in the cell centers is as low as 1.52wt% (Table 9). The cell walls contain precipitates of θ'-phase (Figure 53) that contribute to the high average Cu-content in these regions. However, between the precipitates, the Cu concentration in the cell wall falls as low as 2.18wt% (Table 12). Hence, both cell center and cell wall pitting are due to local copper impoverishment.

No preferential pitting behavior was observed in a 9°<001> tilt boundary bicrystal containing a more dilute Cu concentration of 0.54wt%. Consistent, with this, the Eprot and Epit of the as-grown bicrystal (Table 18) were close to those of the comparable homogenized bicrystal (Table 17). The absence of preferential pitting phenomena is attributed to the fact that any local inhomogeneities in the copper content of the matrix will be relatively small in dilute alloys and insufficient to have a pronounced effect on pitting behavior.

4.4.3 Aged Bicrystals

Aged bicrystals of the 4.2wt% Cu alloy exhibited a microstructure that is typical of the peak-aged condition. The 9°<001> tilt boundary contained large precipitates of θ-phase and the interior of each component of the bicrystal contained a finer dispersion of θ'-phase, as shown in Figure 58. Thus, the Cu content of the matrix had been depleted to form the precipitates. Therefore, based on the effect of Cu on pitting potentials, the Epit
and $E_{\text{prot}}$ of the aged alloy should be typical of a matrix with a Cu content lower than 4.2 wt%. Figure 65 confirmed that these potentials were lower than those of the comparable homogenized alloy bicrystal. Also, Figure 65 showed that $E_{\text{pit}}$ and $E_{\text{prot}}$ of the aged tilt boundary were very similar to those of the aged crystal interior, indicating that the Cu concentration profile and the minimum Cu concentration of the matrix in these regions were very similar to those of the grain boundary. Based on the concentration profiles of Figure 60, the minimum Cu content of the matrix within the individual component single crystals is expected to be located close to the precipitate interface.

Following pitting tests on 0.5 M NaCl, a line of pronounced pits was observed along the tilt boundary and along a few {111} traces (see Figures 69 and 71). Each line was attributed to precipitates falling out of the surface after pitting corrosion of the adjacent matrix. The presence of $\theta'$-phase along the {111} traces was attributed to nucleation and growth of precipitates at dislocations. Other workers have observed that the $\theta'$ precipitates concentrate in clusters along slip planes.(145)

### 4.4.4 Addition of NO$_3^-$

Consistent with the beneficial effects of nitrate additions on pitting behavior of single crystals, the addition of 0.5M [NO$_3^-$] to 0.5 M NaCl raised the pitting potential of $9^\circ <001>$ tilt boundaries. The $E_{\text{pit}}$ values of boundaries in the homogenized alloy bicrystals were raised relative to those in nitrate-free solutions over the whole range of Cu compositions that were studied. This is evident from a comparison between figures 65 and 84, where it is seen that the relative benefit (ie increase in potential, $\Delta E_{\text{pit}}$) is less pronounced at the higher Cu concentrations. For example, from Table 22, the $\Delta E_{\text{pit}}$ was $\sim$367 mV for Al and $\sim$280 mV for the 4.2 wt% Cu alloy.

Comparing Figure 64, with 65 and 84 shows that the $E_{\text{pit}}$ values of the tilt boundary for the as-grown and aged 4.2 wt% Cu alloy are raised by the NO$_3^-$ addition. The $E_{\text{pit}}$ values are not as high as the comparable homogenized alloy, partly due to the lower Cu content in the matrix at the boundary. Also, the relative benefit of NO$_3^-$ is not as high, e.g. $\Delta E_{\text{pit}}$ was 178 mV and 172 mV for the as-grown and aged boundaries respectively. This latter effect may be due to the precipitates acting as preferential sites for adsorption of NO$_3^-$ ions.
The results suggest that there is some benefit to be derived by nitrate additions in practical corrosion situations where Al-Cu alloys are exposed to chloride solutions. This is particularly true for the situation where the beneficial effect of solid solution Cu on pitting behavior has been removed by the precipitation of \( \theta \) or \( \theta+\theta' \) phases that have depleted the matrix of Cu.
The present investigation has shown that corrosion in Al and Al-Cu alloys is dependent on crystal structure, sample composition and bath chemistry.

5.1 Pitting Corrosion of Single Crystals:

(1) Effect of crystallographic orientation

The Epit and pit density of Al is a function of the crystallographic orientation of the surface. The susceptibility to pitting progressively decreases for orientations \{111\}, \{011\} and \{001\} respectively.

Pitting attack leads to pit morphologies in which the sides of the pit are \{001\} facets, independent of the orientation of the crystal.

The Eprot is independent of the crystallographic orientation of the electrode surface and independent of the amount of coulomb charge for pit propagation. Eprot is determined by the behavior of \{001\} facets in the local chloride-enriched pit environment. Eprot is, in effect, the Epit for the \{001\} surface in a solution of the same composition as the pit solution.

(2) Effect of Cl⁻ concentration

Increasing the Cl⁻ concentration of the bulk solution shifts both the Epit and Eprot to more active potentials by 140 mV/decade and 72 mV/decade respectively. The hysteresis between Epit and Eprot diminishes with increasing Cl⁻ concentration.

Pit density is increased by increasing Cl⁻ concentration of the bulk solution. This is a result of a higher degree of the adsorption competitiveness of the Cl⁻ species on the less favorable sites within the pre-existing flaw and the subsequent enhancement of the dissolution at these sites.
(3) Effect of pH

Decreasing pH slightly lowers the $E_{\text{pit}}$ of Al(001) in 0.5M NaCl solution by 5.2 mV/pH unit. The decrease of pH has no effect on $E_{\text{prot}}$, due to the overwhelmingly higher concentration of Cl$^-$, as compared to the concentration of OH$^-$ in a solution of pH 2.5 and 6.5.

(4) Effect of NO$_3^-$

Addition of NO$_3^-$ ions inhibits pitting corrosion on all three low index crystal surfaces by substantially shifting both $E_{\text{pit}}$ and $E_{\text{prot}}$ to more noble potentials. The NO$_3^-$ species inhibits most effectively on (001) and least effectively on (111) surfaces. The anisotropic behavior of $E_{\text{pit}}$ that is observed in the uninhibited solution persists in the presence of NO$_3^-$ ions.

The addition of NO$_3^-$ ions also reduces the pit density and changes the pit morphology on the crystal surface where access of the NO$_3^-$ ions is sufficient. The (001) faceted pit changes to a more irregular shape.

The inhibiting effect of NO$_3^-$ ions was produced by the competing of NO$_3^-$ ions with Cl$^-$ ions for adsorption sites at the metal substrate within the oxide flaws. This is followed by the electrochemical reduction of the NO$_3^-$ ions to produce adsorbed film-forming OH$^-$ species which enhance the repassivation process.

(5) Effect of Cu

Alloying with Cu raises both the $E_{\text{pit}}$ and $E_{\text{prot}}$ of the homogenized alloys through the blockage of active dissolution sites by the inert Cu atoms at the metal surface within the oxide flaws.

The anisotropic pitting corrosion behavior of pure Al disappeared when it was alloyed with Cu due to the high $E_{\text{pit}}$ value of the alloy.

The value of $E_{\text{pit}}$ increased monotonically with Cu within the range of compositions examined. $E_{\text{prot}}$ progressively increases with increasing Cu content to
1.42 wt%Cu above which it remains constant. Above 1.42 wt%Cu the inside of the pits are saturated with Cu atoms due to the preferential leaching of the active Al atoms.

When the alloy composition is raised above 0.54 wt% Cu, the pit density increases and the pit facets change from \{001\} to irregular spongy surfaces.

The effect of Cu additions on the corrosion behavior is attributed to the following, (a) The increase in \(E_{p_{\text{pit}}}\) due to the effect of blockage of the active dissolution sites by the Cu atoms, (b) The preferential leaching of the active Al atoms, (c) The presence of Cu atoms at the metal surface hindering the formation of an Al oxide film in the immediate vicinity, thus increasing the density of flaws in the original oxide film.

5.2 Mechanism of pitting corrosion of Al

A model of pitting corrosion is proposed. It is based on the local kinetic balance between the repassivation process produced by the OH\(^-\) ions, and the dissolution process, enhanced by the Cl\(^-\) ions, at the bare metal surface in the base of the pre-existing oxide flaws.

It is proposed that the rates (\(R\)) of the dissolution process are dependent on the substrate orientation. The rates of dissolution are in the order \(R\{111\}\rangle R\{100\}\rangle R\{001\}\) for a given potential and Cl\(^-\) activity at the metal-solution interface.

The proposed kinetic model of pitting corrosion in Al accounts for the effects of the bulk solution chemistry and metal alloy composition on the corrosion behaviour.

5.3 Pitting Corrosion and Intergranular Corrosion of Bicrystals

(1) Solute segregation in as-grown and aged bicrystals

Cu is segregated in both the as-grown and aged bicrystals. In the as-grown crystals the solute is concentrated along the walls of a cellular substructure, and depleted in the cell centers. The cell structure is a result of constitutional supercooling ahead of the advancing interface during solidification. \(\theta\) and \(\theta'\) precipitates are formed during the cooling period after crystal growth due to a solid phase transformation at the cell walls or
nodes where Cu is concentrated. As the θ phase grows, it depletes the surrounding region of Cu.

For the aged bicrystal, grain boundary precipitates (θ-phase) with Cu depleted zone are present. θ'-phase precipitates (parallel to {001}) were formed within the individual component single crystals. The θ' precipitates are expected to be associated with a Cu depleted zone similar to the grain boundary precipitates.

(2) Effect of grain boundaries on corrosion

No preferential pitting corrosion or intergranular corrosion occurs at a homogenized tilt boundary. The exception is a 0.1 wt% Cu bicrystal having a <001> tilt boundary of 28° which pits preferentially along the boundary. This is attributed to non-equilibrium depletion of Cu at the high angle tilt boundary.

(3) Effect of Cu solute distribution on corrosion

The Epit values of the boundary and the grain interior of the as-grown and the aged 90°<001> tilt bicrystals of 4.2 wt% Cu are lower than the Epit of the boundary in the homogenized bicrystal of the same Cu content. This is due to the segregation of Cu in the as-grown and the aged bicrystals. The Epit of the crystal is determined by the lowest Cu content region in the sample.

Severe intergranular corrosion occurs on the as-grown 90°<001> tilt bicrystal of 4.2 wt% Cu. Preferential attacks also occur at the cell centers and cell walls in the component single crystals. The preferential attack is attributed to the Cu depletion and the associated lower Epit in these regions.

Preferential pitting corrosion occurs at the tilt boundary and along a few {111} traces within the component single crystals of aged 90°<001> tilt bicrystals of 4.2 wt% Cu. These preferential attacks are caused by Cu depletion and the lower Epit value of the regions adjacent to the grain boundary and grain interior precipitates.
(4) Effect of NO$_3^-$

Addition of 0.5M [NO$_3^-$] to 0.5M NaCl raises the $E_{pit}$ of crystals containing tilt boundaries. The magnitude of the increase in the $E_{pit}$ is dependent on the Cu content and thermal history of the crystals.

Nitrate addition to the corrosion environment is of benefit in practical situations when Al-Cu alloys are exposed to chloride solutions.
BIBLIOGRAPHY


Bibliography

70. E.H. Dix, and H.H. Richardson, Trans AIME, 73, 560 (1926).
77. O.P. Arora, G.R. Ramagopal, and M. Metzger, Trans. AIME, 224, 541 (1962).
Australian Academy of Sciences, Canberra, 1, 396 (1974).
103. J.Y. Boos and C. Goux, Localized Corrosion, NACE -3, R.Staehle, B.Brown, J.Kruger,
105. B. Chalmers, Proc. Royal Soc. A, 196, 64 (1948); Also, B. Chalmers, Canadian J. of
Physics, 31, 132 (1953).
108. J.W.Colby, MAGIC Program, BellTelephone Labs.,Inc.
111. J. Philibert and R. Tixier, Proc. 5th Int. Cong. On X-Ray Optics and Microanalysis,
Bibliography


140. R. Bakish and W.D. Robertson, Trans. AIME, 206, 1278 (1956).


Publication (Presentation)

1. M. Yasuda, Chung-Hung Tien, and S. Haraaya,
   "The Role of Chloride in Electroplating of Nickel," The
   annual conference, Electrochemical Soc. of Japan,
   1977.

2. M. Yasuda, D. Tromans and F. Weisinger,
   "Grain Boundary Segregation and Corrosion
   of Al-Cu Alloy Bridgelds," 24th
   Annual Conference of Metallurgists, CIM. Poster

Awards

1975-1977 Japan Rotary Club Scholarship.
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   AMP - Japan, 10th Technical
   Conference, 1981
1985 "First Prize Poster Section," 24th
   Annual Conference of Metallurgists,
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1988